THE PHOTOCHEMISTRY OF AMIDES AND PHTHALIMIDES

by

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PART III

Experimental Results

EXPERIMENTAL

Microanalyses were performed by Dr. Franz Kasler of the University of Maryland, Department of Chemistry. Mass spectra were performed by either Dr. Robert Lustig or Dr. Martha Gay at the University of Maryland on a DuPont 492 double focusing magnetic scanning mass spectrophotometer. Spectra were usually low resolution and taken at 70 ev ionization potential unless otherwise noted.

Infrared spectra were taken on either a Beckman IR-8 infrared spectrophotometer or a Perkin Elmer 337 Grating infrared spectrophotometer in matched 0.1 mm thickness sodium chloride cells. Deuterochloroform or spectrograde carbon tetrachloride were used as solvents and in reference cells. Other pure liquid samples were taken neat between two sodium chloride plates.

NMR spectra were obtained on a Varian A-60D NMR spectrophotometer with deuterochloroform solutions unless otherwise noted with tetramethylsilane as an internal standard.

Ultraviolet and visible spectra were obtained on a Cary 15 ultraviolet spectrophotometer in matched 10 mm quartz cells. Spectrograde cyclohexane and absolute ethanol were used as solvents.

Analytical gas chromatography was performed on a Varian Aerograph 1200 series with a flame ionization detector. A Houston Instruments Omniscribe recorder with electronic integrator or a Sargent recorder with disc integrator were

used to quantify analytical results through a system of response factors calculated for each compound of interest. Preparative gas chromatography was performed on a Varian Aerograph Model 90-P with a thermal conductivity detector. A list of the 1/8" and 1/4" columns used in the analytical and preparative chromatography is presented in Appendix I.

Liquid chromatography was performed on a DuPont Instruments Model 830 Liquid Chromatograph with an ultraviolet detector whose absorbance detectability was 1×10^{-9} at 254 nm. A Sargent recorder with disc integrator was used for qualitative and quantitative work. The column used was a 12" × 3/8" silica gel column (Zipak). Elution solvents were ethyl acetate (redistilled) and spectro-quality methylene chloride. Special septa from Lawshe were necessary for high pressure work with organic solvents.

Preparation of N-alkylamides and N-arylamides

With only the exceptions noted later all N-alkyl and N-aryl amides were prepared by the following general procedure:

In a 500 ml three-neck flask fitted with reflux condenser, pressure equilibrating addition funnel, stopper, and magnetic stirrer, 160 ml 10% aqueous NaOH were vigorously stirred with 0.20 moles of amine in 75 ml tetrahydrofuran. The acid chloride* (0.2 moles) was mixed with 90 ml tetrahydrofuran in the addition funnel. The reaction flask was cooled in a water-ice bath, and at reduced temperature the acid chloride solution was added dropwise with stirring. When the addition was completed, the reaction mixture was stirred at room temperature an additional two to twelve hours.

The two layers were separated, and the lower aqueous phase was extracted with three 100 ml portions of ether. The organic phases were combined and dried over anhydrous Na_2SO_4. After gravity filtration, the filtrate was concentrated as far as possible on the rotovap with steam. The residue was then vacuum distilled twice. The yields were 78-96%.

*The acid chlorides were prepared by refluxing one mole of the appropriate acid with 1.5 moles thionyl chloride, unless otherwise noted. The excess thionyl chloride was distilled, followed by acid chloride distillation from the pot.

A. N-hexylhexanoamide: b.p. 133-5°/1-1.5 mm; 90% yield

NMR: ($CDCl_3$) 0.6-1.15 δ(t, 6H, CH_3), 1.15-2.0 δ(m, 14H, CH_2), 2.0-2.45 δ(t, 2H, CH_2 α to C=O), 3.0-3.5 δ(q, 2H, N-C-H), 6.4-7.0 δ(m broad, 1H, NH).

IR: (neat) 3400-3200 (N-H stretch), 3100, 2930, 2920, 2870 (C-H stretch), 1640 (C=O stretch), 1550, 1460, 1380, 1260, 725 cm^{-1}.

B. N-hexyloctanoamide: b.p. 135°/.25 mm; 86% yield

NMR: ($CDCl_3$) 0.7-1.1 δ(t J=5Hz, 6H, CH_3), 1.1-2.0 δ(m broad, 18H, CH_2), 2.0-2.4 δ(t J=6Hz, 2H, CH_2 α to C=O), 3.0-3.5 δ(q, 2H, N-CH_2), 7.5-7.9 δ(t J=6Hz, 1H, NH).

IR: (neat) 3400-3200 (N-H stretch), 3100, 2970, 2940, 2860 (C-H stretch), 1640 (C=O stretch), 1550, 1450, 1380, 1260, 1225, 1195, 1150, 1110, 725 cm^{-1}.

C. N-hexylbutyramide: b.p. 142-4°/4 mm; 85% yield

NMR: ($CDCl_3$) 0.7-1.15 δ(2 overlapping t, 6H, CH_3), 1.15-2.05 δ(m broad, 10H, CH_2), 2.05-2.40 δ(t J=7Hz, 2H, CH_2 α to C=O), 3.0-3.5 δ(q J=6.5Hz, 2H, N-CH_2), 6.8-7.4 δ(t broad, 1H, NH).

IR: (neat) 3500-3200 (N-H stretch), 3090, 2970, 2950, 2930, 2870 (C-H stretch), 1640 (C=O stretch), 1540, 1460, 1375, 1325, 1290, 1210, 1150, 1110, 1060, 890, 725 cm^{-1}.

D. N-butylhexanoamide: b.p. 136°/3.8 mm; 85% yield

NMR: ($CDCl_3$) 0.7-1.15 δ(t, 6H, CH_3), 1.15-2.1 δ(m broad, 10H, CH_2), 2.1-2.5 δ(t J=7Hz, 2H, CH_2 α to C=O), 3.0-3.4 δ(q, 2H, N-CH_2), 6.4-6.9 δ(t broad, 1H, NH).

IR: (neat) 3500-3200 (N-H stretch), 3100, 2970, 2940, 2880 (C-H stretch), 1640 (C=O stretch), 1550, 1460, 1380, 1300, 1255, 1230, 1190, 1150, 1110, 980, 730 cm^{-1}.

E. N-hexyl-4-phenylbutyramide*: b.p. 190°/1.8 mm; 84% yield

NMR: ($CDCl_3$) 0.7-1.1 δ(t, 3H, CH_3), 1.1-1.9 δ(m broad, 8H, CH_2), 1.9-2.3 δ(t J=6Hz, 2H, CH_2 α to C=O), 2.4-2.8 δ(t J=6.5Hz, 2H, benzylic), 3.0-3.5 δ(q, 2H, N-CH_2), 6.8-7.4 δ(m broad, 6H, phenyl and N-H).

IR: (neat) 3400-3200 (N-H stretch), 3100, 3080, 3040, 2960, 2940, 2860 (C-H stretch), 1640 (C=O stretch), 1545, 1500, 1455, 1380, 1255, 1200, 1150, 1075, 1030, 740, 700 (monosubstituted benzene) cm^{-1}.

F. N-2-phenylethylhexanoamide: b.p. 186-8°/3.6 mm; 92% yield

NMR: ($CDCl_3$) 0.7-1.1 δ(t J=6Hz, 3H, CH_3), 1.1-1.9 δ(m broad, 6H, CH_2), 2.0-2.35 δ(t J=6Hz, 2H, CH_2 α C=O), 2.6-3.0 δ(t J=7Hz, 2H, benzylic), 3.3-3.8 δ(d of q, 2H, N-CH_2), 6.2-6.8 δ(m, 1H, NH), 7.0-7.5 δ(m, 5H, phenyl).

IR: (neat) 3400-3200 (N-H stretch), 3100, 3080, 3050, 2960, 2940, 2860 (C-H stretch), 1640 (C=O stretch), 1545, 1500, 1455, 1380, 1255, 1200, 1150, 1075, 1030, 740, 705 (monosubstituted benzene) cm^{-1}.

*Special preparation of the acid chloride

G. N-hexylproprionamide: b.p. 137°/5 mm; 81% yield (proprionic anhydride not proprionyl chloride)

NMR: ($CDCl_3$) 0.7-1.9 δ(m and 2 sets of triplets J=6 and 7.5Hz, 14H, CH_3 and CH_2), 2.0-2.5 δ(q J=7.5Hz, 2H, $CH_2\alpha$ to C=O), 3.0-3.5 δ(q J=6Hz, 2H, N-CH_2), 5.9-6.8 δ (m broad, 1H, N-H).

IR: (neat) 3500-3200 (N-H stretch), 3100, 2970, 2930, 2860 (C-H stretch), 1640 (C=O stretch), 1460, 1380, 1270, 1240, 1200, 1150, 1130, 1100, 1060, 920, 800, 725 cm^{-1}.

H. N-methylhexanoamide: b.p. 150°/17 mm; 88% yield

NMR: ($CDCl_3$) 0.7-1.1 δ(t J=5.5Hz, 3H, CH_3), 1.1-2.0 δ (m, 6H, CH_2), 2.0-2.5 δ(t J=6.5Hz, 2H, CH_2 α to C=O), 2.7-3.0 δ(d J=4.5Hz, 3H, N-CH_3), 7.4-8.1 δ(m broad, 1H, N-H).

IR: (neat) 3500-3200 (N-H stretch), 3100, 2970, 2940, 2870 (C-H stretch), 1640 (C=O stretch), 1555, 1465, 1450, 1410, 1380, 1330, 1295, 1260, 1220, 1185, 1160, 1110, 1060, 970, 725 cm^{-1}.

I. N-octylhexanoamide: b.p. 145-8°/0.5 mm; 80% yield

NMR: ($CDCl_3$) 0.7-1.1 δ(t J=5.5Hz, 6H, CH_3), 1.1-2.0 δ (m broad, 18H, CH_2), 2.1-2.5 δ(t J=6Hz, 2H, CH_2 α to C=O), 3.0-3.5 δ(q, 2H, N-CH_2), 6.4-6.8δ(m broad, 1H, NH).

IR: (neat) 3400-3200 (N-H stretch), 3100, 2965, 2935, 2860 (C-H stretch), 1640 (C=O stretch), 1550, 1450, 1380, 1255, 1225, 1190, 1150, 1110, 725 cm^{-1}.

J. N-ethylhexanoamide: b.p. 122-3°/4 mm; 85% yield

NMR: ($CDCl_3$) 0.7-2.0 δ(m and 2t J=6Hz and 7.5Hz, 12H, CH_3 and CH_2), 2.0-2.4 δ(t J=6Hz, 2H, CH_2 α to C=O), 3.0-3.6 δ(quintet J=7.5Hz, 2H, N-CH_2), 7.5-8.0 δ(m, 1H, NH).

IR: (neat) 3500-3200 (N-H stretch), 3100, 2970, 2930, 2870 (C-H stretch), 1635 (C=O stretch), 1540, 1460, 1380, 1325, 1280, 1250, 1210, 1150, 1130, 1110, 1095, 1060, 930, 890, 725 cm^{-1}.

K. N-hexylacetamide: b.p. 121-5°/3.5 mm; 95% yield

NMR: ($CDCl_3$) 0.7-1.1 δ(t J=5Hz, 3H, CH_3), 1.1-1.9 δ(m broad, 8H, CH_2), 1.9-2.1 δ(s, 3H, CH_3-C=O), 3.0-3.45 δ (q J=7Hz, 2H, N-CH_2), 6.6-7.3 δ(m broad, 1H, NH).

IR: (neat) 3500-3200 (N-H stretch), 3080, 2920, 2860 (C-H stretch), 1640 (C=O stretch), 1550, 1455, 1430, 1360, 1290, 1190, 1145, 1120, 1090, 1030, 990, 720 cm^{-1}.

L. N-2-heptylhexanoamide: b.p. 152°/4.5 mm; 78% yield

NMR: ($CDCl_3$) 0.65-1.9 δ(t J=5.5Hz, d J=7Hz and m broad, 23H, CH_3-CH_2, CH_3-CH and CH_2), 2.0-2.4 δ(t J=6.5Hz, 2H, CH_2-C=O), 3.65-4.35 δ(m broad, 1H, CH-N), 5.2-5.9 δ(m broad, 1H, N-H).

IR: (neat) 3400-3180 (N-H stretch), 3080, 2970, 2960 (C-H stretch), 1640 (C=O stretch), 1540, 1460, 1380, 1290, 1250, 1185, 1160, 1120, 1100, 1080, 960, 900, 725 cm^{-1}.

M. N-isobutylhexanoamide: b.p. 136-7°/4 mm; 85% yield

NMR: ($CDCl_3$) 0.7-1.1 δ(t and d J=6Hz, 9H, CH_3), 1.1-2.0 δ(m broad, 7H, CH_2 and CH), 2.1-2.5 δ(t J=6.5Hz, 2H, CH_2-C=O), 2.85-3.25 δ(t J=6Hz, 2H, N-CH_2), 7.3-7.8 δ(t, 1H, NH).

IR: (neat) 3400-3200 (N-H stretch), 3080, 2960, 2940, 2870 (C-H stretch), 1640 (C=O stretch), 1550, 1460, 1375, 1250, 1180, 1155, 970, 725 cm^{-1}.

N. N-hexyl-4-methylvaleramide: b.p. 156-8°/3.8 mm; 80% yield

NMR: ($CDCl_3$) 0.7-1.1 δ(t and d J=6Hz, 9H, CH_3), 1.1-1.9 δ(m broad, 11H, CH_2 and CH), 2.0-2.4 δ(t J=7Hz, 2H, CH_2 α to C=O), 3.0-3.4 δ(q J=6Hz, 2H, N-CH_2), 6.8-7.3 δ(t, 1H, NH).

IR: (neat) 3400-3180 (N-H stretch), 3100, 2960, 2930, 2870 (C-H stretch), 1640 (C=O stretch), 1550, 1465, 1380, 1370, 1340, 1330, 1305, 1275, 1240, 1200, 1180, 1150, 1130, 1115, 1030, 725 cm^{-1}.

O. N-hexyl-2-methylvaleramide: b.p. 122-4°/2.5 mm; 82% yield

NMR: ($CDCl_3$) 0.65-1.9 δ(2t J=6Hz d J=7Hz and m broad, 21H, CH_3 and CH_2), 2.0-2.7 δ(m, 1H, CH α to C=O), 3.05-3.5 δ(q J=6Hz, 2H, CH_2-N), 5.8-6.4 δ(m broad, 1H, NH).

IR: (neat) 3450-3200 (N-H stretch), 3090, 2960, 2930, 2870 (C-H stretch), 1640 (C=O stretch), 1550, 1460,

1380, 1370, 1305, 1250, 1220, 1150, 1115, 1100, 1000, 985, 720, 695 cm^{-1}.

P. N-hexylvaleramide: b.p. 145°/3.9 mm; 94% yield

NMR: ($CDCl_3$) 0.65-1.2 δ(2 overlapping t J=6Hz, 6H, CH_3), 1.1-2.0 δ(m broad, 12H, CH_2), 2.0-2.4 δ(t J=6.5Hz, 2H, CH_2 α to C=O), 3.0-3.5 δ(q J=6Hz, 2H, N-CH_2), 7.3-7.8 δ(m, 1H, N-H).

IR: (neat) 3450-3180 (N-H stretch), 3100, 2970, 2940, 2875 (C-H stretch), 1640 (C=O stretch), 1550, 1460, 1440, 1380, 1260, 1225, 1195, 1150, 1135, 1110, 1065, 1030, 960, 920, 720 cm^{-1}.

Q. N-2-heptylacetamide: b.p. 125-28°/3.7 mm; 90% yield

NMR: ($CDCl_3$) 0.7-1.65 δ(m, t J=5.5Hz, and d J=7Hz, 14H, CH_3 and CH_2), 1.85-2.05 δ(s, 3H, CH_3-C=O), 3.7-4.2 δ(m, 1H, CH-N), 5.5-6.3 δ(m broad, 1H, N-H).

IR: (neat) 3600-3200 (N-H stretch), 1640 (C=O stretch), 1550, 1440, 1370, 1290, 1200, 1150, 1135, 1075, 1040, 970, 830, 725 cm^{-1}.

R. N,N-dihexylhexanoamide: b.p. 155-57°/1 mm; 87% yield

NMR: ($CDCl_3$) 0.6-2.0 δ(t J=5Hz and m broad, 33H, CH_3 and CH_2), 2.1-2.5 δ(t J=Hz, 2H, CH-C=O), 3.0-3.6 δ(m, 4H, CH_2-N).

IR: (neat) 2960, 2920, 2850 (C-H stretch), 1640 (C=O stretch), 1460, 1420, 1375, 1295, 1250, 1180, 1140, 1100, 720 cm^{-1}.

S. N,N-dihexylacetamide: b.p. 124°/1 mm; 96% yield

NMR: ($CDCl_3$) 0.6-2.0 δ(t J=5Hz and m broad, 22H, CH_3 and CH_2), 2.1 δ(s, 3H, CH_3-C=O), 3.0-3.6 δ(m, 4H, CH_2-N).

IR: (neat) 2960, 2930, 2860 (C-H stretch), 1640 (C=O stretch), 1460, 1420, 1380, 1360, 1300, 1260, 1225, 1200, 1105, 990, 725 cm^{-1}.

T. N-methyl-N-butylhexanoamide: b.p. 111-112°/3 mm; 90% yield

NMR: ($CDCl_3$) 0.7-2.0 δ(m broad, 16H, CH_3 and CH_2), 2.1-2.6 δ(t J=7Hz, 2H, CH_2-C=O), 2.8-3.1 δ(2s, 3H, CH_3-N), 3.1-3.6 δ(m, 2H, CH_2-N).

IR: (neat) 2960, 2940, 2865 (C-H stretch), 1645 (C=O stretch), 1460, 1400, 1380, 1300, 1260, 1210, 1150, 1105, 1080, 730 cm^{-1}.

U. N-methyl-N-butylacetamide: b.p. 95°/1.4 mm; 82% yield

NMR: ($CDCl_3$) 0.7-1.9 δ(m broad, 7H, CH_3 and CH_2), 2.0-2.2 δ(s, 3H, CH_3-C=O), 2.8-3.1 δ(2s, 3H, CH_3-N), 3.15-3.55 δ(2q, 2H, CH_2-N).

IR: (neat) 2960, 2930, 2870 (C-H stretch), 1640 (C=O stretch), 1470, 1430, 1400, 1360, 1305, 1270, 1260, 1225, 1170, 1110, 1090, 1060, 1020, 755, 730 cm^{-1}

V. N-isobutylbenzamide: b.p. 152-4°/1 mm; 98% yield

NMR: ($CDCl_3$) 0.75-1.05 δ(d J=6.5Hz, 6H, CH_3), 1.55-2.3 δ(heptet J=7Hz, 1H, $CH_2(CH_3)_2$), 3.15-3.4 δ(t J=6.5Hz,

2H, N-CH_2), 7.1-8.1 δ(m broad, 6H, phenyl and N-H).
IR: (KBr) 3300 (N-H stretch), 2980, 2950, 2900 (C-H stretch), 1650 (C=O stretch), 1550, 1510, 1475, 1440, 1400, 1380, 1300, 1250, 1180, 1110, 940, 740, 710 (monosubstituted benzene) cm^{-1}.

Preparation of 4-Phenylbutyryl Chloride

Freshly distilled thionyl chloride (20 ml) was added slowly to 26 g 4-phenylbutyric acid in 250 ml round bottom flask fitted with reflux condenser and magnetic stirrer. The reaction mixture was melted on the steam bath, and allowed to react at room temperature for two hours. After a seven-hour reflux, the thionyl chloride was removed by distillation at atmospheric pressure. Vacuum distillation yielded 28.5 g 4-phenylbutyryl chloride at 134°/11 mm.

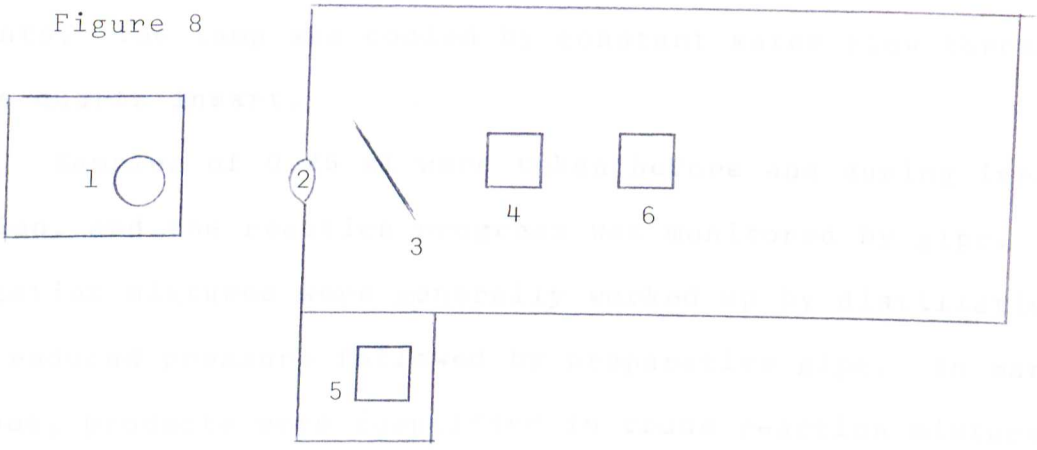
Photolysis Light Sources

A. Hanovia 450 W medium pressure mercury vapor arc.

B. A circular array (radius 19 cm) of 10 General Electric 15 Watt G15T8 germicidal lamps (ca. 90% of the total energy of wavelength less than 760 nm lies in a narrow band at 254 nm).

C. Bausch and Lomb monochromator with grating 1200 grooves/minute and with adjustable wavelength selector for black box (Figure 8) irradiations.

Figure 8



1. Monochromator
2. Quartz collimating lens
3. Optically clear quartz reflector
4. Sample
5. Reference cell
6. Backup cell

Photolysis Procedures for Amides

Type A

Two percent solutions, by weight, of amides in solvent were introduced to photocontainers with quartz water jacket inserts. The photocontainer was fitted with magnetic stirrer, septa, and stoppered condenser, and samples were purged for periods of one-half to two hours with dry nitrogen prior to irradiation.

Irradiations were conducted under positive nitrogen pressure with a Hanovia 450 W medium pressure mercury vapor arc. The irradiation periods varied with individual experiments. The lamp was cooled by constant water flow through the quartz insert.

Samples of 0.25 ml were taken before and during irradiation, and the reaction progress was monitored by glpc. Reaction mixtures were generally worked up by distillation at reduced pressure followed by preparative glpc. In many cases, products were identified in crude reaction mixtures by coinjection on two different columns.

Type B

Type B photolyses were carried out in 6" × 12 mm with 1 mm thickness quartz tubes fitted with rubber septa (which were covered with aluminum foil). Tubes were purged for varying periods with dry nitrogen through a needle inside a larger gauge vent needle. Samples were taken from the tubes with nitrogen-purged syringes. The tubes were either

irradiated with the Hanovia lamp by suspension beside the quartz well, or with the Source B light. An alternate method was irradiation with either light source by equally spacing the tubes in the merry-go-round apparatus. The reaction mixtures were analyzed by glpc.

Type C

This photolysis was similar to the Type B except the photocontainers were larger. (This type of photolysis was usually used when highly volatile products were to be analyzed in preparative scale reactions). These tubes were either quartz or vycor as indicated in the individual experiments. Each tube was fitted with a rubber septum, which was wired on and covered with aluminum foil. The volumes of solution varied, but all were purged with dry nitrogen for one-half to one hour. The tubes were irradiated by suspension beside the quartz well or with Source B light. The vapor phase was then analyzed by chilling the tube and removing the vapor under vacuum. The residues were analyzed by glpc and worked up as in the Type A photolysis.

Type D

Type D photolyses were also similar to Type B photolyses. These reactions were run in special cylindrical vessels constructed with two circular quartz windows and a long neck, which was usually fitted with a septum. The samples were purged with nitrogen as in a Type B photolysis.

These vessels were used only in "black box" irradiations where either quantum yields were measured or where specific wavelength irradiation was desired.

Type E

This type of photolysis was conducted in vessels whose preparation is described in the section on freeze-pump-thaw photolysis vessels. This method completely removed oxygen from the photolysis solutions. After the tubes were sealed, irradiations were carried out in the merry-go-round apparatus with either type of light. Duplicates of each solution were run as verification for results. The weakness of this method was that no samples could be taken. Once the tubes were opened, the irradiation was completed.

Preparation of Photolysis Vessels for Freeze-Pump-Thaw Degassing Method

Photolysis vessels for freeze-pump-thaw degassing, one of the most efficient methods for the removal of oxygen from samples (especially important in quantum yield measurements where oxygen acts as a quencher), ideally would be sealed quartz tubes. The cost for such vessels would be prohibitive since they could be used only once. The photolysis tubes must also be uniform in height, wall thickness, and diameter. Alternately, quartz tubes could be joined to regular glass tubes, and the regular portion sealed in vacuo. The requirements for joining the glass to the quartz, however, were that the bond between the two be strong enough to withstand a powerful vacuum and that the tubes be separable by simple means after irradiation.

This type of photolysis cell was prepared as follows: 15-20 cm lengths of glass tubing, 1 mm thickness and 12 mm outer diameter, were cut perpendicular with a wheel causing neither cracks nor chips. These tubes were constricted in the center by drawing and compressing (to insure thick walls in the constriction). These constricted tubes were then aligned flush with the grated end of #9 Pyrex "0" ring joints in a frame, and Dure "EPX-1" epoxy glue was applied in a wide strip to overlap the junction. Every half hour for two hours the frame was turned over to insure complete

and fairly uniform coverage of the junction by the glue. The seal was then allowed to "set" at room temperature for an additional four hours.

Six in. × 12 mm outer diameter (1 mm thickness) quartz tubes were then glued to the other end of the constricted tubes in a similar manner to the first seals. When the second seals had "set", the tubes were then cured overnight in an oven at 75°. The seals were then tested under a vacuum of 1 micron for an hour. This testing served a dual purpose in that it removed any residual solvent from the glue after slight heating with a heat gun for several minutes, and showed which tubes could withstand the vacuum of freeze-pump-thaw.

Samples were introduced through the "O" ring joint by a long fine syringe. After the irradiation, the tubes were cooled in ice, covered with a towel, and crunched open with pliers. When the samples had been removed,* the "O" ring joings and quartz tubes were recovered by melting the epoxy seals in hot DMF.

*Samples which required external standards were divided immediately into one ml aliquots.

Photolysis of N-hexylhexanoamide in Dioxane

A solution of four grams N-hexylhexanoamide, 1, in 210 ml spectrograde dioxane was irradiated in a Type A photolysis for 125 hours with the Hanovia lamp. Samples were taken at irregular intervals and analyzed immediately.

Coinjection of authentic samples of pentane and 1-butene on Column M at 35-40° showed peaks at 5 and 3 minutes respectively. Confirmation was obtained on Column L at 35-40°. Absence of 1-hexene was shown in the reaction mixture when an authentic sample was compared on Column M at 35-40°.

Glpc on Column M at 180° showed three major product peaks. Hexylamine, hexanal, hexylpentylamine, hexanoamide, and N-hexylacetaminde were not the major products. The solvent was removed by distillation at atmospheric pressure. Vacuum distillation yielded three main fractions: 0.3 ml 80-90°/5 mm, 0.4 ml 90-115°/5 mm, and 0.6 ml 120-155°/5 mm.

Although all fractions contained the first product, the second contained the fewest other contaminants. Preparative glpc on Column N at 105° yielded one major peak, which was verified as the first product. NMR contained 3 regions, 3.2-4.0 δ integrating 8, a pair of doublets integrating 3 at 1.0-1.2 δ, and a broad singlet at 2.6 δ integrating 1. The IR showed a dioxyl band at 1115 cm^{-1} and an OH band at 3600 cm^{-1}. The molecular weight by mass spec was m^{+}/e 132.

On Column C at 110° the liquid collected on the first pass split into two peaks. A second pass on Column R at 110° separated the two peaks. The two doublets were simplified to a doublet for each peak. On the basis of the following spectra the two products were characterized as the two diastereomers of α-methyl dioxane methanol, 2 and 3.

NMR: ($CDCl_3$) 1.13 δ (d J=6Hz, 3H, CH_3), 2.73 δ (s broad, 1H, OH), 3.3-4.0 δ (m broad, 8H, O-C-H).

IR: (CCl_4) 3600, 3500 (OH stretch), 2980, 2870 (C-H stretch), 1115 (dioxyl) cm^{-1}.

MASS SPEC: m^+/e 132(P, 4%), 117(3%), 114(4%), 102(10%), 101(2%), 99(4%), 89(17%), 88(38%), 87(100%), 86(30%), 74(2%), 73(4%), 71(7%), 70(3%), 69(3%), 59(17%), 58(18%), 57(22%), 45(98%), 44(45%), 43(65%), 41(12%), 32(88%), 31(34%), 29(15%), 28(100%).

NMR: ($CDCl_3$) 1.13 δ(d J=6.5Hz, 3H, CH_3), 2.28 δ(s broad, 1H, OH), 3.4-4.1 δ(m broad, 8H, O-C-H).

IR: (CCl_4) 3600, 3500 (O-H stretch), 2970, 2865 (C-H stretch), 1115 (dioxyl) cm^{-1}.

MASS SPEC: m^+/e 132(P, 6%), 117(4%), 114(5%), 102(13%), 101(2%), 99(4%), 89(14%), 88(38%), 87(base, 100%), 86 (30%), 74(2%), 73(7%), 72(2%), 71(5%), 70(2%), 69(3%), 59(13%), 58(11%), 57(13%), 45(49%), 44(18%), 43(26%), 41(5%), 32(11%), 31(8%), 29(4%), 28(24%).

The third nearly solid fraction was redissolved in dioxane and tested on Column M at 180°. This fraction contained mostly the second and third products. The fraction was passed on Column N at 125°.

The second product was characterized by its spectra and analysis as one of the diastereomeric dimers of dioxane, 4, m.p. 155°.

NMR: ($CDCl_3$) 3.2-4.2 δ(m, O-C-H).

IR: ($CDCl_3$) 2970, 2920, 2860 (C-H stretch), 1560, 1450, 1275, 1220, 1120 (dioxyl), 790, 740, 710 cm^{-1}.

MASS SPEC: m^+/e 174(P, 4%), 143(5%), 130(7%), 99(5%), 88(5%), 87(base, 100%), 86(68%), 73(20%), 71(5%), 70 (5%), 59(9%), 58(8%), 57(11%), 55(7%), 45(12%), 44(9%), 43(30%), 41(10%), 39(5%), 31(29%), 30(9%), 29(15%), 28(78%), 27(17%).

Anal: Calculated for $C_8H_{14}O$: C 55.16; H 8.10;
Found: C 55.43; H 8.30.

The third product was characterized by its spectra and analysis as the other diastereomer, 5, m.p. 117°.

NMR: ($CDCl_3$) 3.3-4.0 δ(m, O-C-H).

IR: ($CDCl_3$) 2980, 2920, 2870 (C-H stretch), 1560, 1460, 1260, 1125 (dioxyl), 1100, 875 cm^{-1}.

MASS SPEC: m^+/e 174(P, 12%), 143(6%), 130(4%), 115(5%), 99(8%), 88(5%), 87(base, 100%), 86(69%), 73(24%), 71(4%), 70(3%), 59(6%), 58(4%), 57(6%), 55(4%), 45(5%), 43(10%), 41(3%), 31(5%).

Anal: Calculated for $C_8H_{14}O_4$: C 55.16; H 8.10;
Found: C 55.15; H 8.30.

Reduction of N-hexylvaleramide

The product of carbon monoxide extrusion from N-hexylhexanoamide would be N-pentylhexylamine, the product of lithium aluminum hydride reduction of N-hexylvaleramide. Lithium aluminum hydride, 3.75 g, was added to a flame-dried 250 ml 3-neck flask fitted with addition funnel, mechanical stirrer, and reflux condenser. At 0°, N-hexylvaleramide, 0.7 g in 45 ml dry ether, was added dropwise with stirring. The reaction mixture was stirred overnight at room temperature. At 0°, 4.6 ml ethanol were added, followed by equal quantities of water and ether.

The reaction mixture was extracted with three 50 ml portions of ether. The ether extracts were combined, dried over anhydrous $MgSO_4$, and concentrated under vacuum. Vacuum distillation yielded 5.8 g N-pentylhexylamine at 72-77°/15 mm. Retention time on Column H at 150° was 11½ min. and on Column M at 140° was 15 minutes.

NMR: ($CDCl_3$) 0.7-1.1 δ(t, 6H, CH_3), 1.1-2.0 δ(m broad, 15H, CH_2 and N-H), 2.4-2.9 δ(t, 4H, N-CH_2).

IR: (neat) 3400, 3280 (N-H stretch), 2940, 2900, 2840, 2780, 2770 (C-H stretch), 1450 (C-N bend), 1360, 1135, 1110, 710 cm^{-1}.

Photolysis II of N-hexylhexanoamide

A solution of 2.5 g N-hexylhexanoamide in 250 ml dioxane was irradiated in a Type B photolysis for 144 hours with the Hanovia lamp. The tube was cooled to -20° in an ethanol-dry ice-water slurry. Gas IR of the vapor phase showed carbon monoxide and dioxane but no alkene (1-butene).

Photolysis III of N-hexylhexanoamide

A solution containing 1.000 g N-hexylhexanoamide and 0.4045 g hexadecane was diluted to 100 ml with spectrograde dioxane. A five ml portion of this sample was dissolved in 15 ml dioxane in a Type D photolysis vessel. The mixture was purged an hour and irradiated with 230 nm light from the monochromator. Samples were taken at 0, 4, 10 and 26 hours. Disappearance of starting material was monitored by glpc on Column M at 180°.

The results are shown in Table IX. The reaction occurred much slower with the higher (270 nm) wavelength irradiation. An undiluted sample of the 100 ml solution was also irradiated with 270 nm light for 125 hours. After glpc analysis on samples taken at 0, 24, 61, and 125 hours on Column M at 180°, no observable reaction had occurred. The ratio of amide to standard areas remained constant at between 1.70 and 1.80.

Table IX

Percent Decomposition for N-hexylhexanoamide in Dioxane

(2300Å Irradiation)

Time (Hours)	Area Amide	Area Standard	Ratio	Avg.	% Decomposition
0	278	160	1.74		
0	265	156	1.70		
0	284	162	1.75	1.74	0
0	287	163	1.76		
4	137	86	1.59		
4	122	78	1.56	1.58	9
10	180	133	1.35		
10	124	100	1.24		
10	140	114	1.22	1.27	27
10	144	113	1.27		
26	129	107	1.20		
26	137	113	1.21	1.17	33
26	107	97	1.10		

Photolysis IV of N-hexylhexanoamide

A solution of 1.4035 g N-hexylhexanoamide and 0.6560 g hexadecane in 200 ml spectrograde dioxane (0.7% solution) was irradiated in a Type A photolysis for 110 hours with a Corex filtered Hanovia lamp. Samples were taken at 0, 4, 13, 22, and 110 hours and monitored by glpc on Column M at 180°.

Time (Hours)	Area Amide	Area Standard	Ratio	Avg.	% Decomposition
0	328	221	1.53		
0	329	225	1.46	1.47	0
0	349	241	1.45		
0	346	238	1.45		
4	302	217	1.39		
4	349	249	1.40	1.39	5.4
4	316	227	1.39		
13	240	174	1.38		
13	251	182	1.38	1.37	6.9
13	307	227	1.35		
22	301	224	1.34		
22	290	219	1.32	1.34	8.9
22	321	234	1.37		
110	251	194	1.25		
110	242	190	1.27	1.29	12.3
110	253	192	1.31		

Photolysis V of N-hexylhexanoamide

A solution of 3.0521 g N-hexylhexanoamide and 1.3022 g hexadecane in 500 ml spectrograde dioxane (0.6% solution) was irradiated in a Type A photolysis conducted for 117 hours using a Vycor filtered Hanovia lamp. Samples were taken at 0, 15, 100, and 117 hours and monitored by glpc on Column M at 180°.

Time (Hours)	Area Amide	Area Standard	Ratio	Avg.	% Decomposition
0	113	69	1.63		
0	292	183	1.59	1.61	0
0	318	198	1.61		
16	193	134	1.44		
16	185	131	1.41	1.42	11.8
16	151	107	1.41		
100	220	217	1.01		
100	240	236	1.02	1.04	35.4
100	217	201	1.08		
117	222	223	1.00		
117	201	200	1.00		
117	197	203	.97	.99	38.5
117	223	228	.98		

Photolysis of N-hexylhexanoamide in Methanol

A solution of 4 g of N-hexylhexanoamide in 250 ml spectrograde methanol was irradiated in a Type A photolysis for 16 hours with the Hanovia lamp. Samples were taken at 10 and 16 hours. Glpc studies of both samples on Column M at 35° revealed no 1-hexene, and the same column at 180° showed no detectable amounts of hexanal, hexylamine, hexanoamide, N-hexylacetamide, or N-hexylpentylamine, the products of primary conventional photodecomposition.

Photolysis II of N-hexylhexanoamide in Methanol

A solution of 0.5070 g N-hexylhexanoamide, 0.1559 g hexadecane, and 210 ml spectrograde methanol was purged an hour with dry nitrogen in a Vycor tube fitted with a rubber septum. The mixture was irradiated in a Type B photolysis with 2537Å light (Source B) for 75 hours. Samples were taken at 16½, 24, 54½, and 75 hours. Glpc analysis of the samples on Column M at 180° revealed only a slight decrease in starting material concentration (Table X).

Table X

Decomposition of N-hexylhexanoamide in Methanol (2537Å)

Time (hours)	Area Amide	Area Standard	Ratio	Avg.	% Decomposition
0	91	42	2.17		
0	184	84	2.19	2.15	0
0	162	78	2.08		
0	192	89	2.16		
16½	412	193	2.13		
16½	359	168	2.14	2.14	.5
16½	388	181	2.14		
24	375	187	2.02		
24	405	198	2.05	2.04	5.1
24	397	193	2.06		
54½	363	185	1.96		
54½	414	203	2.04	2.00	7.0
54½	392	196	2.00		
75	402	201	2.00		
75	356	185	1.92	1.97	8.4
75	352	176	2.00		

Photolysis of Acetaldehyde in Dioxane

A solution of 10 g acetaldehyde and 200 ml spectro-grade dioxane was purged with nitrogen for an hour in an ice bath. A Type A photolysis was carried out at 0° C for 12 hours with the Hanovia light. Samples were taken during the course of the reaction and analyzed by glpc on Column M at 35-40°. When most of the acetaldehyde was decomposed, the reaction was stopped.

The dioxane was removed by distillation at atmospheric pressure. The residue was vacuum distilled, and four fractions were collected: A. 55-60°/17 mm, B. 90-104°/17 mm, C. 104-117°/17 mm, and D. 117-130°/17 mm. Both fractions C and D contained white solid, which was shown by coinjection on Column M to be 4 and 5.

The major product of the reaction was most abundant in fraction C. Fraction C was passed on Column N at 100°. The collected liquid had a doublet of doublets at 1.05-1.20 δ. An additional pass on Column N at 65-72° yielded two overlapping peaks, which were further purified by a third pass on the same column at the same temperature. In each liquid, the doublet of doublets was simplified to a single doublet, and the spectral data was identical with that obtained for the diastereomers of α-methyl dioxane methanol, 2 and 3.

Photolysis of Hexanal in Dioxane

A solution of 2.0 g hexanal in 200 ml spectrograde dioxane was purged with nitrogen for 45 minutes. A Type A photolysis was conducted with the Hanovia lamp for 90 minutes. Samples were taken every 30 minutes. Coinjection on Column M at 35-40° showed rapid production of acetaldehyde followed by equally rapid disappearance. Two other large peaks with shorter retention times than dioxane were identified also by coinjection as 1-butene and pentane (as expected). The results were confirmed by subsequent coinjection on Column L at 40°.

An additional 5 g hexanal were added to the reaction mixture. After another one hour nitrogen purge, the irradiation was continued for 10 hours with a Corex filtered Hanovia lamp. Glpc showed almost total starting material decomposition.

The dioxane was removed by distillation at atmospheric pressure. Vacuum distillation of the residue yielded five fractions of which two .1 g 85-110°/18 mm and .3 g 110-130°/18 mm contained $\underset{\sim}{2}$ and $\underset{\sim}{3}$. The fractions were passed on Column N at 110-112°, and the alcohols were collected. The diastereomers were separated by 2 passes on Column R at 112-115°. The spectral data confirmed that these were the dioxane alcohols $\underset{\sim}{2}$ and $\underset{\sim}{3}$.

Dimers $\underset{\sim}{4}$ and $\underset{\sim}{5}$ were also produced in the reaction and identified by coinjection.

Photolysis of Dioxane

Spectrograde dioxane, 200 ml, was purged for an hour with dry nitrogen and irradiated with the Hanovia lamp in a Type A photolysis for 200 hours. Samples were removed during the course of the reaction and glpc analysis on Column B at 140° revealed slow generation of four main product peaks at 8, 12, 15, 23, and 31 minutes respectively, as well as a small peak whose size remained relatively constant. Coinjection of authentic samples of the two alcohols, 2 and 3, and the two dimers, 4 and 5 showed these to be the four increasing product peaks. These results were confirmed by subsequent coinjection on Column H at 130°.

The dioxane was removed by distillation at atmospheric pressure. The residue was vacuum distilled to yield a fraction 0.4 ml 100-120°/17 mm greatly enriched with 2 and 3. The residue of the vacuum distillation contained mostly dimers.

The residue was redissolved in dioxane and passed on Column N at 125°. The two major product peaks were separated. The first peak, m.p. 155°, had spectral data matching the dimer, 4, obtained in the N-hexylhexanoamide photodecomposition in dioxane.

The liquid fraction containing 2 and 3 was passed on Column N at 105°. This collected liquid was split into two peaks and collected on Column R at 110°. As further confirmation of the coinjection data, the spectral data on

the two peaks matched that of authentic 2 and 3 samples. The fifth small peak was not identified and disappeared after distillation.

Photolysis of Octyloxyacetaldehyde in Dioxane

A solution of 4 g 100% octyloxyacetaldehyde in 230 ml spectrograde dioxane was purged with nitrogen for ½ hour and irradiated in a Type A photolysis for 12 hours with the Hanovia lamp. Samples were taken at 15, 30, 45, 90, 210, and 420 minutes.

Heptane was identified by coinjection on Column F and Column D at room temperature. In addition, acetaldehyde and 1-hexene were identified in the 15 minute and 30 minute samples under the same conditions. Glpc coinjection on Column F at 110° and 150° and on Column D at 105° and 150° identified 2, 3, 4, and 5 as major products.

Photolysis of N-hexylproprionamide in Dioxane

A solution of 10 g N-hexylproprionamide, 6, in 500 ml spectrograde dioxane was purged with nitrogen for an hour and irradiated for 112 hours with the Hanovia lamp. Glpc showed only slight product formation, and the irradiation was continued for 92 hours. Glpc on Column H at 105° and Column B at 110° showed the presence of 2, 3, 4, and 5 and an additional product.

The solvent was removed by distillation at atmospheric pressure. Vacuum distillation of the residue yielded fractions <110°/15 mm, 115-138°/15 mm and 140-158°/15 mm. The second fraction was passed on Column P at 105°, and the unidentified peak was repassed on Column Q at 130°. Spectra of the isolated compounds were consistent for those of the diastereomers of α-ethyl dioxane methanol, 7, and 8, listed in the next section.

Photolysis of Proprionaldehyde

A solution of 10 g freshly distilled proprionaldehyde in 220 ml spectrograde dioxane was purged with dry nitrogen for an hour in a Type A photolysis apparatus. The solution was then irradiated for 10 hours with a quartz filtered 450 W Hanovia lamp. Glpc on Column A at 120° revealed 4 major peaks, the dioxane dimers and two shorter retention time peaks. The solvent was removed by distillation at atmospheric pressure, and the residue was vacuum distilled. Four fractions were collected: 25-60°/15 mm (.5 g), 70-100°/15 mm (.6 g), 102-119°/15 mm (2.7 g), and 122-150°/15 mm (1.3 g partially solidified). The last two fractions contained most of the unidentified products at about 30% on Column R at 135°.

Glpc on Column A at 135° showed fractions 3 and 4 to contain different percentages of the two products. On Column H at 110°, however, they were not cleanly separated.

The two fractions were passed on Column P at 100-104°, and the large peaks at 30 minutes were collected in both fractions. The NMR revealed the possibility of two diastereomeric alcohols. The sample was repassed under the same conditions. The two products were separated finally by two passes on Column Q at 125° as the diastereomers of α-ethyl dioxane methanol, 7 and 8.

NMR: ($CDCl_3$) 0.7-1.2 δ(t, 3H, CH_3), 1.2-2.0 δ(m, 2H, CH_2), 3.1-3.9 δ(broad m, 9H, OH and H-C-O).

IR: (CCl_4) 3600, 3450 (O-H stretch), 2960, 2920, 2860 (C-H stretch), 1450, 1400, 1350, 1290, 1275, 1230, 1140, 1120 (dioxyl), 1095, 1050, 975, 960, 910, 875, 860, 640 cm^{-1}.

MASS SPEC: m^+/e 146(3%), 128(1.5%), 117(22%), 99(4%), 89(14%), 88(61%), 87(100%), 86(35%), 73(7%), 59(62%), 58(21%), 57(47%), 45(61%), 44(62%), 43(46%), 31(62%), 29(33%), 28(29%).

Anal: Calculated for $C_7H_{14}O_3$: C 57.51; H 9.65;

Found: C 57.70; H 9.87.

and

NMR: ($CDCl_3$) 0.7-1.2 δ(t, 3H, CH_3), 1.2-2.0 δ(m, 2H, CH_2), 3.1-3.9 δ(broad m, 9H, OH, and H-C-O).

IR: (CCl_4) 3610, 3500 (O-H stretch), 2970, 2920, 2870 (C-H stretch), 1450, 1300, 1280, 1260, 1230, 1120 (dioxyl), 1100, 1050, 970, 950, 910, 880, 640 cm^{-1}.

MASS SPEC: m^+/e 146(3.8%), 128(1.0%), 117(18.2%), 99 (1.0%), 89(11.3%), 88(60.4%), 87(100%), 86(29.6%),

73(6.9%), 59(67.9%), 58(17.0%), 57(36.5%), 45(90.6%), 44(98.1%), 43(37.7%), 41(24.5%), 31(75.5%), 29(25.8%), 28(22.0%), 27(17.6%).

Anal: Calculated for $C_7H_{14}O_3$: C 57.51; H 9.65;
Found: C 57.35; H 9.95.

Photolysis of Isobutyraldehyde

A solution of 10 g isobutyraldehyde and 220 ml spectrograde dioxane was purged with dry nitrogen for an hour in a Type A photolysis apparatus and irradiated for 10 hours with a quartz filtered 450 W Hanovia lamp. Glpc on Column H at 130° showed one main product peak with a retention time corresponding to the alcohols from previous aldehyde experiments. The solvent was removed by distillation at atmospheric pressure. Vacuum distillation of the residue yielded four fractions: <80°/5 mm (18 g); 80-98°/5 mm (1.2 g), 98-120°/5 mm (1.3 g), and 120-150°/5 mm (1.5 g). Glpc on Column H at 150° showed fractions 2 and 3 contained 30-40% product and 1 and 4 15% product with many impurities.

Fraction 2 was passed twice on Column P at 115-120° in 70-80 µl quantities, and the peaks at 30 minutes were collected. NMR showed the mixture to be predominantly one diastereomer of α-isopropyl dioxane methanol. The two diastereomers 9 and 10 were separated by two passes on Column Q at 120-135° and identified as the diastereomers of α-isopropyl dioxane methanol.

NMR: ($CDCl_3$) 0.9-1.05 δ(d J=7Hz, 6H, CH_3), 1.4-1.9 δ(m, 1H, $(CH_3)_2$-C-H), 2.3-2.6 δ(s, 1H, OH), 2.9-4.0 δ(broad m, 8H, H-C-O).

IR: (CCl_4) 3600, 3490 (O-H stretch), 2960, 2900, 2860 (C-H stretch), 1465, 1460, 1445, 1380, 1360, 1355, 1290, 1275, 1260, 1245, 1230, 1170, 1115 (dioxyl), 1100, 1080, 1070, 1055, 1030, 995, 940, 910, 895, 870, 640 cm^{-1}.

MASS SPEC: m^+/e 160(1.5%), 145(0.4%), 142(0.4%), 127 (1.1%), 117(31.1%), 99(5.6%), 89(22.6%), 88(58.9%), 87 (81.1%), 86(23.0%), 73(24.4%), 71(19.3%), 59(20,7%), 58(11.1%), 57(19.3%), 55(22.6%), 45(95.6%), 44(100%), 43(23%), 41(23%), 31(35%), 29(16.3%), 28(23%), 27(17.8%).

Anal: Calculated for $C_8H_{16}O_3$: C 59.97; H 10.07;
Found: C 59.71; H 10.12.

and

NMR: ($CDCl_3$) 0.9-1.05 δ(d J=6Hz, 6H, CH_3), 1.4-1.9 δ(m, 1H, $(CH_3)_2$-C-H), 2.15-2.35 δ(s, 1H, OH), 2.9-4.0 δ(broad m, 8H, O-C-H).

IR: (CCl_4) 3600, 3500 (O-H stretch), 2960, 2900, 2860 (C-H stretch), 1465, 1445, 1385, 1365, 1350, 1310, 1300, 1275, 1260, 1240, 1220, 1170, 1145, 1110 (dioxyl), 1100, 1065, 1025, 1000, 975, 960, 915, 895, 870, 640 cm^{-1}.

MASS SPEC: m^+/e 160(2%), 145(0.6%), 142(0.6%), 127(1.2%), 117(20.4%), 99(4.1%), 89(22.4%), 88(51%), 87(63.3%), 86(22.4%), 73(30.6%), 71(14.3%), 59(16.3%), 58(10.2%), 57(16.3%), 55(20.4%), 45(87.8%), 44(100%), 43(24.5%), 41(20.4%), 31(34.7%), 29(12.2%), 28(30.6%), 27(14.3%).

Preparation of N-hexylhexanoamide-α-d_1

Hexanoic acid was labelled in the α-position by the method of Pfeiffer and Silbert.[67] A 45 ml sample of dry diisopropylamine and 100 ml dry THF were reacted at 0° with 25.8 ml butyllithium (90% in hexane) under positive nitrogen pressure in a 500 ml 3-neck flask fitted with addition funnel, reflux condenser, and magnetic stirrer. The reaction mixture was stirred an additional half hour at 0°, and a mixture of 27 ml freshly distilled hexamethylphosphoramide, 18.7 ml freshly distilled hexanoic acid, and 45 ml dry THF were added slowly with stirring to the lithium diisopropylamide.

When the reaction had stirred for six hours at 0°, 20 ml D_2O were added dropwise, and the reaction mixture was stirred overnight. After acidification to pH 5, the reaction mixture was extracted with four 100 ml portions of anhydrous ether, and the organic phases were combined, dried, and concentrated. Vacuum distillation of the residue yielded 12.9 g (73% yield) hexanoic acid at 108-112°/15 mm, which was 42% α-d_1, labelled by NMR.

NMR: 0.6-1.1 δ(t J=5Hz, 3H, CH_3), 1.1-2.0 δ(m broad, 6H, CH_2), 2.0-2.6 δ(t J=6.5Hz, 1.58H, CH_2-C=O and CHD-C=O), 11.6 δ(s, .85-.9H, OH and OD).

The labelled acid was converted to the acid chloride by standard thionyl chloride treatment. Labelled acid (9.0g) was treated with 10.5 ml distilled thionyl chloride.

The stirred mixture was refluxed for twelve hours, and seven grams (69%) acid chloride 152-154°/760 mm were collected.

A solution of 6.5 g hexanoyl chloride (labelled) in 15 ml dry THF was added dropwise with stirring to a mixture of 5.1 g hexylamine, 30 ml 10% aqueous NaOH, and 20 ml THF. The mixture was stirred at room temperature an additional ten hours. The layers were separated, and the aqueous phase was extracted with four 75 ml portions of ether. The standard workup followed by vacuum distillation yielded 8.5 g (88% yield) labelled N-hexylhexanoamide at 135°/0.7 mm, which was shown to be 28% α-d_1 (by mass spec) and 30% α-d_1 (by NMR).

NMR: ($CDCl_3$) 0.7-1.1 δ(t J=5Hz, 6H, CH_3), 1.1-2.0 δ(m broad, 14H, CH_2), 2.0-2.4 δ(t J=6Hz, 1.7H, CH_2-C=O), 3.05-3.5 δ(q, 2H, CH_2-N), 5.6-6.5 δ(m broad, 1H, NH).

IR: (neat) 3300 (N-H stretch), 3090, 2940, 2860 (C-H stretch), 1640 (C=O stretch), 1545, 1460, 1440, 1380, 1325, 1300, 1260, 1225, 1200, 1150, 1110, 725 cm^{-1}.

MASS SPEC: molecular ion 29% d_1 (20 ev, 50/a), m^+-29 28.5% d, (70 ev, 300/a), and m^+-43 28% d_1 (70 ev, 300/a).

Photolysis of N-hexylhexanoamide-α-d_1

A solution of 3.8 g N-hexylhexanoamide-α-d_1, and 230 ml spectrograde dioxane was irradiated in a Type A photolysis for 90 hours with the Hanovia lamp. Only slight decomposition of starting material had occurred by glpc on Column A at 180°. When additional irradiation gave only slight further decomposition, a new lamp was used for an additional 48 hours.

The irradiation was stopped with about 50% starting material decomposition. The dioxane was removed by distillation at atmospheric pressure. The residue was vacuum distilled, and a fraction (1 ml) was collected at 90-130°/17 mm. This fraction was passed twice on Column Q at 110-12°. One peak was collected, which was shown by NMR to be one of the diastereomeric alcohols.

In the mass spec, the size of the 132 and 133 (P and P-1) peaks were compared in the partially labelled alcohol and in the unlabelled alcohol. The ratio of the 133 peak to the 132 peak in the labelled alcohol was 0.136 as compared with 0.092 in the unlabelled alcohol. The difference is a deuterium enrichment of 4.4%. Since the amide was 28% labelled α-d_1, (4.4/28) or 15% of the alcohol came from amide decomposition, while the remaining 85% of the alcohol arose from solvent decomposition.

NMR: ($CDCl_3$) 0.9-1.2 δ(d, 2.7H, CH_3), 2.6-2.7 δ(s, 1H, OH), 3.3-4.05 δ(m, 8H, O-C-H).

MASS SPEC: m^+/e 133(13.6%), 132(100%), and 132(P, 4%), 87(base, 100%).

Photolysis of N-hexylhexanoamide in Cyclohexane

A solution of 4 g N-hexylhexanoamide in 230 ml spectrograde cyclohexane was purged one hour with dry nitrogen, and a 0-hour sample showed only solvent and starting material by glpc on Column A at 180°. A Type A irradiation was carried out for 115 hours, and the reaction progress was monitored by glpc. After 46 hours' irradiation there was substantial starting material loss and product formation. Only slight additional product formation was observed in the subsequent 69-hour irradiation period. There were four major product peaks of retention time: 7 min., 12 min., 31 min., and 40 min. on Column A at 110°.

The solvent was removed by careful distillation at atmospheric pressure up to 85°. Vacuum distillation of the residue yielded four fractions: .1 ml A <90°/18 mm; .25 ml B 90-115°/18 mm: 1 ml C 115-135°/18 mm; and 2 ml D 135-150°/18 mm.

Fraction A contained mostly the product of retention time 7 min. Fraction A was then passed on Column Q at 110° and then repassed on the same column at 80°. The liquid collected was shown on Column A at 100° and Column H at 110° to be essentially pure. The spectral data of the liquid had in the mass spec its m^+/e 140 and large peaks

83, 82 (cyclohexyl, cyclohexenyl) and only hydrocarbon bands in the IR. The spectra matched that of N-butylcyclohexane, 11.

NMR: ($CDCl_3$) 0.7-1.1 δ(t, 3H, CH_3), 1.1-2.2 δ(m, 17H, CH_2 or ).

IR: (CCl_4) 2960, 2930, 2860, 1450, 1250, 860 cm^{-1}.

MASS SPEC: m^+/e 140(24%), 111(7.6%), 97(3.8%), 96(7.0%), 84(9.6%), 83(100%), 82(89%), 81(14%), 69(17%), 67(39%), 56(20%), 55(94%), 43(11%), 41(44%), 39(18%).

Fraction B contained the first product and the product of retention time 12 min. Fraction B was passed on Column Q at 110°, and the second peak was collected. The liquid was then repassed on the same column at 80°. The liquid collected was shown to be essentially pure on Column A at 100° and Column H at 110°. Spectral data for the second product was similar to that of the first product except the m^+/e 154. Spectra were identical to those of an authentic sample of N-pentylcyclohexane, 12.

NMR: ($CDCl_3$) 0.7-1.1 δ(t, 3H, CH_3), 1.1-2.2 δ(m, 19H, CH_2 or ).

IR: (CCl_4) 2960, 2930, 2860, 1450, 1250, 860 cm^{-1}.

MASS SPEC: m^+/e 154(29%), 152(3.2%), 125(2.8%), 97(7.1%), 96(6.0%), 84(7.9%), 83(100%), 82(75%), 81(9.9%), 67(29%), 55(75%), 43(19%), 41(54%), 39(23%).

Fraction D contained almost exclusively the product of retention time 40 minutes. The size of the fraction (2 ml) and glpc traces indicated the 40 minute product was

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the major product of the reaction. Fraction D was passed on Column Q at 110° (the largest peak was collected) and repassed on the same column at 95°. The collected product was shown to be essentially pure on Column A at 100° and Column H at 110°. Spectral data of this product was similar to the other two except in the mass spec m^+/e 166. The spectra of this compound were identical to the authentic sample of bicyclohexyl, 14.

NMR: ($CDCl_3$) 0.7-2.2 δ(m, ⟨S⟩-H axial or equitorial).

IR: (CCl_4) 2960, 2930, 2860, 1445, 1245, 860 cm^{-1}.

MASS SPEC: m^+/e 166(57%), 140(23%), 112(100%), 98(19%), 84(18%), 83(57%), 82(100%), 81(15%), 67(43%), 57(29%), 56(27%), 55(67%), 43(38%), 42(19%), 41(60%), 39(19%), 29(20%).

Fraction C contained mostly the product with a 31 minute retention time and some of the product previously identified as bicyclohexyl. Fraction C was passed on Column Q at 110°. The product was essentially pure on Column A at 100°, but Column H at 110° showed the peak to have several components. The peak was repassed on Column P at 125°. One of the products was shown by spectral data to be an alcohol m^+/e 128. Spectra were identical with an authentic sample of 1-cyclohexylethanol, 13.

NMR: ($CDCl_3$) 0.7-2.2 δ(m, 14H (doublet sticks out 0.9-1.3)), 2.4-3.2 δ(m, 1H, ⟨S⟩), 3.2-3.7 δ(m, 1H, H-C-O).

IR: (CCl_4) 3650, 3300 (O-H stretch), 2930, 2860 (C-H stretch), 1450, 1370, 1240, 1150, 1100, 900 cm^{-1}.

MASS SPEC: (Low ev) m^+/e 128(0.3%), 127(0.6%), 126 (1.6%), 113(12%), 110(33%), 95(10%), 84(20%), 83(17%), 82(100%), 67(10%), 45(50%).

Another peak was identified as methyl cyclohexyl ketone by matching spectral data with an authentic sample.

NMR: ($CDCl_3$) 0.7-2.4 δ(m, (singlet sticks out 2δ)).

IR: (CCl_4) 2930, 2860 (C-H stretch), 1705 (C=O stretch), 1450 cm^{-1}.

MASS SPEC: (Low ev) m^+/e 127(3.5%), 126(11%), 113(14%), 110(38%), 82(base), 45(70%), 95(11%), 84(16%), 83(19%), 82(100%).

Other components were present but not identified.

Photolysis II of N-hexylhexanoamide in Cyclohexane

A solution of 2 g N-hexylhexanoamide in 120 ml cyclohexane was stirred in a quartz tube fitted with a rubber septum, and purged for an hour with dry nitrogen. A Type B photolysis was carried out for 30 hours with quartz filtered Hanovia light. After 28 hours a sample was carefully taken to avoid loss of any of the vapor phase. Glpc on Column A at 115° and 185° showed product formation and starting material disappearance. The reaction mixture was irradiated two additional hours.

The photolysis tube was cooled to -80°C in a dry ice-acetone bath. At the reduced temperature a gas sample was taken, and the gas phase IR showed the presence of carbon monoxide.

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Photolysis of N-hexylhexanoamide in Cyclohexane (Quantitative)

N-hexylhexanoamide, 0.6646 g, and standards eicosane, 0.1606 g, and hexadecane, 0.0771 g were carefully weighed and quantitatively transferred with 200 ml spectrograde cyclohexane. The stirred reaction mixture was purged with nitrogen for an hour, and a Type A photolysis was performed. Samples, 0.5 ml, were taken at 0, 4, 8, and 13 hours. (Because the standards are alkanes with secondary hydrogens, they must be kept at low concentration to prevent competition with the solvent).

The samples were analyzed immediately by glpc on Column A at 110-115°. The major products, butylcyclohexane, pentylcyclohexane, and bicyclohexyl, were identified by coinjection. Quantitative determination of starting material versus eicosane and product formation versus hexadecane was performed on Column A at 185° and at 110-115° respectively.

The molar response factors at the respective temperatures for butylcyclohexane, pentylcyclohexane, and bicyclohexyl vs. hexadecane and hexadecane and hexylhexanoamide vs. eicosane are shown in Table XI.* The amount of the products produced was calculated as follows:

*The fact that the area ratio for hexadecane vs. eicosane did not change indicates that neither was present in sufficient concentration to compete in the reaction with cyclohexane (constant area ratio .49).

Table XI

Response Factors for the Products of the Photodecomposition of 1 in Cyclohexane

Compound	Weight	Moles Compound	Std.	Moles Standard	Ratio	Area Comp.	Area Std.	Area Ratio	Molar Response Factor
Butylcyclo-hexane	0.0230	1.64×10^{-4}	Hex.	1.51×10^{-4}	1.09	164	278		
						304	505		
						341	562	.59	1.85
						357	622		
						194	682		
Pentylcy-clohexane	0.0259	1.68×10^{-4}	Hex.	1.51×10^{-4}	1.11	196	278		
						364	505		
						413	562	.71	1.57
						424	622		
						475	682		
Bicyclo-hexyl	0.0232	1.40×10^{-4}	Hex.	1.51×10^{-4}	0.93	174	278		
						328	505		
						378	562	.64	1.45
						384	622		
						436	682		

Table XI (Continued)

Compound	Weight	Moles Compound	Std.	Moles Standard	Ratio	Area Comp.	Area Std.	Area Ratio	Molar Response Factor
Hexadecane	0.0771	3.41×10^{-4}	Eic.	5.7×10^{-4}	0.60	94	191		
						146	294		
						115	233	.49	1.22
						117	238		
						110	224		
N-hexyl-hexano-amide	0.6646	3.34×10^{-3}	Eic.	5.7×10^{-4}	5.86	622	204		
						725	238		
						705	224	3.09	1.90
						593	191		
						917	294		

$$(1)\quad \text{Molar response Factor} = \frac{\frac{\text{Moles Compound}}{\text{Moles Standard}}}{\frac{\text{Area Compound}}{\text{Area Standard}}}$$

$$(1a)\quad \text{Area Ratio} = \frac{\text{Area Compound}}{\text{Area Standard}}$$

$$(2)\quad \text{Molar Response Factor} = \frac{\text{Moles Compound}}{\text{Moles Standard} \times \text{Area Ratio}}$$

$$(3)\quad \text{Moles Compound} = \text{Molar Response Factor} \times \text{Area Ratio} \times \text{Moles Standard}$$

The area and moles of each product at each sample time is shown on Tables XII and XIII.

From the number of moles of product and from percentage of amide decomposition the percent yield for each product at the different times was calculated as follows:

% yield product = moles product/moles reacted amide $\times 100$.

$$\text{Moles Reacted Amide} = \frac{\frac{\text{Area Amide at } T_1}{\text{Area Standard at } T_1}}{\frac{\text{Area Amide at 0 hours}}{\text{Area Standard at 0 hours}}}$$

$$= \frac{\text{Area Ratio at } T_1}{\text{Area Ratio at 0 hours}} \times \text{Moles Amide at 0 hours}$$

$$\% \text{ Yield Product} = \frac{\text{Moles Product} \times \text{Area Ratio at 0 hours} \times 100}{\text{Moles Amide at 0 hours} \times \text{Area Ratio at } T_1}$$

Using the above equations the number of moles of decomposed amide at 4, 8, and 13 hours was 6.7×10^{-4}, 1.16×10^{-3}, and 1.5×10^{-3} respectively. The percent yield for each product at the three times is shown in Table V on page 68.

Table XII

Product to Standard Area Ratios in the Photodecomposition of 1 in Cyclohexane

Time Hours	Area Butyl-cyclohexane	Area Pentyl-cyclohexane	Area Bicyclo-hexyl	Area Standard	Butyl/ Std.	Pentyl/ Std.	Bicyclo / Std.
4	12	41	331	808	0.015	0.052	0.41
	11	40	317	773	0.014	0.052	0.41
				Avg.	0.015	0.052	0.41
8	31	92	655	825	0.036	0.11	0.79
	23	69	500	632	0.036	0.11	0.79
	29	89	627	820	0.035	0.11	0.77
				Avg.	0.036	0.11	0.78
13	41	94	780	651	0.063	0.14	1.20
	39	90	771	628	0.062	0.14	1.22
				Avg.	0.063	0.14	1.21

Table XIII

Product Yields in the Photodecomposition of 1 in Cyclohexane

Time Hours	Moles Butyl-cyclohexane	Moles Pentyl-cyclohexane	Moles Bicyclo-hexyl
4	9.5×10^{-6}	2.7×10^{-5}	2.0×10^{-4}
8	2.3×10^{-5}	5.9×10^{-5}	3.9×10^{-4}
13	3.9×10^{-5}	7.8×10^{-5}	6.0×10^{-4}

Photolysis of Acetaldehyde in Cyclohexane

Acetaldehyde (25 g) was dissolved in 500 ml spectrograde cyclohexane and purged with dry nitrogen for ½ hour. A Type A irradiation was carried out for 26 hours with the Hanovia lamp. (The photolysis vessel was cooled in an ice water bath to prevent vaporization of the acetaldehyde.) The reaction mixture contained two major products by glpc on Column H at 135°.

The solvent was distilled at atmospheric pressure. Two other fractions were collected, 185-195°/760 mm and 125-135°/10 mm. Glpc on Column H at 135° showed the first fraction contained primarily one of the peaks while the second fraction contained the other.

The high boiling fraction was passed on Column P at 125°. The largest peak was collected and repassed on the same column at the same temperature. The product was essentially pure on Column H at 135°. Spectral data matched that of 14. Coinjection of an authentic sample of bicyclohexyl and the original reaction mixture on Column A at 125° and Column H at 135° showed that the major product peak was indeed 14.

The lower boiling fraction showed bands for OH and carbonyl in the IR after being passed on Column P at 123°. The liquid was repassed on Column Q at 125°. The two peaks were subsequently identified by their spectra as 1-cyclohexylethanol and cyclohexyl methyl ketone. Spectra for these

products were given previously.

Quantitative Determination on Acetaldehyde Photoreduction in Cyclohexane

In order to put the yields of products from the previous experiment in proper perspective, quantitative determinaton of the yield of cyclohexyl methyl ketone and 1-cyclohexylethanol was carried out. A sample of 3.5 g acetaldehyde and 0.1021 g hexadecane was dissolved in 210 ml spectrograde cyclohexane in a Type A photolysis apparatus. The apparatus was immersed in ice water; the reaction mixture was purged 45 minutes with dry nitrogen, and the solution was irradiated 3½ hours with the Hanovia lamp at the reduced temperature (glpc showed nearly total starting material conversion). The final irradiated sample was analyzed on Column H at 140° at attenuation 16×10^{-10}. The results are shown in Table XIV below. An additional .2137 g hexadecane were added, making the total standard 0.3158 g.

Table XIV

Quantitative Determination on Acetaldehyde Photoreduction in Cyclohexane

Product Area	Standard Area	Ratio	Standard Wt.	Product Wt.
335	56	5.98	.102	.73
273	46	5.94	.102	.73
276	47	5.87	.102	.72
182	96	1.90	.316	.72
166	85	1.95	.316	.74
188	100	1.88	.316	.72

The combined yield of .73 g represents for alcohol and ketone (10.2 g theoretical yield) a maximum 7.2% yield of the photoreduction of acetaldehyde in cyclohexane. (The amount of alcohol produced × 13.9 represents the amount of acetaldehyde produced in the amide decomposition reactions.)

Photolysis of N-hexylproprionamide in Cyclohexane

A solution of 10 g N-hexylproprionamide in 500 ml spectrograde cyclohexane was purged with nitrogen for two hours and irradiated in a Type A photolysis for 18 hours with the Hanovia lamp. Glpc coinjection verified formation of bicyclohexyl (major), 14, 1-cyclohexylpropanol, and cyclohexyl ethyl ketone. Only slight formation of proprionamide was detected. No methylcyclohexane was detected.

Photolysis of Proprionaldehyde in Cyclohexane

A solution of 10 g freshly distilled proprionaldehyde in 200 ml spectrograde cyclohexane was purged 15 minutes with dry nitrogen and irradiated in a Type A photolysis for 20 hours with the Hanovia lamp. Additional proprionaldehyde, 10 g, was added, the mixture purged with nitrogen for an hour, and the irradiation continued for an additional 20 hours.

Glpc of the reaction mixture on Column H at room temperature showed that methylcyclohexane was a trace product. At 105° on Column H there were two major products. The solvent was removed by distillation at atmospheric pressure, the residue was vacuum distilled, and three fractions were collected: 83°/13 mm, 85-97°/13 mm, and 104-130°/13 mm.

Preparative glpc of the second fraction on Column Q at 130° gave two peaks, which were collected. The first peak was characterized by its spectra as ethyl cyclohexyl ketone (m^+/e 140). Spectral properties and glpc coinjection on Column H and Column B of an authentic sample of the ketone verified the structure assignment.

The second peak was shown by mass spec to contain two components in unequal amounts, which were separated by glpc on Column P at 130° and collected. The first peak was characterized by comparison with an authentic sample of 1-cyclohexylpropanol. The second peak and major product of the reaction was characterized by its spectra (m^+/e 166) as 14.

Solvent Effects on Type II Photodecomposition of N-hexylhexanoamide

The following solutions were prepared with eicosane and N-hexylhexanoamide then diluted to 25 ml with the solvent indicated.

Sample	Eicosane	N-hexylhexanoamide	Solvent
1	0.0136	0.0502	cyclohexane
2	0.0135	0.0505	diisopropyl ether
3	0.0136	0.0502	dioxane
4	0.0137	0.0503	acetonitrile
5	0.0137	0.0504	methanol

Each solution was added to two quartz tubes in five ml aliquots. The tubes were then fitted with rubber septa and degassed five minutes with dry nitrogen.

The irradiation was carried out in a merry-go-round apparatus with a quartz-filtered Hanovia 450 W mercury vapor lamp. Samples were taken with nitrogen-purged syringes at 4, 10, and 21 hours. The important retention times were 51 min. (N-hexylhexanoamide), 31 min. (eicosane), and 17 and 19 min. respectively for hexanoamide and N-hexylacetamide (the expected products of Type II decomposition). The data showing percentage decomposition versus time are plotted in Figure 3.

The method for determination of response factors for hexanoamide and hexylacetamide is shown below. The conver-

sion factor for converting response factors from hexadecane to eicosane as standard is also shown.

Eq. 1 $$\frac{\frac{\text{moles AI}}{\text{moles Eicosane}}}{\frac{\text{Area AI}}{\text{Area Eicosane}}} = RF_1$$

Eq. 2 $$\frac{\frac{\text{moles Eicosane}}{\text{moles Hexadecane}}}{\frac{\text{Area Eicosane}}{\text{Area Hexadecane}}} = RF_2$$

Eq. 3 $$\frac{\frac{\text{moles } A_2}{\text{moles Hexadecane}}}{\frac{\text{Area } A_2}{\text{Area Hexadecane}}} = RF_3$$

From table: $RF_1 = 1.7$, $RF_2 = .82$ and $RF_3 = 3.4$

Solving for moles A_2 (hexanoamide and hexylacetamide)

Eq. 4 $$\text{moles } A_2 = \frac{RF_3 \times \text{moles Hexadecane} \times \text{Area } A_2}{\text{Area Hexadecane}}$$

All terms are known except moles Hexadecane/Area Hexadecane. Solving for moles Hexadecane/Area Hexadecane in Eq. 2 yields:

$$\text{Eq. 5} \qquad \frac{\text{moles Hexadecane}}{\text{Area Hexadecane}} = \frac{\text{moles Eicosane}}{\text{Area Eicosane} \times RF_2}$$

Substitution of Eq. 5 into Eq. 4 gives an expression for moles product where all terms are known.

$$\text{Eq. 6} \qquad \text{moles } A_2 = \frac{RF_3 \times \text{Area } A_2 \times \text{moles Eicosane}}{\text{Area Eicosane} \times RF_2}$$

Table XV

Molar Response Factors for Products from Type II Photodecomposition of N-hexylhexanoamide (Hexadecane)

Compound	Moles Compound $\times 10^4$	Moles Standard $\times 10^4$	Ratio	Cmpd.	Std.	Ratio	Avg.	M.R.F.*
N-hexyl-hexano-amide	25.5	6.90	3.69	91	42	2.2	2.2	1.7
	25.5	6.90		184	84	2.2		
	25.5	6.90		162	78	2.1		
	25.5	6.90		192	89	2.2		
Hexano-amide	6.92	2.24	3.09	99	125	.79	.80	3.9
	6.92	2.24		84	105	.80		
	6.92	2.24		110	138	.80		
	6.92	2.24		93	116	.80		
	6.92	2.24		99	124	.80		
N-hexyl-acet-amide	6.90	2.35	2.94	144	141	1.02	1.04	2.8
	6.90	2.35		136	130	1.04		
	6.90	2.35		117	111	1.05		
	6.90	2.35		132	130	1.02		
	6.90	2.35		137	131	1.05		
Eicosane	5.70	3.41	1.67	224	110	2.04	2.03	.82
	5.70	3.41		238	117	2.03		
	5.70	3.41		294	146	2.01		
	5.70	3.41		233	115	2.03		

*M.R.F. = Molar Response Factor

Table XVI

Solvent Effects on the Photodecomposition of N-hexylhexanoamide

Sample	Tube	Time (hours)	Std.	Amide	Ratio	Average	%Decomposition
1	A	0	100	276	2.76	2.75	0
1	B	0	335	910	2.75		
1	A	4	700	935	1.34	1.36	50.6
1	B	4	549	754	1.37		
1	A	10	423	303	.72	.74	73.1
1	B	10	336	257	.76		
1	A	21	189	58	.31	.30	89.1
1	B	21	449	130	.29		
2	A	0	350	949	2.71	2.72	0
2	B	0	340	925	2.72		
2	A	4	367	842	2.29	2.29	15.8
2	B	4	172	393	2.29		
2	A	10	462	882	1.91	1.92	29.5
2	B	10	436	840	1.93		
2	A	21	202	330	1.63	1.63	40.1
2	B	21	512	835	1.63		
3	A	0	477	1320	2.77	2.76	0
3	B	0	289	796	2.75		
3	A	4	343	864	2.52	2.53	8.3
3	B	4	196	497	2.54		
3	A	10	425	810	1.91	1.92	30.5

Table XVI (Continued)

Sample	Tube	Time (hours)	Std.	Amide	Ratio	Average	% Decomposition
3	B	10	485	930	1.92		
3	A	21	368	448	1.22	..23	55.4
3	B	21	450	560	1.24		
4	A	0	267	730	2.73	2.74	0
4	B	0	335	920	2.75		
4	A	4	278	473	1.70	1.69	38.3
4	B	4	326	549	1.68		
4	A	10	221	275	1.24	1.22	55.5
4	B	10	285	343	1.20		
4	A	21	362	284	.78	.78	71.6
4	B	21	311	239	.77		
5	A	0	177	485	2.74	2.76	0
5	B	0	285	792	2.78		
5	A	4	276	605	2.19	2.16	21.7
5	B	4	533	1138	2.14		
5	A	10	431	670	1.55	1.55	43.8
5	B	10	615	958	1.56		
5	A	21	227	209	.92	.93	66.6
5	B	21	257	240	.93		

Table XVII

Solvent Effects on Percentage Type II Reactions

Sample	Tube	Time (hours)	Area Product	Area Standard	Ratio	Average	Moles Prod. $\times 10^{-6}$	Moles Starting Mat'l. Decomp. $\times 10^{-5}$	% Yield Type II Product
1	A	4	16	700	.022	.022	3.5	12.6	2.8
1	B	4	12	549	.022				
1	A	10	23	423	.054	.052	8.3	18.4	4.5
1	B	10	17	336	.050				
1	A	21	11	189	.058	.058	9.2	22.5	4.1
1	B	21	26	449	.058				
2	A	4	2	367	.0054	.0056	.89	4.0	2.2
2	B	4	1	172	.0058				
2	A	10	11	462	.024	.024	3.8	7.5	5.0
2	B	10	10	436	.023				
2	A	21	6	202	.030	.030	4.7	10.0	4.7
2	B	21	15	512	.029				

Table XVII (Continued)

Sample	Tube	Time (hours)	Area Product	Area Standard	Ratio	Average	Moles Prod. $\times 10^{-6}$	Moles Starting Mat'l. Decomp. $\times 10^{-5}$	% Yield Type II Product
3	A	4	0	343	0.	0.	0.	2.09	0.
3	B	4	0	196	0.				
3	A	10	17	425	.040	.040	6.4	7.7	8.3
3	B	10	19	485	.031				
3	A	21	22	368	.060	.059	9.5	14.0	6.8
3	B	21	26	450	.058				
4	A	4	4	278	.014	.015	2.4	9.7	2.5
4	B	4	5	326	.015				
4	A	10	10	221	.045	.042	6.7	14.0	4.8
4	B	10	11	285	.039				
4	A	21	16	362	.044	.043	6.9	18.0	3.8
4	B	21	13	311	.042				

Table XVII (Continued)

Sample	Tube	Time (hours)	Area Product	Area Standard	Ratio	Average	Moles Prod. $\times 10^{-6}$	Moles Starting Mat'l. Decomp. $\times 10^{-5}$	% Yield Type II Product
5	A	4	0	276	0.				
5	B	4	0	533	0.	0.	0.	5.5	0.
5	A	10	5	431	.012				
5	B	10	5	615	.010	.011	1.8	11.0	1.6
5	A	21	4	227	.018				
5	B	21	4	257	.016	.017	2.7	17.0	1.6

Photolysis of N-hexylacetamide

A solution of 4 g N-hexylacetamide in 200 ml spectrograde dioxane was irradiated under Type A conditions for 145 hours with the Hanovia lamp. Samples were taken with nitrogen purged needles, and before the lamps were started again, the reaction mixture was purged with nitrogen an additional 15 minutes.

The reaction progress was followed by glpc on Column M at 180°. The products were identified by coinjection on Column M at 110° and 150°, on Column G at 110° and 180°. The retention times for the diastereomeric alcohols, 2 and 3, were 5½ minutes on Column M at 110° and 6 minutes on Column G at 110°. The retention times for the dimers, 4 and 5, were 7½ and 9 minutes on Column G at 150° and 6 and 6½ minutes on Column M at 150°.

Competitive Photolysis of N-hexylacetamide vs. N-hexylhexanoamide

N-hexylacetamide, 0.7016 g, hexadecane, 0.7023 g, and N-hexylhexanoamide, 2.0575 g, were stirred an hour in 210 ml spectrograde dioxane then purged with dry nitrogen for two hours. A Type A irradiation was conducted for 12 hours. Samples were taken at 0, 4, 8, and 12 hours.

It was determined by the following logic that if the ratio of N-hexylacetamide/standard to N-hexylhexanoamide/standard remained constant, the two amides decomposed at the

same rate and that N-hexylacetamide was then not an intermediate of N-hexylhexanoamide decomposition.

$$\frac{\dfrac{\text{Area N-hexylacetamide } t_1}{\text{Area Standard } t_1}}{\dfrac{\text{Area N-hexylhexanoamide } t_1}{\text{Area Standard } t_1}} = K = \frac{\dfrac{\text{Area N-hexylacetamide } t_0}{\text{Area Standard } t_0}}{\dfrac{\text{Area N-hexylhexanoamide } t_0}{\text{Area Standard } t_0}}$$

Cancelling like terms yields:

$$\frac{\text{Area N-hexylacetamide } t_1}{\text{Area N-hexylhexanoamide } t_1} = \frac{\text{Area N-hexylacetamide } t_0}{\text{Area N-hexylhexanoamide } t_0}$$

The fact that this equality is established insures that any loss from N-hexylhexanoamide at any time will be accompanied by a similar loss from N-hexylacetamide.

The reaction mixture was analyzed on Column M at 180°. The results are given in Table XVIII and showed that the decomposition rate, i.e. the ratio, was fairly constant as shown:

At 4 hours	At 8 hours	At 12 hours
$\frac{\text{N-hexylacetamide}}{\text{Standard}} = .462$	$\frac{\text{N-hexylacetamide}}{\text{Standard}} = .427$	$\frac{\text{N-hexylacetamide}}{\text{Standard}} = .348$
$\frac{\text{N-hexylhexanoamide}}{\text{Standard}} = 1.85$	$\frac{\text{N-hexylhexanoamide}}{\text{Standard}} = 1.72$	$\frac{\text{N-hexylhexanoamide}}{\text{Standard}} = 1.52$
$\frac{\text{N-hexylacetamide}}{\text{N-hexylhexanoamide}} = .25$	$\frac{\text{N-hexylacetamide}}{\text{N-hexylhexanoamide}} = .25$	$\frac{\text{N-hexylacetamide}}{\text{N-hexylhexanoamide}} = .25$

These results show that N-hexylacetamide is probably not an important intermediate of N-hexylhexanoamide decomposition.

Table XVIII

Competitive Photodecomposition of 1 and N-hexylacetamide

Time (Hours)	Area Standard	Area N-hexyl-hexanoamide	Ratio	Avg.	Area N-hexyl-acetamide	Ratio	Average
0	144	324	2.25		85	.59	
0	152	334	2.20		95	.62	
0	147	328	2.23	2.23	87	.59	.59
0	178	396	2.22		107	.60	
0	123	278	2.26		69	.56	
4	114	200	1.75		49	.43	
4	67	120	1.79	1.85	27	.40	.46
4	129	240	1.86		67	.52	
4	113	225	1.99		54	.48	
8	134	229	1.71		62	.46	
8	129	225	1.74	1.72	56	.43	.43
8	128	215	1.68		55	.43	
8	132	230	1.74		51	.39	
12	139	220	1.58		55	.40	
12	143	217	1.52	1.52	51	.36	.38
12	161	236	1.47		61	.38	
12	163	247	1.52		64	.39	

Competitive Photodecomposition of N-hexylhexanoamide vs. 1-Hexene in Dioxane

Cyclohexane (0.8698 g), 1-hexene (1.0682 g), hexadecane (1.0435 g), and N-hexylhexanoamide (3.5013 g) were dissolved in 210 ml spectrograde dioxane and purged for 45 minutes with dry nitrogen. A Type A photolysis was carried out for 98 hours with the Hanovia light. Samples were taken at 0, 6, 17, 40, 65.5, and 98 hours and immediately analyzed by glpc. Disappearance of 1-hexene vs. cyclohexane was monitored on Column I at 60°. Decomposition of amide and production of product vs. hexadecane were monitored on Column M at 160°, and the results were shown in Tables XIX and XX.

The rates of decomposition for 1-hexene and N-hexylhexanoamide are roughly shown in Figure 4, which is a graph of the ratio of each vs. the appropriate standard. The rates of decomposition should parallel the decrease in ratio. Accordingly the 1-hexene concentration decreased very rapidly to an optimum level, and the rate of disappearance leveled off. The amide decomposed at a constant slower rate.

Three major products besides the diastereomeric alcohols, 2 and 3, were formed, the dimers and an additional product of dioxane and 1-hexene (characterized later). The rate of production for the dimers was low but constant, which paralleled the disappearance of amide. The rate of production of the addition product was initially high but

Table XIX

Rate of Photodecomposition of 1-hexene vs. N-hexylhexanoamide

Time (Hrs.)	Area 1-hexene	Area Std.	Ratio	Avg.	% Decom-position	Area Amide	Area Std.	Ratio	Avg.	% Decom-position
0	170	180	.94			699	345	1.94		
0	156	162	.96			684	351	1.95		
0	159	165	.96	.96	0	534	278	1.92	1.94	0
0	182	183	.94			605	312	1.94		
0	161	167	.96			640	330	1.94		
6	53	64	.82			330	625	1.89		
6	97	116	.83	.83	14	362	677	1.88	1.89	2.6
6	100	120	.83							
17	104	184	.57			598	324	1.84		
17	110	194	.57	.57	41	630	339	1.85	1.84	5.2
17	60	104	.58			632	343	1.84		

Table XIX (Continued)

Time (Hrs.)	Area 1-hexene	Area Std.	Ratio	Avg.	% Decomposition	Area Amide	Area Std.	Ratio	Avg.	% Decomposition
40	38	87	.44			473	275	1.72		
40	108	251	.43	.43	55	588	351	1.68	1.69	13
40	107	246	.43			587	355	1.65		
40						502	295	1.70		
65.5	68	235	.29			352	248	1.42		
65.5	73	252	.29	.29	70	393	273	1.44	1.43	26
65.5	70	242	.29			492	342	1.44		
98	49	210	.23			460	357	1.29		
98	65	265	.24			405	304	1.33		
98	56	229	.24	.24	75	339	247	1.32	1.30	33
98						484	380	1.27		

Table XX

Product Production for the Photolysis of 1-hexene vs. 1

Time (Hrs.)	Area Standard	Area Addition Product	Ratio	Avg.	Area Dimers	Ratio	Avg.
0	-	-	-		-	-	-
6	330	12	.036	.036	-	-	-
6	362	13	.036		-	-	
17	324	34	.10		3	.009	
17	339	37	.11	.11	3	.009	.009
17	343	39	.11		3	.009	
40	275	40	.15		5	.018	
40	351	53	.15	.15	6	.017	.018
40	355	52	.15		6	.017	
65.5	248	42	.17		8	.032	
65.5	273	45	.17	.17	9	.033	.033
65.5	342	56	.16		12	.035	
98	357	64	.18		17	.048	
98	304	56	.18	.18	15	.049	0.048
98	257	48	.19		12	.047	
98	380	68	.18		19	.050	

tapered off, as would be expected when the 1-hexene concentration was lowered.

Distillation of the solvent followed by a vacuum distillation yielded at 110-114°/7 mm 1.5 g of a fraction, which contained mostly the addition product of 1-hexene and dioxane. The fraction was passed on Column O at 110°. The NMR showed dioxyl and alkyl regions while the IR showed no alcohol or carbonyl. The molecular weight by mass spec was 172, and another important fragment was 87 (dioxyl). The data tentatively identified the product as 1-hexyldioxane, 15.

NMR: ($CDCl_3$) 0.65-1.15 δ (t, 3H, CH_3), 1.2-2.4 δ (m, 10H, CH_2), 3.2-4.0 δ (m, 7H, H-C-O).

IR: ($CDCl_3$) 2970, 2925, 2860 (C-H stretch), 1665, 1460, 1370, 1275, 1115 (dioxyl), 1100, 860-900, 710-790 cm^{-1}.

MASS SPEC: m^+/e 172(22%), 97(18%), 96(12%), 87(100%), 86(16%), 85(10%), 59(14%), 45(10%), 44(13%), 43(15%), 41(22%), 32(16%), 31(14%), 29(17%), 28(42%), 27(15%).

Photolysis of 1-hexene in Dioxane

An authentic sample of 1-hexyldioxane was prepared by the method of Elad,[69] which projected five percent yield for the photochemical addition of alkene to dioxane. A sample of 1-hexene, 17 g, was dissolved in 210 ml dioxane. After the reaction mixture was purged an hour with dry nitrogen, a Type A photolysis was carried out for 38 hours with the

Hanovia lamp.

The solvent was distilled off and vacuum distillation yielded 1 g 100-117°/5 mm of mostly one component. The liquid was passed on Column O at 115°. The spectral and analytical data identified the product as 1-hexyldioxane and confirmed the identity of the addition product in the previous experiment.

NMR: ($CDCl_3$) 0.7-1.15 δ (t, 3H, CH_3), 1.2-2.4 δ (m, 10H, CH_2), 3.2-4.0 δ (m, 7H, H-C-O).

IR: ($CDCl_3$) 2970, 2930, 2860 (C-H stretch), 1670, 1460, 1375, 1275, 1115 (dioxyl), 1100, 860-900, 710-790 cm^{-1}.

MASS SPEC: m^+/e 172(21%), 115(6.5%), 113(9.1%), 97(18%), 96(13%), 88(6.5%), 87(100%), 85(16%), 85(39%), 81(65%), 70(5.2%), 69(13%), 68(5.2%), 67(7.8%), 66(3.9%), 59(14%), 58(7.8%), 57(7.8%), 56(3.1%), 55(10%), 45(10%), 44(13%), 43(14%), 42(8.9%), 41(23%), 32(16%), 31(14%), 29(17%), 28(42%), 27(14%).

Anal: Calculated for $C_{10}H_{20}O_2$: C 69.73; H 11.69;
Found: C 69.77; H 11.46.

Photolysis of N-hexyloctanoamide

A solution of 10 g N-hexyloctanoamide in 500 ml dioxane was irradiated in a Type A photolysis for 250 hours. Samples were taken at 0, 24, 48, 72, 108, and 250 hours and immediately analyzed by glpc.

Analysis by coinjection of authentic samples showed the presence of 1-hexene and heptane on Column M at 35° (6½ and 14 minutes respectively). The results were confirmed on Column L at 35°.

There were four main products between the solvent and the starting material on Column M at 180°. All four increased as the irradiation progressed. The diastereomeric alcohols, 2 and 3, were identified by coinjection of an authentic sample on Column M at 110° (retention time 5½ min.) and on Column G at 140° (retention time 4½ min.). The dimers, 4 and 5, were also identified by coinjection of authentic samples on Column M at 150° (retention times 6 and 6½ min.) and on Column G at 150° (retention times 7½ and 9 min.). The fourth product was neither N-hexylacetamide nor octanoamide, the expected products of initial Type II cleavage.

The solvent was removed by distillation at atmospheric pressure. The residue was vacuum distilled and a small fraction was collected, .2 g 100-12°/5 mm. The liquid was passed on Column N at 110°, and the second major component was collected. The NMR, IR, and glpc retention times of the collected peak matched that of 1-hexyldioxane, 15.

Photolysis of N-methylhexanoamide

A solution of 3.0 g N-methylhexanoamide in 200 ml dioxane was irradiated in a Type A photolysis for 112 hours with the Hanovia lamp. Samples were taken at 0, 6, 17, 57, and 112 hours. Glpc analysis on Column M at 110° and 150° and Column G at 150° showed that alcohols 2 and 3, and dimers 4 and 5 were present as the major products. N-methylacetamide did not appear as a major product.

Photolysis II of N-methylhexanoamide

A solution of 2.5g N-methylhexanoamide in 210 ml dioxane in a quartz tube stoppered with a rubber septum was irradiated in a Type B photolysis for 75 hours with the Hanovia lamp. The photolysis vessel was cooled in a dry ice-acetone bath. Gas IR of the vapor phase after 75 hours' irradiation showed carbon monoxide and no substantial quantity of the initial Type I product, methylamine.

Photolysis of N-hexyl-2-methylvaleramide

A solution of 2 g N-hexyl-2-methylvaleramide in 200 ml spectrograde dioxane was purged with nitrogen for an hour and irradiated in a Type A photolysis for 71 hours with the Hanovia lamp. Glpc analysis of the reaction mixture on Column H at 110° showed production of seven products.

The products retention time 27 and 32½ min. on Column M at 110° (Column C at 150°- retention times 17 and 24 minutes) were identified by coinjection as 4 and 5. Under the same glpc conditions 2 and 3 were identified by coinjection. The products at retention time 10 minutes on Column H at 110° were verified as 7 and 8 by coinjection on Column C at 150° which showed peaks at 9 and 14 minutes.

Photolysis Products of Alkyl Amides

Nitrogen purged 2% solutions of the amides in spectrograde dioxane were irradiated in Type A photolysis for periods varying from 75-140 hours with the Hanovia lamp. The following amides were irradiated with the observed results: N-ethylhexanoamide, N-butylhexanoamide, N-hexylbutyramide, N-2-heptylhexanoamide, N-2-heptylacetamide, N-isobutylhexanoamide, N-hexyl-4-methylvaleramide, and N-octylhexanoamide. The products 2, 3, 4, and 5 were detected by glpc coinjection on Column B at 105° and 140° and on Column H at 110° and 150°.

Determination of Carbon Monoxide and Volatile Products for N-alkylamides Photodecomposition

A nitrogen purged solution of 2.5 g amide in 210 ml spectrograde dioxane* was irradiated in a Type B photolysis for 50-125 hours with the Hanovia lamp. The sealed reaction mixture was cooled in a dry ice-acetone bath. Gas IR of the vapor phase showed the presence of carbon monoxide and dioxane in all cases but no alkenes. This procedure was conducted for N-hexylacetamide, N-hexyloctanoamide, N-hexylbutyramide, N-hexylproprionamide, N-octylhexanoamide, N-ethylhexanoamide, N-hexyl-4-phenylbutyramide, β-phenylethylhexanoamide, N,N-dihexylhexanoamide, N-methyl-N-butylhexanoamide, N-hexyl-2-methylvaleramide, N-hexyl-4-methylvaleramide, N-isobutylhexanoamide, hexanoamide, butyramide, octanoamide, proprionamide, and 4-phenylbutyramide.

*Also N-hexylhexanoamide and N-propylhexanoamide in cyclohexane.

Relative Photoreactivity of the γ-Position in Amides

The following solutions were prepared:

Amide	Wt. Amide	Wt. Std. (eicosane)	Sample
N-isobutylhexano-amide	0.0490	0.0254	1
N-hexyl-4-methyl-valeramide	0.0548	0.0254	2
N-hexylhexanoamide	0.0553	0.0254	3

The samples were then diluted to 25 ml with sodium-dried t-butanol. Three 4 ml samples of each solution were added to the freeze-pump-thaw vessel described previously. After 5 freeze-pump-thaw cycles the 9 tubes were sealed and equally spaced in the merry-go-round apparatus. The samples were then irradiated with the Hanovia lamp for 129.5 min. The tubes were opened, and the samples were analyzed on Column C at 170°. The results are shown in Table XXI.

The ratio of amide/standard after irradiation to amide/standard at 0 hours gives the % decomposition.* Type II products were not produced by any of the three amides. (Changing to a tertiary site on the carbonyl or nitrogen side did not increase the Type II although the incipient radical would be more stable.) The rate of reaction as seen by the percentage decompositions shown in Table XXI was not altered by changing the γ-position from secondary to tertiary.

*Ratio T_1/T_0 is .895 for N-isobutylhexanoamide, .894 for N-hexyl-4-methylvaleramide, and .894 for N-hexylhexanoamide.

Table XXI

Relative Photoreactivity of the γ-Position in Amides

Sample	Tube	Time (Hrs.)	Area Amide	Area Standard	Ratio	Avg.
1	0	0	835	742	1.13	
1	0	0	952	840	1.13	
1	0	0	831	732	1.14	1.14
1	0	0	872	764	1.14	
1	0	0	937	820	1.14	
2	0	0	656	407	1.61	
2	0	0	1757	1105	1.59	1.60
2	0	0	1965	1231	1.60	
2	0	0	1854	1162	1.60	
3	0	0	1725	1078	1.60	
3	0	0	2029	1270	1.60	1.60
3	0	0	2054	1282	1.60	
3	0	0	1969	1231	1.60	
1	A	2.16	794	775	1.02	
1	B	2.16	694	692	1.00	1.02
1	C	2.16	551	531	1.03	
2	A	2.16	1169	816	1.43	
2	B	2.16	658	461	1.42	1.43
2	C	2.16	1680	1175	1.43	
3	A	2.16	733	510	1.44	
3	B	2.16	1925	1342	1.43	1.43
3	C	2.16	1818	1273	1.43	

Photolysis of Hexanoamide

A solution of 2 g hexanoamide in 200 ml spectrograde dioxane was irradiated in a Type A photolysis for 90 hours. Samples were taken at irregular intervals, at 0 hours, and when the irradiation was completed.

The progress of the reaction was monitored by glpc on Column M at 150°. Products were identified by coinjection with authentic samples. The products identified were the alcohols 2 and 3 and the dimers 4 and 5. Retention times and column conditions were identical to those used in the photolysis of N-hexylacetamide (page 293).

Photolysis of Octanoamide

A solution 1.9 g octanoamide in 200 ml spectrograde dioxane was irradiated in a Type A photolysis for 80 hours with the Hanovia lamp. The alcohols 2 and 3 were identified by coinjection on Column M at 110° and Column G at 170° at 5 min. and 3 min. respectively. The dimers 4 and 5 were identified by coinjection on Column M at 160° at 5 min. and 6 min. and on Column G at 180° at 6 min. and 7 min. Coinjection of 1-hexene with a 5-hour sample on Column M at 65° showed that the expected Type II product was not a major low boiling component.

The reaction mixture was worked up in the general fashion. A fraction was collected, b.p. 105-120°/760 mm (0.5 g). This fraction was passed on Column at 80°. It had the

following spectral data and was tentatively identified as 15.

Photolysis of Butyramide

A solution of 2 g butyramide in 210 ml spectrograde dioxane was irradiated in a Type A photolysis for 120 hours with the Hanovia lamp. The major products were the alcohols, 2 and 3, and the dimers, 4 and 5, which were identified by coinjection under the conditions given previously. An additional product was characterized by its spectra as ethyldioxane.

NMR: ($CDCl_3$) 0.7-1.15 δ(t, 3H, CH_3), 1.15-2.7 δ(quartet of doublets, 2H, CH_2), 3.1-3.95 δ(m, 7H, H-C-O).

IR: (CCl_4) 2970, 2920, 2870, (C-H stretch), 1470, 1385, 1250, 1115 (dioxyl), 1100, 860-940, 650-800 cm^{-1}.

MASS SPEC: m^+/e 116(81%), 88(18%), 87(91%), 86(18%), 73(3.7%), 71(7.4%), 59(67%), 58(78%), 57(100%), 56(26%), 45(46%), 44(15%), 43(35%), 41(33%), 31(41%), 29(39%), 28(65%).

Photolysis of 4-phenylbutyramide

A solution of 2 g 4-phenylbutyramide in 200 ml spectrograde dioxane was purged 1½ hours with dry nitrogen and irradiated for 56 hours in a Type A photolysis. Column G at 125° showed only negligible amounts of styrene and no detectable propylbenzene or α-tetralone, the product of photochemical ring closure of 4-phenylbutyraldehyde. Coinjection of authentic samples of 2 and 3 on Column M at 115° (5 min.) and Column G (6 min.) showed the alcohols were a major product. Coinjection of the dimers on Column M at 150° (7½ and 9 min.) and Column G at 180° (6 and 7 min.) proved that these were the other major products.

Photolysis of N,N-dihexylhexanoamide

A solution of 4 g N,N-dihexylhexanoamide in 210 ml spectrograde dioxane was purged with nitrogen for an hour and irradiated in a Type A photolysis for 68 hours with the Hanovia lamp. Reaction progress was monitored by glpc on Column H at 200°. Samples were taken at 13, 20, 31, and 68 hours and immediately analyzed. Glpc again showed multiple products.

Three volatile products were identified by coinjection at low temperature. On Column H at 35-40° and Column M at 40°, 1-butene was identified at 3 minutes and 2 minutes respectively. Pentane was identified under the same conditions on Column H at 5 minutes and Column M at 2½ minutes.

Identification of 1-hexene was made on Column H at 9 minutes (6 minutes at 40°) and Column M at 4 minutes.

Coinjection on Column H at 200° at 8 minutes showed the presence of N,N-dihexylacetamide and on Column C at 200° at 36 minutes. N-hexylhexanoamide was identified by coinjection on Column H at 200° at 12 minutes and on Column C at 200° at 47 minutes. N-hexylacetamide was also shown to be a major product by coinjection (Column C at 200° at 19 min.).

The dimers 4 and 5 and alcohols 2 and 3 were again identified. N,N-dihexylamine (an initial Type I product) was identified by coinjection on Column H at 200° at 4 minutes and on Column M at 140° at 19 minutes.

Photolysis of N-methyl-N-butylhexanoamide

A solution of 4 g N-methyl-N-butylhexanoamide in 210 ml spectrograde dioxane was purged with nitrogen for an hour and irradiated in a Type A photolysis for 48 hours with the Hanovia lamp. Reaction progress was monitored by glpc on Column H at 200°. Samples were taken at 9, 18, 31, and 48 hours. More than eleven products with retention times greater than the solvent were formed as shown on Column H at 150°.

Immediately after the 18 hour sample was taken, two volatile products were verified by coinjection at low temperature. On Column H at 35-40° and on Column M at 40°, 1-butene was identified at 2½ minutes and 2 minutes respec-

tively. Pentane was shown to be present on Column H at 35-40° at 5 minutes and on Column M at 40° at 3 minutes. (Although retention times were short, column conditions were such to give good separation of analogous short chained alkanes and alkenes.)

Several of the longer retention time products were also identified by coinjection. N-butylhexanoamide was identified at 28 minutes on Column H at 150°, and the results were verified on Column C at 200°. Coinjection under the same conditions showed the presence of N-methylhexanoamide on Column H and Column C at 9½ and 16 minutes respectively. N-methyl-N-butylacetamide under the same conditions appeared at 8 minutes on Column H, and the results were verified on Column C.

Dimers $\underset{\sim}{4}$ and $\underset{\sim}{5}$ and alcohols $\underset{\sim}{2}$ and $\underset{\sim}{3}$ were present. The most significant result of the experiment was verification of an initial Type I product, N-methyl-N-butylamine at five minutes on Column H at 150° and at seven minutes on Column M at 140°.

Preparation of Unsymmetrical Anilide Imides

A. Preparation of N-acetylbutyranilide

N-acetylbutyranilide was prepared by a method analogous to that of Heyns and Pyrus.[74] In a 500 ml 3-neck flask fitted with magnetic stirrer, addition funnel, and reflux condenser, 2.4 g magnesium were stirred with 75 ml anhydrous ether. Ethyl bromide, 11 g, in 10 ml anhydrous ether were added slowly. When the addition was completed, the reaction mixture was stirred an additional 45 minutes at room temperature. The flask was cooled in an ice bath, and 12 g acetanilide were added slowly with stirring. When this addition was completed, the reaction mixture was recooled in an ice bath, and 10 g freshly distilled butyryl chloride were added dropwise. The reaction mixture was stirred at reduced temperature for ½ hour and heated in a warm water bath an additional 3½ hours. (Heavy salt deposits made stirring difficult.)

The mixture was recooled, and 50 ml water were added slowly. The layers were separated, and the aqueous phase was extracted with three 75 ml portions of ether. The organic extracts were combined and washed with sodium carbonate solution to remove excess amide. The organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was vacuum distilled, and the fraction 165-70°/14 mm (18 g) was collected. This fraction was redistilled and four fractions were collected: <95°/.3 mm,

95-105°/.3 mm, 105-113°/.5 mm, and 113-118°/.6 mm. The second fraction contained almost pure N-acetylbutyranilide. Further purification was attained by passing the second fraction on Column P at 160-165°. The impurity removed was N,N-diacetylaniline.

NMR: ($CDCl_3$) 0.7-1.1 δ (t J=6.5Hz, 3H, CH_3), 1.3-1.9 δ (m, 2H, CH_2), 2.2-2.7 δ (s+t, 5H, CH_3-C=O and CH_2-C=O), 6.9-7.75 δ (m, 5H, phenyl).

IR: (CCl_4) 3080, 3050, 2970, 2940, 2880 (C-H stretch) 1710 (C=O stretch), 1600, 1530, 1525, 1490, 1440, 1370, 1310, 1285, 1280, 1240, 1210, 1140, 1095, 1075, 1035, 1020, 920, 900, 690 (monosubstituted benzene) cm^{-1}.

MASS SPEC: m^+/e 206(P+1, 1.1%), 205(P, 4.8%), 164(1.7%), 163(14%), 162(0.8%), 148(2.3%), 136(6.7%), 135(63%), 134(2.3%), 94(9.7%), 93(100%), 92(4.6%), 91(2.9%), 77 (3.4%), 71(9.7%), 66(4.6%), 65(5.5%), 51(4.2%), 43(35%), 41(8.4%), 39(6.3%), 32(6.7%), 28(32%), 27(8.0%).

B. Preparation of N-acetyl-N-butyryl-3-α,α,α-trifluoromethylaniline

To a 250 ml three-neck flask, fitted with an addition funnel, reflux condenser, and magnetic stirrer, 1.2 g Mg in 25 ml anhydrous ether were added. Ethyl bromide, 6 g, in 15 ml anhydrous ether were added slowly. The mixture was stirred 90 minutes at room temperature then cooled to 0°C. To the reaction mixture 8.5 g 3-α,α,α-trifluoromethylacetanilide were added slowly with stirring at 0°C. When the addition

of the amide was completed, the reaction mixture was stirred in a water bath for 2 hours at 50°C.

The reaction mixture was then cooled to 0° in an ice bath. Freshly distilled butyryl chloride, 5 g, in 15 ml anhydrous alcohol were added dropwise. When this addition was completed, the reaction mixture was reheated to 50° and stirred overnight. The reaction mixture was then recooled.

The layers were separated after 25 ml water were added and the aqueous phase was extracted with five 25 ml portions of ether. The organic layers were combined, washed with aqueous sodium carbonate, dried over anhydrous Na_2SO_4, and concentrated under vacuum. Vacuum distillation yielded five fractions: <115°/1 mm, 115-118°/1 mm, 118-120°/1 mm, 121-123°/1 mm, and 127-131°/1 mm. The third and fourth fractions contained mostly N-acetyl-N-butyryl-3-α,α,α-trifluoromethylaniline with a small amount of 3-α,α,α-trifluoromethylbutyranilide and N,N-diacetyl-3-α,α,α-trifluoromethylaniline. The imide was further purified by preparative glpc on Column P at 170-175°.

NMR: ($CDCl_3$) 0.7-1.15 δ(t J=6.5Hz, 3H, CH_3), 1.35-2.0 δ (hextet, J=6.5Hz, 2H, CH_2), 2.2-2.7 δ(s and m, 5H, CH_3-C=O and CH_2-C=O), 7.15-7.8 δ(m, 4H, phenyl).

IR: ($CDCl_3$) 2980, 2940, 2890 (C-H stretch), 1710 (C=O stretch), 1600, 1530, 1490, 1440, 1370, 1330, 1310, 1210, 1175, 1140, 1070, 1035 cm^{-1}.

Photolysis of N-acetylbutyranilide

A solution of 0.45 g unpurified N-acetylbutyranilide in 42 ml spectrograde dioxane was purged in a quartz tube with nitrogen for an hour and irradiated in a Type B photolysis for 104 hours with Source B light. Glpc of the reaction mixture on Column H at 140° showed three main products as well as acetanilide and N,N-diacetylaniline in minor amounts. Butyranilide, an expected Type II product, was absent. The acetanilide and N,N-diacetylaniline peak sizes decreased in the course of the reaction as opposed to an expected buildup of the Type II products.

The photolysis mixture was concentrated under vacuum at 50-60° to a volume of 4 ml. The residue was then purified by preparative glpc on Column P at 140-150°, and the three product peaks were collected (retention times 9 min., 18-19 min., and 52-55 min.).

The first peak was tentatively identified by its spectra as o-acetoaniline and confirmed by comparison of these spectra with literature spectra and spectra of an authentic sample.

The second peak m^+/e 163 was consistent with o-aminobutyrophenone (the para isomer whose retention time was identical to the starting material was not collected). The spectra of the second peak were identical with those for the ortho isomer prepared by alternate means.

The third and major peak was characterized by its NMR as primary Photo-Fries products of the starting material. The products were tentatively identified as the o and p isomers of acetobutyranilide and butyroacetanilide. The mass spec showed 205 to be the parent while IR showed two carbonyl bands and the N-H band of amides. Repeated attempts to separate the isomers by glpc and tlc proved futile.

Photolysis II of N-acetylbutyranilide

A solution of 0.2 g freshly purified N-acetylbutyranilide* in 42 ml spectrograde dioxane was purged with nitrogen for an hour and irradiated for 42 hours in a Type B photolysis with Source B light. Samples were taken at 3, 6, 14, 25, and 42 hours with nitrogen purged syringes. Glpc analysis of these samples on Column H at 140° showed the same three major products of the previous reaction by coinjection. Acetanilide and N,N-diacetylaniline, which were virtually absent from the zero hour sample were, by contrast, only minor products.

Preparation of o-acetoaniline

o-acetoaniline was prepared by the method of D. Elad.[78] A solution of 40 g recrystallized acetanilide in 1900 ml

*Column P 160-165°.

dry methanol* was purged with nitrogen for 1 hour and irradiated in a Type A photolysis for 44 hours with the Hanovia lamp. The solvent was removed under vacuum.

The residue was steam distilled, and the first 1000 ml of distillate were collected. The distillate was saturated with sodium chloride and extracted with four 200 ml portions of ether.

The ether extracts were combined and concentrated under vacuum to 150 ml. The concentrated ether solution was washed with two 200 ml portions of 10% HCl. The acidic washings were made basic (pH 10) with 10% NaOH. The resulting solution was extracted with four 150 ml portions of ether. The ether extracts were combined, dried over anhydrous $MgSO_4$, and concentrated under vacuum to 5 ml. The residue was passed on Column P at 130°. The product was collected, and had spectral properties consistent for o-acetoaniline.

Photolysis of N-acetyl-N-butyryl-3-α,α,α-trifluoromethylaniline

A solution of 0.2 g freshly purified** N-acetyl-N-butyryl-3-α,α,α-trifluoromethylaniline in seven ml spectrograde dioxane was purged for 20 min. with nitrogen and irradiated in a Type C photolysis for 48 hours with Source B light (2537Å). Glpc of the reaction mixture on Column H

*Spectrograde methanol stored three days over anhydrous $MgSO_4$ and seven days over molecular sieves.

**Column P 160-165°.

at 160° showed that the expected Type II products, 3-α,α,α-trifluoromethylacetanilide and N,N-diacetyl-3-α,α,α-trifluoromethylaniline, were no more than minor products during the course of the reaction. In addition, the large number of major products made individual product isolation impossible.

Preparation of N-alkylphthalimides (General Procedure)

N-alkylphthalimides were prepared by the method of Sheehan and Bolhofer[144] unless otherwise noted. Primary or secondary alkyl bromide, 0.2 moles, was stirred with 210 ml DMF (freshly distilled from P_2O_5) in a 500 ml round bottom flask, fitted with magnetic stirrer and reflux condenser. Powdered potassium phthalimide, 0.2 moles, was added slowly with stirring. The mixture was then refluxed at bath temperature 150°C for 14 hours. The reaction mixture was then cooled and poured into ice water.

This 2-phase system was then extracted with four 100 ml portions of chloroform. The combined chloroform layers were washed with 200 ml 0.2N aqueous NaOH solution to remove any unreacted phthalimide. The basic layer was then washed with three 50 ml portions of $CHCl_3$. The $CHCl_3$ extracts were combined, dried over anhydrous sodium sulfate, and concentrated under vacuum. Vacuum distillation yielded pure products which usually solidified on standing.

A. N-propylphthalimide: m.p. 55°; b.p. 128-132°/.8-.9 mm; 78% yield.

NMR: 0.7-1.15 δ(t J=7Hz, 3H, CH_3), 1.25-2.1 δ(m, 2H, CH_2), 3.45-3.85 δ(t J=7Hz, 2H, N-CH_2), 7.4-8.05 δ(m, 4H, phenyl).

IR: (CCl_4) 2980, 2950, 2880 (C-H stretch), 1775, 1715 (C=O stretch), 1470, 1440, 1390, 1365, 1340, 1190, 1175, 1055, 945, 860, 715 (disubstituted benzene) cm^{-1}.

UV: (EtOH) λ max 292(ε = 1900), 241(ε = 11,200) 232(ε = 15,300), 219(ε = 40,900) and minimum near 252-254(ε = 524).

B. N-ethylphthalimide: m.p. 78-79°; b.p. 135-137°/2-3 mm; 80% yield

NMR: 1.1-1.5 δ(t J=7Hz, 3H, CH_3), 3.5-4.0 δ(q J=7Hz, 2H, CH_2-N), 7.5-8.0 δ(m, 4H, phenyl).

IR: (CCl_4) 3000, 2960, 2890 (C-H stretch), 1775, 1710 (C=O stretch), 1475, 1445, 1400, 1380, 1355, 1340, 1205, 1190, 1175, 1090, 1035, 895, 880, 720 (disubstituted benzene) cm^{-1}.

UV: (EtOH) λ max 292 (ε = 1940), 241(ε = 12,400), 232(ε = 16,100), 219(ε = 41,100) and minimum near 252-254(ε = 644).

C. N-isobutylphthalimide: m.p. 92-93°; b.p. 137-142°/1.2-1.4 mm; 61% yield

NMR: 0.65-0.95 δ(d J=7Hz, 6H, CH_3), 1.5-2.4 δ(m broad, 1H, CH), 3.25-3.5 δ(d J=7Hz, 2H, N-CH_2), 7.4-7.85 δ (m, 4H, phenyl).

IR: (CCl_4) 2980, 2950, 2890 (C-H stretch), 1780, 1725, 1715 (C=O stetch), 1470, 1440, 1400, 1390, 1365, 1355, 1320, 1310, 1195, 1175, 1060, 910, 715 (disubstituted benzene) cm^{-1}.

UV: (EtOH) λ max 292(ε = 2030), 241(ε = 8160), 232(ε = 10,900), 219(ε = 28,900) and minimum at 252-254(ε = 717).

D. N-tert-butylphthalimide: m.p. 80° (from hexane); 80% yield

Preparation of Tert-butyl Urea

Tert-butyl urea was prepared in order to prepare a tertiary alkyl phthalimide[102]. In a one-liter 3-neck flask, fitted with a thermometer, mechanical stirrer, and addition funnel, 105 ml (1.98 moles) concentrated sulfuric acid were stirred. Finely powdered urea, 60 g, was added slowly with stirring, the temperature being maintained at 20-25°C in an ice bath. Tert-butyl alcohol, 188 ml (2 moles), was added dropwise from the addition funnel at a rate which maintained the temperature between 20 and 25°. After stirring an additional half hour at room temperature, the reaction mixture was allowed to stand for 16 hours.

The reaction mixture was poured slowly over 1500 ml cracked ice and water. Aqueous NaOH (160g/750 ml H_2O) was added slowly at less than 25° to a change of Congo red paper. The mixture was then cooled to 10°, and the solid was filtered and washed with two 100 ml portions of cold water. After drying as much as possible the solid was recrystallized from water. Yield 37.8g; m.p. 179-181°.

Preparation of N-tert-butylphthalimide

Phthalic anhydride, 50 g, and 17.5 g tert-butyl urea were well mixed in a mortar. The contents were transferred to a 1-liter Erlenmeyer, which was immersed in a bath previously heated to 200°C. The mixture melted and was

maintained at this temperature for ten minutes, then heated to 240° for 5 minutes (gas liberated). The flask was removed from the heat, cooled to 65°, and 100 ml 95% ethanol were added, partially dissolving the contents.

A 20% Na_2CO_3 solution was added until alkaline to litmus, and the mixture was diluted with water to 1 liter. The solid was collected and dissolved in hot petroleum ether (b.p. 68-70°). Water that separated was removed, and the solution was filtered on cooling to 25°. The supernatant was concentrated to 1/3 volume and chilled. Tert-butylphthalimide, 24.1 g, was collected on cooling.

NMR: 1.6-1.85 δ(s, 9H, $3CH_3$), 7.55-7.9 δ(m, 4H, phenyl).

IR: (CCl_4) 2990 (C-H stretch), 1775, 1715 (C=O stretch), 1470, 1370, 1350, 1320, 1260, 1215, 1175, 1105, 1090, 1015, 875, 720 (disubstituted benzene) cm^{-1}.

UV: (EtOH) λ max 292(ε = 1610), 241(ε = 10,200), 232(ε = 15,000), 219(ε = 39,900) and minimum at 252-254(ε = 447).

E. N-isopropylphthalimide: m.p. 79-81°; b.p. 126-127°/4.6 mm; 65% yield

NMR: 1.35-1.65 δ(d J=7Hz, 6H, CH_3), 4.15-4.19 δ(heptet J=7Hz, 1H, N-CH), 7.55-7.95 δ(s broad, 4H, phenyl).

IR: (CCl_4) 2990, 2950, 2890 (C-H stretch), 1775, 1710 (C=O stretch), 1615, 1470, 1460, 1385, 1370, 1355, 1330, 1295, 1200, 1170, 1140, 1085, 1040, 940, 875, 835, 715 (disubstituted benzene) cm^{-1}.

UV: (EtOH) λ max 292(ε = 1720), 241(ε = 11,200), 232(ε = 15,500), 219(ε = 41,000) and minimum at 252-254(ε = 447).

F. N-2-methylbutylphthalimide (Racemic): b.p. 128-132°/ 0.7 mm; 79% yield

Racemic N-2-methylbutylphthalimide was prepared by the general method from racemic 2-methyl-1-bromobutane. Pyridine, 350 ml, and 45 g 2-methyl-1-butanol were stirred at 0°. Freshly recrystallized (Skelly B) tosyl chloride, 190 g, was added slowly to the chilled mixture, and the mixture was refrigerated (at 0°) for 36 hours.

The mixture was poured into 250 ml water, ice and dilute HCl. The mixture was then extracted with four 150 ml portions of ether (until no foaming occurred). The ether extracts were combined and washed with two 250 ml portions of 6N HCl. The ether layers were combined, and the acid aqueous phase was extracted with two 100 ml portions of ether. The combined ether layers were washed with two 100 ml portions of saturated sodium carbonate solution. These aqueous phases were extracted with three 150 ml portions of ether.

All organic layers were combined and dried over anhydrous sodium sulfate. The resulting liquid was concentrated as far as possible under vacuum with steam (essentially quantitative by weight). The NMR of the residue matched that of an authentic sample.

2-methylbutyl tosylate, 40 g, was dissolved in 100 ml spectrograde acetone. To this stirred mixture was added a solution of 30 g lithium bromide in 200 ml acetone slowly at room temperature. The resultant mixture was then

stirred for 18 hours at 50°.

The mixture was poured over 150 ml water, and the organic layer removed. The aqueous phase was then extracted with four 100 ml portions of ether. The organic phases were combined and dried over anhydrous sodium sulfate. Distillation at 118-121°/760 mm yielded 21.8 g 2-methyl-1-bromobutane. The NMR matched an authentic sample.

The phthalimide was prepared by the general method listed on page 321. Vacuum distillation yielded 20.2 g racemic 2-methyl-butylphthalimide at 128-132°/.7 mm.

NMR: 0.7-2.3 δ(m broad, 9H, CH_3, CH_2, and CH), 3.35-3.65 δ(d J=7Hz, 2H, N-CH), 7.6-8.0 δ(m, 4H, phenyl).

IR: (neat) 2980, 2940, 2890 (C-H stretch), 1775, 1710 (C=O stetch), 1610, 1460, 1435, 1400, 1380, 1360, 1265, 1185, 1155, 1060, 1025, 1000, 965, 910, 790, 765, 720, 710, 630 cm^{-1}.

UV: (EtOH) λ max 292(ε = 1780), 241(ε = 10,900), 232(ε = 14,800), 219(ε = 41,500), and minimum at 251-254(ε = 457).

H. N-2-methylbutylphthalimide (Optically Active): b.p. 126-132°/0.7 mm; 82% yield

An analogous procedure for preparation of racemic N-2-methylbutylphthalimide was used to prepare the optically active compound. Optically active alcohol, 10 g, 45 g. tosyl chloride, and 125 ml pyridine were refrigerated for 30 hours. The isolation of optically active tosylate yielded 27 g after the previous workup.

Optically active tosylate, 20 g, was stirred at 50° for 18 hours with lithium bromide. Optically active bromide, 6.5 g, was isolated.

Optically active bromide, 5.0 g, was used to prepare the optically active phthalimide by the general procedure. Vacuum distillation yielded 5.8 g optically active N-2-methylbutylphthalimide at 126-132°/0.7 mm.

NMR: 0.75-2.3 δ(m broad, 9H, $2CH_3$, CH_2, and CH), 3.5-3.7 δ(d, 2H, N-CH_2), 7.6-8.05 δ(m, 4H, phenyl).

IR: (neat) 2980, 2940, 2880 (C-H stretch), 1775, 1710, (C=O stretch), 1610, 1470, 1435, 1400, 1380, 1360, 1265, 1185, 965, 925, 910, 790, 765, 725, 715 (disubstituted benzene), 625 cm^{-1}.

UV: (EtOH) λ max 292(ε = 1790), 241(ε = 10,900), 232(ε = 14,900), 219(ε = 41,500), and minimum at 251-254(ε =458).

I. N-sec-butylphthalimide: b.p. 110-112°/0.5 mm; 62% yield

NMR: 0.7-1.05 δ(t J=7Hz, 3H, CH_3), 1.35-1.6 δ(d J=7Hz, 3H, CH_3), 1.65-2.1 δ(m, 2H, CH_2), 3.95-4.6 δ(m, 1H, N-CH), 7.55-8.0 δ(m, 4H, phenyl).

IR: (neat) 2980, 2950, 2890 (C-H stretch), 1775, 1755, 1705 (C=O stretch), 1610, 1365, 1295, 1260, 1235, 1190, 1170, 1145, 1135, 1090, 1050, 1000, 960, 910, 880, 790, 720 cm^{-1}.

UV: (EtOH) λ max 292(ε = 1810), 241(ε = 10,400), 237(ε = 10,000), 232(ε = 14,000), 220(ε = 40,000), 217(ε = 37,500), and a minimum at 251-254(ε = 523).

J. N-butylphthalimide: m.p. 40-42°; b.p. 153-154°/2.7 mm; 75% yield

NMR: 0.7-1.15 δ(t J=Hz, 3H, CH_3), 1.15-2.0 δ(m broad, 4H, CH_2), 3.5-3.9 δ(t J=7Hz, 2H, N-CH_2), 7.5-8.0 δ(m, 4H, phenyl).

IR: (CCl_4) 2980, 2950, 2880 (C-H stretch), 1770, 1715 (C=O stretch), 1470, 1440, 1395, 1375, 1365, 1340, 1190, 1175, 1055, 945, 865, 715 (disubstituted benzene) cm^{-1}.

UV: (EtOH) λ max 297(ε = 1680), 292(ε = 1760), 241(ε = 11,100), 232(ε = 15,100), 219(ε = 42,000), and minimum at 251-254(ε = 473).

K. N-2-propenylphthalimide: m.p. 70-72°; b.p. 124-127°/1.5 mm; 87% yield

NMR: 4.15-4.4 δ(t of d 1.5Hz and 5.0Hz, 2H, N-CH_2-C=C), 5.0-5.4 δ(m, 2H, C=CH_2), 4.55-6.25 δ(m broad, 1H, C-CH=CO), 7.5-7.9 δ(m, 4H, phenyl).

IR: (CCl_4) 3090, 2990, 2930 (C-H stretch), 1775, 1720 (C=O stretch), 1470, 1435, 1385, 1335, 1320, 1190, 1175, 1115, 1065, 985, 935 (=CH_2), 710(disubstituted benzene) cm^{-1}.

UV: (EtOH) λ max 292(ε = 1910), 241(ε = 12,000), 232(ε = 16,200), 219(ε = 45,500), and minimum at 252-254(ε = 463).

L. N-methylphthalimide: m.p. 134°; 62% yield

NMR: 3.1-3.25 δ(s, 3H, N-CH_3), 7.55-8.0 δ(m, 4H, phenyl).

IR: (CCl_4) 2960 (C-H stretch), 1775, 1725 (C=O stretch), 1470, 1435, 1385, 1255, 1005, 715 (disubstituted ben-

zene) cm^{-1}.

UV: (EtOH) λ max 292(ε = 1910), 241(ε = 12,000), 232(ε = 16,200), 219(ε = 45,500), and minimum at 251-254(ε = 463). (Cyclohexane) λ max 298(ε = 1430), 289(ε = 1590), 240(ε = 12,100), 236(ε = 9810), 232(ε = 13,000), 219(ε = 24,300), 214(ε = 25,600), and minimum at 247-250 nm at 254(ε = 474).

UV Data on Phthalimides

The following data was collected on the phthalimides, photoproducts, and related compounds shown below on a Cary 15 UV spectrophotometer. The spectra were used to determine concentrations for quantum yields and specifically to determine the molar absorptivity of each compound at 254 nm, the wavelength of irradiation. These spectra were run in 1 cm path UV cells with spectrograde ethanol as solvent.

Compound	λ max	Absorbance	Concentration	ε (liters/ mole-cm)
N-propylphthal-imide	292	1.010	5.3×10^{-4}	1,900
	241	.237	2.1×10^{-5}	11,200
	232	.325	2.1×10^{-5}	15,300
	219	.867	2.1×10^{-5}	40,900
	254	.278	5.3×10^{-4}	524
N-ethylphthal-imide	292	1.03	5.3×10^{-4}	1,940
	241	.262	2.1×10^{-5}	12,400
	232	.342	2.1×10^{-5}	16,100
	219	.872	2.1×10^{-5}	41,100
	254	.342	5.3×10^{-4}	644
N-isobutyl-phthalimide	292	1.02	5.0×10^{-4}	2,030
	241	.164	2.0×10^{-5}	8,160
	232	.218	2.0×10^{-5}	10,900
	219	.580	2.0×10^{-5}	28,900
	254	.360	5.0×10^{-4}	717

Compound	λmax	Absorbance	Concentration	ε (liters/mole-cm)
N-tert-butyl-phthalimide	292	.825	5.1×10^{-4}	1,610
	241	.208	2.0×10^{-5}	10,200
	232	.306	2.0×10^{-5}	15,000
	219	.813	2.0×10^{-5}	39,900
	254	.229	5.1×10^{-4}	447
N-isopropyl-phthalimide	292	.945	5.5×10^{-4}	1,720
	241	.246	2.2×10^{-5}	11,200
	232	.342	2.2×10^{-5}	15,500
	219	.903	2.2×10^{-5}	41,000
	254	.246	5.5×10^{-4}	447
N-2-methylbutyl-phthalimide (racemic)	292	.864	4.8×10^{-4}	1,780
	241	.210	1.9×10^{-5}	10,900
	232	.286	1.9×10^{-5}	14,800
	219	.800	1.9×10^{-5}	41,500
	254	.221	4.8×10^{-4}	457
N-2-methylbutyl-phthalimide (optically active)	292	.865	4.8×10^{-4}	1,790
	241	.210	1.9×10^{-5}	10,900
	232	.288	1.9×10^{-5}	14,900
	219	.803	1.9×10^{-5}	41,500
	254	.220	4.8×10^{-4}	458
N,N-dibenzoyl isobutylamine	254	.365	3.2×10^{-5}	11,500
	249	.380	3.2×10^{-5}	12,000
	239	.367	3.2×10^{-5}	11,600
	224	.420	3.2×10^{-5}	13,200
	219	.430	3.2×10^{-5}	13,600
	215	.420	3.2×10^{-5}	13,200

Compound	λ max	Absorbance	Concentration	ε(liters/ mole-cm)
N-sec-butyl-phthalimide	292	1.03	5.7×10^{-4}	1,810
	241	.240	2.3×10^{-5}	10,400
	237	.230	2.3×10^{-5}	10,000
	232	.322	2.3×10^{-5}	14,000
	220	.921	2.3×10^{-5}	40,000
	217	.862	2.3×10^{-5}	37,500
	254	.298	5.7×10^{-4}	523
N-butylphthal-imide	297	.825	4.9×10^{-4}	1,680
	292	.860	4.9×10^{-4}	1,760
	241	.221	2.0×10^{-5}	11,100
	232	.301	2.0×10^{-5}	15,100
	219	.840	2.0×10^{-5}	42,000
	254	.232	4.9×10^{-4}	473
N-methylphthal-imide (EtOH)	292	.552	3.0×10^{-4}	1,840
	241	.152	1.2×10^{-4}	12,700
	232	.194	1.2×10^{-5}	16,200
	219	.518	1.2×10^{-5}	43,200
	254	.148	3.0×10^{-4}	493
N-methylphthal-imide (cyclohexane)	298	.671	4.7×10^{-4}	1,430
	289	.745	4.7×10^{-4}	1,590
	240	.449	3.7×10^{-5}	12,100
	236	.363	3.7×10^{-5}	9,810
	232	.48	3.7×10^{-5}	13,000
	219	.899	3.7×10^{-5}	24,300
	214	.946	3.7×10^{-5}	25,600
	254	.223	4.7×10^{-4}	474

Compound	λ max	Absorbance	Concentration	ε(liters/ mole-cm)
N-2-propenylphthal-imide	292	1.07	5.6×10^{-4}	1,910
	241	.264	2.2×10^{-5}	12,000
	232	.357	2.2×10^{-5}	16,200
	219	1.00	2.2×10^{-5}	45,500
	254	.315	5.6×10^{-4}	463
3,4-benzo-6,7-dihydro(1H)aze-pine-2,5-dione	326	.079	4.7×10^{-4}	168
	282	.576	4.7×10^{-4}	1,230
	235	.344	3.8×10^{-5}	9,050
	207	.958	3.8×10^{-5}	25,200
	254	.236	3.8×10^{-5}	6,210
(2-methyl) 3,4-benzo-6,7-dihydro-7-methyl(1H)aze-pine-2,5-dione	322	.070	4.4×10^{-4}	159
	284	.491	4.4×10^{-4}	1,120
	236	.258	3.6×10^{-5}	7,170
	209	.794	3.6×10^{-5}	22,100
	254	.132	3.6×10^{-5}	3,670
(2,2-dimethyl) 3,4-benzo-6,7-dihydro-7,7-di-methyl(1H)aze-pine-2,5-dione	330	.042	4.0×10^{-4}	105
	292	.635	4.0×10^{-4}	1,590
	245	.275	3.2×10^{-5}	8,590
	237	.287	3.2×10^{-5}	8,810
	213	.866	3.2×10^{-5}	27,100
	254	.225	3.2×10^{-5}	7,030
(3-methyl) 3,4-benzo-6,7-dihydro-6-methyl (1H)azepine-2,5-dione	326	.071	5.3×10^{-4}	134
	282	.630	5.3×10^{-4}	1,190
	236	.157	2.1×10^{-5}	7,440
	211	.420	2.1×10^{-5}	19,900
	254	.069	2.1×10^{-5}	3,270

Compound	λ max	Absorbance	Concentration	ε(liters/ mole-cm)
(3,3-dimethyl)	322	.080	5.4×10^{-4}	148
3,4-benzo-6,7-	279	.770	5.4×10^{-4}	1,430
dihydro-6,6-	235	.350	4.3×10^{-5}	8,140
dimethyl(1H)	210	1.16	4.3×10^{-5}	27,000
azepine-2,5-	254	.15	4.3×10^{-5}	3,490
dione				

Photolysis Procedures for Phthalimides

Type A

Solutions, 0.5-1.0% (by weight), were introduced to the same photocontainer used in amide photolyses. The solutions were purged with dry nitrogen for periods of from 15 minutes to an hour.

The irradiations were conducted with Source A light for periods varying from 1/2 hour to 18 hours. Samples, 0.25 ml, were taken at random irradiation times from the drain at the bottom of the photocontainer. Reaction progress was monitored by TLC or by liquid chromatography. The solvent systems varied with the individual experiments. In general, workup of these experiments was by evaporation of the solvent under vacuum followed by either column chromatography or preparative TLC.

Type B

Type B photolyses were conducted in the Type B vessels used for amides. The tubes were purged as before. Samples were irradiated by either of the two procedures used for amides. Analyses of photolysates were conducted by glpc, lc, and TLC.

Type C

Type C photolyses were similar to Type B photolyses except the volumes of solution were larger. The solutions were magnetically stirred while being purged 1 hour with dry nitrogen. Samples were taken with nitrogen purged syr-

inges. Irradiations were conducted either with Source B light or by suspension next to a quartz well with the Hanovia lamp. Photolysis mixtures were then analyzed by NMR, TLC, lc, and glpc (in cases where starting material loss was quantified).

Type D

Type D photolyses were quantum yield determinations conducted in the black box. A special side tube as shown in Figure 9 (Page 381) was fashioned to remove oxygen from the system more effectively by five freeze-pump-thaw cycles. The solutions were magnetically stirred and irradiated for varying periods with Source C (at 254 nm) light. The samples were analyzed by lc. A further explanation is given in the section on ferrioxalate actinometry on page 357.

Type E

Type E photolyses were also quantum yield and reaction efficiency determinations. The same vessels were used as in Type E for amides. Oxygen was removed by four freeze-pump-thaw cycles. Vessels were irradiated with Source B light, and reaction mixtures were analyzed by glpc and quantum yields by lc. (The expanded analysis procedure is given in the cyclopentanone actinometry section.)

Type F

Type F photolyses were similar to Type A except that the standard condenser was replaced with a dry ice condenser

to condense volatile gases such as butadiene or isobutylene into the reaction mixture. The photocontainer was immersed in ice water during irradiation with the Hanovia lamp. (The volume of gas condensed was measured by difference.) The photolysis mixtures were analyzed as in the Type A photolyses.

Photolysis of N-propylphthalimide in Acetonitrile

A solution of 1.5 g N-propylphthalimide in 230 ml spectrograde acetonitrile was purged with nitrogen for an hour and irradiated in a Type A photolysis for 10 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed two products, R_f = 0.75 and 0.35.

The reaction mixture was evaporated to dryness under vacuum, and NMR of the residue showed signals in the vinylic region as well as a doublet in the alkyl region. The residue was redissolved in a minimum amount of methylene chloride and methanol, and the products were isolated by preparative TLC (2 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride). There were three bands, and the top R_f = ~0.9 band was identified by NMR as starting material.

The second band, R_f = 0.7-0.8, was worked up, and the oil was further purified by preparative TLC (2 plates 500 micron thickness, 15% ethyl acetate - 85% methylene chloride). The oil (~0.1 g) was identified by its spectra as 3-dihydrophthalimido-1-propene.

NMR: ($CDCl_3$) 3.6-4.0 δ (m, 2H, N-CH_2), 4.9-5.3 δ (m, 3H, -CH=CH_2), 5.65-5.8 δ (s broad, 1H, OH), 7.3-7.8 δ (m, 5H, phenyl and N-CH-O).

IR: ($CDCl_3$) 3580, 3540, 3380-3260 (O-H stretch), 2940, 2920 (C-H stretch), 1780, 1735, 1700, 1690 (C=O stretch), 1470, 1440, 1420, 1300, 1210, 1170, 1130, 1040 cm^{-1}.

The third band R_f = 0.4-0.6 was worked up in the usual fashion with methylene chloride and ethyl acetate. The isolated oil contained a characteristic doublet in the alkyl region. Further purification of the oil was attained by preparative TLC (2 plates 500 micron thickness, 18% ethyl acetate - 82% methylene chloride) followed by the usual work-up with ethyl acetate and methylene chloride. The white crystalline solid, 0.15 g, m.p. 161-162°, (from benzene/Skelly B) was identified by its spectra as 3,4-benzo-6,7-dihydro-6-methyl(1H)azepine-2,5-dione,* 36.

NMR: ($CDCl_3$) 1.15-1.4 δ(d J=7Hz, 3H, CH_3), 2.65-3.25 δ(m, 1H, CH-C=O), 3.25-3.7 δ(m, 2H, N-CH_2), 7.45-8.5 δ(m, 5H, phenyl and N-H).

IR: (KBr) 3220 (N-H stretch), 3080, 3000, 2970, 2940, 2900, 2870 (C-H stretch), 1680, 1655, 1620 (C=O stretch), 1590, 1560, 1440, 1400, 1370, 1345, 1320, 1270, 1235, 1215, 1170, 1045, 1000, 970, 915, 895, 865, 790, 760, 750, 710 cm^{-1}.

MASS SPEC: m^+/e 189(P, 19%), 174(25%), 149(10%), 148(Base, 100%), 130(35%), 105(13%), 104(45%), 103(14%), 77(14%), 76 (28%), 51(9%), 50(15%), 45(48%), 43(23%), 42(11%), 32(12%).

*Retention time on LC (12% ethyl acetate-88% methylene chloride, flow rate 20 drops/70 sec.) ~55 min.

UV: (EtOH) λ max 326(ε = 134), 282(ε = 1190), 236(ε = 7440), 211(ε = 19,900), and at 254(ε = 3270).

Photolysis of N-propylphthalimide in Tert-butanol

A solution of 1.2 g N-propylphthalimide in 220 ml sodium-dried tert-butanol was purged with nitrogen for an hour and irradiated in a Type A photolysis for 11 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed one product, R_f = ~0.35.

The reaction mixture was evaporated to dryness under vacuum. NMR again showed the characteristic alkyl doublet. Preparative TLC of the residue (2 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride) yielded one band, R_f = ~0.4-0.6, which was worked up in the usual manner. The spectral properties of the 0.1 g (m.p. 160°) isolated product were identical to those of 3,4-benzo-6,7-dihydro-6-methyl(1H)azepine-2,5-dione, 36.

Photolysis of N-ethylphthalimide in Acetonitrile

A solution of 1.5 g N-ethylphthalimide and 230 ml spectrograde acetonitrile was purged with nitrogen for an hour and irradiated in a Type A photolysis for 9½ hours with a Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed one product, R_f = 0.3.

The reaction mixture was evaporated to dryness under vacuum. NMR of the residue showed three major signals:

2-3δ, 3-4δ, and phenyl signals. The residue was dissolved in a minimum amount of methylene chloride and methanol, and the product was isolated by preparative TLC (3 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride). The band R_f = 0.25-0.45 was worked up in the usual manner with methylene chloride and ethyl acetate and further purified by preparative TLC (2 plates 500 micron thickness, 16% ethyl acetate - 84% methylene chloride). The single band R_f = 0.2-0.4 was worked up as before. The recovered solid 0.15 g, m.p. 162-163° was characterized by its spectral data as 3,4-benzo-6,7-dihydro(1H)azepine-2,5-dione, 37*.

NMR: ($CDCl_3$) 2.75-3.25 δ(t J=6.5Hz, 2H, CH_2-C=O), 3.3-3.8 δ(q J=6.5Hz, 2H, CH_2-N), 7.25-8.1 δ(m, 4H, phenyl), 8.1-8.6 δ(t, 1H, N-H).

IR: (KBr) 3275, 3180 (N-H stretch), 3060, 3030, 2920, 2870 (C-H stretch), 1640 (C=O stretch), 1590, 1460, 1390, 1350, 1330, 1270, 1220, 1150, 1085, 1030, 890, 750, 700 cm^{-1}.

MASS SPEC: m^+/e 175(P, 15%), 174(9%), 160(7%), 133(12%), 105(12%), 104(10%), 83(7%), 77(10%), 76(6%), 59(11%), 56(7%), 55(14%), 54(8%), 44(Base, 100%), 43(13%), 42(8%), 41(23%), 32(32%).

UV: (EtOH) λ max 326(ε = 168), 282(ε = 1230), 235(ε = 9050), 207(ε = 25,200), and at 254(ε = 6210).

*Retention time by LC 80 min. (12% ethyl acetate - 88% methylene chloride, flow rate 20 drops/40 sec.).

Photolysis of N-ethylphthalimide in tert-butanol

A solution of 1.5 g N-ethylphthalimide in 220 ml sodium-dried tert-butanol was purged with nitrogen for an hour and irradiated in a Type A photolysis for 12 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed one product R_f = ~0.3.

The reaction mixture was evaporated to dryness under vacuum. Preparative TLC (2 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride) yielded ~0.1 g white solid, R_f = 0.2-0.4. The solid was further purified by preparative TLC (20% ethyl acetate - 80% methylene chloride). The white crystalline solid, ~0.1 g, R_f = 0.2-0.4, m.p. 160-161° had spectral properties identical to 3,4-benzo-6,7-dihydro(1H)azepine-2,5-dione, 37.

Photolysis of N-isobutylphthalimide in Acetonitrile I

A solution of 1.5 g N-isobutylphthalimide in 230 ml spectrograde acetonitrile was purged two hours with nitrogen and irradiated in a Type A photolysis for 16 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed three products, R_f = 0.75, 0.65, and ~0.4.

The reaction mixture was evaporated to dryness under vacuum. Preparative TLC of the residue (two plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride). The band R_f = 0.65-0.75 was worked up in the

usual manner. The collected oil, ~.2 g, was further purified by preparative TLC (12% ethyl acetate - 88% methylene chloride). Following the usual workup ~0.1 g crystalline solid, m.p. 65-67°, was identified by its spectra as 3-dihydrophthalimido-2-methyl-1-propene, 38.

NMR: ($CDCl_3$) 1.6-1.75 δ(s, broad, 3H, CH_3), 3.6-4.0 δ(2s broad, 2H, N-CH_2-C=C), 4.6-4.9 δ(m, 2H, C=CH_2), 5.5-5.65 δ(s broad, 1H, OH), 7.1-7.7 δ(m, 5H, phenyl and N-CH-O).

IR: ($CDCl_3$) 3450, 3380-3260 (O-H stretch), 2980, 2970, 2940, 2920, 2860 (C-H stretch), 1690 (C=O stretch), 1440, 1420, 1300, 1210, 1140, 1040 cm^{-1}.

The second band of the first plates R_f 0.4-0.55 was worked up with methylene chloride and ethyl acetate. The residue, 0.3 g, was redissolved in a minimum of methylene chloride and further purified by preparative TLC (two plates 1000 micron thickness, 80% methylene chloride - 20% ethyl acetate). Following the general workup the white residue was collected and recrystallized twice from acetonitrile. The white crystalline solid, m.p. 165-167°, 0.2 g, was identified by its spectra as 3,4-benzo-6,7-dihydro-6,6-dimethyl(1H)azepine-2,5-dione, 39.

NMR: ($CDCl_3$) 1.2-1.35 δ(s, 6H, CH_3) 3.25-3.5 δ(d J=6.5Hz, 2H, N-CH_2), 7.5-8.3 δ(m, 5H, phenyl and N-H).

IR: (KBr) 3200 (N-H stretch), 3080, 2980, 2970, 2930, 2920, 2890 (C-H stretch), 1665 (C=O stretch), 1600, 1570,

1475, 1465, 1455, 1400, 1380, 1345, 1320, 1280, 1225, 1185, 1070, 995, 960, 940, 915, 820, 780, 730, 710 cm^{-1}.

MASS SPEC: m^+/e 203(P, 3%), 174(15%), 159(14%), 148(Base, 100%), 130(23%), 115(3%), 105(8%), 104(13%), 77(12%), 76(18%), 56(63%), 51(7%), 50(9%), 44(52%), 41(23%), 39(8%), 32(10%).

UV: (EtOH) λ max 322(ε = 1.48), 279(ε = 1430), 235(ε = 8140), 210(ε = 27,000), and at 254(ε = 3490).

Photolysis of N-isobutylphthalimide in Acetonitrile II

A solution of 2.5 g N-isobutylphthalimide in 230 ml spectrograde acetonitrile was purged with nitrogen for two hours and irradiated in a Type A photolysis for 16 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed three products with R_f = 0.75, 0.65, and ~0.4.

The reaction mixture was evaporated to dryness under vacuum. The residue was redissolved in a minimum of methylene chloride and loaded on a 40 × 4 cm silica gel column. The column was eluted with 1000 ml methylene chloride to remove the remaining starting material. The column was eluted with a second liter of methylene chloride, and 0.2 g white solid, m.p. 130°, was recovered. NMR showed only a phenyl signal and IR matched that of phthalic anhydride (m.p. 130°).

Elution with one liter 10% ethyl acetate - 90% methylene chloride and one liter 20% ethyl acetate - 80% methylene chloride yielded 0.15 g yellow solid. The solid was further purified by preparative TLC (two plates 1000 micron thickness, 15% ethyl acetate - 85% methylene chloride). Spectra of the isolated compound were identical to those of 3-dihydrophthalimido-2-methyl-1-propene, 38.

The column was eluted with 2 liters 20% ethyl acetate - 80% methylene chloride and 1 liter 40% ethyl acetate - 60% methylene chloride. The recovered yellow solid, 0.35 g, was redissolved in a minimum amount of methylene chloride and purified by preparative TLC (20% ethyl acetate - 80% methylene chloride). The single band, R_f 0.4-0.55, was worked up with methylene chloride and ethyl acetate in the standard manner. The white solid had spectral properties identical to 3,4-benzo-6,7-dihydro-6,6-dimethyl(1H)azepine-2,5-dione, 39.

Photolysis of N-isobutylphthalimide in tert-butanol

A solution of 1.5 g N-isobutylphthalimide in 220 ml sodium dried tert-butanol was purged with nitrogen for an hour and irradiated in a Type A photolysis for 11 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed only one major product whose R_f matched 39. Absence of phthalic anhydride was not verified. Lc (flow rate = 20 drops/40 sec., 12% ethyl

acetate - 88% methylene chloride) coinjection of authentic samples showed 39 to be the major product and 38 only to be present in very minor quantities. NMR of the evaporated reaction mixture had the characteristic alkyl singlet of 39 but no vinylic signals. Isolation of the major product by preparative TLC (20% ethyl acetate - 80% methylene chloride) yielded a white crystalline solid R_f = 0.4-0.55 with spectral properties identical to 39.

Photolysis of N-isopropylphthalimide in Acetonitrile

A solution of 1.5 g N-isopropylphthalimide in 230 ml spectrograde acetonitrile was purged with nitrogen for an hour and irradiated in a Type A photolysis for ten hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed one product, R_f = 0.35.

The reaction mixture was evaporated to dryness under vacuum. NMR of the residue showed an alkyl doublet at ~1.3δ. The residue was redissolved in a minimum amount of methylene chloride and ethyl acetate. Preparative TLC (2 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride) yielded ~0.2 g yellow oil, R_f = 0.3-0.5. The oil was further purified by preparative TLC (2 plates 500 micron thickness, 20% ethyl acetate - 80% methylene chloride). The product was isolated after the usual workup. The white crystalline solid, m.p. 220°

(from benzene/Skelly B) was characterized by its spectra as 3,4-benzo-6,7-dihydro-7-methyl(1H)azepine-2,5-dione, 40*.

NMR: ($CDCl_3$) 1.2-1.4 δ(d J=6.5Hz, 3H, CH_3), 2.7-2.95 δ(m, 3H, CH_2-C=O and CH-N), 6.4-7.1 δ(m, broad, 1H, N-H), 7.1-7.9 δ(m, 4H, phenyl).

IR: (KBr) 3300, 3200 (N-H stretch), 3080, 2990, 2930, 2880 (C-H stretch), 1685 (C=O ketone stretch), 1655 (C=O amide stretch) 1600, 1570, 1450, 1395, 1330, 1290, 1240, 790, 760, 700, 615 cm^{-1}.

MASS SPEC: m^+/e 189(P, 34%), 174(23%), 149(9%), 148(64%), 147(36%), 146(66%), 130(18%), 129(11%), 118(16%), 105(16%), 104(45%), 90(10%), 77(14%), 76(34%), 51(11%), 50(17%), 49(7%), 45(Base, 100%), 44(13%), 43(22%), 42(11%), 39(9%), 32(40%).

UV: (EtOH) λ max 322(ε = 159), 284(ε = 1,120), 236(ε = 7,170), 209(ε = 22,100) and at 254 nm(ε = 3,160).

Photolysis of N-isopropylphthalimide in tert-butanol

A solution of 1.5 g N-isopropylphthalimide in 220 ml sodium-dried tert butanol was purged with nitrogen for an hour and irradiated in a Type A photolysis for 11 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed one product, R_f = ~0.4.

*Retention time by Lc (12% ethyl acetate - 88% methylene chloride), flow rate 20 drops/70 sec.) was 46 min.

(Lc with 12% ethyl acetate - 88% methylene chloride showed only one major product with a retention time ~45 min.)

The reaction mixture was evaporated to dryness under vacuum. Preparative TLC (2 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride) yielded a product whose spectral properties matched those of 3,4-benzo-6,7-dihydro-7-methyl(1H)azepine-2,5-dione, 40.

Photolysis of N-tert-butylphthalimide in Acetonitrile

A solution of 1.5 g N-tert-butylphthalimide in 230 ml spectrograde acetonitrile was purged an hour with dry nitrogen and irradiated in a Type A photolysis for 11 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed one major product, R_f = 0.45.

The reaction mixture was evaporated to dryness under vacuum. NMR of the residue showed two alkyl signals other than starting material. Preparative TLC of the residue (2 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride) yielded a band, R_f = 0.45-0.6, which was worked up in the usual manner with methylene chloride and ethyl acetate. The residue was purified further by preparative TLC using the previous conditions. The third purification step was also preparative TLC (1 plate 1000 micron thickness, 15% ethyl acetate - 85% methylene chloride). The white crystalline solid, ~.15 g, m.p. 158-159°,

was characterized by its spectra as 3,4-benzo-6,7-dihydro-7,7-dimethyl(1H)azepine-2,5-dione, 41.

NMR: ($CDCl_3$) 1.25-1.45 δ(s, 6H, CH_3), 3.05-3.2 δ(s, 2H, CH_2-C=O), 7.4-8.4 δ(m, 5H, phenyl and N-H).

IR: (KBr) 3280, 3190 (N-H stretch), 3070, 3050, 3000, 2990, 2930, 2900 (C-H stretch), 1645 (C=O stretch), 1595, 1570, 1475, 1440, 1390, 1280, 1235, 1165, 985, 810, 775, 760, 710, 690, 630, 610 cm^{-1}.

MASS SPEC: m^+/e 203(P, 60%), 188(27%), 187(11%), 148(64%), 147(Base, 100%), 146(25%), 130(20%), 105(16%), 104(45%), 76(40%), 50(15%), 44(35%), 42(13%), 32(9%).

UV: (EtOH) λ max 330(ε = 105), 292(ε = 1590), 245(ε = 8590), 237(ε = 8810), 213(ε = 27,100), and at 254(ε = 7030).

Photolysis of N-tert-butylphthalimide in tert-butanol

A solution of 1.5 g N-tert-butylphthalimide in 220 ml sodium-dried tert-butanol was purged for an hour with nitrogen and irradiated in a Type A photolysis for 10½ hours with the Hanovia lamp. Lc analysis (12% ethyl acetate - 88% methylene chloride) showed that only one major product was produced.

The reaction mixture was evaporated to dryness under vacuum. Preparative TLC (2 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride) yielded one band R_f = 0.5-0.6, which was worked up in the usual manner.

The white crystalline solid, m.p. 157-159°, had identical IR and NMR spectra with the 7,7-dimethyl compound 41.

Photolysis of N-butylphthalimide in Acetonitrile

A solution of 2 g N-butylphthalimide in 230 ml spectrograde acetonitrile was purged with nitrogen ½ hour and irradiated in a Type A photolysis for 11 hours with the Hanovia lamp. Analytical TLC (30% ethyl acetate - 70% methylene chloride) showed one major product R_f = ~0.3 and two minor products, R_f = 0.65 and ~0.7.

The reaction mixture was evaporated under vacuum, and NMR of the residue showed small vinyl signals. The residue was then redissolved in a minimum amount of methylene chloride and methanol and eluted on a 4 cm × 40 cm silica gel column. After the column was eluted with one liter 50% hexane - 50% methylene chloride and 2 liters methylene chloride, the unreacted starting material, 0.7 g, was recovered. The column was eluted with 425 ml 1% ethyl acetate - 99% methylene chloride and 500 ml 10% ethyl acetate - 90% methylene chloride to remove unreacted starting material.

The minor products were removed from the column by elution with one liter 20% ethyl acetate - 80% methylene chloride (the last 100 ml contaminated with the major product). A yellow oil <0.1 g was collected and repurified by preparative TLC (14% ethyl acetate - 86% methylene

chloride). The oil was characterized by its spectra as the cis and trans isomers of 1-dihydrophthalimido-2-butene.

NMR: ($CDCl_3$) 1.5-1.8 δ(d J 4.5Hz, 3H, CH_3), 3.3-3.8 δ and 4.1-4.6 δ(2 m, <2H, N-CH_2), 5.3-5.65 δ(m, 2H, -CH=CH- cis and trans), 5.65-5.85 δ(s broad, 1H, OH), 7.25-7.9 δ(m, 5H, phenyl and N-CH-O).

IR: ($CDCl_3$) 3420, 3280 (O-H stretch), 2980, 2930 (C-H stretch), 1665 (C=O stretch), 1600, 1480, 1390, 1285 cm^{-1}.

The major product, 0.3 g, was contained in two liters 50% ethyl acetate - 50% methylene chloride. The product was further purified by preparative TLC (2 plates 1000 micron thickness, 22% ethyl acetate - 78% methylene chloride). On the basis of spectra, melting point, and lc data* the product was identified as 3,4-benzo-6,7-dihydro(1H)azepine-2,5-dione, 37.

Photolysis of N-sec-butylphthalimide in Acetonitrile

A solution of 0.7 g N-sec-butylphthalimide in 220 ml spectrograde acetonitrile was purged with nitrogen for an hour and irradiated in a Type A photolysis for 7½ hours with the Hanovia lamp. Analytical TLC (20% ethyl acetate - 80% methylene chloride) showed two products, R_f = 0.05 and 0.13 and R_f = 0.15 and 0.6 (30% ethyl acetate - 70% methylene chloride).

*Retention time 80 min. (20 drops/50 sec., 12% ethyl acetate - 88% methylene chloride).

The reaction mixture was evaporated to dryness under vacuum. NMR of the residue revealed vinylic as well as alkyl signals. The residue was dissolved in a minimum amount of methylene chloride, and the products were separated from the starting material by preparative TLC (2 plates 1000 micron thickness, 19% ethyl acetate - 81% methylene chloride). There were three main resultant bands. The top band was identified by NMR as starting material.

The second band R_f = 0.7 was worked up with methylene chloride. NMR of the band contained vinylic signals and was similar to other dihydrophthalimide alkene alcohols. The product was further purified by preparative TLC (2 plates 250 micron thickness, 11% ethyl acetate - 89% methylene chloride). The band R_f = 0.35-0.6 was worked up with methylene chloride to yield a light yellow oil and white crystals,which were again purified by preparative TLC (1 plate 500 micron thickness, 12% ethyl acetate 88% methylene chloride). The resultant lower band (following methylene chloride workup) was tentatively identified by NMR and IR as 3-dihydrophthalimido-1-butene.

NMR: ($CDCl_3$) 1.3-1.5 δ(d J=6Hz, 3H, CH_3), 4.5-4.9 δ(m, 1H, N-CH), 4.9-5.3 δ(2 m, 3H, $-CH=CH_2$), 5.7-5.9 δ(s broad, 1H, OH), 7.2-7.7 δ(m, 5H, N-CH-O and phenyl).

IR: ($CDCl_3$) 3400, 3280 (O-H stretch), 2960, 2920 (C-H stetch), 1660 (C=O stretch), 1600, 1385, 1285 cm^{-1}.

The third band R_f = 0.3-0.55 (first plates) was worked up in the usual manner. The residue, 0.25 g, was redissolved in a minimum amount of methylene chloride and further purified by preparative TLC (2 plates 1000 micron thickness, 15% ethyl acetate - 85% methylene chloride). The single band, R_f = 0.2-0.4, was worked up in the usual manner with methylene chloride and methanol, and the solid was recrystallized twice from benzene/hexane. The structure was assigned as the cis and trans isomers of 3,4-benzo-6,7-dihydro-6,7-dimethyl(1H)azepine-2,5-dione, 43, on the basis of the spectral data and melting point, 172-214°.

NMR: ($CDCl_3$) 1.05-1.45 δ(3 d J=7Hz, 6H, CH_3), 2.5-3.0 δ (m, 1H, cis and trans O=C-C-H), 3.4-3.9 δ(p of d J=7Hz, and 2Hz, 1H, N-CH), 4.05-4.45 δ(m, 1H, N-CH), 6.9-8.2 δ(2 m broad and m, 5H, phenyl and N-H).

IR: ($CHCl_3$) 3420, 3220 (N-H stretch), 3080, 3000, 2980, 2950, 2900 (C-H stretch), 1685, 1660 (C=O stretch), 1600, 1570, 1480, 1450, 1390, 1375, 1360, 1290, 970 cm^{-1}.

MASS SPEC: m^+/e 203(P, 4%), 188(4%), 174(11%), 161(16%), 160(Base, 100%), 159(10%), 148(58%), 147(10%), 132(21%), 131(13%), 130(26%), 105(23%), 104(54%), 103(10%), 78(8%), 77(18%), 76(25%), 56(49%), 51(11%), 50(14%), 44(99%), 41(18%).

Anal: Calculated for $C_{12}H_{13}NO_2$: C, 70.91%; H, 6.45%; N, 6.89%; Found: C, 70.97%; H, 6.63%; N, 6.82%.

Photolysis of Inactive N-2-methylbutylphthalimide (I)

A solution of 1.5 g optically inactive N-2-methylbutylphthalimide in 230 ml spectrograde acetonitrile was purged with nitrogen for an hour and irradiated in a Type A photolysis for 14 hours with a Hanovia lamp. Analytical TLC of the reaction mixture (30% ethyl acetate - 70% methylene chloride) showed minor products, R_f = 0.6-0.8 and one major product, R_f = ~0.4.

The reaction mixture was evaporated to dryness under vacuum. NMR of the residue showed an alkyl doublet. The residue was dissolved in minimum amount of methylene chloride and methanol. The major product was isolated after purification by preparative TLC (2 plates 1000 micron thickness, 20% ethyl acetate - 80% methylene chloride). The product was characterized by lc and spectral data as 3,4-benzo-6,7-dihydro-6-methyl(1H)azepine-2,5-dione, 36.

Photolysis of Inactive N-2-methylbutylphthalimide (II)

A solution of 2 g optically inactive N-2-methylbutylphthalimide in 230 ml spectrograde acetonitrile was purged with nitrogen for an hour and irradiated in a Type A photolysis for 15 hours with the Hanovia lamp. Analytical TLC of the reaction mixture was similar to the previous reaction.

The reaction mixture was evaporated to dryness under vacuum. The residue was redissolved in a minimum amount of methylene chloride and eluted with three liters methylene chloride. The last 1½ liters contained a white solid identified by IR and melting point as phthalic anhydride. The major product was again characterized by its spectra following preparative TLC as 36.

Photolysis of Inactive N-2-methylbutylphthalimide and cis-1,3-pentadiene

A solution of 1 g optically inactive N-2-methylbutylphthalimide and 8 g freshly distilled cis-1,3-pentadiene in 210 ml sodium-dried tert-butanol was purged with nitrogen for 15 minutes and irradiated in a Type A photolysis for 3 3/4 hours with a Corex filtered Hanovia lamp. (The short irradiation period, filter, and triplet quencher was expected to stop secondary Type II reactions and allow isolation of 3,4-benzo-6,7-dihydro-6-ethyl-6-methyl(1H)azepine-2,5-dione). Analytical TLC of the reaction of the reaction mixture (30% ethyl acetate - 70% methylene chloride and 20% ethyl acetate - 80% methylene chloride) showed several products, R_f = 0.4-0.8. Lc analysis showed that 36 was a minor product compared with two shorter retention time (more highly alkylated) peaks.

The reaction mixture was evaporated to dryness under vacuum. The major product was purified three times by

preparative TLC (10% ethyl acetate - 90% methylene chloride, 7% ethyl acetate - 93% methylene chloride, and 5% ethyl acetate - 95% methylene chloride). NMR of the residue, following workup, showed no O-H but vinyl signals as well as the usual alkyl and phenyl signals. IR showed no OH or NH bands characteristic of either the azepinedione or the dihydro phthalimido alkene alcohol, analogous to the work of Kanaoka. (Lc analysis of the product showed that more than one component was present.)

Quantum Yields for N-alkylphthalimides

The quantum yield of any photochemical reaction is a measure of the reaction's efficiency (the more efficient the reaction, the higher the quantum yield). The quantum yield is defined to be the ratio of moles of product to the quantity of light incident on the photolysis sample. In these studies, the moles of product formed could either be measured with an internal hydrocarbon standard, by glpc, or with an external aromatic standard such as benzamide by high pressure liquid chromatography. The quantity of light could either be measured by the actinometry methods of Dunion and Trumbore[105] or the method of Parker and Hatchard.[107] Both of these methods are detailed below.

The method of Dunion and Trumbore employs cyclopentanone actinometry. Cyclopentanone is photochemically converted to 4-pentenal at 2537Å in a reaction whose quantum yield has been accurately determined as 0.37 ± 0.02. From the definition above, the quantity of light incident on the sample would be moles 4-pentenal/Φ or moles 4-pentenal/.37.

Moles 4-pentenal could be determined by response factors. An authentic sample of 4-pentenal was obtained by photolysis of cyclopentanone followed by distillation and subsequent glpc preparation. Molar response factors were determined using nonane as a standard.

Several solutions of cyclopentanone and nonane were irradiated in sealed tubes in the merry-go-round apparatus

with Source B light for 12 hours. The quantity of 4-pentenal produced was determined to be 3.64×10^{-4} moles by the following equation:

$$\text{moles 4-pentenal} = \text{Response Factor} \times \text{moles nonane} \times \frac{\text{area 4-pentenal}}{\text{area nonane}}$$

This quantity divided by 0.37 gave the light quantity incident on all the samples as 9.83×10^{-4} einsteins.

The second method employs ferrioxalate actinometry and is effective in the irradiation range of interest, 250-255 nm. The irradiation of a sulfuric acid solution of potassium ferrioxalate results in the reduction of iron from its ferric to ferrous state. The quantity of ferrous ions and subsequently the quantity of light can be determined by the complexation of ions. The quantity of light or einsteins (moles of photons) is equal to the product of the ferrous ions produced and the quantum yield at 254 nm for ferrioxalate decomposition (which has been accurately determined at 1.25).

There are two methods for measuring einsteins with this type of actinometry, the split ratio method and the direct irradiation method. The difference lies in the absence of the quartz reflector and reference cell in the direct irradiation method shown in Figure 8. The light source is effective for 200 hours and provides the 254 nm light for irradiations in this study. For both methods the light from the monochromator is collimated through a quartz

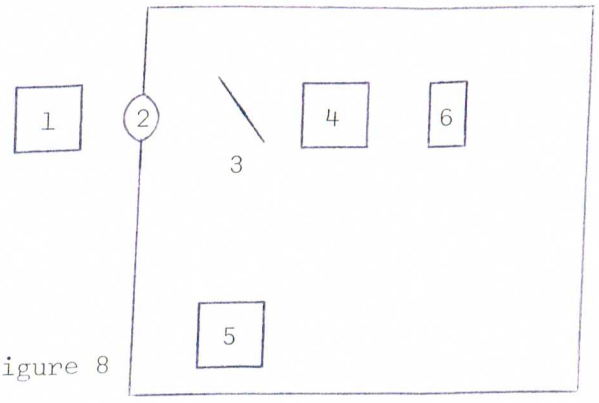


Figure 8

1. Monochromator
2. Quartz collimating lens
3. Optically clear quartz reflector
4. Sample cell
5. Reference cell
6. Backup cell

lens, and the resultant parallel rays are either split by the reflector in the split ratio method or impinge directly on the sample cell in the direct irradiation method.

For both ferrioxalate methods standard solutions must be prepared:

1. Actinometer solution: Potassium ferrioxalate, 0.006M, was prepared by dissolving 2.94 g solid $K_3Fe(C_2O_4)_3$ in 800 ml distilled water. Sulfuric acid, 100 ml 1N, was added slowly, and the solution was diluted to 1 liter with distilled water.

2. Indicator solution: 0.1% 1,10-phenanthrolene in distilled water.

3. Buffer solution: Sulfuric acid, 360 ml 1N was added slowly to 600 ml 1N sodium acetate, and the combined mixture was diluted to 1 liter with water.

The actinometer solution must be stored in the dark, and all work must be done either in the dark or with photographic red light due to photosensitivity of the ferrioxa-

late solution. All dilutions and washings must be done with distilled water.

In both methods, the light intensity or photons per second impinging on the sample cell was measured as follows: A known volume V_1 of actinometer solution (must fill reaction vessel) was irradiated at the desired wavelength, 254 nm, for a time t, measured in seconds. When the irradiation of the ferrioxalate solution was completed, an aliquot of the photolyte of V_2 was pipetted into a volumetric flask. To this aliquot, 2 ml indicator solution and a volume equal to V_2 of the buffer solution were added. The mixture was then diluted to the mark, which defined V_3 as the volume of the flask. The blank was prepared of unirradiated actinometer in the same proportions as the irradiated sample. Both solutions were allowed to stand at room temperature for an hour.

The number of moles of ferrous ions was determined spectrophotometrically. At 510 nm the absorbance A was related by Beer's law to the moles of ferrous ions $n_{Fe^{++}}$ as follows:

$$A = b \times \varepsilon \times c \quad \text{(where } b = 1 \text{ cm and } \varepsilon = 1.1 \times 10^4 \text{ liters/mole-cm)}$$

$$C = \frac{A}{b \times \varepsilon} = \frac{A}{1.1 \times 10^4}$$

$$n_{Fe^{++}} = \frac{A}{1.1 \times 10^4} \times \frac{V_1 V_3}{V_2}$$

(where once again V_1 is the volume of actinometer photolyzed, V_2 is volume of the aliquot taken, and V_3 is the diluted volume).

The intensity or quantity of light (photons) per unit time (sec) can be determined as:

$$I = \frac{\text{moles of ferrous ions}}{1.25 \text{ moles/einstein} \times t}$$

$$\text{since einsteins} = \frac{\text{moles of ferrous ion}}{\Phi} \quad \text{and } \Phi = 1.25$$

where t is the time of photolysis

Substituting from an earlier equation:

$$I = \frac{\dfrac{A}{1.1 \times 10^4} \times \dfrac{V_1 V_3}{V_2}}{t}$$

The split ratio was controlled by the angle of the quartz reflector, which split the light beam into two unequal components. The small component of the beam was deflected into the reference cell, (5) which monitored the light entering the sample cell. The backup cell (6) determined the portion of the larger beam not trapped by the sample cell. The split ratio is defined as the ratio of the light entering the sample cell less the backup cell to the light in the reference cell.

The split ratio was calculated before and after each phthalimide photolysis. The split ratio was determined experimentally as follows. Three cells were filled with actinometer (4), a 9 ml cell, and (5) and (6), 32 ml cells as shown in Figure 8. The cells were irradiated as shown in the diagram for 30 minutes, and samples were prepared for spectrophotometric analysis as described previously. It is essential for quantifying the light impingent on the sample cell that the split ratio remain constant before and after a photolysis run.

From the absorbance measured for the three cells and the dilutions used, the split ratio was calculated by the following equations:

$$\text{Split Ratio} = \frac{\text{Moles } Fe^{2+}_{\text{Sample}} - \text{Moles } Fe^{2+}_{\text{Backup}}}{\text{Moles } Fe^{2+}_{\text{Reference Cell}}}$$

It was experimentally determined that all the light was absorbed by the sample cell so the split ratio could then be defined as:

$$\text{Split Ratio} = \frac{\text{Moles } Fe^{2+}_{\text{Sample}}}{\text{Moles } Fe^{2+}_{\text{Reference}}}$$

Further substitution yielded an equation, which could be solved with experimental values:

$$\text{Split Ratio} = \frac{A_{\text{Sample}} \quad \frac{V_1 V_3}{V_2}}{A_{\text{Reference}} \quad \frac{V_1 V_3}{V_2}}$$

The data for three split ratios is given in Table XXII. The subsequent calculations show the consistency of the split ratios and therefore the quantum yield determinations.

The sample whose quantum yield was to be determined was prepared as stated on page 359. The reference and back-up cells were filled with actinometer solution. The irradiation was conducted for 30 hours, and the absorbance of the two actinometer cells was measured after the standard preparation. Two separate but identical 30-hour irradiations were conducted consecutively. The quantities of light were calculated by the following equations:

$$\text{Moles } Fe^{2+} = \frac{V_1 V_3}{V_2} \times \frac{A}{\varepsilon} \quad \text{where } \varepsilon = 1.1 \times 10^4$$

$$\text{Einsteins} = \frac{\text{Moles } Fe^{2+}_{\text{Reference}}}{\Phi\ Fe^{2+}} \times \text{Split Ratio} - \frac{\text{Moles } Fe^{2+}_{\text{Backup}}}{\Phi\ Fe^{2+}}$$

$$= \frac{\text{Moles } Fe^{2+}_{\text{Reference}} \times \text{Split Ratio} - \text{Moles } Fe^{2+}_{\text{Backup}}}{\Phi\ Fe^{2+}}$$

$$= \frac{\text{Moles } Fe^{2+}_{\text{Reference}} \times \text{Split Ratio} - \text{Moles } Fe^{2+}_{\text{Backup}}}{1.25}$$

Substitution gives the quantity in terms experimentally determined.

$$\text{Einsteins} = \frac{A_{\text{Reference}} \frac{V_1 V_3}{V_2} \times \text{Split Ratio} - A_{\text{Backup}} \frac{V_1 V_3}{V_2}}{1.1 \times 10^4 \times 1.25}$$

The data and calculations are shown in Table XXIII.

Table XXII

Split Ratio Determinations

Split Ratio #1 (15 minutes)

Cell	Volume(V_1)	Aliquot(V_2)*	Dilution(V_3)*	Absorbance
Sample	12.00	1.00	50.00	.174
Reference	32.00	10.00	25.00	.036
Backup	32.00	12.00	25.00	.000

$$\text{Split Ratio \#1} = \frac{\frac{.174 \times 12.00 \times 50.00}{1.1 \times 10^4 \times 1.00}}{\frac{.036 \times 32.00 \times 25.00}{1.1 \times 10^4 \times 10.00}} - 0 = 36.2$$

*Volumes in ml

Table XXII (Continued)

Split Ratio #2 (30 minutes)

Cell	Volume (V_1)*	Aliquot (V_2)*	Dilution	Absorbance
Sample	12.00	1.00	50.00	.38
Reference	32.00	10.00	25.00	.08
Backup	32.00	12.00	25.00	.00

$$\text{Split Ratio \#2} = \frac{\frac{.38 \times 12.00 \times 50.00}{1.1 \times 10^4 \times 1.00}}{\frac{.08 \times 32.00 \times 25.00}{1.1 \times 10^4 \times 10.00}} - 0 = 35.8$$

Split Ratio #3 (30 minutes)

Cell	Volume (V_1)*	Aliquot (V_2)*	Dilution	Absorbance
Sample	12.00	1.00	50.00	.385
Reference	32.00	10.00	25.00	.08
Backup	32.00	12.00	25.00	.00

$$\text{Split Ratio \#3} = \frac{\frac{.385 \times 12.00 \times 50.00}{1.1 \times 10^4 \times 1.00}}{\frac{.08 \times 32.00 \times 25.00}{1.1 \times 10^4 \times 10.00}} - 0 = 36.1$$

Average Split Ratio = 36.00

*Volumes in ml

Table XXIII

Determination of Light Quantity by Split Ratio

(Run 1) 30.00 hours

$$\text{Einsteins} = \frac{1}{1.25 \times 1.1 \times 10^4}\left(\frac{V_1V_3}{V_2} A_{\text{Reference}} \times \text{Split Ratio} - \frac{V_1V_2}{V_3} \times A_{\text{Backup}}\right)$$

$A_{\text{Reference}} = .60 \quad V_1 = 32.00 \quad V_2 = 1.00 \quad V_3 = 50.00$

$A_{\text{Backup}} = .42 \quad V_1 = 32.00 \quad V_2 = 2.00 \quad V_3 = 50.00$

$$*\text{Einsteins} = \frac{.032 \times .050}{1.25 \times 1.1 \times 10^4} \quad \frac{.60}{.001} \times 36.00 - \frac{.42}{.002}$$

$$= 1.17 \times 10^{-7} \times 2.14 \times 10^4$$

$$= 2.50 \times 10^{-3} \text{ einsteins}$$

(Run 2) 30.00 hours

$A_{\text{Reference}} = .58 \quad V_1 = 32.00 \quad V_2 = 1.00 \quad V_3 = 50.00$

$A_{\text{Backup}} = .41 \quad V_1 = 32.00 \quad V_2 = 2.00 \quad V_3 = 50.00$

$$*\text{Einsteins} = \frac{.032 \times .050}{1.25 \times 1.1 \times 10^4} \quad \frac{.58}{.001} \times 36.00 - \frac{.41}{.002}$$

$$= 1.17 \times 10^{-7} \times 2.07 \times 10^4$$

$$= 2.4 \times 10^{-3} \text{ einsteins}$$

*Within a run V_1 and V_3 are always equal and may be factored out. Because concentrations are in moles/liter the volumes V_1, V_2, and V_3 must be converted to liters.

The second method for determination of light quantity using ferrioxalate actinometry is the direct irradiation method. The quartz reflector was removed. This method requires careful determination of the irradiation time. The intensity, which has been previously defined, was measured before and after each determination. Since these intensities were constant, the quantity of light impinging on the photolysis sample was calculated to be the product of the intensity and the irradiation time (in seconds) less the light not absorbed (which is measured accurately by the backup cell).

The intensities were calculated by measuring the absorbance of the sample and backup cells for an irradiation period of exactly 30 minutes (1800 seconds). The intensities were calculated for the equation and following experimental data.

Run #1

$A_R = .39 \quad V_1^* = .012 \quad V_2^* = .50 \quad V_3^* = .050$

$A_B = .0 \quad V_1^* = .032 \quad V_2^* = .012 \quad V_3^* = .025$

$\varepsilon = 1.1 \times 10^4 \quad t = 1800 \text{ sec} \quad \Phi = 1.25$

$$\text{Intensity} = \frac{.39 \times .012 \times .050}{1.1 \times 10^4 \times 1.25 \times .001 \times 1.8 \times 10^3}$$

$$= 9.45 \times 10^{-9} \text{ einsteins/sec.}$$

*Volume in ml

Run #2

$A_R = .391 \quad V_1^* = .012 \quad V_2^* = .001 \quad V_3^* = .050$

$A_B = 0 \quad V_1^* = .032 \quad V_2^* = .012 \quad V_3^* = .025$

$$\text{Intensity} = \frac{.391 \times .012 \times .050}{1.1 \times 10^4 \times 1.25 \times .001 \times 1.8 \times 10^3} = 9.48 \times 10^{-9}$$

Run #3

$A_R = .388 \quad V_1^* = .012 \quad V_2^* = .001 \quad V_3^* = .050$

$A_B = 0 \quad V_2^* = .032 \quad V_2^* = .012 \quad V_3^* = .025$

$$\text{Intensity} = \frac{.388 \times .012 \times .050}{1.1 \times 10^4 \times 1.25 \times .001 \times 1.8 \times 10^3} = 9.41 \times 10^{-9}$$

Average Intensity $= 9.44 \times 10^{-9}$ einsteins/sec.

The number of moles of product in a photochemical reaction or the numerator of the quantum yield equation could be determined by glpc with an internal hydrocarbon standard such as eicosane or hexadecane. This method serves the double purpose of monitoring starting material disappearance or percentage conversion, as well as product formation. In order to measure the amount of product formation, an authentic sample of product must be isolated for determination of a response factor with the selected hydrocarbon.

*Volume in ml

The moles of product formation is defined as:

$$\text{Moles Product} = \frac{\text{Response Factor} \times \text{Moles Standard} \times \text{Area Product}}{\text{Area Standard}}$$

An alternate method for the determination of product formation, high pressure liquid chromatography with UV detector, can be used when the product has a phenyl moiety, i.e. UV absorption at 254 nm. An aliquot of photolyte is mixed with an aliquot of a standard solution of an external aromatic standard, such as benzamide. As before, the response factor of the product and the standard must be determined as shown in the previous equation. (Liquid chromatography on a silica gel column offers the advantages of separation of any components which can be separated by silica gel TLC, and separation of thermally unstable components.) The difficulties encountered are: selection of a solvent system, selection of a flow rate, and maintaining control of the instrument long enough to cure the column with the solvent (1 day prior to any quantitative work)*. This method, because of possible interference of an aromatic standard, cannot quantitatively measure starting material conversion straight away. (The problem may be circumvented by mixing an aliquot of the solution before photolysis with an aliquot of the standard solution and comparing the area ratios before photolysis with those after).

*One additional problem may arise if water from reverse phase liquid chromatography comes in contact with the silica gel column. The column becomes deactivated and is only reactivated by slow elution with increasingly nonpolar solvent systems.

The ring expansion products could not be separated from alkyl phthalimides by glpc. A compromise was effected where starting material conversion was determined by glpc, and product formation was determined by liquid chromatography. The overall efficiency of ring expansion was determined by a combination of the two methods where moles of product formed were compared to moles of starting material decomposed. The ring expansion products 36, 37, 39, 40, and 41 were isolated by the methods stated on pages 337 to 355. The response factors for the ring expansion products as determined on a silica gel column with a 12% ethyl acetate and 88% methylene chloride solvent system are shown in Table XXIV. (Samples of the products were purified until only one peak was present.) The flow rates are also shown in the table.

Table XXIV

Response Factors of Ring Expansion Products

Compound	Flow Rate (drops/sec)	Standard	Moles Compound	Moles Standard	Ratio
3,4-benzo-6,7-dihydro-6-methyl(1H) azepine-2,5-dione 36	20/70	benzamide	5.39×10^{-5}	1.22×10^{-4}	.44
3,4-benzo-6,7-dihydro-6,6-dimethyl(1H) azepine-2,5-dione 39	20/40	benzamide	4.48×10^{-5}	1.11×10^{-4}	.40
3,4-benzo-6,7-dihydro(1H) azepine-2,5-dione 37	20/40	benzamide	8.85×10^{-5}	1.14×10^{-4}	.78
3,4-benzo-6,7-dihydro-7,7-dimethyl(1H)azepine-2,5-dione 41	20/50	benzamide	4.72×10^{-5}	8.26×10^{-5}	.57
3,4-benzo-6,7-dihydro-7-methyl (1H)azepine-2,5-dione 40	20/70	m-methoxy-benzamide	5.39×10^{-5}	8.61×10^{-5}	.63

Table XXIV (Continued)

Compound	Area Compound	Area Standard	Ratio	Avg.	Molar Response Factor
3,4-benzo-6,7-dihydro-6-methyl(1H)azepine-2,5-dione 36	236	93	2.54	2.53	.175
	269	107	2.52		
	164	65	2.52		
3,4-benzo-6,7-dihydro-6-6-dimethyl(1H)azepine-2,5-dione 39	460	260	1.77	1.81	.223
	408	220	1.85		
	562	311	1.81		
3,4-benzo-6,7-dihydro(1H)azepine-2,5-dione 37	501	143	3.50	3.47	.224
	960	277	3.47		
	986	286	3.45		
3,4-benzo-6,7-dihydro-7,7-dimethyl(1H)azepine-2,5-dione 41	478	105	4.55	4.56	.125
	569	125	4.55		
	568	114	4.58		
	377	82	4.60		
	401	88	4.56		
	678	149	4.55		
3,4-benzo-6,7-dihydro-7-methyl(1H)azepine-2,5-dione 40	228	135	1.69	1.72	.363
	265	152	1.74		
	136	79	1.72		
	181	109	1.67		
	106	60	1.77		

Quantum Yields by Cyclopentanone Actinometry I

A 25 ml solution of .1608 g N-ethylphthalimide and 0.0420 g hexadecane in sodium-dried tert-butanol was divided into three 4 ml portions, which were introduced by syringe to the freeze-pump-thaw photolysis vessels. After 4 freeze-pump-thaw cycles, two of the samples were irradiated for 12 hours with the cyclopentanone samples.

The tubes were opened, and a 1 ml aliquot was taken from each. The aliquots were allowed to air evaporate as far as possible in vials. An aliquot of .9 ml .0502 g/100 ml benzamide in methylene chloride was added. The following results were obtained on the silica gel column using 12% ethyl acetate and 88% methylene chloride at 20 drops/40 sec. flow rate.

Tube	Area Product	Area Standard	Ratio	Avg.
1	178	240	.742	.765
	201	255	.789	
2	145	188	.771	.763
	167	221	.756	

	Moles Standard	Moles Prod./ml	Total Moles Product
1	3.73×10^{-6}	6.39×10^{-7}	2.56×10^{-6}
2	3.73×10^{-6}	6.32×10^{-7}	2.52×10^{-6}

With the light quantity for 12 hours in Source B (2537Å) being 9.35×10^{-4} einsteins, the quantum yield for N-ethylphthalimide is 0.0026.

Quantum Yields by Cyclopentanone Actinometry II

The following solutions were prepared:

Solution	N-alkyl-phthalimide or Imide	Phthalimide (g)	Standard (g) (Eicosane)
1	n-propyl	.1600	.0399
2	ethyl	.1608	.0408
3	isobutyl	.1600	.0402
4	isopropyl	.1598	.0400
5	tert-butyl	.1603	.0405
6	N,N-dibenzoyl-isobutylamine	.2422	.0408

The solutions were then diluted to 25 ml with sodium-dried tert-butanol. Two 4 ml samples of each solution were introduced to the freeze-pump-thaw photolysis vessels. After four freeze-pump-thaw cycles the tubes were sealed, equally spaced in the merry-go-round apparatus, and irradiated for exactly 12 hours with Source B (2537Å) light.

The tubes were opened and two 1 ml aliquots of each were immediately removed for product analysis. The aliquots were air evaporated as much as possible before the aliquot of standard was added.

Samples of the photolyte and unirradiated solutions were compared to determine percentage starting material conversion. The results along with glpc Column D conditions are shown in Tables XXV and XXVI.

The number of moles of standard in solution for each product analysis is described by the following equation:

$$\text{moles standard} = \frac{v \times c}{m}$$

where v = volume of aliquot, c = concentration of solution (in the same units as the volume), and m = molecular weight.

The moles of standard for each photolysis tube are calculated below. Benzamide, which was recrystallized from hexane, was the standard for all products except 40. m-methoxybenzamide, which was shown to be pure by lc, NMR, and melting point was used as a standard for the isopropylphthalimide quantum yield determination.

Solution 1: v = 1 ml c = 0.0524 g/50 ml m = 121 g/mole

$$\text{moles benzamide} = \frac{1 \times 0.0524/50}{121} = 8.6 \times 10^{-6}$$

Solution 2: v = 0.9 ml c = 0.0502 g/100 ml m = 121 g/mole

$$\text{moles benzamide} = \frac{0.9 \times 0.0502/100}{121} = 3.7 \times 10^{-6}$$

Solution 3: v = 0.9 ml c = 0.0502 g/100 ml m = 121 g/mole

$$\text{moles benzamide} = \frac{0.9 \times .0502/100}{121} = 3.7 \times 10^{-6}$$

Solution 4: v = 1 ml c = 0.1009 g/100 ml m = 151 g/mole

$$\text{moles of methoxybenzamide} = \frac{1 \times 0.1009/100}{151} = 6.6 \times 10^{-6}$$

Solution 5: Due to the large amount of product formation, two aliquots were added.

v = 0.9 ml c = 0.0502 g/100 ml and v = 1 ml

c = 0.0524 g/ 50 ml m = 121 g/mole

$$\text{moles of benzamide} = \frac{0.9 \times 0.0502/100 + 1 \times 0.0524/50}{121}$$

$$= \frac{4.52 \times 10^{-4} + 1.048 \times 10^{-3}}{121}$$

$$= \frac{1.50 \times 10^{-3}}{121}$$

$$= 1.23 \times 10^{-5}$$

The area ratio is then the only unknown term in the equation:

moles product = moles standard × molar response factor × area ratio

This quantity is the moles of product in the 1 ml aliquot. The total moles of product produced must be 4 times the quantity from the equation. The relative areas, flow rates, moles product/ml, and total moles of product for each photolysis tube are shown in Table XXVII.

The quantity of light used for the 12 hour irradiation was 9.35×10^{-4} einsteins. The reason this light quantity

could be used was a comparison of the quantum yield for N-ethylphthalimide in this experiment and in the previous experiment. The moles of product produced, as well as starting material converted, coincided for the same irradiation time. The quantum yields are shown in Table VII, where tert-butyl has the highest quantum yield.

Efficiency of the reaction is defined to be the ratio of moles of product produced to moles of starting material decomposed. The results are shown in Table VIII with the tert-butyl being the most efficient and the isobutyl the least.

Table XXV

Percent Conversion of N-alkylphthalimides in Quantum Yield Determination

(0 Hours)

Solution	Column Temperature	Area Phthalimide	Standard	Ratio	Avg.
1	190°	131	53	2.47	2.44
1		143	59	2.43	
1		595	245	2.43	
1		618	254	2.43	
2	170°	569	245	2.32	2.30
2		604	264	2.29	
2		561	242	2.32	
2		690	302	2.28	

Table XXV (Continued)

Solution	Column Temperature	Area Phthalimide	Standard	Ratio	Avg.
3	170°	689	204	2.65	2.72
3		363	132	2.75	
3		263	95	2.77	
3		283	105	2.70	
4		297	120	2.48	2.50
4		296	118	2.51	
4		726	290	2.50	
4		755	300	2.52	
5		330	124	2.66	2.68
5		310	114	2.72	
5		320	119	2.69	
5		360	136	2.65	
6	(Column H) 252°	611	227	2.69	2.68
6		533	196	2.72	
6		315	117	2.69	
6		311	119	2.64	

Table XXVI

Percent Starting Material Conversion in Quantum Yield Determination (12 Hrs. Irradiation)

Solution	Tube	Area Phthalimide	Area Standard	Ratio	Avg.	% Conversion
1	A	182	86	2.11	2.09	14.7
1	A	215	102	2.11		
1	B	237	115	2.06		
2	A	508	243	2.09	2.10	8.9
2	A	356	169	2.11		
2	B	634	302	2.10		
2	B	645	307	2.10		
3	A	458	213	2.15	2.15	21.1
3	A	398	186	2.14		
3	B	396	183	2.16		
3	B	431	203	2.13		
4	A	219	97	2.26	2.26	9.6
4	A	245	108	2.27		
4	B	313	139	2.25		
4	B	290	128	2.27		
5	A	287	140	2.05	2.04	23.9
5	A	523	257	2.04		
5	B	508	252	2.02		
5	B	489	239	2.05		

Table XXVI (Continued)

Solution	Tube	Area Phthalimide	Area Standard	Ratio	Avg.	% Conversion
6	A	307	116	2.65	2.68	(0.2)
6	A	310	115	2.70		
6	B	315	117	2.69		
6	B	311	117	2.67		

Table XXVII

Moles of Ring Expansion Product

in Quantum Yield by Cyclopentanone Actinometry II

Solution	Tube	Flow Rate (drops/sec)	Area Product	Area Standard	Ratio	Avg.	Moles $\times 10^{-7}$/ml	Total Moles $\times 10^{-6}$
1	A	20/70	128	115	1.11	1.11	16.7	6.68
1	A		126	111	1.15			
1	B		175	159	1.10			
2	A	20/40	174	132	.76	.76	6.3	2.5
2	A		200	154	.77			
2	B		92	70	.76			
2	B		165	125	.76			
3	A	20/40	287	121	2.37	2.35	19.5	7.8
3	A		338	143	2.36			
3	B		389	166	2.34			
3	B		409	175	2.34			

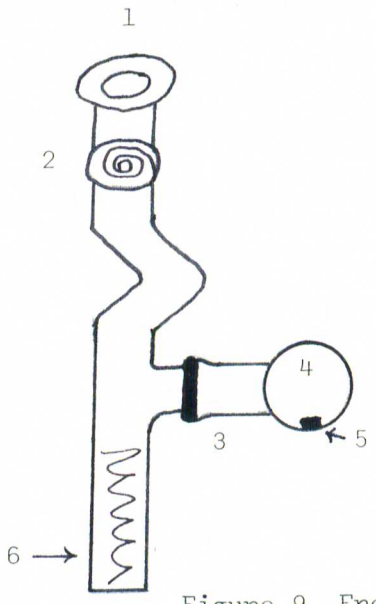
Table XXVII

(Continued)

Solution	Tube	Flow Rate (drops/sec)	Moles Product	Moles Standard	Ratio	Avg.	Moles $\times 10^{-7}$ ml	Total Moles $\times 10^{-6}$
4	A	20/50	144	186	.77	.77	18.4	7.38
4	A		147	189	.78			
4	A		152	198	.77			
4	B		113	144	.78			
4	B		104	141	.79			
4	B		203	271	.75			
5	A	20/70	520	138	3.77	3.75	57.7	23.1
5	A		397	106	3.75			
5	B		266	71	3.75			
5	B		379	101	3.75			

Quantum Yield by Ferrioxalate Actinometry I

A 25 ml solution was prepared with 0.0411 g eicosane, .1603 g tert-butylphthalimide, and sodium-dried tert-butanol. A 9 ml sample in the freeze-pump-thaw photolysis vessel (Figure 9) was carried through five freeze-pump-thaw cycles.



1. "O-ring" joint
2. stopcock
3. photolysis cell
4. quartz window
5. magnetic stirrer
6. freeze – pump-thaw vessel (as shown during degassing, when perpendicular photolyte drains into photolysis cell)

Figure 9. Freeze-Pump-Thaw-Vessel for Quantum Yield Determination

The vessel in Figure 9 had a #9 Pyrex "O ring" joint with "O ring" rubber washer and was detachable from the "black box" quartz irradiation vessel. (The reaction must be periodically checked to prevent freezing of the reaction mixture.) This apparatus also may be reused after cleaning as the final sealing is with a stopcock rather than destructive sealing with a torch. (Special care must be taken when opening or closing the stopcock to prevent breaking the vacuum.) As in the determination of light quantity during irradiation, the reaction mixture was agitated magnetically.

The first photolysis was carried out for 30 hours with Source C light at 254 nm. Two 1 ml aliquots were taken and concentrated as far as possible. A 1 ml aliquot of 0.0524 g/50 ml (benzamide in methylene chloride) was added to relate the area ratios to 8.6×10^{-6} moles. The area results and moles of product produced are given below. (Once again the quantity only represented the number of moles in the 1 ml aliquot.)

The solvent system was once again 12% ethyl acetate 88% methylene chloride, but the flow rate was 20 drops/45 sec.

Area Product	Area Standard	Ratio	Avg.	Moles/ml	Total Moles Produced
287	121	2.37			
345	146	2.36	2.33	2.51×10^{-5}	2.26×10^{-5}
394	174	2.27			
429	185	2.32			

The second run was a repeat of the first. A 9 ml aliquot of the solution used in the first run was taken through five freeze-pump-thaw cycles. The irradiation was conducted for 30 hours after determination of the second split ratio, and two 1 ml aliquots were taken and evaporated slowly on a steam bath. One ml of the standard solution (0.0524 g/50 ml) was added to each aliquot. The area results and product formation are shown on the following page.

Area Product	Area Standard	Ratio	Avg.	Moles/ml	Total Moles Produced
542	232	2.32			
184	78	2.36			
214	91	2.35	2.35	2.52×10^{-6}	2.7×10^{-5}
416	178	2.34			
402	171	2.36			

Both runs were made on the same sample concentration, with the same wavelength light, and for the same irradiation period. The product yields for each reaction differed only in the third place, which further verified the consistency of the two runs. The data on light quantity by split ratio gave the quantum yield for tert-butylphthalimide as 0.0093 which was the right magnitude but differed from the quantum yield determined by cyclopentanone actinometry by a factor of 2.5.

The split ratios determined experimentally and those calculated by others in previous experiments also differed by a factor of 2.5. When the split ratios were determined no light reached the backup cell, and the light intensity was constant in the sample cell at 9.48×10^{-9} einsteins/sec. By the direct irradiation method, the einsteins impinging on the sample in 30 hours (108,000 sec.) was 1.02×10^{-3} einsteins. The quantum yields were then calculated to be .0222 and .02223 or an average of 0.0223. This quantity is consistent with the quantum yield from cyclo-

pentanone actinometry for the decomposition of N-tert-butylphthalimide. The consistency showed cyclopentanone actinometry to be a viable method for determination of quantum yields in N-alkylphthalimides.

Quantum Yield by Ferrioxalate Actinometry II

A 25 ml solution was prepared with 0.1600 g tert-butylphthalimide, 0.0412 g eicosane, and sodium-dried tert-butanol. A 9 ml portion of the solution in the photolysis vessel used in the previous experiment was taken through five freeze-pump-thaw cycles. The light intensity was checked before and after each run again because a new bulb was used. The sample was then irradiated for 15 hours with Source C light at 254 nm with no quartz reflector, only a backup cell. The workup for product analysis was the same (8.6×10^{-6} moles of benzamide).

The intensities were measured without the quartz reflector on the sample and backup cells for exactly 30 minutes. The intensity calculations were determined by the sample cell since no light reached the backup ($A_{backup} = 0$). (Once again $\Phi = 1.25$ at 254 nm and $\varepsilon = 1.1 \times 10^{-4}$ l/mole-cm.)

Run 1

$A = 0.475 \quad V_1 = .0120\ l \quad V_2 = 1.0\times10^{-3} \quad V_3 = .0500 \quad t = 1800$ sec

$$\text{Intensity} = \frac{.475 \times .0120 \times .0500}{1.25 \times 1.1\times10^{-4} \times 1800 \times 1.0\times10^{-3}} = 1.1\times10^{-8} \text{ ein./sec.}$$

Run 2

$A = 0.476 \quad V_1 = 0.0120\ l \quad V_2 = 1.00 \times 10^{-3}\ l \quad V_3 = 0.0500\ l$

$t = 30.01$ min. $= 1801$ sec.

$$\text{Intensity} = \frac{0.476 \times .0120 \times 0.0500}{1.25 \times 1.1 \times 10^{4} \times 1.0 \times 10^{-3} \times 1801} = 1.1 \times 10^{-8} \text{ ein./sec.}$$

The intensities were consistent, hence the light quantity was once again the product of the intensity and the irradiation time in seconds less the light not absorbed. The absorbance of the backup cell at a dilution of 12 to 25 ml was 0.01, therefore that term was negligible. The light quantity was then 54,000 sec. of 1.1×10^{-8} einsteins/sec. or 5.94×10^{-4} einsteins.

As previously stated, the product analysis was carried out as in previous analyses. The results are shown in the following table:

Area Product	Area Standard	Ratio	Avg.	Moles/ml	Total Moles Produced
54	39	1.39			
47	33	1.39	1.40	1.51×10^{-6}	1.36×10^{-5}
112	80	1.39			
109	76	1.43			

The quantum yield for tert-butylphthalimide was calculated to be 0.02229 from the above data. These results are

consistent with the previous ferrioxalate quantum yield determination and also the cyclopentanone actinometry determination. A second run of ferrioxalate (II) could not verify the first because the sample froze during irradiation. The quantum yields, although low, were consistent, and certain reactions were quite efficient.

Photolysis of Active N-2-methylbutylphthalimide I

A solution of 0.4805 g N-2-methylbutylphthalimide and 0.1203 g hexadecane in 130 ml sodium-dried tert-butanol in a quartz tube was purged with nitrogen for an hour and irradiated in a Type B photolysis for 21 hours. Glpc (Column F, 190°) analysis of a zero hour and an irradiated sample showed 11-12% starting material conversion.

The solvent was distilled at atmospheric pressure, and the residue was then passed on Column Q at 175-185°, and unreacted starting material was recovered. (Unirradiated starting material was also purified under similar conditions). Solutions were prepared with 0.1209 g unirradiated and 0.1102 g irradiated starting material each in 5 ml pure ethanol. Comparison of the rotation of the unirradiated with that of the phthalimide recovered after 21 hours' irradiation showed little loss of optical activity ($[\alpha]^{25}_{370}$ = +8.68° at 0 hours and $[\alpha]^{25}_{370}$ = +8.64° at 21 hours).

Photolysis of Active N-2-methylbutylphthalimide II

A solution of 1.4939 g optically active N-2-methylbutylphthalimide and 0.4291 g hexadecane in 100 ml sodium-dried tert-butanol was divided into 5-ml aliquots in quartz tubes. A zero hour sample was retained, and 12 tubes were fitted with rubber septa covered with aluminum foil. Each tube was purged with nitrogen for 10 minutes. The tubes were evenly spaced in the merry-go-round apparatus and irradiated with Source B light.

Two tubes, equally spaced, were removed at 10, 15, 20, 25, and 31 hours. Starting material conversion was monitored by glpc on Column F, and the results are shown in Table XXVIII. ORD studies showed concentric lines, that diverged at low wavelengths. Due to the small differences in starting material conversion absolute rotations could not be determined.*

For each time tubes were removed from the apparatus, two 1 ml aliquots of the reaction mixture were placed in labeled vials and evaporated to dryness. A standard solution of 1 ml of 0.0524 g/50 ml (8.66×10^{-6} moles/ml) recrystallized benzamide in methylene chloride was added to each. Lc analysis of the major product was conducted for

*A change in curve shape would be expected with respect to time if either optically active 3,4-benzo-6,7-dihydro-6-ethyl-6-methyl(1H)azepine-2,5-dione or 3,4-benzo-6,7-dihydro-6-methyl(1H)azepine-2,5-dione were produced-meaning products are inactive.

the various time samples (flow rate 20 drops/65-70 sec., 12% ethyl acetate - 88% methylene chloride), and the results are shown in Table XXIX.

Table XXVIII

Percent Conversion of Optically Active

N-2-methylbutylphthalimide

Sample	Time (Hrs.)	Area Starting Material	Area Standard	Ratio	Avg.	% Conversion
A	0	233	105	2.22		
A	0	248	114	2.18		
A	0	268	122	2.20		
A	0	260	119	2.18	2.19	0
A	0	248	114	2.18		
A	0	262	119	2.20		
A	10.5	372	180	2.07		
A	10.5	320	153	2.09		
A	10.5	280	134	2.09		
B	10.5	257	122	2.10	2.09	4.6
B	10.5	280	133	2.11		
B	10.5	251	120	2.09		
A	15	269	131	2.05		
A	15	234	114	2.05		
B	15	205	100	2.05	2.05	6.4
B	15	206	101	2.04		
B	15	206	101	2.04		
B	15	236	115	2.05		

Table XXVIII (Continued)

Sample	Time (Hrs.)	Area Starting Material	Area Standard	Ratio	Avg.	% Conversion
A	20	249	124	2.01		
A	20	228	113	2.01		
A	20	226	114	1.98	2.00	8.7
B	20	203	102	1.99		
B	20	291	145	2.00		
B	20	287	143	2.00		
A	25.5	277	142	1.95		
A	25.5	295	151	1.95		
B	25.5	182	94	1.94	1.95	11
B	25.5	223	115	1.94		
B	25.5	225	115	1.96		
A	31	234	124	1.89		
A	31	248	132	1.88		
A	31	219	117	1.87	1.88	14.2
B	31	230	122	1.89		
B	31	199	106	1.88		
B	31	225	121	1.86		

Table XXIX

Product Yield from Photolysis of

Optically Active N-2-methylbutylphthalimide

Sample*	Area Product	Area Standard	Ratio	Avg.	Moles** Prod./ml ($\times 10^{-6}$)	Total Moles Product ($\times 10^{-5}$)
A	184	103	1.79			
A	148	82	1.80	1.79	2.7	1.4
A	166	92	1.80			
A	169	96	1.76			
B	121	44	2.75			
B	450	164	2.74			
B	248	89	2.79	2.75	4.2	2.1
B	186	68	2.74			
B	232	85	2.73			
C	258	65	3.91			
C	166	43	3.86	3.88	5.9	2.9
C	167	43	3.88			
C	194	50	3.88			
D	254	54	4.70			
D	247	52	4.75	4.71	7.1	3.6
D	213	46	4.64			
D	217	46	4.64			
D	219	46	4.76			

*A = 10.5 hours; B = 15 hrs.; C = 20 hrs.; D = 25.5 hours; E = 31 hrs.

**Moles product/ml = response factor (.175) × area ratio × moles benzamide (8.7×10^{-6}).

Table XXIX (Continued)

Sample*	Area Product	Area Standard	Ratio	Avg.	Moles** Prod./ml ($\times 10^{-6}$)	Total Moles Product ($\times 10^{-5}$)
E	171	30	5.70			
E	200	35	5.71			
E	194	34	5.71	5.73	8.7	4.4
E	197	35	5.63			
E	194	33	5.88			

*A = 10.5 hours; B = 15 hrs.; C = 20 hrs.; D = 25.5 hours; E = 31 hrs.

**Moles product/ml = response factor (.175) × area ratio × moles benzamide$_{(8.7 \times 10^{-6})}$.

Preparation of N,N-dibenzoylisobutylamine

In a 100 ml 1-neck round bottom flask fitted with reflux condenser and magnetic stirrer, 27 g of N-isobutylbenzamide were liquified, and 40 ml of benzoyl chloride (excess) were added slowly. The stirred mixture was slowly heated to 190-200°C for 17 hours. The excess unreacted benzoyl chloride was removed by vacuum distillation. NMR showed that the residue was 70% product by comparison of starting material triplet at 3.4δ to product doublet for the same N-C-H at 3.9 δ.

Vacuum distillation of the residue yielded 13.9 g impure imide at 155-160°/0.6 mm. The solid was recrystallized three times from hexane and dried under vacuum to yield 9.3g white plates, m.p. 95-97°. Purity can be determined by loss of the farthest downfield multiplet in the phenyl region of the NMR which is simplified to one phenyl multiplet. Glpc on Column H at 200° showed 99.5% purity.

NMR: ($CDCl_3$) 0.9-1.15 δ(d J=6, 5Hz, 6H, CH_3), 1.8-2.7 δ (m, 1H, $(CH_3)_2CH$), 3.85-4.05 δ(d J=7Hz, 2H, N-CH_2-CH), 7.0-7.7 δ(m, 10H, phenyl).

IR: (CCl_4) 3070, 3040, 2970, 2940, 2880 (C-H stretch), 1695, 1665 (C-O stretch), 1600, 1580, 1465, 1450, 1435, 1375, 1360, 1325, 1305, 1240, 1180, 1090, 1075, 1030, 920, 715, 695 (monosubstituted benzene), 660 cm^{-1}.

UV: (EtOH) λ max 249 (ε = 12,000), 239(ε = 11,600), 224(ε = 13,200), 219(ε = 13,600), 215(ε = 13,200), and

at 254 (ε = 11,500).

Photolysis I of N,N-dibenzoylisobutylamine

A solution of 1.5 g N,N-dibenzoylisobutylamine in 200 ml sodium-dried tert-butanol was purged with nitrogen for an hour in a quartz tube fitted with a wired-on septum and magnetic stirrer. The solution was irradiated with Source B light for 150 hours. Samples were taken with nitrogen purged needles at 12, 48, and 96 hours and analyzed by glpc on Column H at 150° and 200°. No product formation or starting material disappearance was observed. TLC showed only one spot under conditions where a ketoamide would separate from starting material.

Photolysis II of N,N-dibenzoylisobutylamine

The solution of 2.5 g N,N-dibenzoylisobutylamine and 240 ml spectrograde acetonitrile was purged with dry nitrogen for 1 1/2 hours. A Type A photolysis was conducted for 92 hours with the Hanovia lamp. On samples taken during the course of the reaction, glpc showed two trace products and one minor product on Column H at 150° and 200°. Coinjection showed the major product to be N-isobutylbenzamide. The R_f of the product also matched that of isobutylbenzamide using TLC with 20% ethyl acetate and 80% methylene chloride.

The solvent was evaporated to five ml. Passage of the solid and liquid on Column O at 190° gave a solid whose NMR also matched isobutylbenzamide.

Quenching Experiment on N-tert-butylphthalimide

The following solutions were prepared:

	Sample 1	Sample 2	Sample 3
tert-butylphthalimide	0.4380 g	0.4394 g	0.4335 g
	-0.2380	-0.2386	-0.2330
	0.2000 g	0.2008 g	0.2005 g
Eicosane	0.2884 g	0.2889 g	0.2829 g
	-0.2382	-0.2384	-0.2333
	0.0502 g	0.0505 g	0.0496 g
Cis-1,3-pentadiene*		23.7531 g	23.2594 g
		-23.5830	-21.5595
		0.1701 g	1.6999 g

All three solutions were diluted to 25 ml with dry tert-butyl alcohol (sodium-distilled). Four ml of each sample were pipetted into quartz tubes which were then fitted with rubber septa. Each sample was degassed 90 seconds with dry nitrogen. The samples were placed in a merry-go-round apparatus and irradiated for 9 hours with 10 General Electric 15 watt G15T8 germicidal lamps (90% of the light <760 nm is 254 nm or 2537Å). Zero-hour samples of each solution

*freshly distilled

were compared with the irradiated samples by glpc on Column F at 170° at attenuation 16 × 10^{-11}. The results are shown in Table XXX.

Percentage Disappearance of Starting Materials

Sample 1: $100 - \frac{2.54}{2.91} \times 100 = 12.7\%$

Sample 2: $100 - \frac{2.37}{2.74} \times 100 = 13.6\%$

Sample 3: $100 - \frac{2.41}{2.87} \times 100 = 15.3\%$

The disappearance of starting material was not appreciably slowed in a 0.1M or a 1M triplet quencher solution over a solution containing no quencher. This indicates that the photodecomposition of tert-butylphthalimide does not arise via the triplet state.

Table XXX

Conversion of tert-butylphthalimide in Quenching Experiment

Sample	Time (hours)	Area Standard	Area Phthalimide	Ratio	Avg.
1	0	348	1007	2.89	2.91
1	0	426	1250	2.93	
1	9	380	961	2.53	
1	9	360	923	2.56	2.54
1	9	349	906	2.59	
1	9	321	799	2.49	
2	0	442	1203	2.72	2.74
2	0	505	1384	2.74	
2	0	430	1181	2.75	
2	0	428	1179	2.75	
2	9	428	1026	2.40	2.37
2	9	452	1071	2.37	
2	9	470	1106	2.35	
3	0	358	1034	2.88	2.86
3	0	397	1129	2.84	
3	9	407	978	2.40	2.41
3	9	367	884	2.41	

Quenching Experiment on N-isobutylphthalimide

The following solutions were prepared:

	Sample 1	Sample 2	Sample 3
Isobutylphthalimide	0.4430 g	0.4423 g	0.4447 g
	-0.2424	-0.2421	-0.2445
	0.2003 g	0.2002 g	0.2002 g
Eicosane	0.2928 g	0.2935 g	0.2963 g
	0.2428	0.2430	0.2453
	0.0500 g	0.0505 g	0.0510 g
Cis-1,3-pentadiene*		24.2697 g	25.7080 g
		-24.0716	-23.9778
		0.1981 g	1.7302 g

All three solutions were diluted to 25 ml with dry tert-butyl alcohol (distilled from sodium). Four ml of each sample were pipetted into quartz tubes, which were then fitted with rubber septa. Each sample was degassed for 90 seconds with dry nitrogen. The septa were covered with aluminum foil, equally spaced in the merry-go-round apparatus, and irradiated for 9 hours with 10 General Electric 15 watt G15T8 germicidal lamps. Zero-hour samples of each solution were compared with irradiated samples of each solution by glpc on Column F at 190° at attenuation 16×10^{-11}. Tubes were numbered as in the previous experiment. The results are shown in Table XXXI.

*freshly distilled

The relative rates of disappearance were calculated as before:

No Quencher: $100 - \frac{2.32}{2.69} \times 100 = 13.8\%$

0.1M Quencher: $100 - \frac{2.18}{2.65} \times 100 = 17.8\%$

1.0M Quencher: $100 - \frac{1.80}{2.73} \times 100 = 34.1\%$

The rate of disappearance was not decreased by quencher but rather accelerated, and the rate of acceleration was increased by increased amounts of quencher. There was the possibility of experimental error since only one tube of each solution was irradiated. The experimental results, however, indicated that the cis-1,3-pentadiene participated either directly or indirectly in the photodecomposition of N-isobutylphthalimide (to a greater extent than in N-tert-butylphthalimide).

Table XXXI

Conversion of iso-butylphthalimide in Quenching Experiment

Sample	Time (hours)	Area Standard	Area isobutyl-phthalimide	Ratio	Avg.
1	0	251	676	2.69	2.69
1	0	229	616	2.69	
1	0	206	554	2.69	
1	9	236	547	2.32	2.32
1	9	234	543	2.32	
1	9	232	537	2.31	
2	0	245	650	2.65	2.65
2	0	240	639	2.66	
2	0	234	616	2.63	
2	9	256	558	2.18	2.18
2	9	252	557	2.21	
2	9	274	590	2.15	
3	0	218	592	2.71	2.73
3	0	211	584	2.74	
3	0	237	650	2.74	
3	9	232	415	1.79	1.80
3	9	240	428	1.80	
3	9	251	451	1.81	

Quenching Check on N-isobutylphthalimide

Four ml aliquots of Sample 1 solution from the N-isobutylphthalimide quenching experiment were pipetted into three quartz tubes and numbered 7-1, 7-2, and 7-3. Four ml aliquots of the Sample 3 solution from the same experiment (containing 1M cis-1,3-pentadiene) were pipetted into three quartz tubes and numbered 8-1, 8-2, and 8-3. Zero hour samples of each solution were retained and numbered 7-0 and 8-0. The six tubes were fitted with rubber septa and degassed for 90 seconds with dry nitrogen. Each septum was covered with aluminum foil, and the tubes were equally spaced in the merry-go-round apparatus. The tubes were then irradiated as in the previous experiment for nine hours (2537Å light).

The zero hour samples were compared with the irradiated samples by glpc on Column F at 190° at attenuation 8×10^{-10}. The results are shown in Table XXXII.

The relative rates of disappearance were calculated as before:

No Quencher (7): $100 - \frac{2.45}{2.83} \times 100 = 13.4\%$

Quencher (8): $100 - \frac{1.79}{2.66} \times 100 = 32.7\%$

These percentages reflected a dramatic increase in the rate of photodecomposition of N-isobutylphthalimide with

1M quencher present (verifying the results of the previous experiment). The reaction is definitely not quenched by cis-1,3-pentadiene.

Table XXXII

Conversion of N-isobutylphthalimide in Quenching Experiment II

Sample	Standard	Starting Material	Ratio	Avg.	
7-0	251	708	2.82	2.83	
	239	678	2.84		
8-0	255	577	2.66	2.66	
	249	660	2.65		
	213	568	2.67		
		Irradiated Samples			
7-1	206	509	2.47	2.44	2.45
	227	547	2.41		
	193	472	2.44		
7-2	208	524	2.47	2.47	
7-3	217	532	2.45		
	183	456	2.49		
8-1	200	363	1.82	1.82	1.79
8-2	238	430	1.81	1.79	
	249	442	1.77		
8-3	258	453	1.76	1.78	
	206	369	1.79		
	206	360	1.75		
	254	460	1.81		

Determination of Product Yields in Quenching Experiments

The yields of ring expansion products for the quenching reactions of N-isobutylphthalimide and N-tert-butylphthalimide were determined by lc. An aliquot of each photolyte was removed and evaporated to dryness, and a one-ml aliquot of standard benzamide in methylene chloride solution (0.1105 g/100 ml) was added. Analysis was conducted with a 12% ethyl acetate-88% methylene chloride solvent system at a flow rate of 20 drops/30 sec.

The calculations were similar to previous experiments where moles product/ml = area ratio × response factor × moles benzamide. In this case, moles benzamide = 9.1×10^{-6}, and the response factors for the two products were .223 and .125 for the 6,6-dimethyl and the 7,7-dimethyl azepinediones respectively. The results of these calculations are shown in Table XXXIII.

Several important observations can be made from these experiments. The rate of starting material disappearance increases with increasing quencher concentration, but the ring expansion product yield decreases. New product peaks in the lc are observed in photolysis solutions with quencher.

Table XXXIII

Product Yields for Quenching Experiments

Material	Quencher Concentration	Area Product	Area Standard	Ratio	Avg.	Area Prod/ml ($\times 10^{-6}$)	Total Moles Product ($\times 10^{-5}$)
t-butyl	0	282	53	5.32			
t-butyl	0	402	73	5.51			
t-butyl	0	351	66	5.32	5.3	6.0	2.4
t-butyl	0	421	83	5.07			
t-butyl	0.1m	291	60	4.85			
t-butyl	0.1m	302	62	4.87	4.86	5.5	2.2
t-butyl	0.1m	296	61	4.85			
t-butyl	1.0m	239	92	2.60			
t-butyl	1.0m	273	103	2.65			
t-butyl	1.0m	256	98	2.61	2.63	3.0	1.2
t-butyl	1.0m	305	115	2.65			
isobutyl	0	235	213	1.10			
isobutyl	0	272	257	1.06			
isobutyl	0	153	144	1.06	1.06	2.2	.87
isobutyl	0	176	169	1.04			
isobutyl	0.1m	69	86	.80			
isobutyl	0.1m	68	86	.79	.79	1.6	.64
isobutyl	0.1m	71	92	.77			
isobutyl	1.0m	28	86	.33			
isobutyl	1.0m	44	132	.33	.33	.67	.28

Photolysis of N-methylphthalimide in Acetonitrile

A solution of 1 g N-methylphthalimide in 230 ml spectrograde acetonitrile was purged with nitrogen for an hour and irradiated in a Type A photolysis for 16 hours with the Hanovia lamp. Analytical TLC of the reaction mixture (30% ethyl acetate-70% methylene chloride) showed no detectable product formation. The reaction mixture was evaporated to dryness under vacuum. NMR of the residue showed only starting material.

Photolysis of N-methylphthalimide in Tert-butanol

A solution of 1 g N-methylphthalimide in 220 ml sodium-dried tert-butanol was purged with nitrogen for an hour and irradiated in a Type A photolysis for 18 hours with the Hanovia lamp. Analytical TLC of the reaction mixture (20% ethyl acetate-80% methylene chloride and 30% ethyl acetate-70% methylene chloride) showed no detectable product formation, only starting material. The reaction mixture was evaporated to dryness under vacuum. NMR of the residue again showed only starting material.

Photolysis of N-methylphthalimide and cis-1,3-pentadiene I

A solution of 1 g N-methylphthalimide and 7 g freshly distilled cis-1,3-pentadiene in 230 ml spectrograde acetonitrile was purged with nitrogen for 15 minutes and irradi-

ated in a Type A photolysis for 7 hours with a Corex filtered Hanovia lamp. Analytical TLC of the reaction mixture (20% ethyl acetate-80% methylene chloride) showed product formation R_f = 0.5 and 0.6.

The reaction mixture was evaporated to dryness under vacuum. The residue was dissolved in a minimum amount of methylene chloride, and partial purification of the products attained by preparative TLC (2 plates 1000 micron thickness, 10% ethyl acetate-90% methylene chloride). The top band was identified by NMR as starting material.

The second and third bands R_f = 0.5 and 0.6 were inseparable even after repeated preparative TLC (5% ethyl acetate-95% methylene chloride). Although the products were not characterized, the NMR of the residue showed alkyl as well as vinylic signals in addition to the phenyl and $N\text{-}CH_3$ signals.

Photolysis of N-methylphthalimide and cis-1,3-pentadiene II

A solution of 1 g N-methylphthalimide and freshly distilled cis-1,3-pentadiene in 220 ml sodium-dried tert-butanol was purged with nitrogen for 15 minutes and irradiated in a Type A photolysis for 7 1/2 hours with a Corex filtered Hanovia lamp. Once again analytical TLC showed product formation, and NMR of the impure products following preparative TLC showed the vinylic and alkyl signals. These two

reactions conclusively proved that the alkene reacted with the phthalimide.

Photolysis of Isobutylene and Phthalimide

A solution of 0.7 g phthalimide in 210 ml spectrograde acetonitrile was purged with nitrogen for 1/2 hour in an ice bath. Isobutylene, 22 ml, were condensed into the reaction mixture. A Type F photolysis was conducted for 5 1/2 hours with the Hanovia lamp. Silica gel TLC on 30% ethyl acetate-70% methylene chloride showed only starting material. The reaction mixture was then evaporated to dryness, and NMR of the residue showed a small concentration of protons in the 1-2 δ region.

The residue was redissolved in a minimum amount of methanol and methylene chloride and streaked on two 20 × 20 cm 1000 micron thickness silica gel plates. The solvents were allowed to thoroughly dry. The plates were then eluted to excess with 20% ethyl acetate-80% methylene chloride. The band between 0.4 and .75 R_f was scraped. (The expected products, 3,4-benzo-6,7-dihydro-6,6-dimethyl(1H) azepine-2,5-dione and 3,4-benzo-6,7-dihydro-7,7-dimethyl (1H)azepine-2,5-dione, which were prepared independently by irradiation of N-isobutylphthalimide and N-tert-butylphthalimide respectively, would be in this region on the plates under the elution conditions).

The scrapings were washed with methylene chloride and methanol. When the solvents were evaporated, NMR did not show the large singlet between 1 and 2 δ indicative of the dimethyl compounds and isobutylene photo-cycloaddition A duplicate sample was irradiated for 5 hours. Product formation was not shown either by NMR or silica gel TLC.

Photolysis of N-methylphthalimide and Furan

A solution of 1 g N-methylphthalimide and 6 g freshly distilled furan in 210 ml spectrograde acetonitrile was purged with dry nitrogen. A Type A photolysis was conducted for 7 hours with the Hanovia lamp. Comparison of a 0 hour sample and an irradiated sample showed only starting material by TLC. The reaction mixture was evaporated to dryness, and the residue was rinsed several times with carbon tetrachloride. NMR of the residue showed only starting material (phenyl to alkyl region 4:3).

Two duplicate samples were irradiated for 6 1/2 and 5 hours respectively. There was no product formation in either when tested by NMR and TLC. (It is perhaps significant that Koch found furan additions to his imino-ethers to be reversible when heated.) When a fourth sample was irradiated for 7 hours, and the solvent was allowed to evaporate at room temperature, there was still no product formation.

Photolysis of N-2-propenylphthalimide

A solution of 1 g N-2-propenylphthalimide in 210 ml spectrograde acetonitrile was degassed for an hour with dry nitrogen. A Type A photolysis was conducted for 17 hours with the Hanovia lamp. Comparison of a 0 hour sample with an irradiated sample on silica gel TLC with 10% ethyl acetate-90% methylene chloride and 30% ethyl acetate-70% methylene chloride showed only starting material.

The reaction mixture was concentrated to dryness, and the residue was redissolved three times in carbon tetrachloride which was evaporated under vacuum. The NMR of the residue showed only unconverted starting material. A duplicate sample of the phthalimide was irradiated under the same conditions for 16 hours with no reaction detectable by NMR or TLC.

Photolysis of N-methylphthalimide and Isobutylene

A solution of 1.5 g N-methylphthalimide and 210 ml spectrograde acetonitrile was purged with nitrogen for 1/2 hour. The reaction mixture was cooled in an ice-salt-water bath, and 14 ml isobutylene were condensed into the reaction nixture. A Type F photolysis was conducted for 2.75 hours with the Hanovia lamp. Analytical TLC (20% ethyl acetate-80% methylene chloride) showed production of one product $R_f = \sim 0.6$.

The reaction mixture was evaporated to dryness under vacuum. NMR of the residue showed no vinylic signals but instead showed one alkyl singlet signal. In addition, a singlet at 3.4-3.5 δ showed $N-CH_2$, but absence of signals 2-3 δ showed no hydrogens α to C=O. The NMR evidence indicated that the isobutylene was added in only one way.

The residue was recrystallized from the acetonitrile, and 0.5 g starting material was recovered. The filtrate was concentrated to dryness under vacuum and redissolved in a minimum amount of methylene chloride. Preparative TLC (2 plates 1000 micron thickness, 11% ethyl acetate-89% methylene chloride) yielded a band R_f 0.45-0.75, which was worked up in the usual fashion with methanol and methylene chloride.

The residue, 0.2 g, was recrystallized three times from hexane. The white crystalline solid, .15 g, m.p. 88-89° was assigned the structure of 3,4-benzo-6,7-dihydro-1,6,6-trimethylazepine-2,5-dione on the basis of the spectral data, 56.

NMR: ($CDCl_3$) 1.2-1.35 δ(s, 6H, CH_3), 3.2-3.35 δ(s, 3H, $N-CH_3$), 3.45-3.55 δ(s, 2H, $N-CH_2$), 7.4-8.1 δ(m, 4H, phenyl).

IR: (CCl_4) 3080, 2970, 2940, 2870 (C-H stretch), 1695 (C=O stretch, ketone), 1660 (C=O stretch, amide), 1600, 1485, 1475, 1430, 1400, 1390, 1355, 1320, 1275, 1205, 1140, 1075, 970, 960, 925, 720 cm^{-1}.

MASS SPEC: m^+/e 217(P, 15%), 176(22%), 175(base, 100%), 163(63%), 160(98%), 147(29%), 133(17%), 131(19%), 117 (22%), 105(24%), 104(53%), 77(36%), 76(53%), 50(19%), 44(97%), 42(44%), 41(53%).

UV: (EtOH) λ max 319(ε = 176), 282(ε = 1660), 234 (ε = 10,400), 210(ε = 25,300), min 273(ε = 1580) and at λ 254(ε = 4180).

Anal: Calculated for $C_{13}H_{15}NO_2$: C, 71.86%, H, 6.96%, N, 6.45%; Found: C, 71.83%; H, 7.20%; N, 6.38%.

Photolysis of N-methylphthalimide and 1,3-butadiene

A solution of 1.5 g N-methylphthalimide and 210 spectrograde acetonitrile was purged with nitrogen for 1/2 hour. The reaction mixture was cooled in an ice-salt-water bath, and 22 ml 1,3-butadiene were condensed into the reaction mixture. A Type F photolysis was conducted for 2.5 hours with the Hanovia lamp. Analytical TLC of the reaction mixture (20% ethyl acetate-80% methylene chloride) showed one product R_f = ~0.6 (R_f = ~0.3 with 10% ethyl acetate-90% methylene chloride).

The reaction mixture was evaporated to dryness under vacuum. NMR of the residue showed two sets of vinyl signals and two sets of doublets in the alkyl region. The ratios of the alkyl signals varied from 1:2 when a Corex filter was used to 1:4 with unfiltered light. The addition prod-

ucts were roughly assigned the structure of the syn and anti isomers of 3,4-benzo-6,7-dihydro-6-ethylidene-1-methylazepine-2,5-dione on the basis of the NMR spectra. The minor product was the syn isomer (which was not isolated)*.

The residue was redissolved in a minimum amount of methylene chloride and the product was purified by preparative TLC (2 plates 1000 micron thickness, 10% ethyl acetate-90% methylene chloride). The minor product (by NMR) was nearly eliminated. The residue was redissolved and preparative TLC (2 plates 1000 micron thickness, 5% ethyl acetate-95% methylene chloride) yielded 0.25 g ring expansion product following the usual workup with methylene chloride. The solid was redissolved in a minimum amount of methylene chloride and recrystallized five times from hexane. The structure of the product, m.p. 109-111°, was assigned on the basis of the spectral data as the anti isomer of 3,4-benzo-6,7-dihydro-6-ethylidene-1-methylazepine-2,5-dione.

NMR: ($CDCl_3$) 1.9-2.1 δ(d J=7Hz, 3H, $=CHCH_3$), 3.1-3.2 δ (s, 3H, $N-CH_3$), 4.15-4.3 δ(s, 2H, $N-CH_2-C=$), 6.9-7.3 δ (q J=7Hz, 1H, $=CH-CH_3$), 7.4-8.0 δ(m, 4H, phenyl).

IR: (CCl_4) 3080, 2990, 2960, 2930, 2880 (C-H stretch), 1680, 1655, 1650 (C=O stretch), 1630 (C=C stretch), 1595, 1480, 1420, 1395, 1360, 1320, 1290, 1260, 1185, 1075, 950, 605 cm^{-1}.

*The syn isomer was characterized by NMR of the evaporated reaction mixture less the signals of the purified anti isomer and starting material.
NMR: ($CDCl_3$) 2.2-2.4 δ(d J=7Hz, 3H, $CH_3-CH=$), 3.1-3.2 δ (s, 3H, $N-CH_3$), 4.0-4.1 δ(s, 2H, $=C-CH_2N$), 6.2-6.7 δ(q J=7Hz, 1H, $=CH-CH_3$), 7.4-8.0 δ(m, 4H, phenyl).

MASS SPEC: m^+/e 215(Base, P, 100%), 200(9.2%), 186(20%), 172(21%), 162(65%), 144(12%), 133(6.1%), 129(10%), 116 (13%), 115(22%), 105(24%), 104(28%), 77(22%), 76(33%), 57(14%), 54(18%), 51(12%), 50(16%), 44(27%), 43(14%), 42(39%).

UV: (EtOH) λ max 340(ε = 109), 289(ε = 3650), 238(ε = 13,700), 219(ε = 15,800), min. 214(ε = 14,700), and at 254(ε = 12,600).

Anal: Calculated for $C_{13}H_{13}NO_2$: C, 72.55%; H, 6.09%; N, 6.51%. Found: C, 72.81%; H, 6.13%; N, 6.35%.

Photolysis of N-methylphthalimide and Ethyl Vinyl Ether

A solution of 0.9 g N-methylphthalimide and 7.2 g freshly distilled ethyl vinyl ether in 210 ml spectrograde acetonitrile was irradiated in a Type A photolysis for 75 minutes without nitrogen purging. Analytical TLC (30% ethyl acetate-70% methylene chloride) showed two products, R_f = 0.2 and 0.65 and R_f = 0.1 and 0.4 (10% ethyl acetate-90% methylene chloride).

The reaction mixture was evaporated to dryness under vacuum. NMR of the residue showed two vinyl doublets but no alkyl region 1.0-2.5 δ (evidently the ethoxy group triplet was absent). The residue was redissolved in a minimum amount of methylene chloride, and preparative TLC of the

liquid (2 plates 1000 micron thickness, 12% ethyl acetate-88% methylene chloride) yielded three main bands where the top band was identified by NMR as starting material.

The second band (R_f = 0.6-0.8) was isolated following the usual workup with methanol and methylene chloride. Preparative TLC (1 plate 1000 micron thickness, 8% ethyl acetate-92% methylene chloride) yielded two bands R_f = 0.4-0.6 and 0.75-0.9. The top band was again identified as starting material. The second band was replated (one plate 1000 micron thickness, 7% ethyl acetate-93% methylene chloride), and once again there were two bands, the top being starting material. The second band was isolated following workup with methylene chloride. The solid, <0.01 g, was combined with the solid from four similarly prepared reaction mixtures. The solid was recrystallized six times from hexane (m.p. 20-30°).

Mass spec of one of the crystals showed peaks at 161 and 159 for maxima, NMR showed a small amount of residual starting material (m^+/e 161). The major component mass 159 contained the pair of vinyl doublets, a singlet 3.4δ and phenyl signals. NMR (100 MHz) decoupling constant J=2-2.5Hz was consistent with geminal coupling although no terminal methylene was present in the IR.* The structure of the minor product was tentatively assigned as 3-methylene-2-methyl-2-azaindanone.

*Another reaction was run under similar conditions. After the first preparative TLC purification, the second band was removed and air-dried. Mass spec of the dried silica gel showed the 161 and 159 peaks indicating that the 159 peak in the previous work was not an artifact.

NMR: ($CDCl_3$) 3.2 δ(s, 3H, N-CH_3), 4.7-4.8 δ(d J=2Hz, 1H, vinylic), 5.0-5.18 δ(d J=2Hz, 1H, vinylic coupled to previous signal), 7.2-7.8 δ(m, 4H, phenyl).

IR: (CCl_4) 2980, 2950, 2900, 2880 (C-H stretch), 1715 (C=O stretch), 1680, 1640, 1480, 1440, 1390, 1320, 1270, 1200, 1170, 1110, 1090, 1045, 1025, 850, 720 cm^{-1}.

MASS SPEC: m^+/e 159P (no further calculation due to starting material contamination).

The third band was isolated following workup with methylene chloride and methanol. NMR of the residue showed no vinyl signals or alkyl signals 1.0-2.5 δ. Further purification was attained by preparative TLC (2 plates 1000 micron thickness, 14% ethyl acetate-86% methylene chloride). The major band was worked up with methylene chloride and ethyl acetate, and recrystallized four times from hexane. On the basis of the spectral data, the white crystalline major product, 0.1 g, (m.p. 79-81°) was assigned the structure of 3,4-benzo-6,7-dihydro-1-methylazepine-2,5-dione.

NMR: ($CDCl_3$) 2.8-3.1 δ(m, 2H, CH_2-C=O), 3.2-3.3 δ(s, 3H, N-CH_3), 3.5-3.8 δ(m, 2H, N-CH_2), 7.3-7.9 δ(m, 4H, phenyl).

IR: (CCl_4) 3080, 2975, 2970, 2880 (C-H stretch), 1695, 1655 (C=O stretch), 1600, 1485, 1470, 1430, 1400, 1390, 1355, 1320, 1275, 1205, 1140, 1075, 1000, 970, 955, 920, 715 cm^{-1}.

MASS SPEC: m^+/e 189(P, 54%), 161(24%), 147(13%), 146 (70%), 118(16%), 117(10%), 105(15%), 104(46%), 90(13%),

77(20%), 76(52%), 51(26%), 50(48%), 45(98%), 44(53%), 43(base, 100%), 32(44%).

UV: (EtOH) λ max 325(ε= 137), 284(ε = 1610), 231(ε = 14,100), 207(ε = 30,100), min 272(ε = 1420), and at 254 (ε = 5480).

Anal: Calculated for $C_{11}H_{11}NO_2$: C, 69.82%; H, 5.86%; N, 7.40%. Found: C, 69.56%, H, 6.13%; N, 7.27%.

PART IV

Spectral Data

APPENDIX 1

List of Glpc Columns

List of GLPC Columns

Column A: 1/8" × 7' Versamid 900, 20% on Chrom W 100/120.

Column B: 1/8" × 6' Versamid 900, 20% on Chrom W 100/120.

Column C: 1/8' × 7' Versamid 900, 20% on Chrom W 60/80.

Column D: 1/8" × 7' Versamid 900, 20% on Chrom W 60/80.

Column E: 1/8" × 3' SE 30, 3% on Varipart.

Column F: 1/8" × 5' SE 30, 3% on Varipart.

Column G: 1/8" × 8' SE 30, 20% on Chrom W 60/80.

Column H: 1/8" × 9' SE 30, 20% on Chrom W 60/80.

Column I: 1/8" × 17' SE 30, 20% on Chrom W 60/80.

Column J: 1/8" × 3' UCON HB 270X, 15% on Chrom W 80/100.

Column K: 1/8" × 9' UCON HB 270X, 15% on Chrom W 80/100.

Column L: 1/8" × 6' XE 60, 10% on Chrom P 80/100.

Column M: 1/8" × 6' DC 550, 15% on Chrom W 80/100.

Column N: 1/4" × 6' DC 550, 15% on Chrom W 80/100.

Column O: 1/4" × 7' SE 30, 30% on Chrom W 30/60.

Column P: 1/4" × 6' SE 30, 20% on Chrom W 60/80.

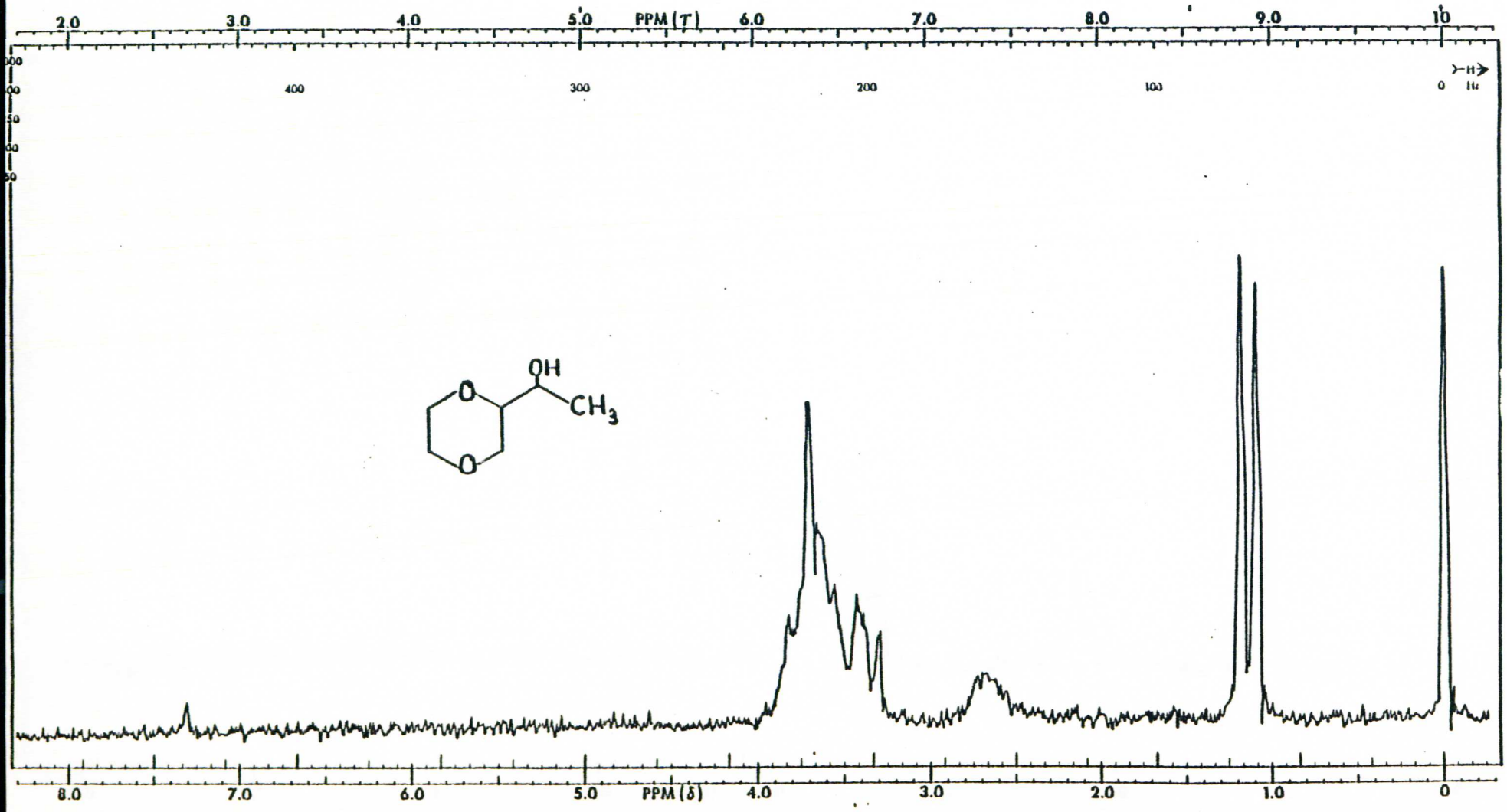
Column Q: 1/4" × 6' Versamid 900, 20% on Chrom W 100/120.

Column R: 1/4" × 6' Versamid 900, 20% on Chrom W 60/80.

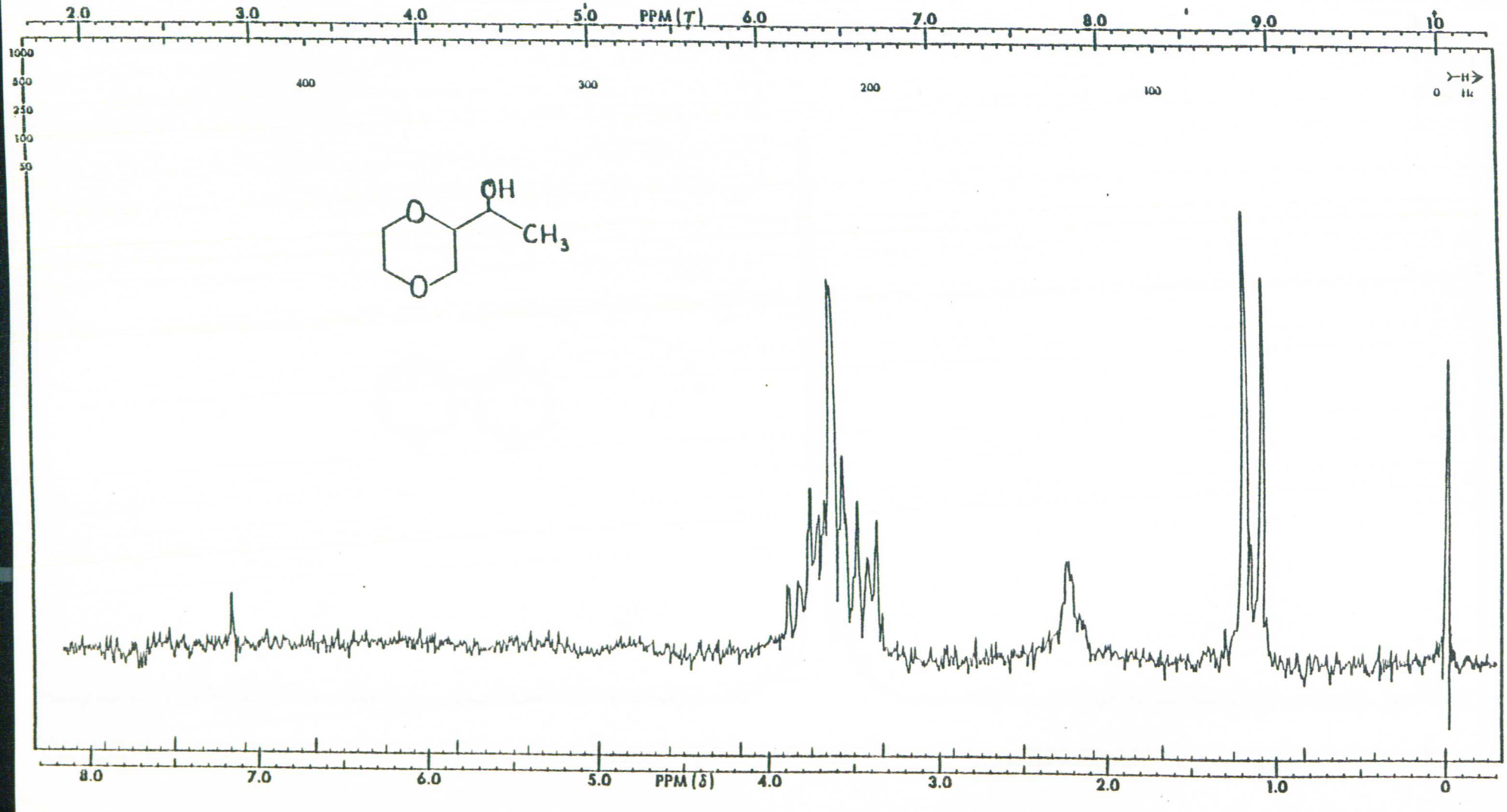
APPENDIX 2

NMR Data

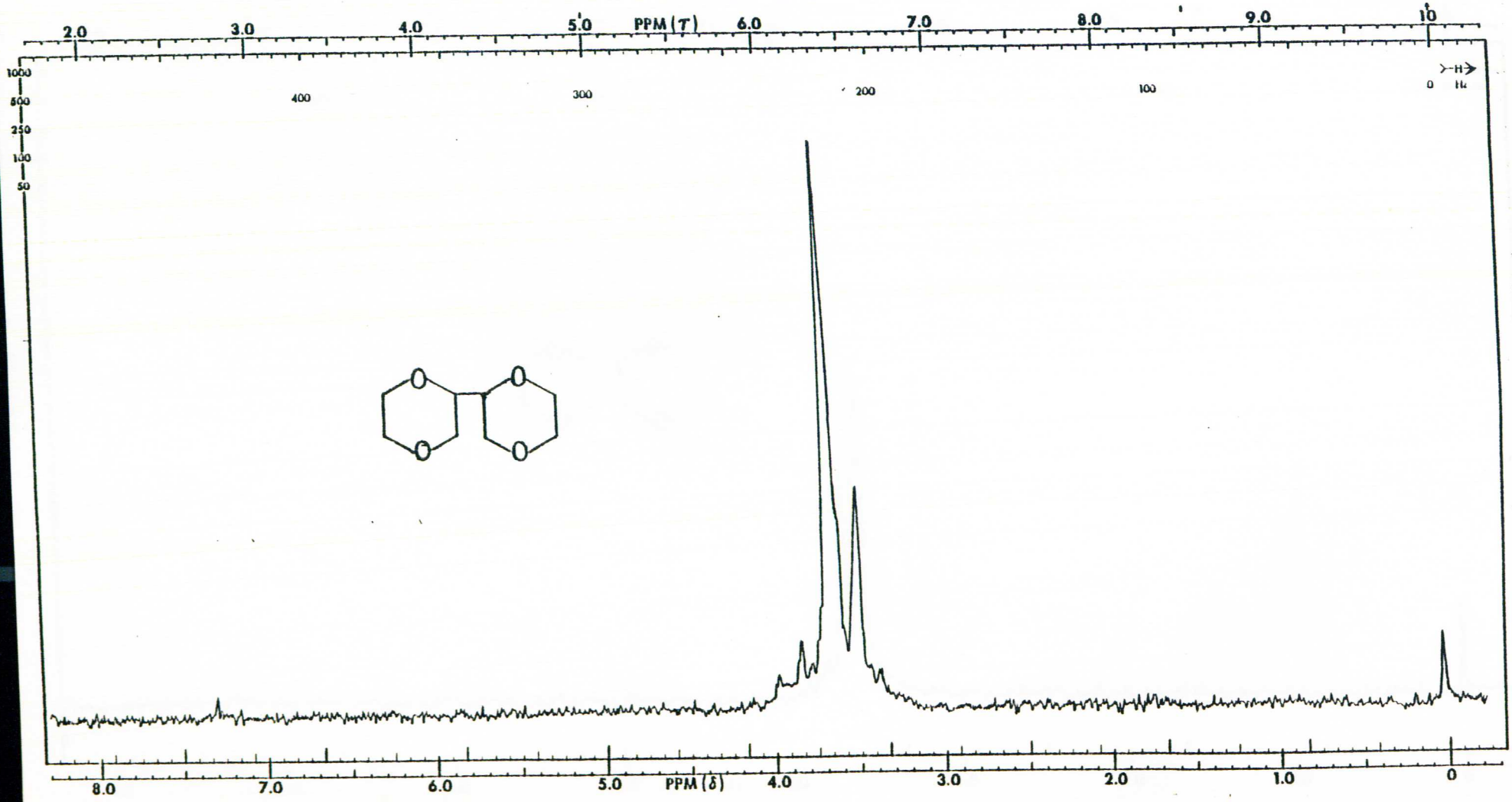
α-methyl dioxane methanol (2)



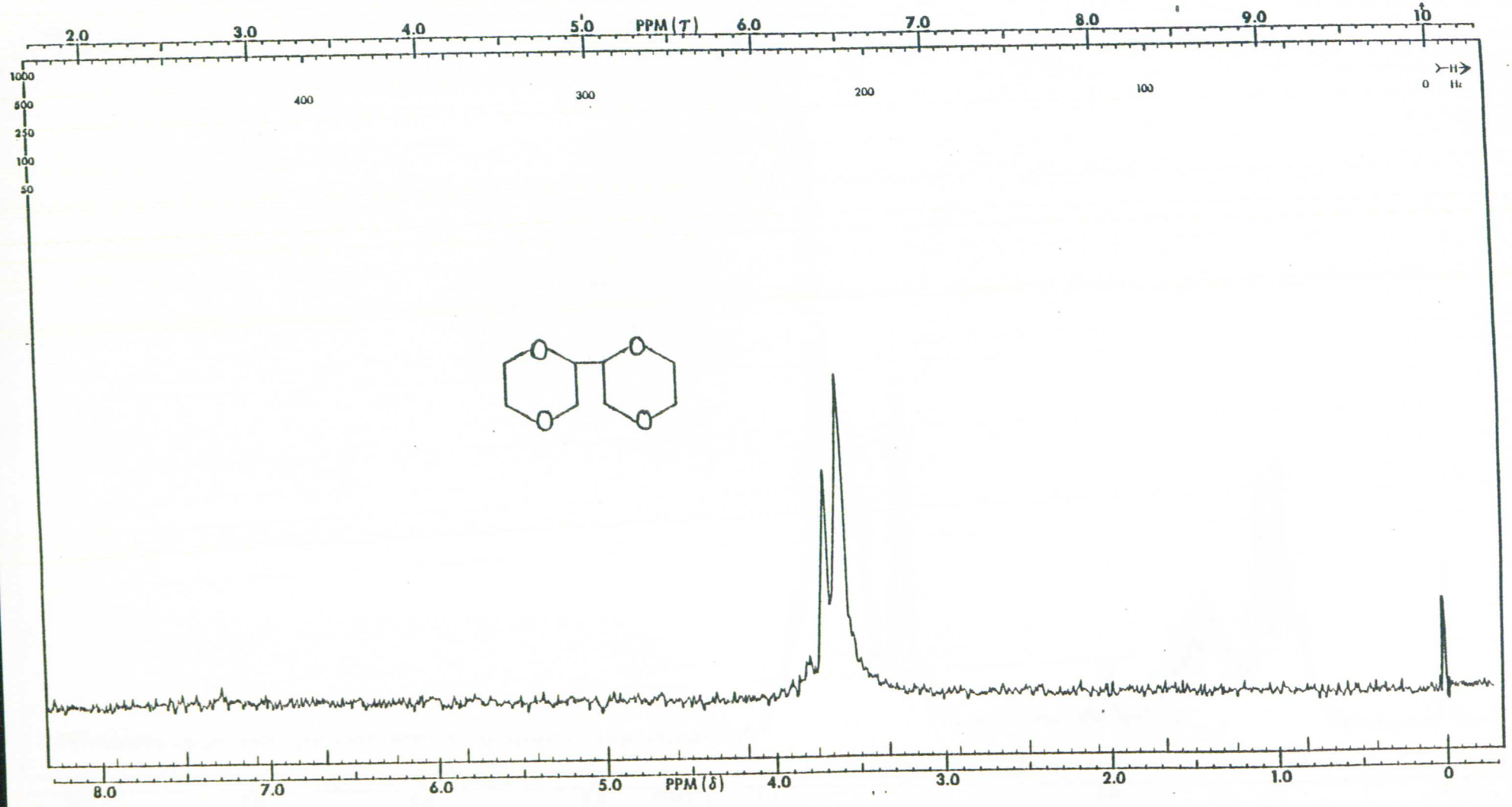
α-methyl dioxane methanol (3)



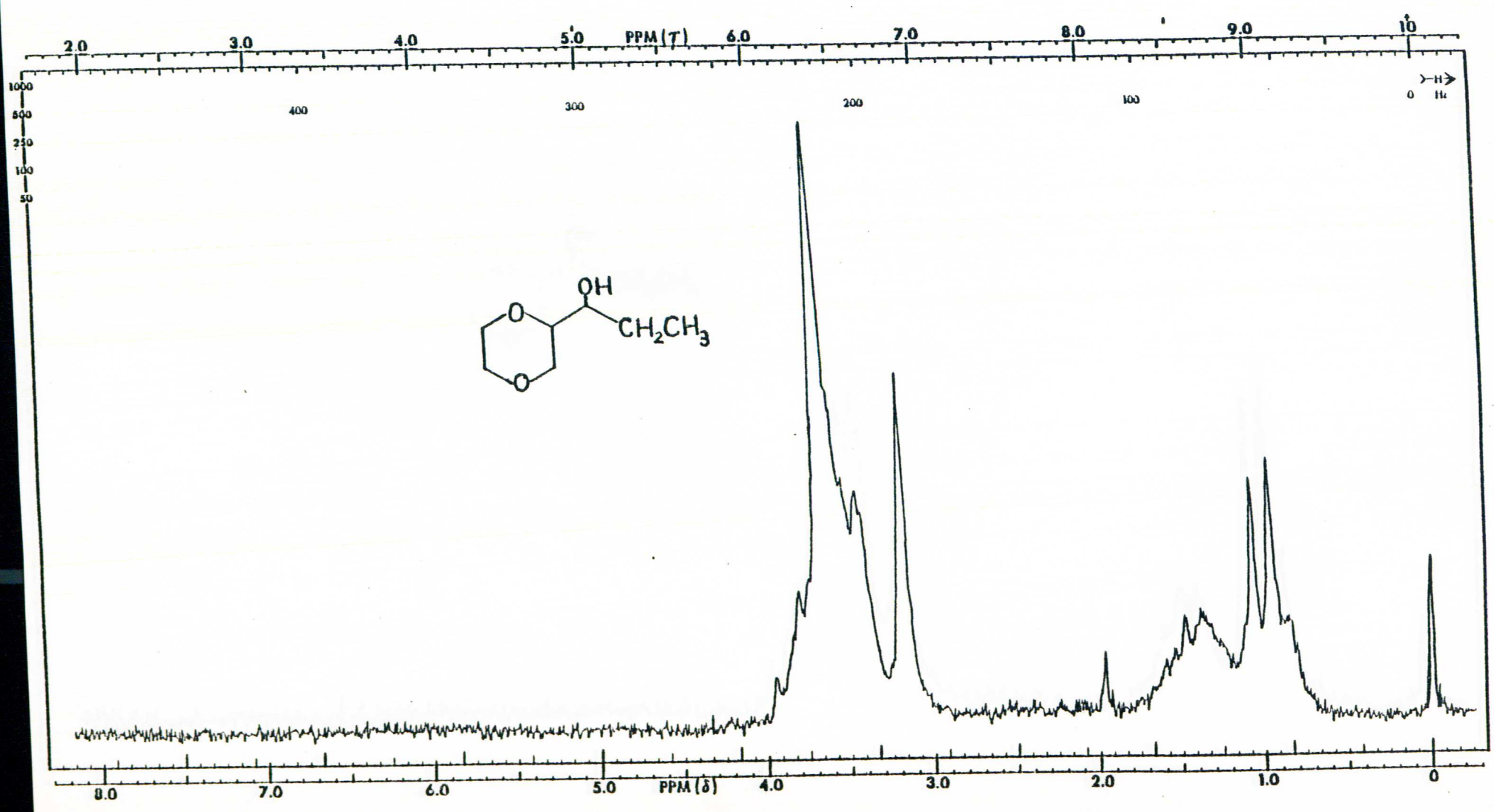
p-dioxyldioxane (4)



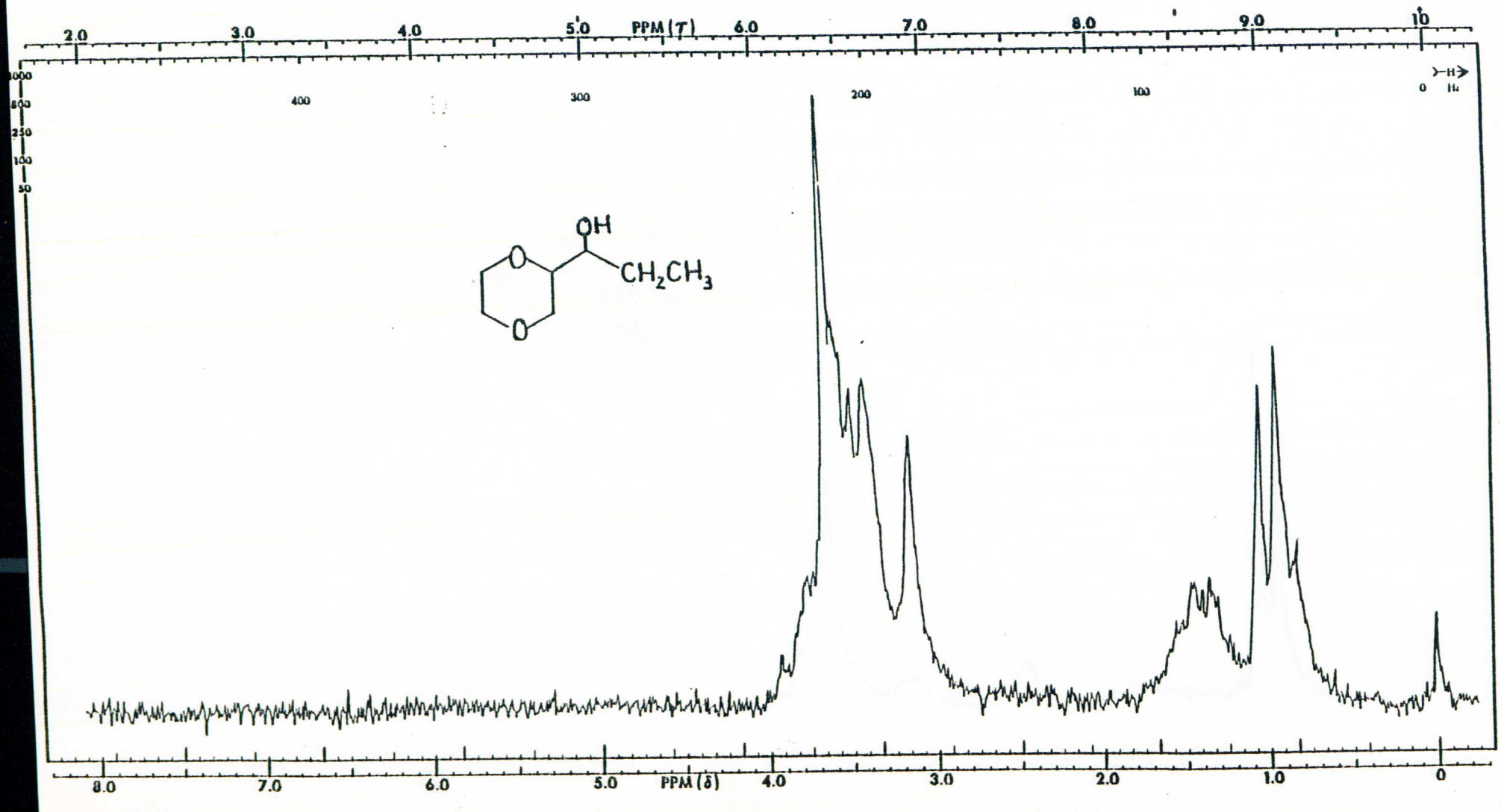
p-dioxyldioxane (5)



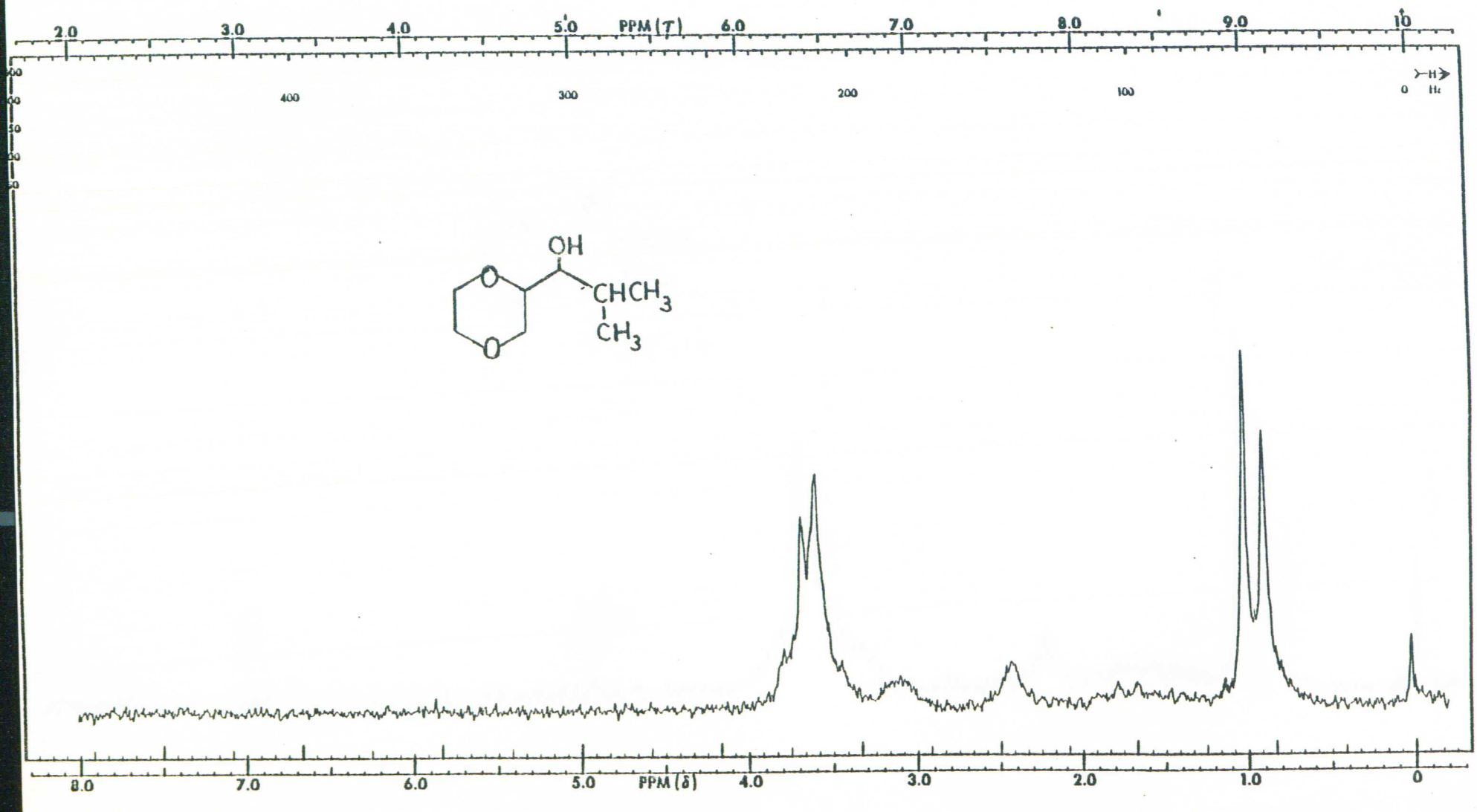
α-ethyl dioxane methanol (7)



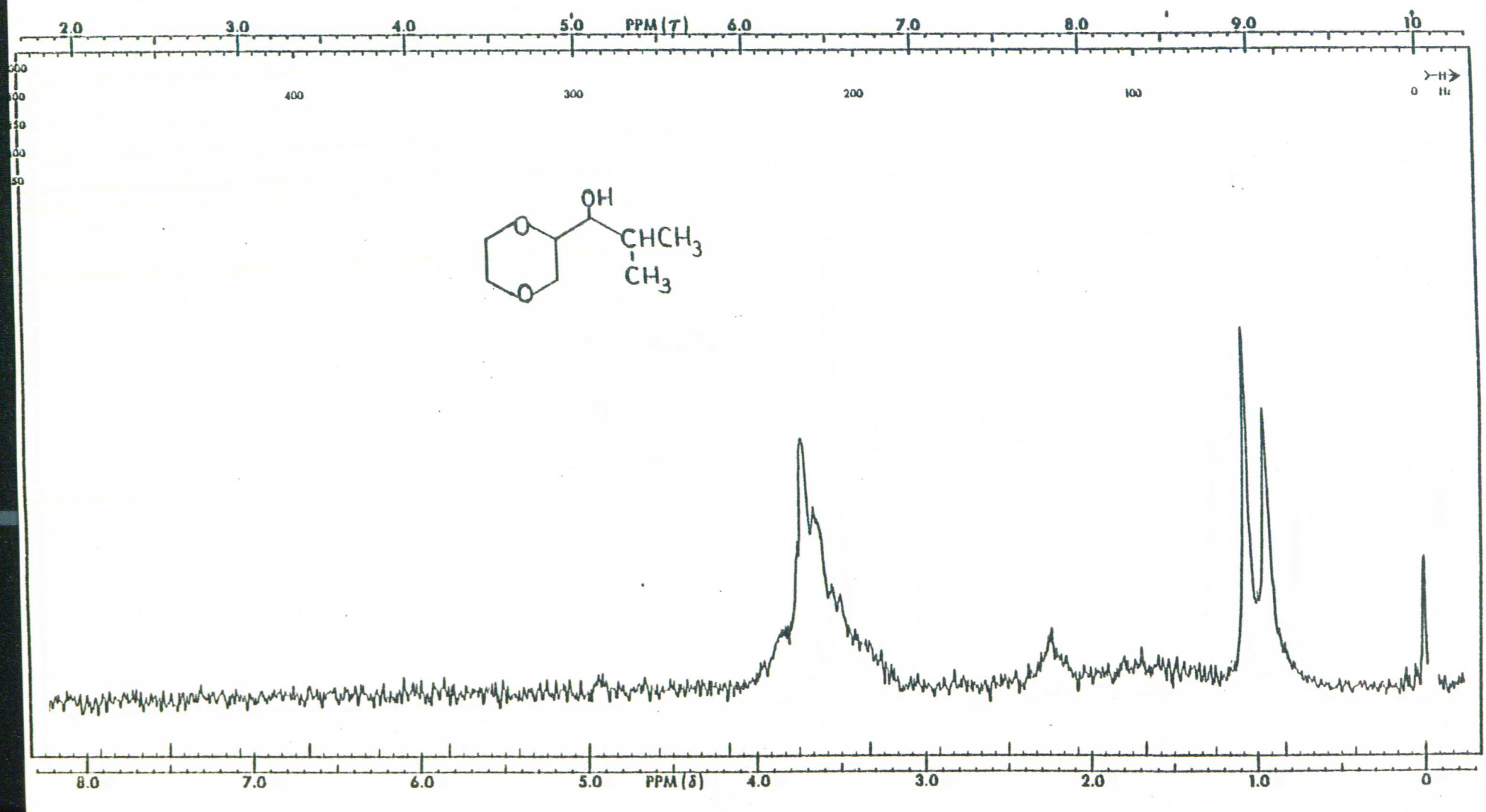
α-ethyl dioxane methanol (8)



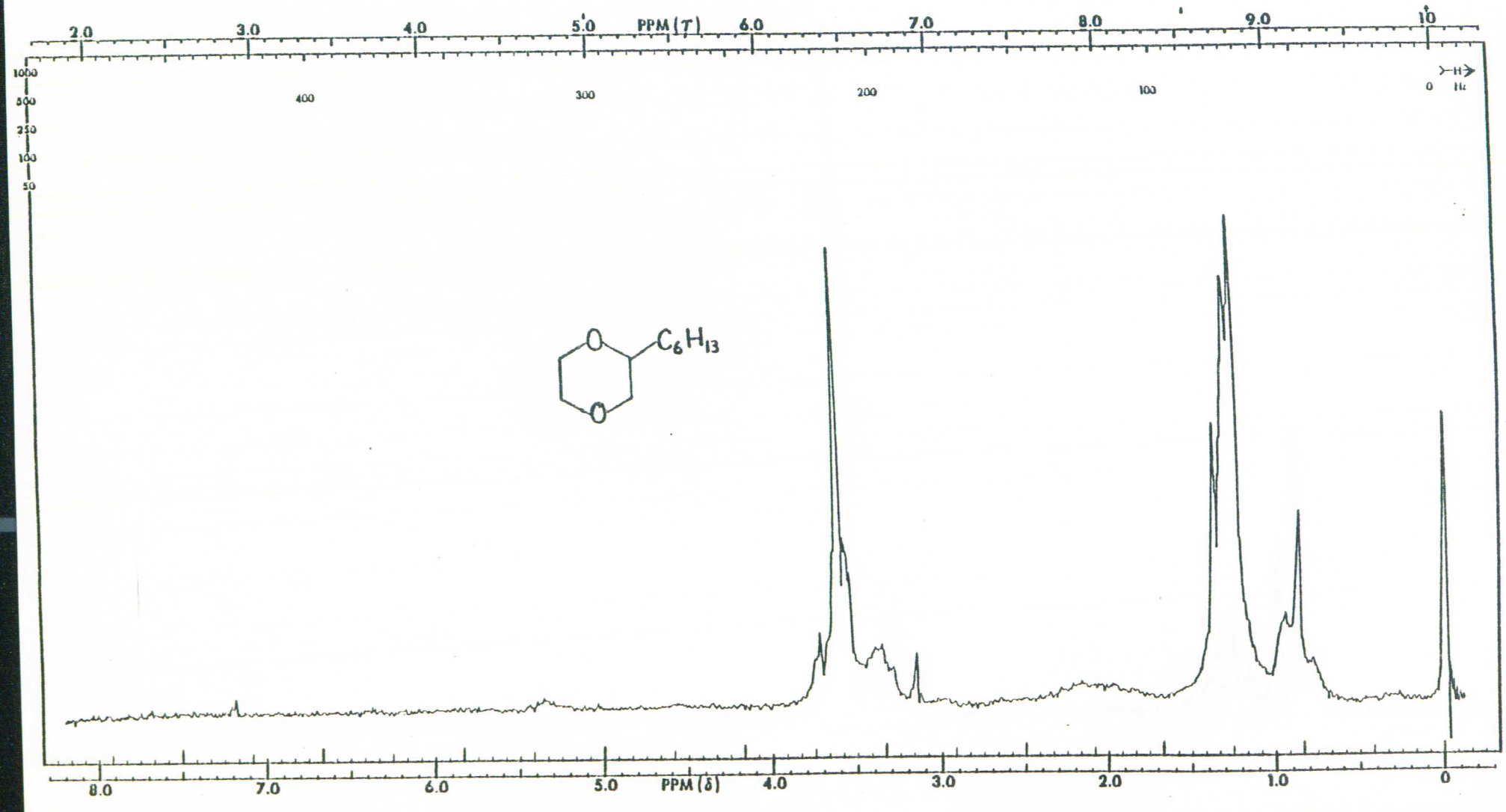
α-isopropyl dioxane methanol (9)



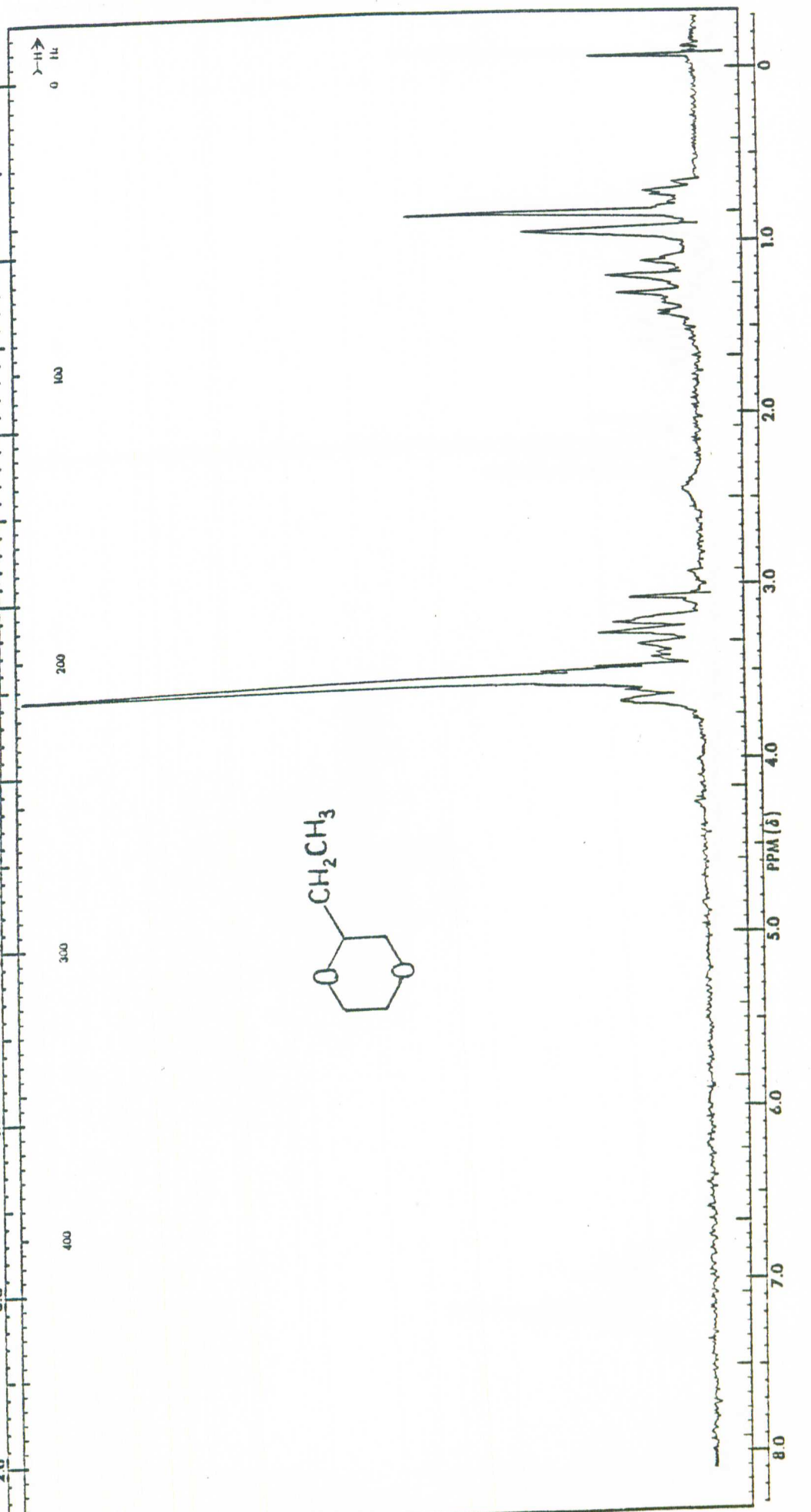
α-isopropyl dioxane methanol (10)



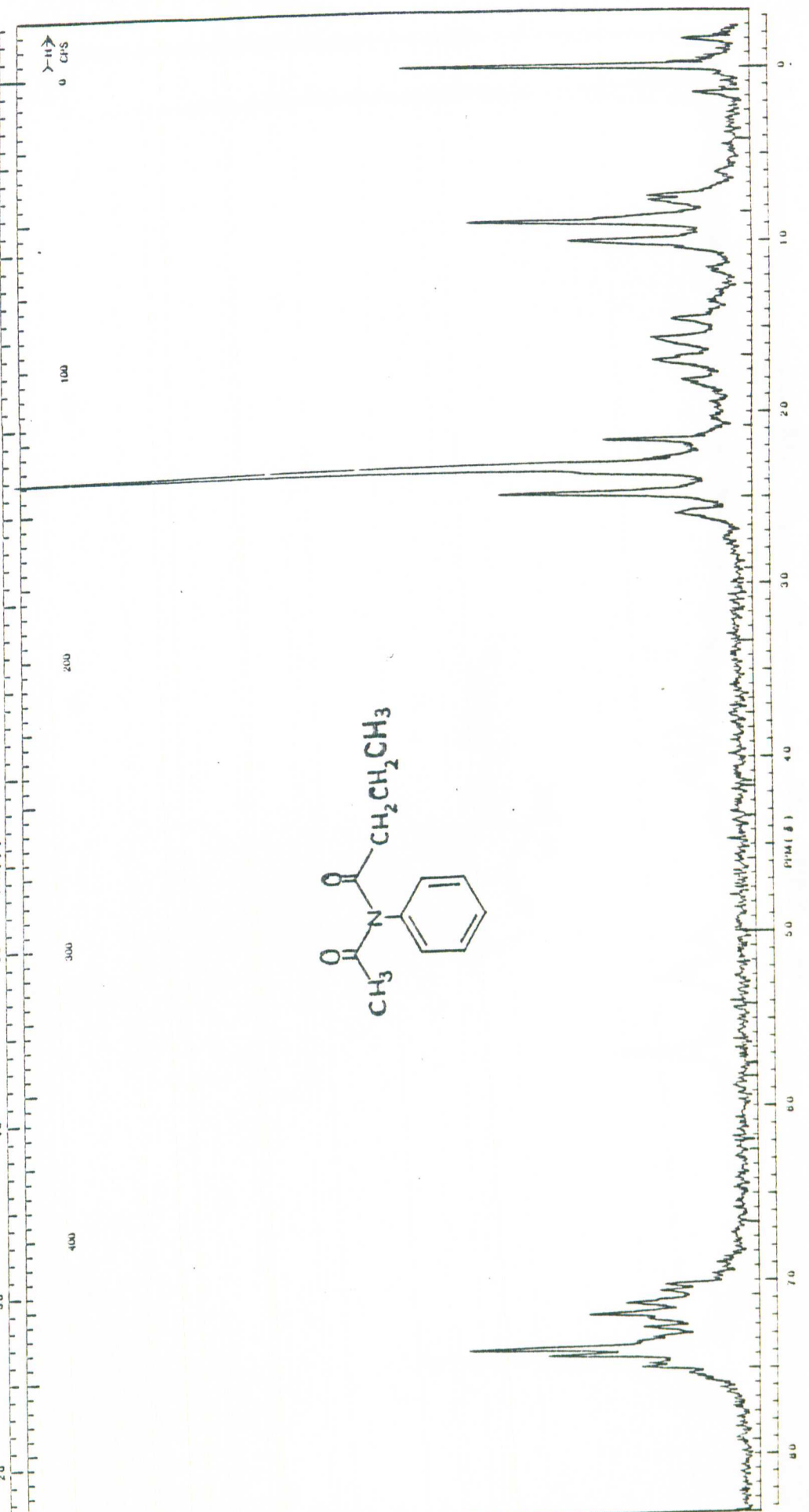
hexyldioxane (15)



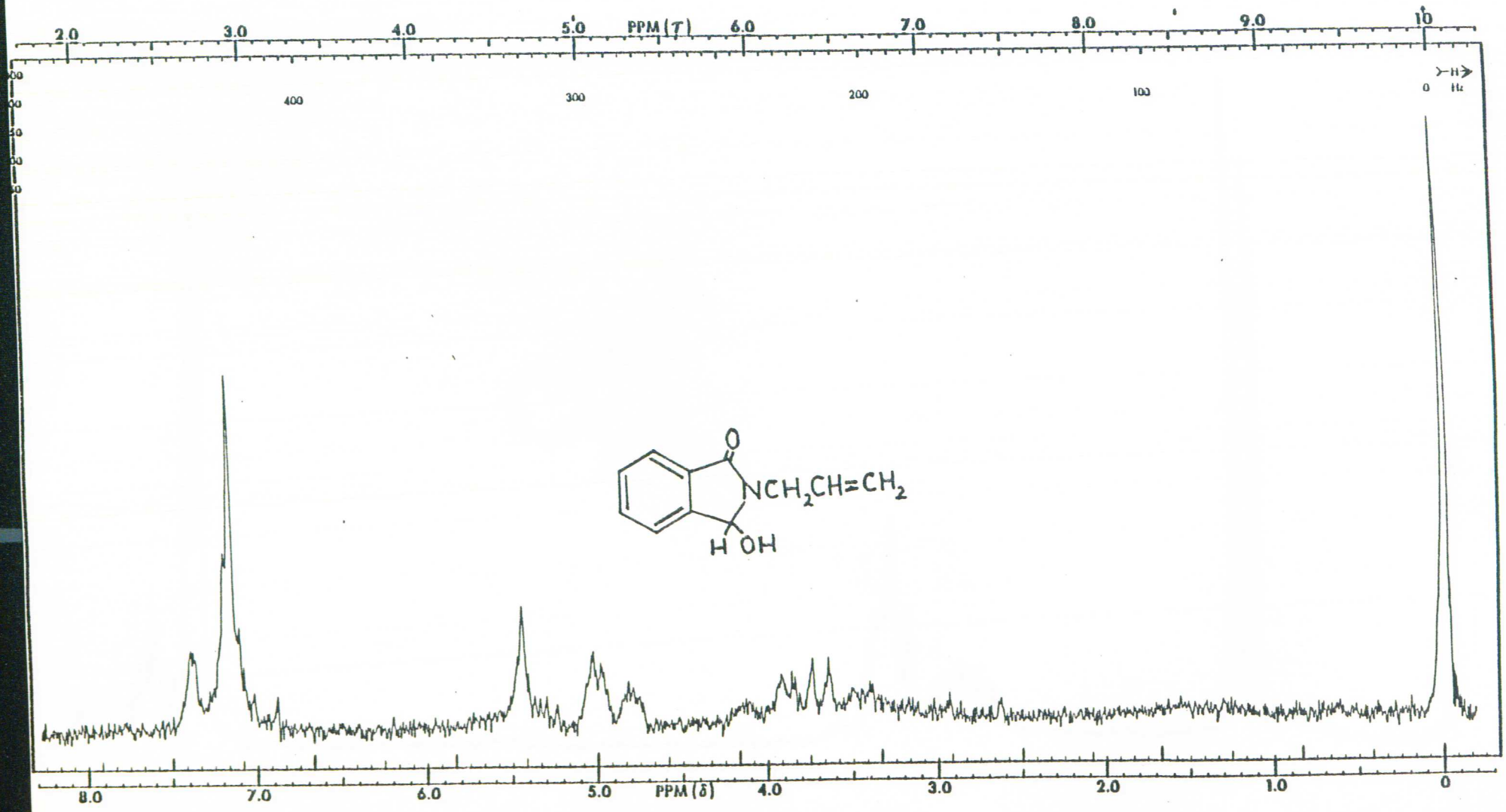
ethyldioxane



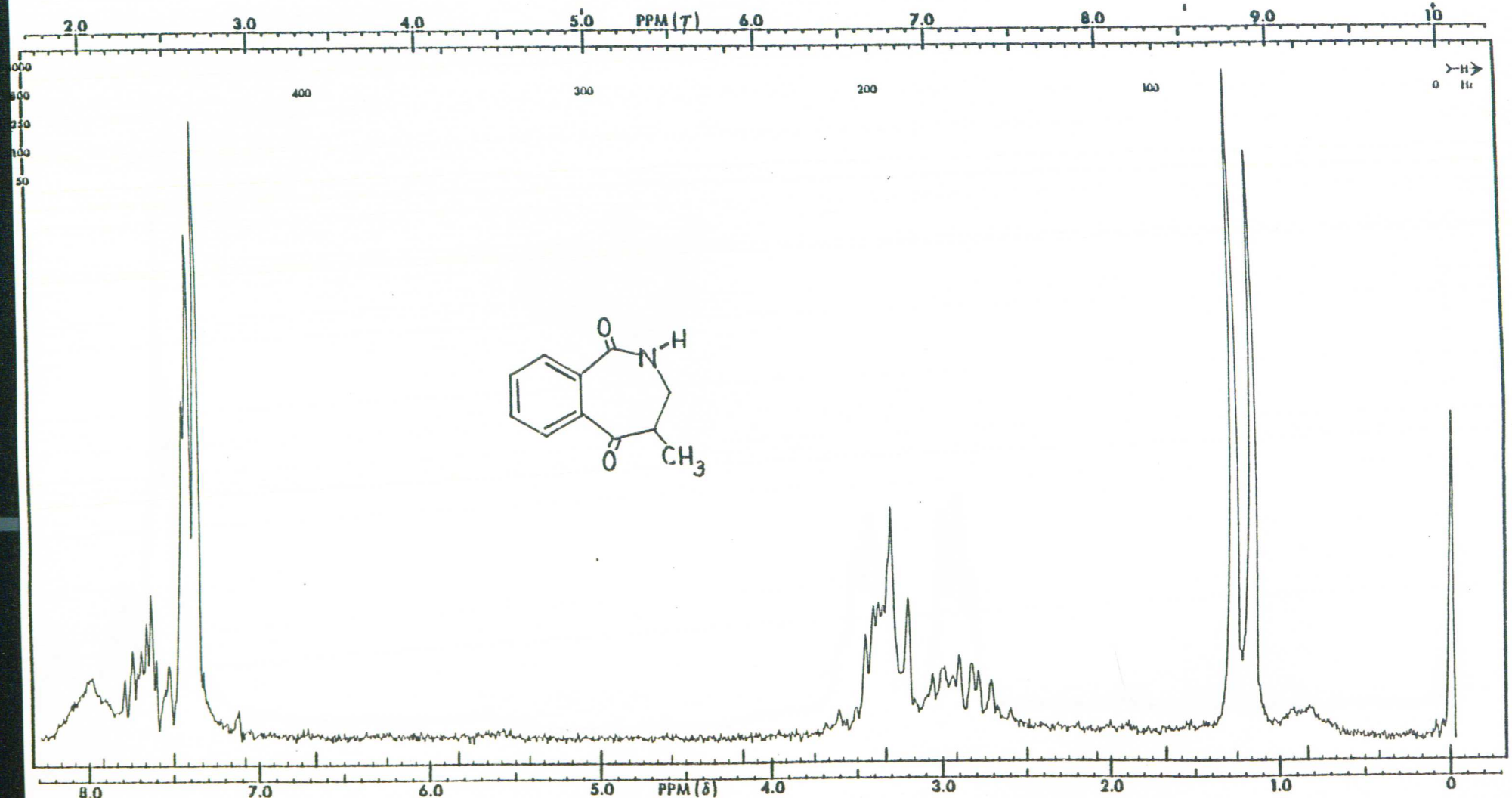
N-acetylbutyranilide.



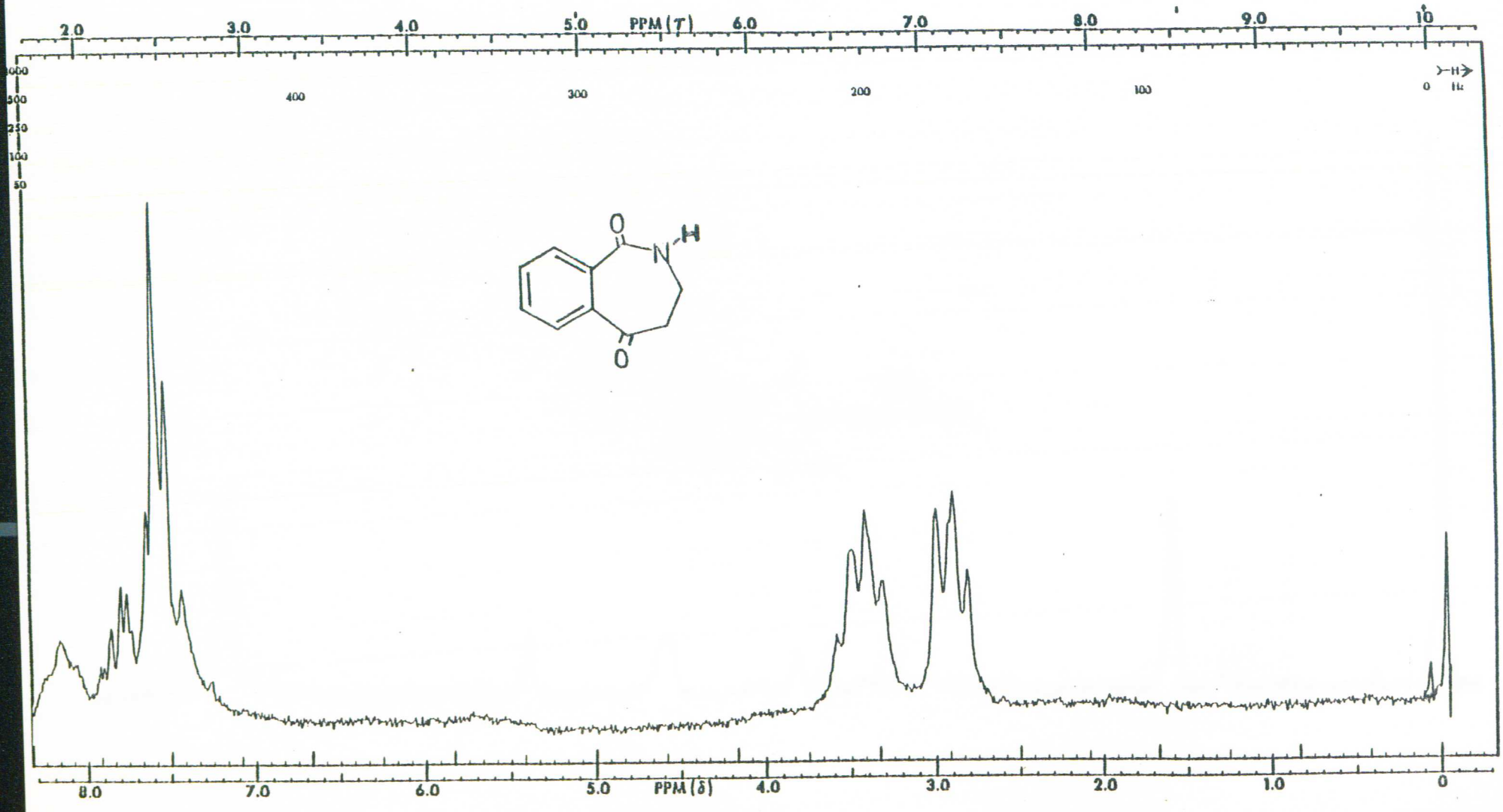
3-dihydrophthalimido-1-propene



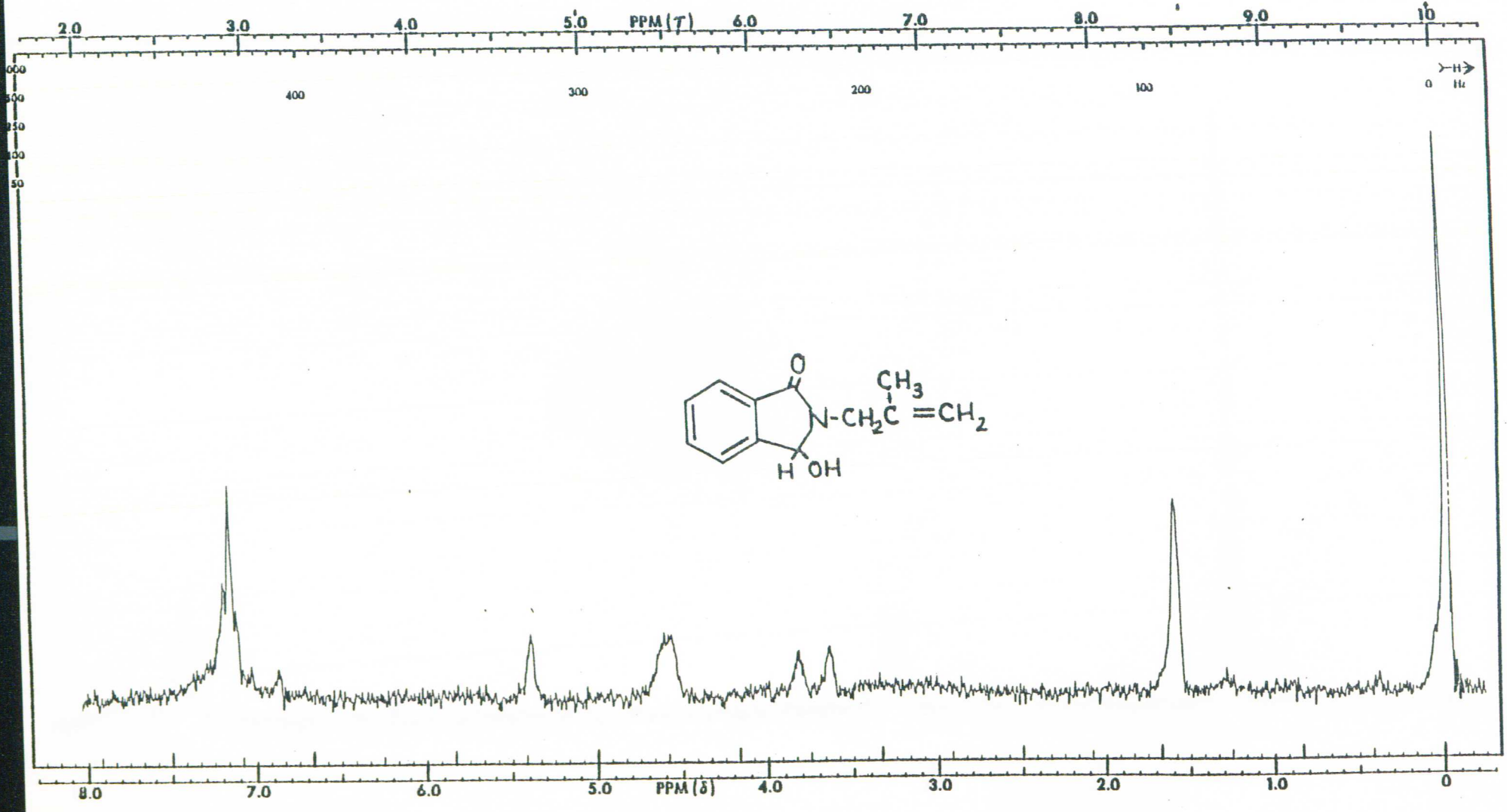
3,4-benzo-6,7-dihydro-6-methyl(1H)azepine-2,5-dione (36)



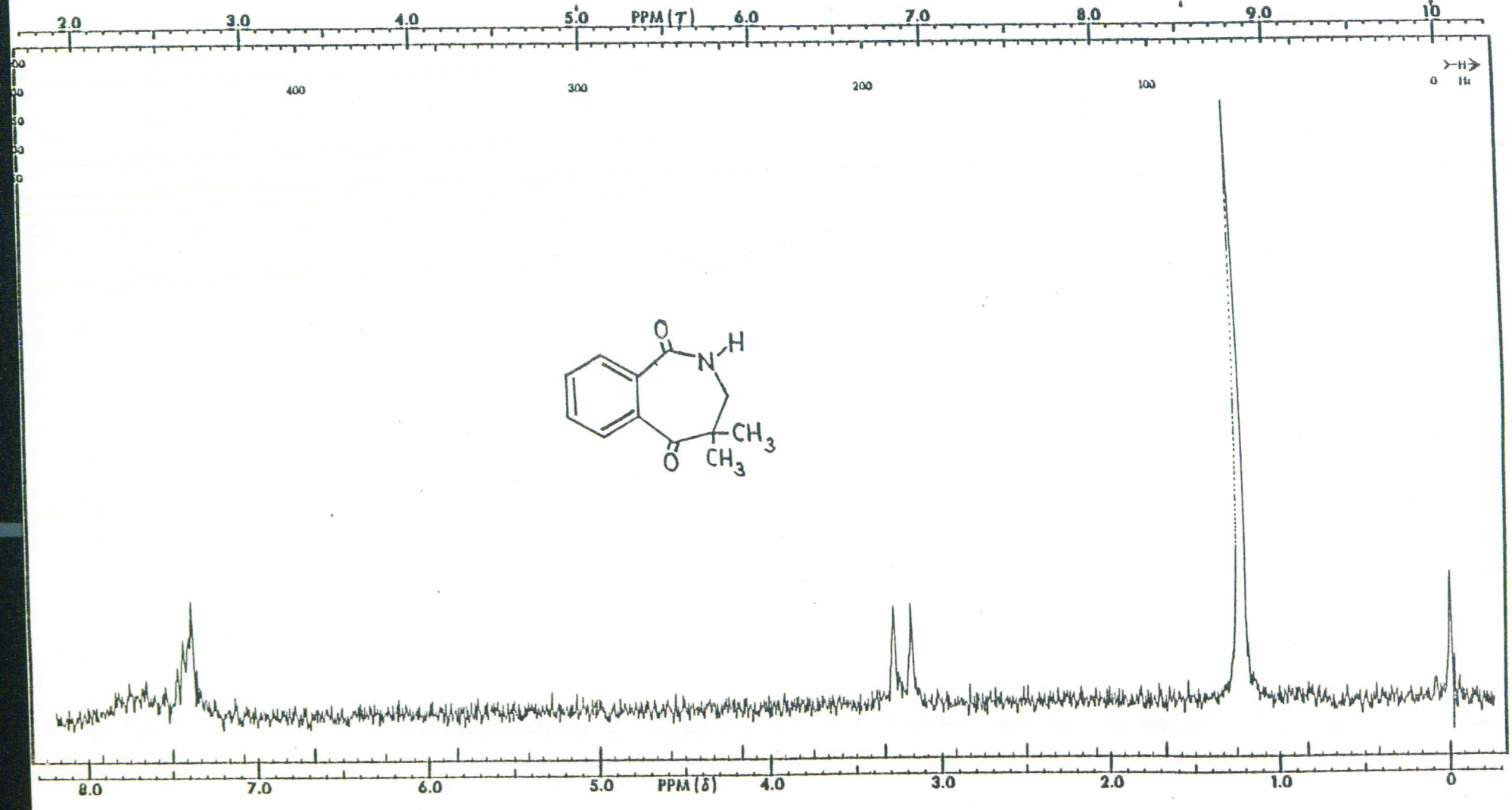
3,4-benzo-6,7-dihydro(1H)azepine-2,5-dione (37)



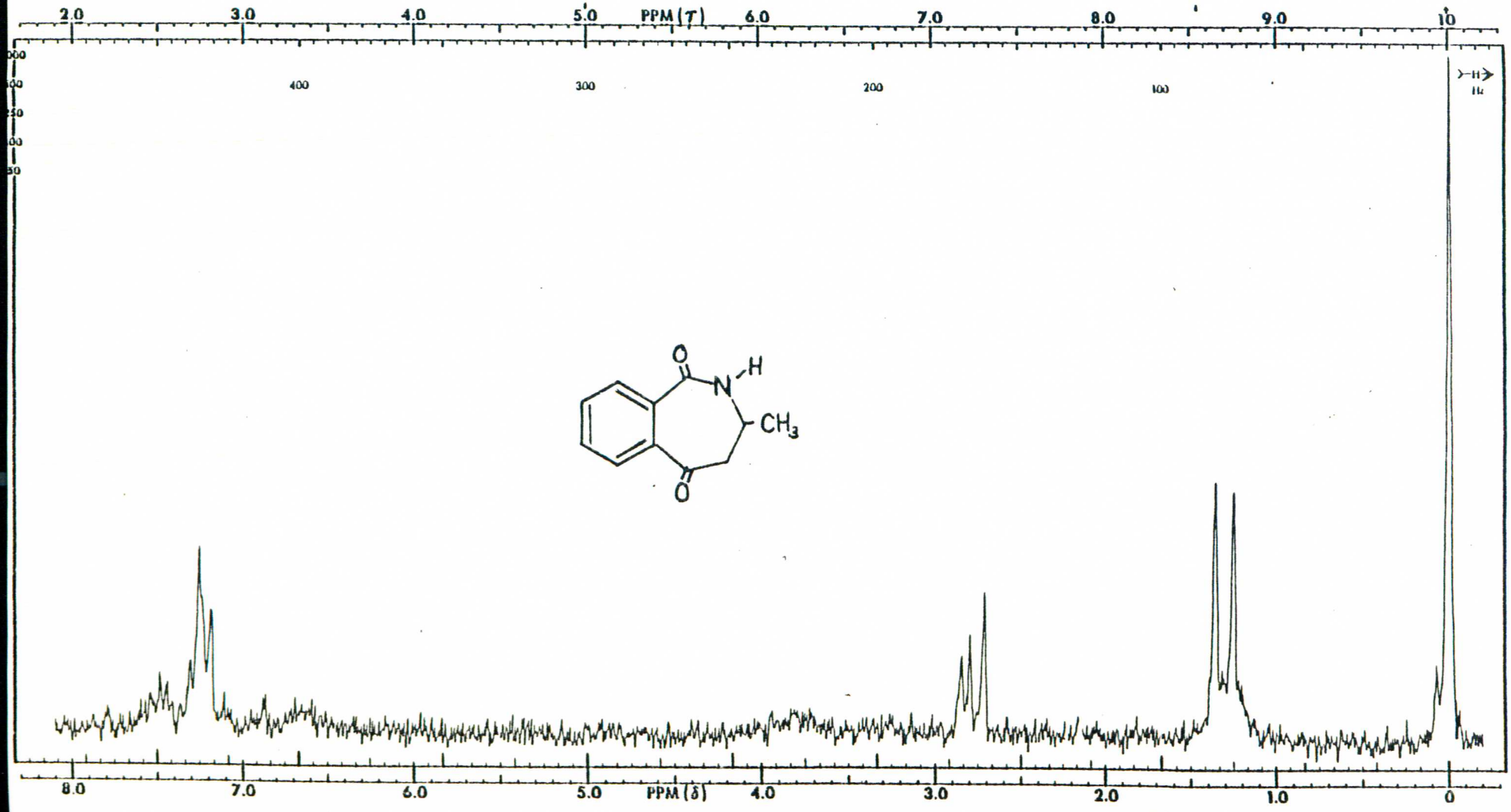
3-dihydrophthalimido-2-methyl-1-propene (38)



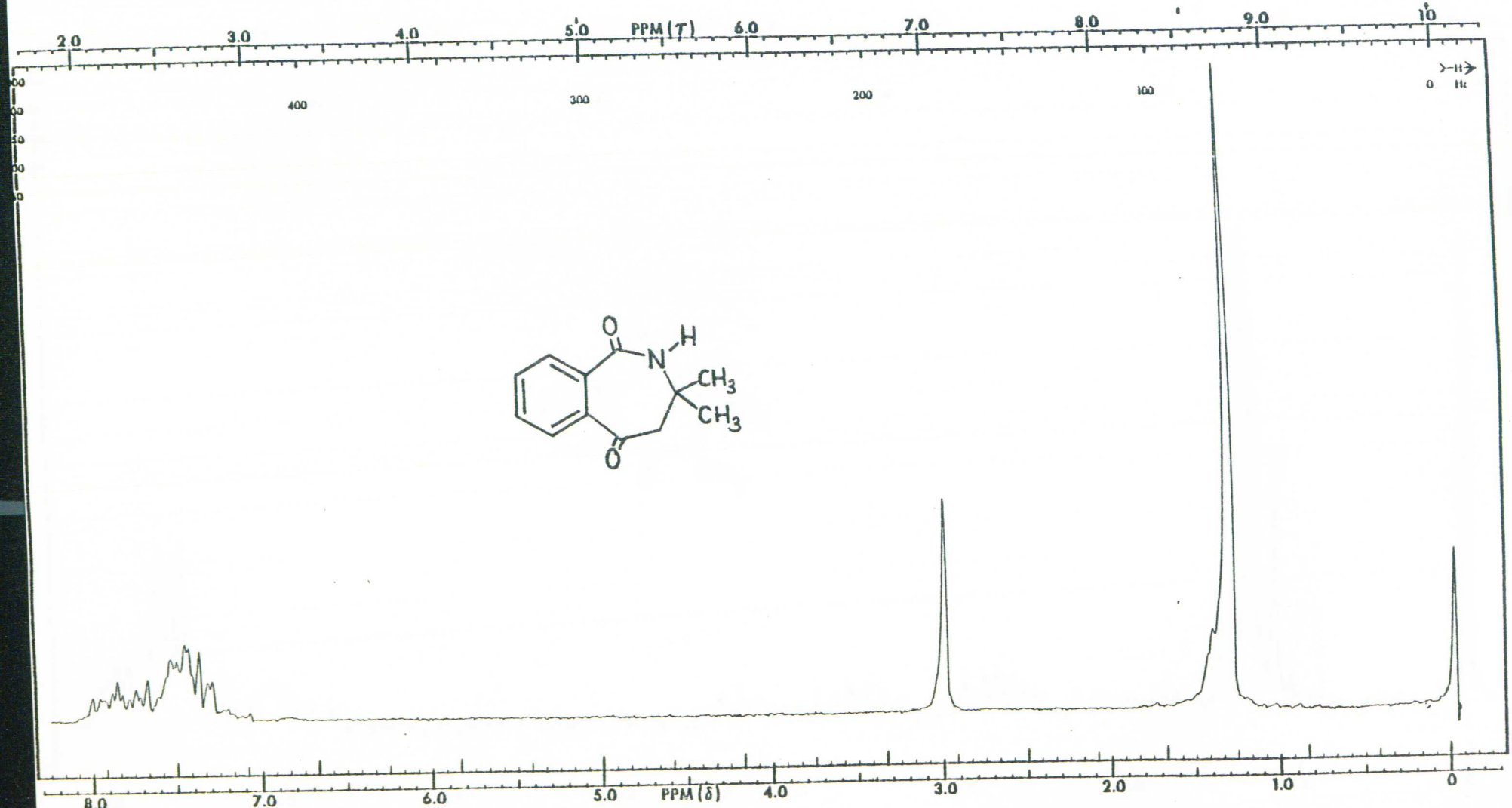
3,4-benzo-6,7-dihydro-6,6-dimethyl(1H)azepine-2,5-dione (39)



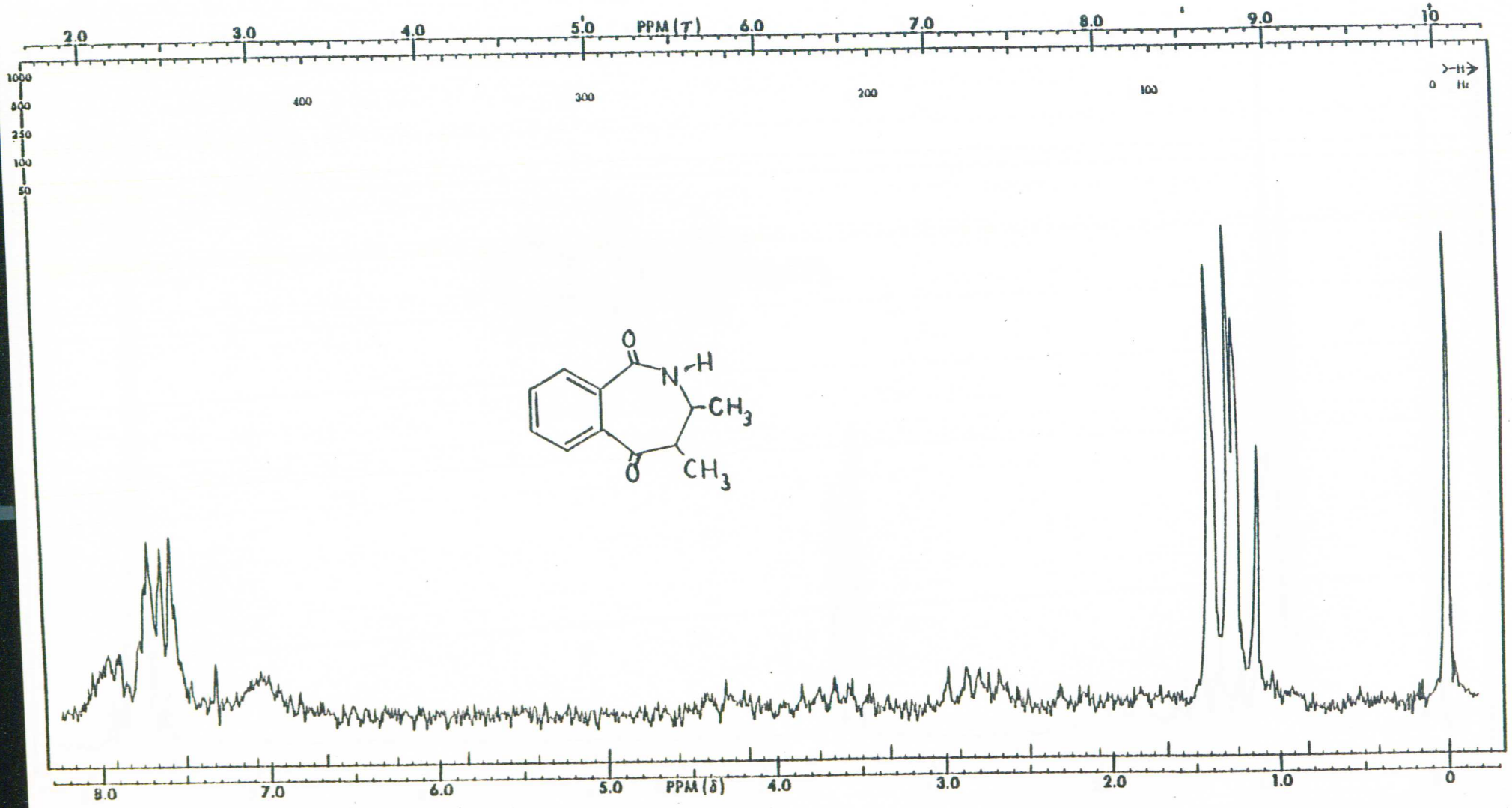
3,4-benzo-6,7-dihydro-7-methyl(1H)azepine-2,5-dione (40)



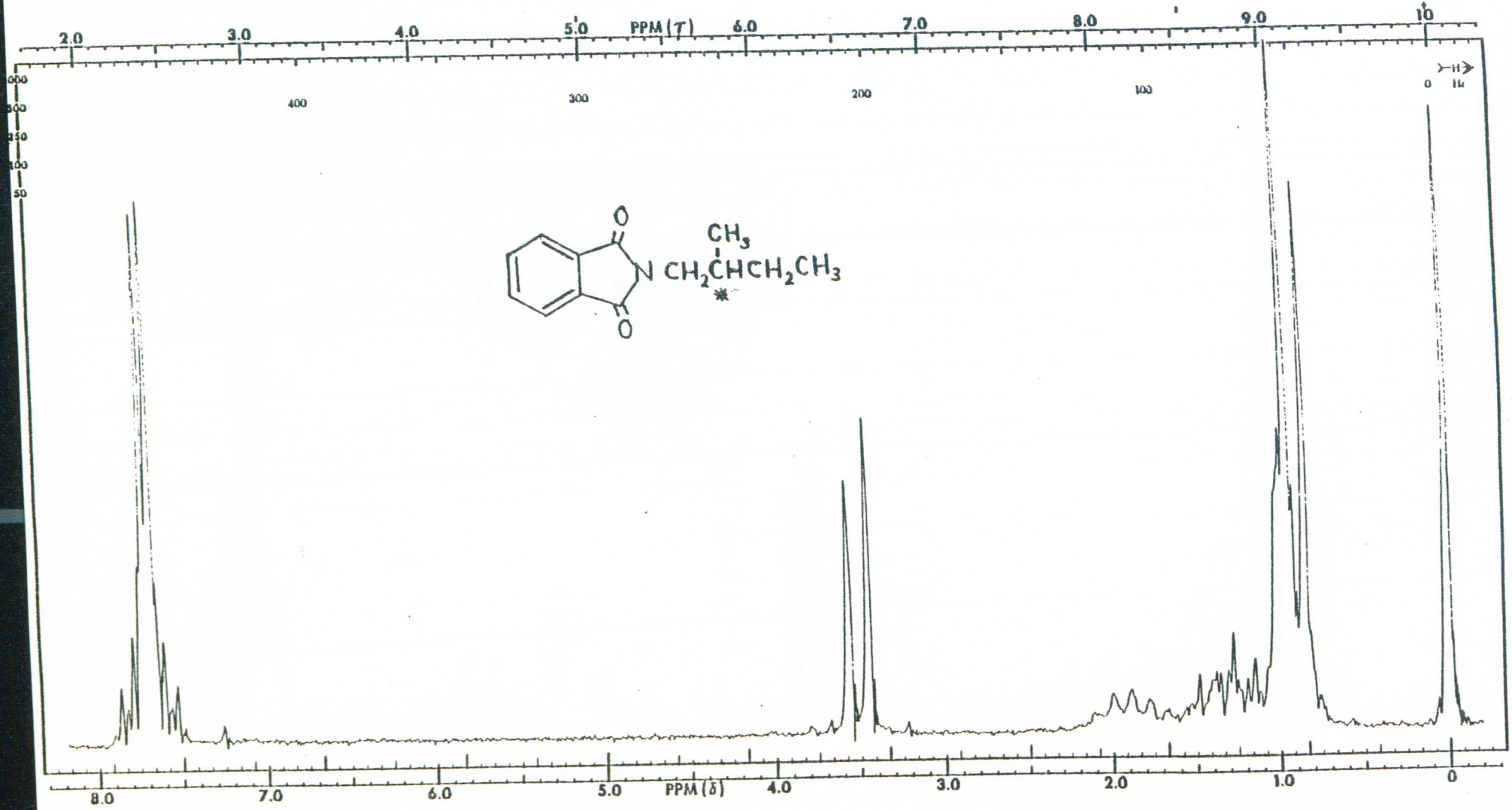
3,4-benzo-6,7-dihydro-7,7-dimethyl(1H)azepine-2,5-dione (41)



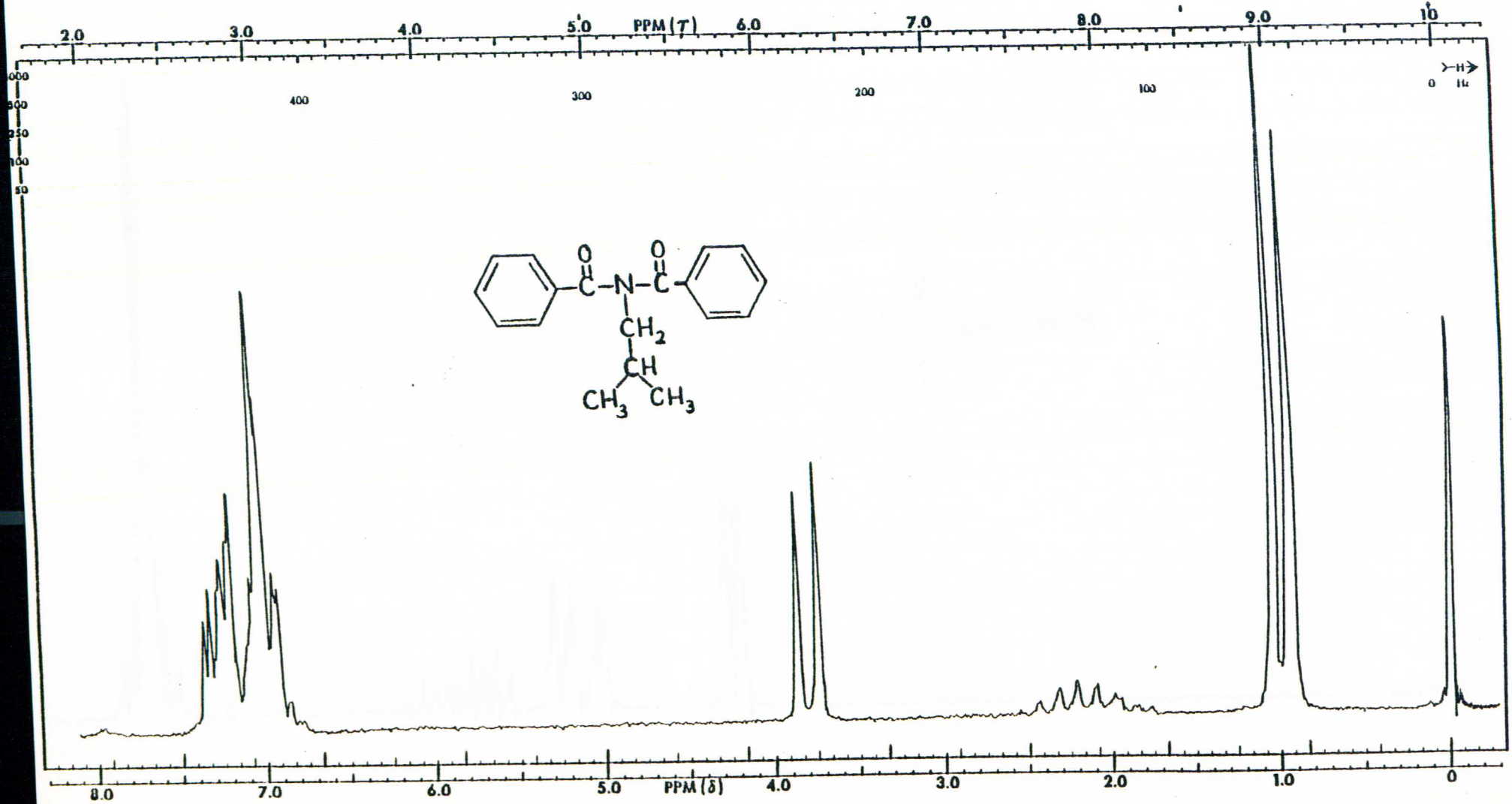
cis and trans-3,4-benzo-6,7-dihydro-6,7-dimethyl(1H)azepine-2,5-dione (43)



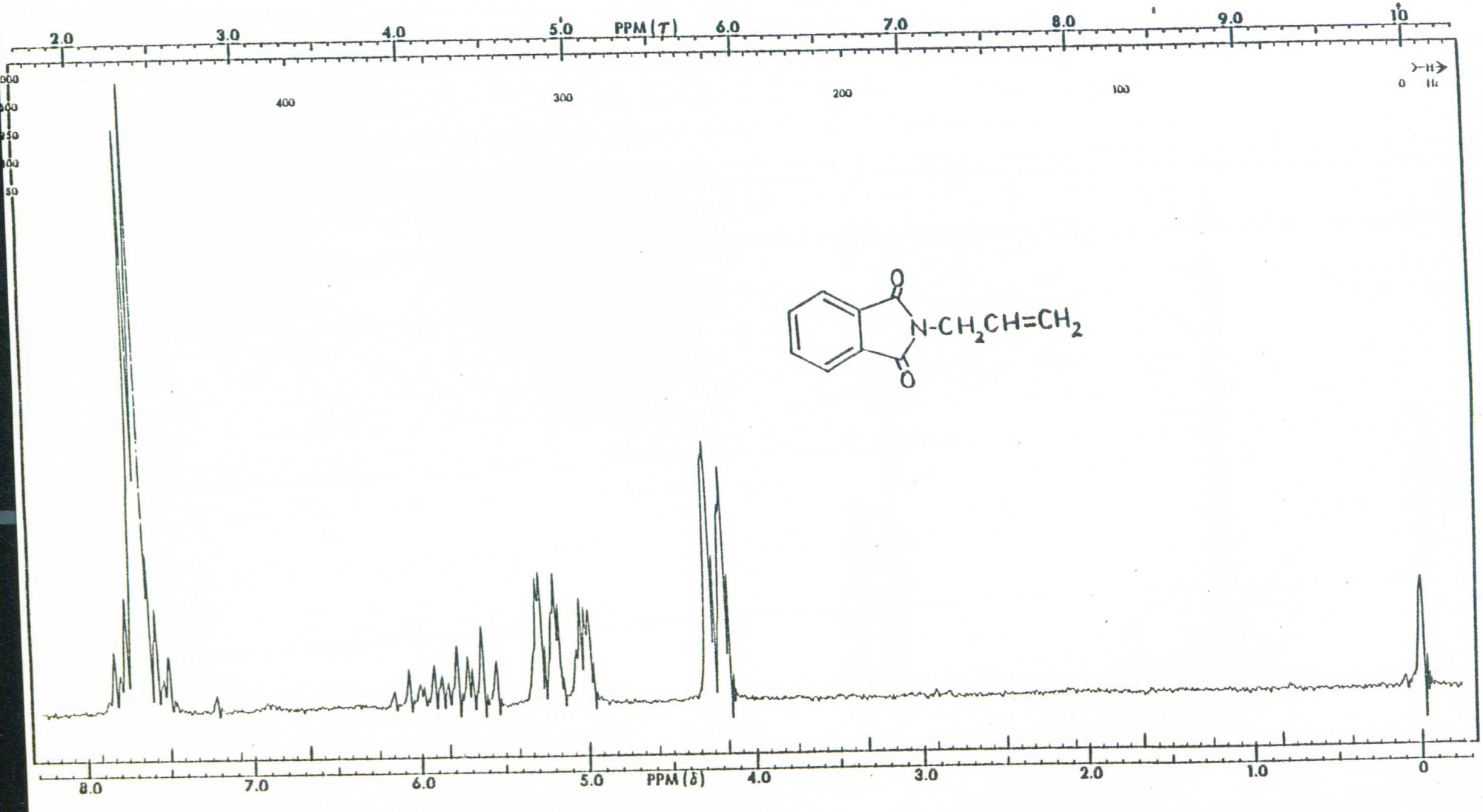
(2S)-(+)-2-methylbutylphthalimide



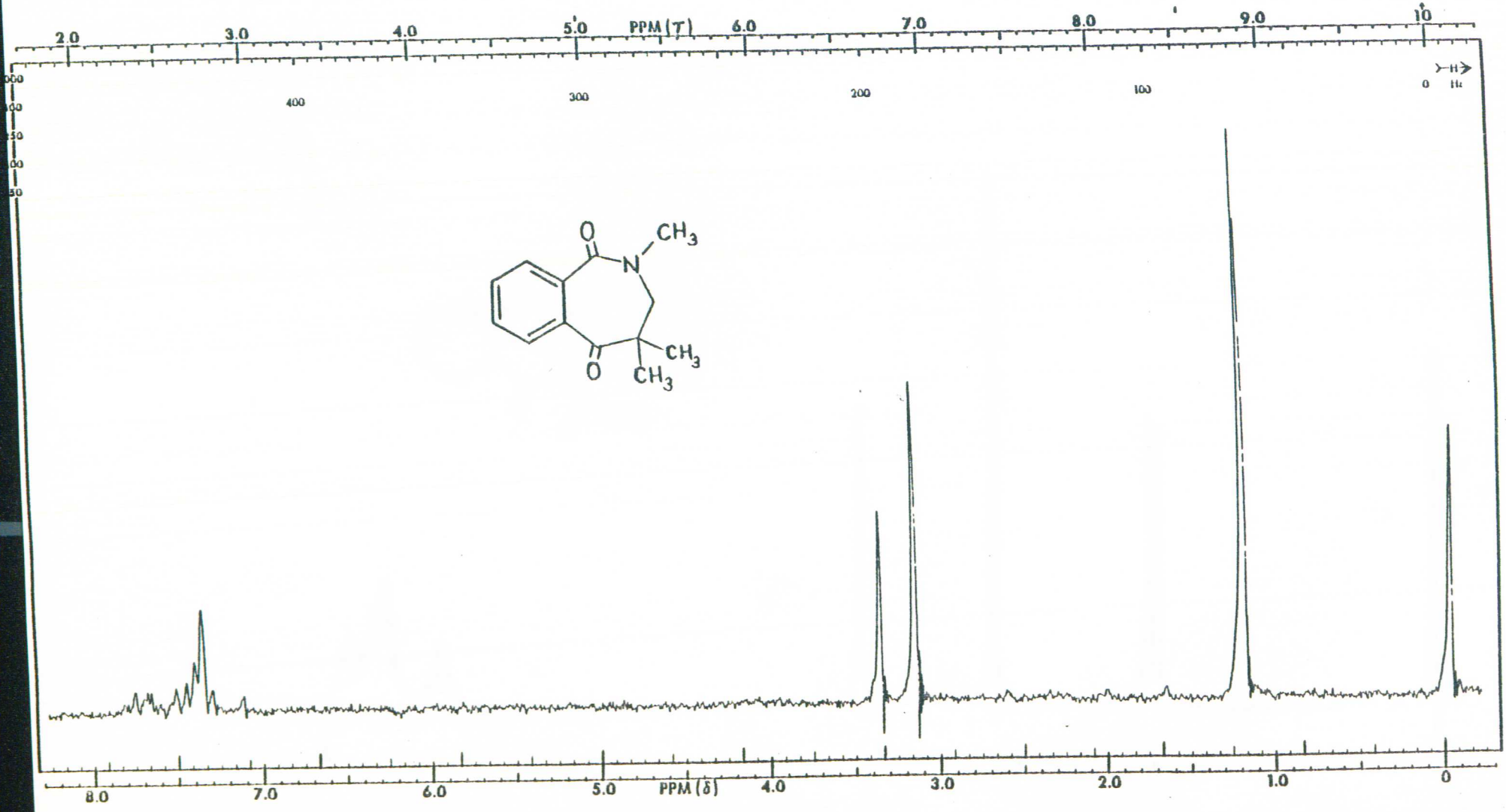
N,N-dibenzoylisobutylamine



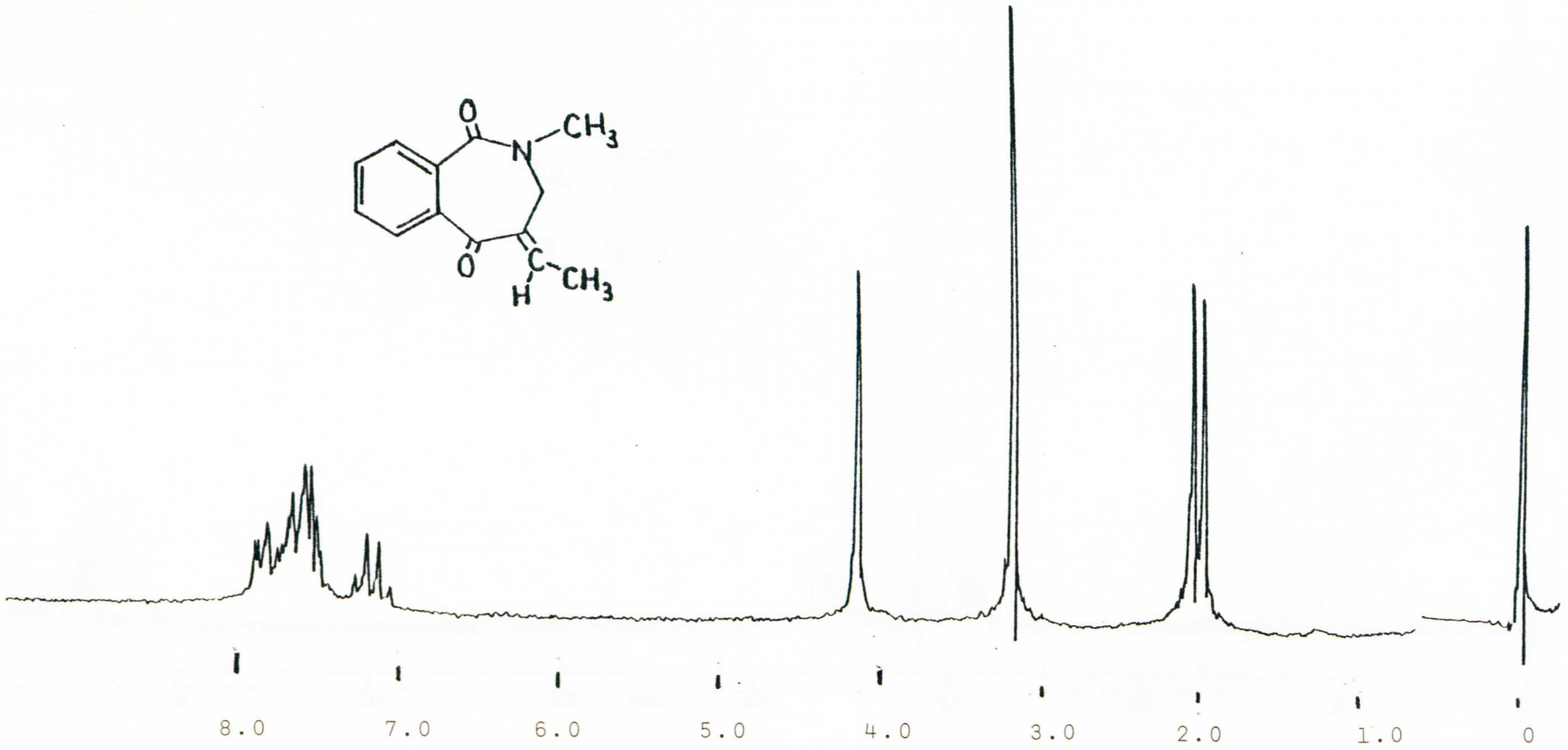
N-2-propenylphthalimide



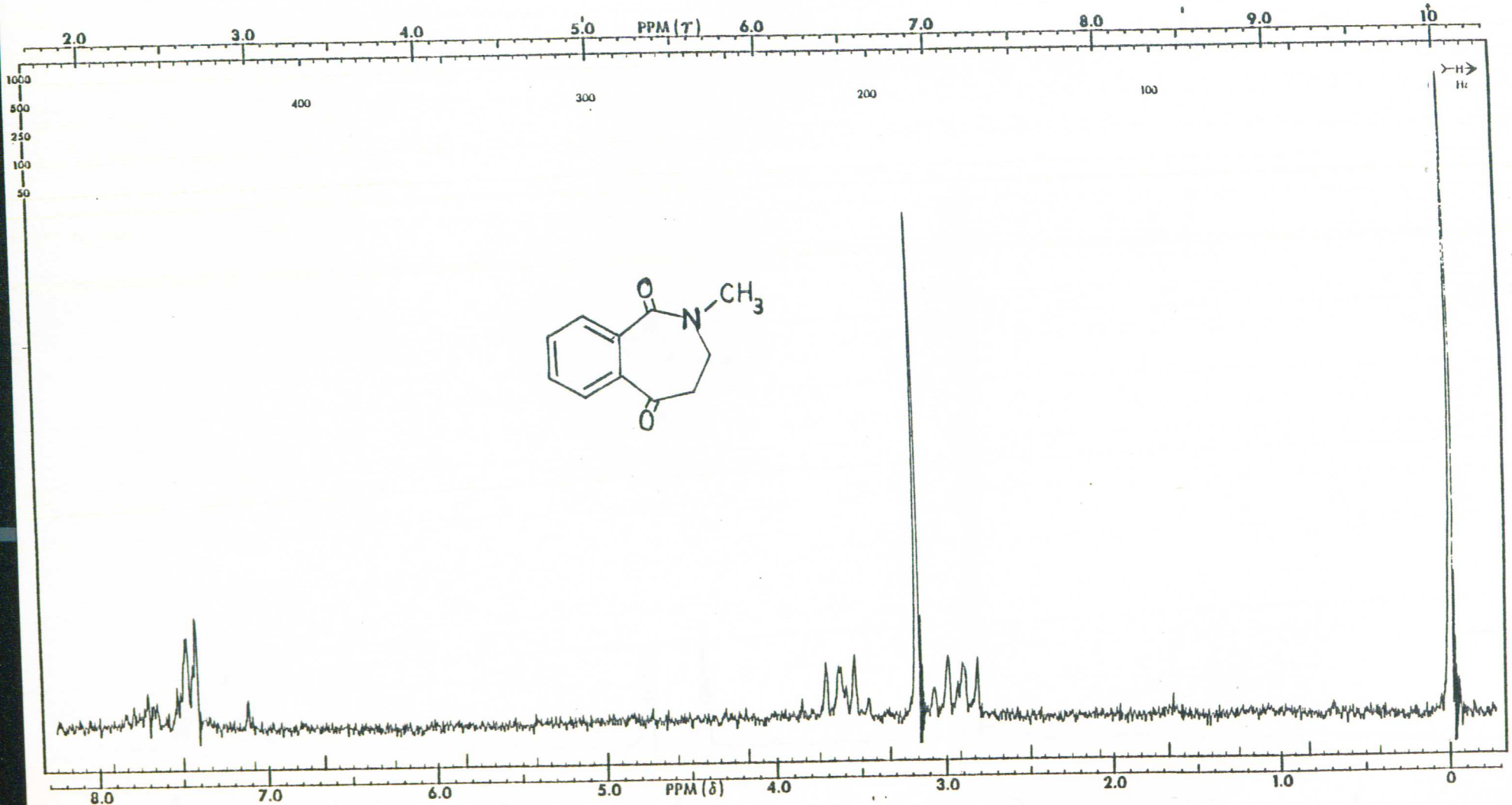
3,4-benzo-6,7-dihydro-1,6,6-trimethylazepine-2,5-dione (56)



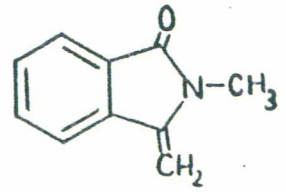
anti-3,4-benzo-6,7-dihydro-6-ethylidene-1-methylazepine-2,5-dione (58)



3,4-benzo-6,7-dihydro-1-methylazepine-2,5-dione (62)



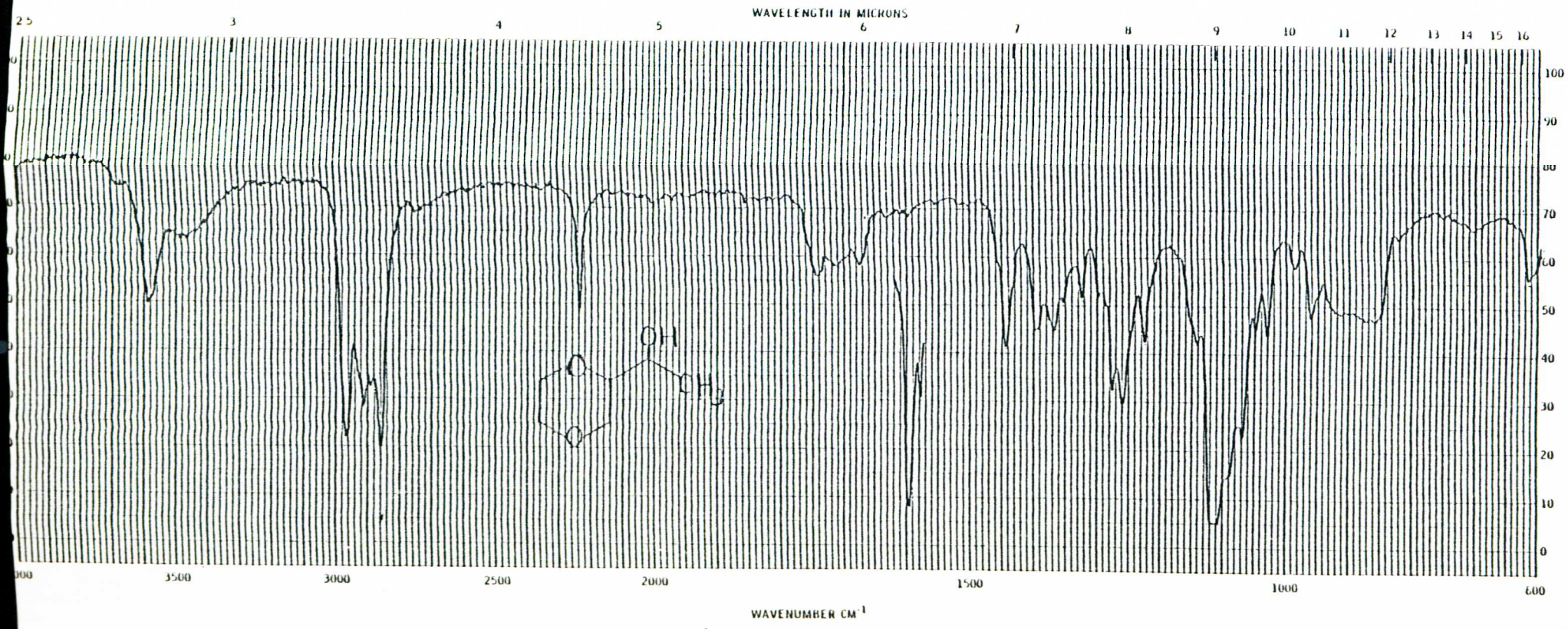
3-methylene-2-methyl-2-azaindanone (63)



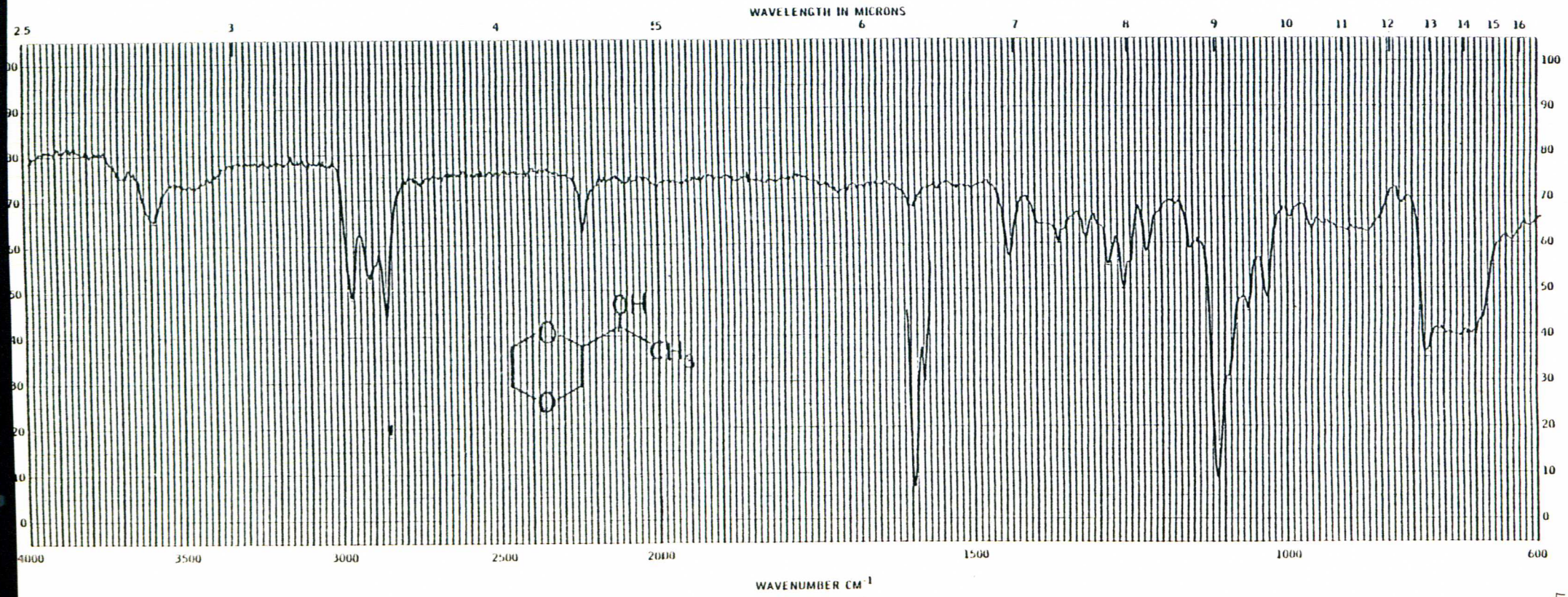
APPENDIX 3

IR Data

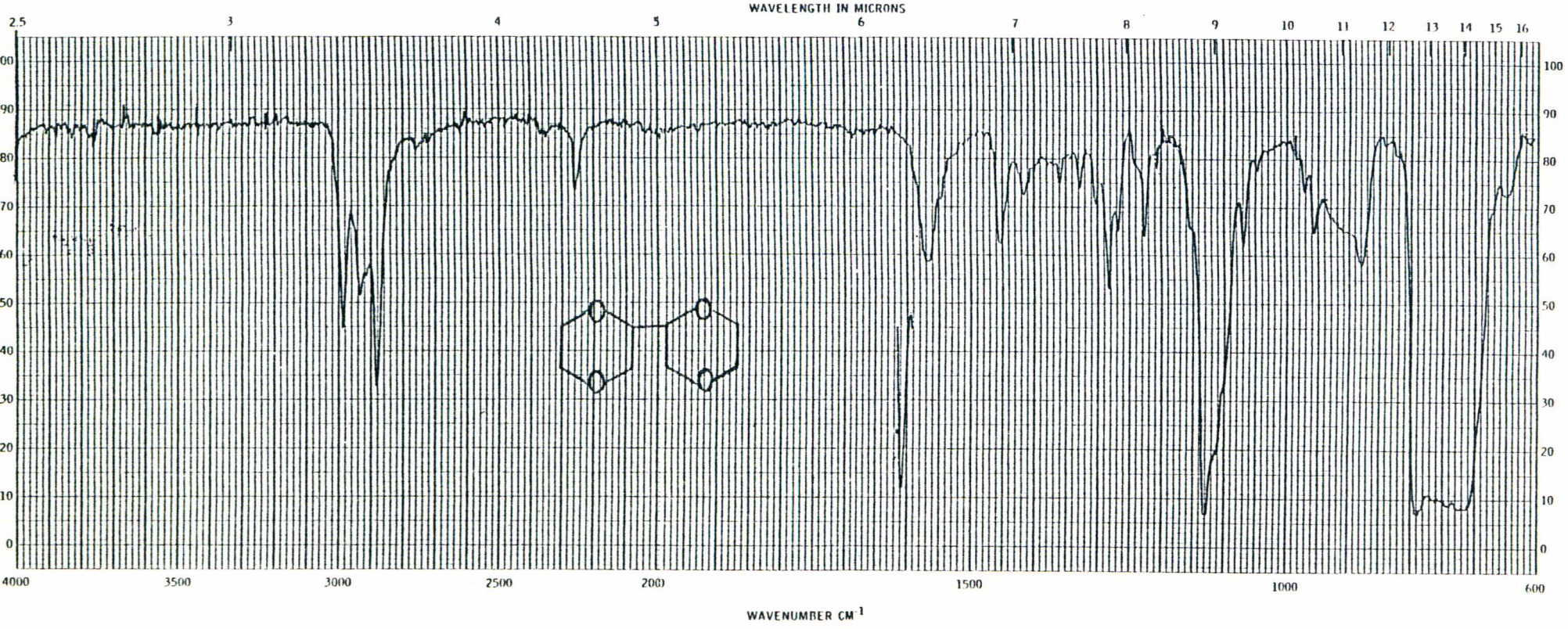
α-methyl dioxane methanol (2)



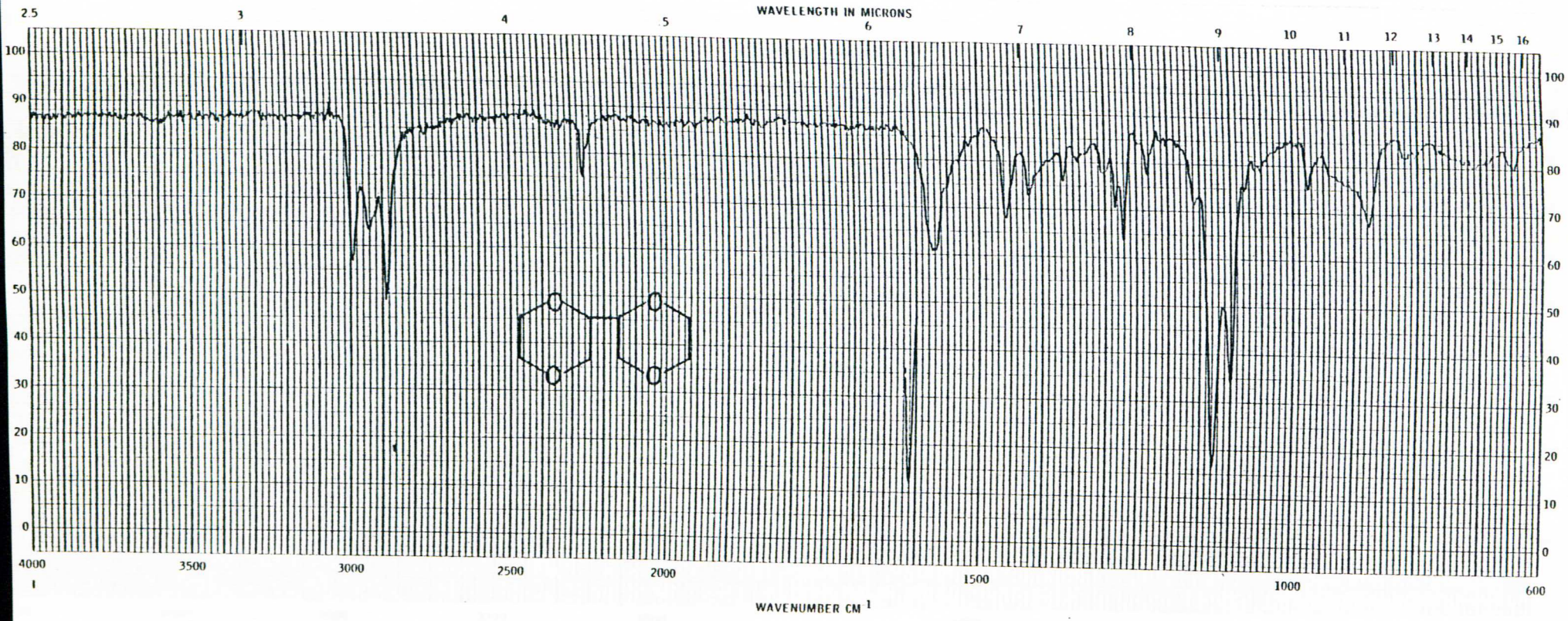
α-methyl dioxane methanol (3)



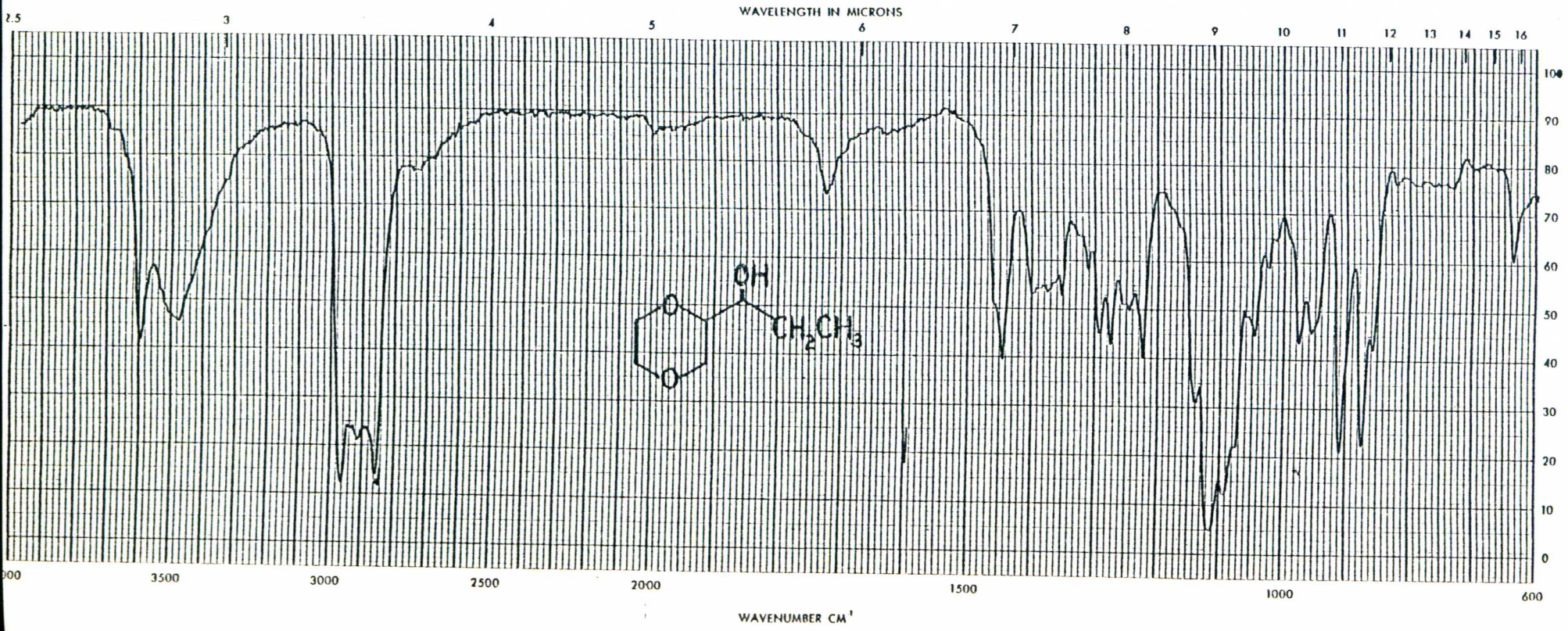
p-dioxyldioxane (4)



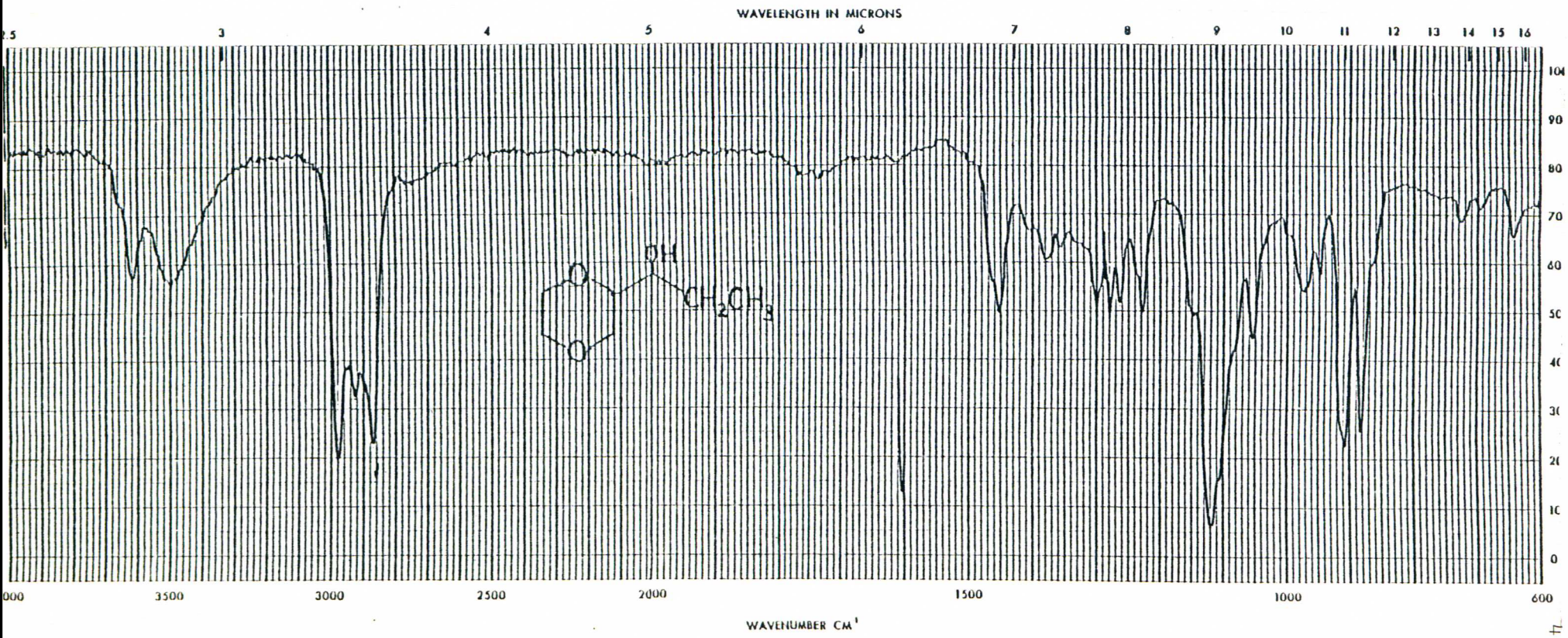
p-dioxyldioxane (5)



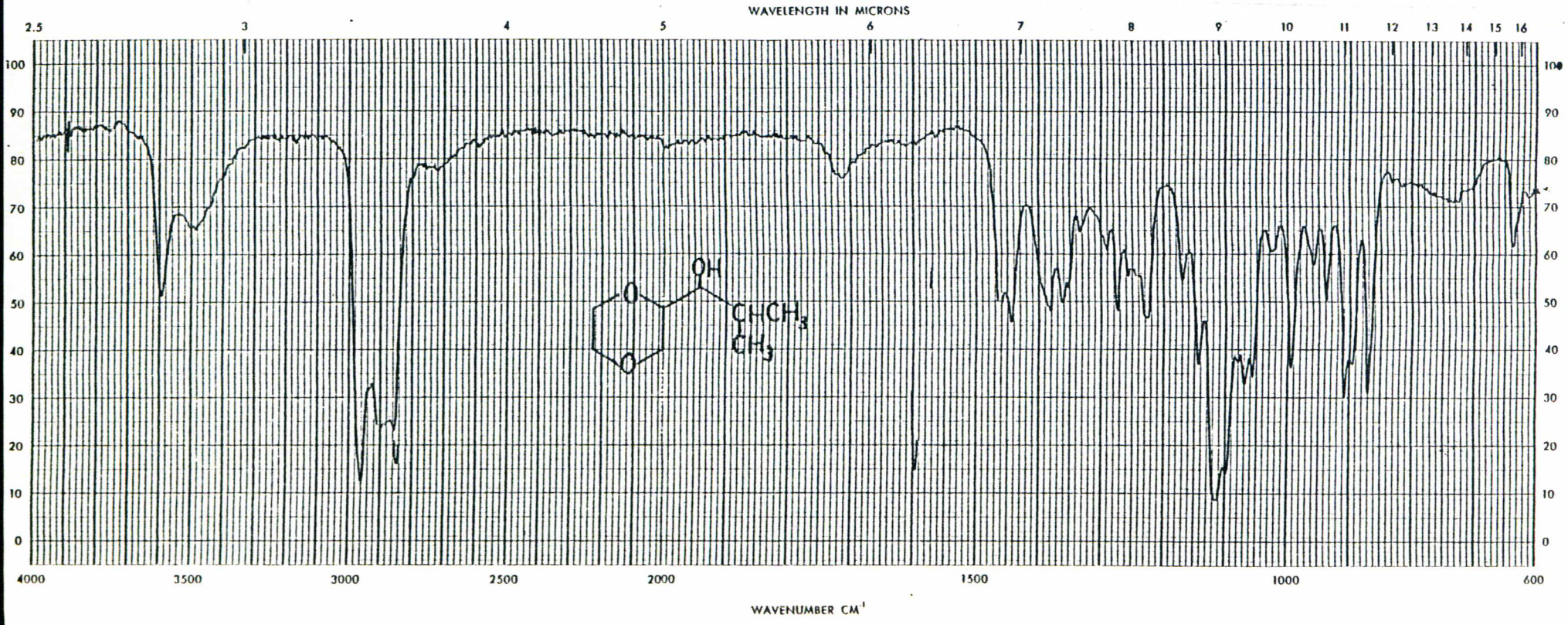
α-ethyl dioxane methanol (7)



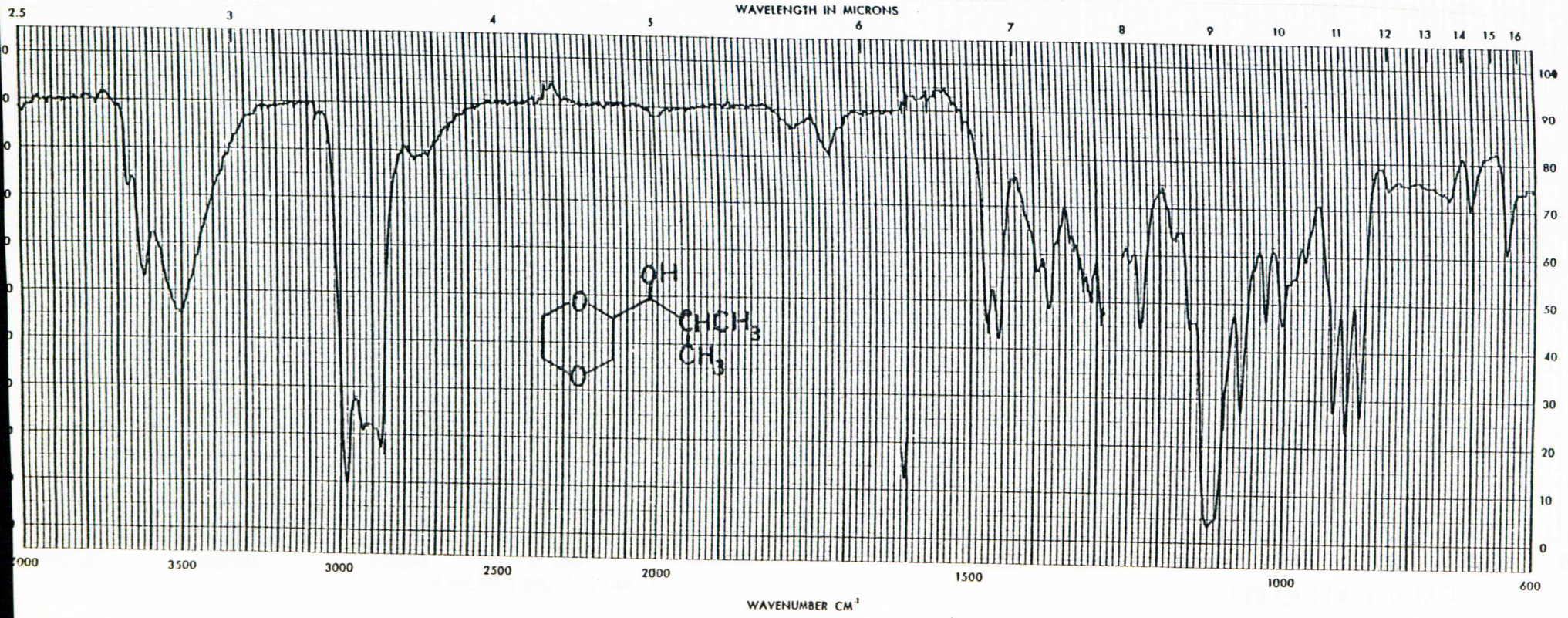
α-ethyl dioxane methanol (8)



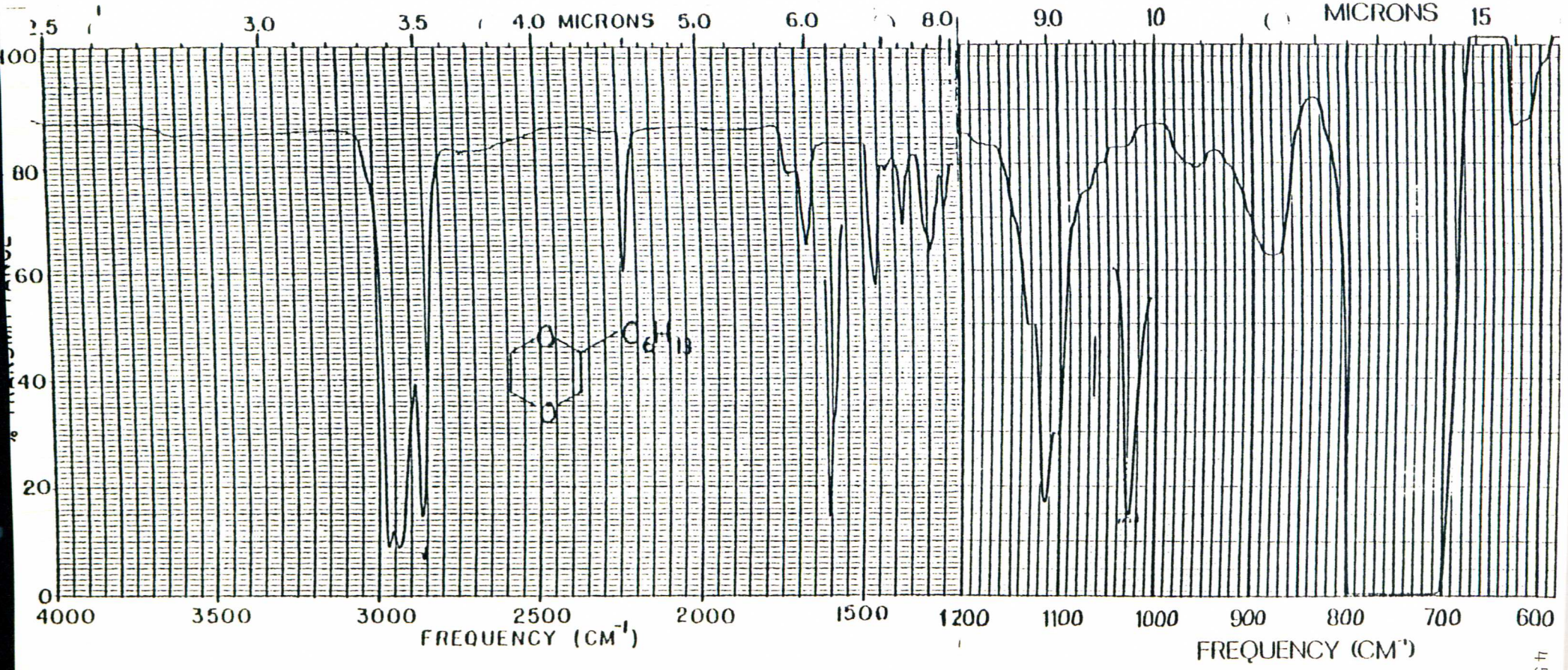
α-isopropyl dioxane methanol (9)



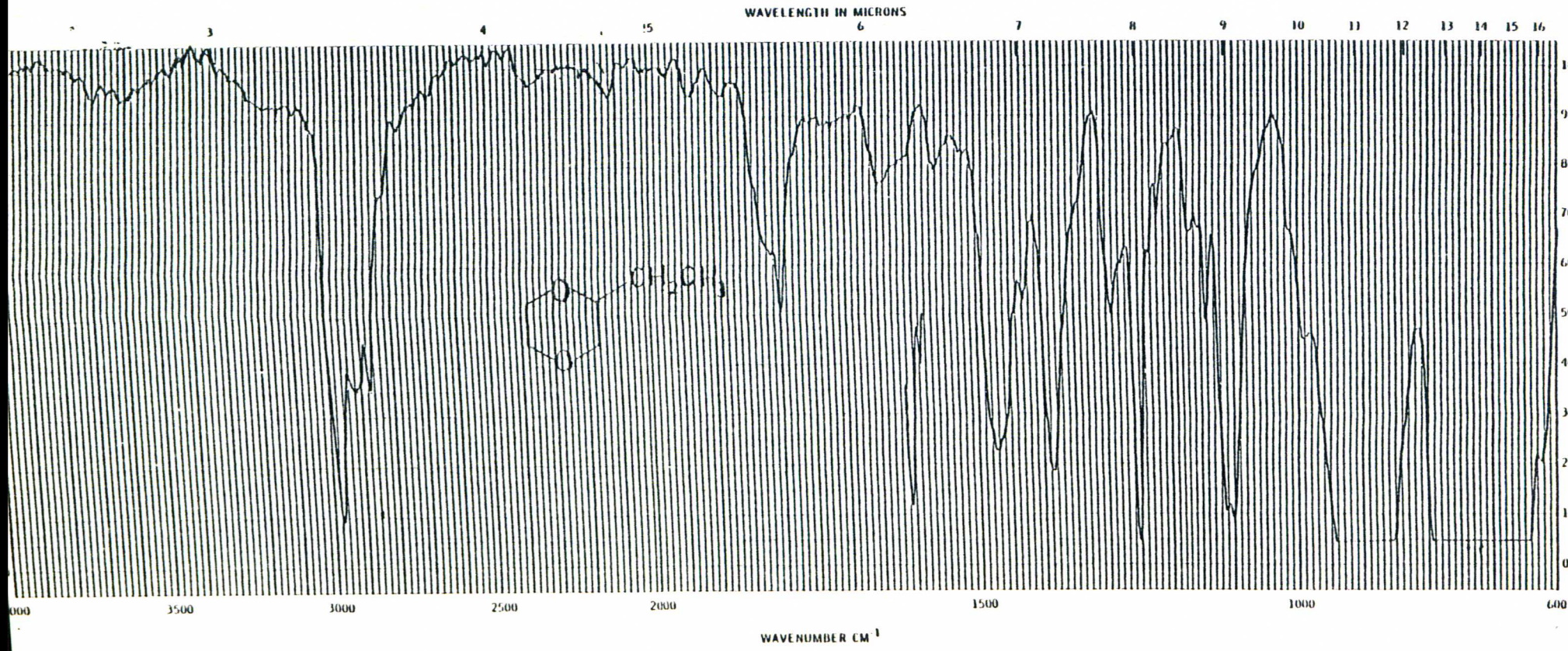
α-isopropyl dioxane methanol (10)



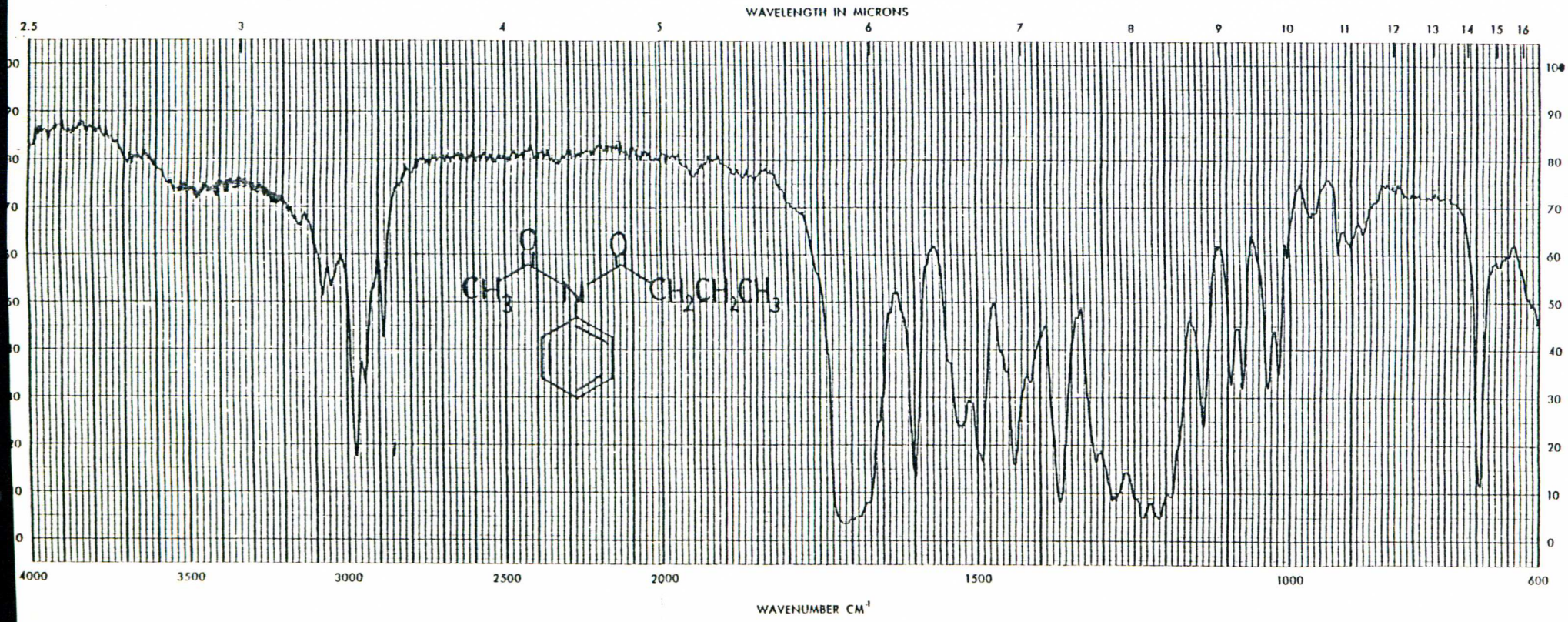
hexyldioxane (15)



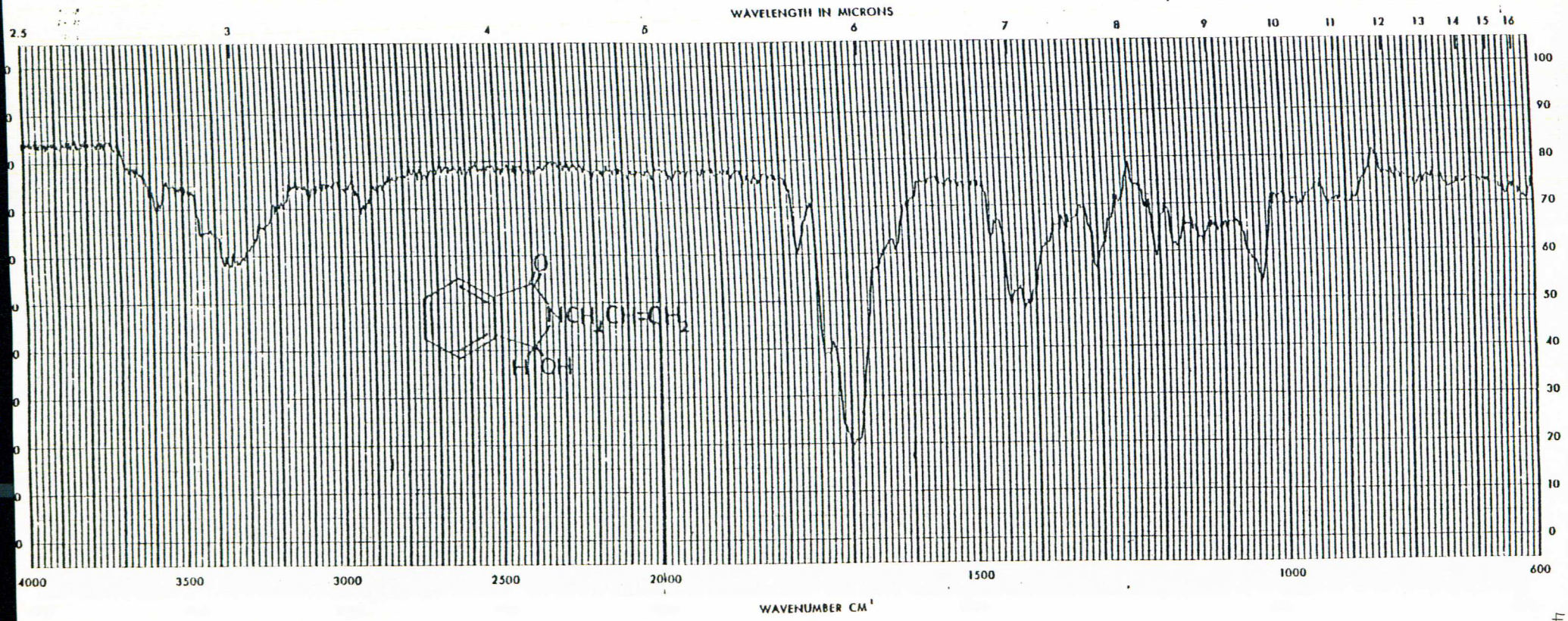
ethyldioxane



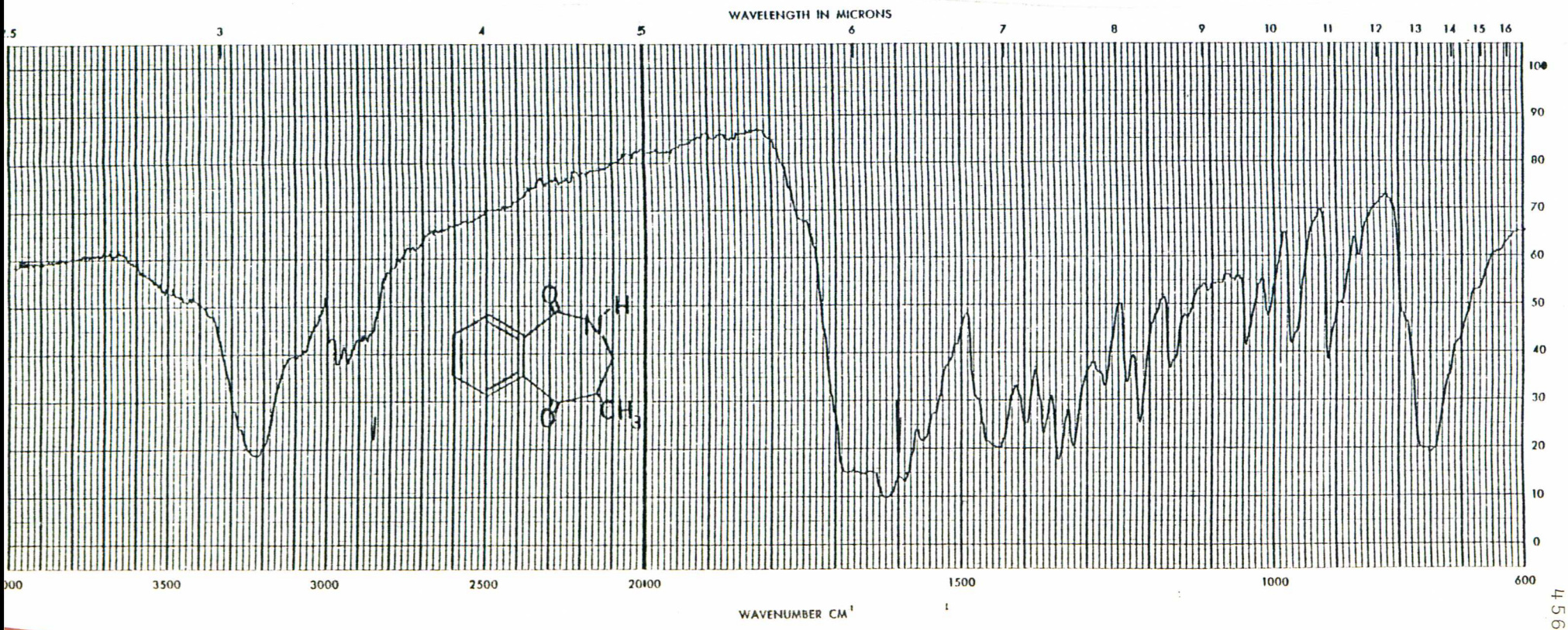
N-acetylbutyranilide



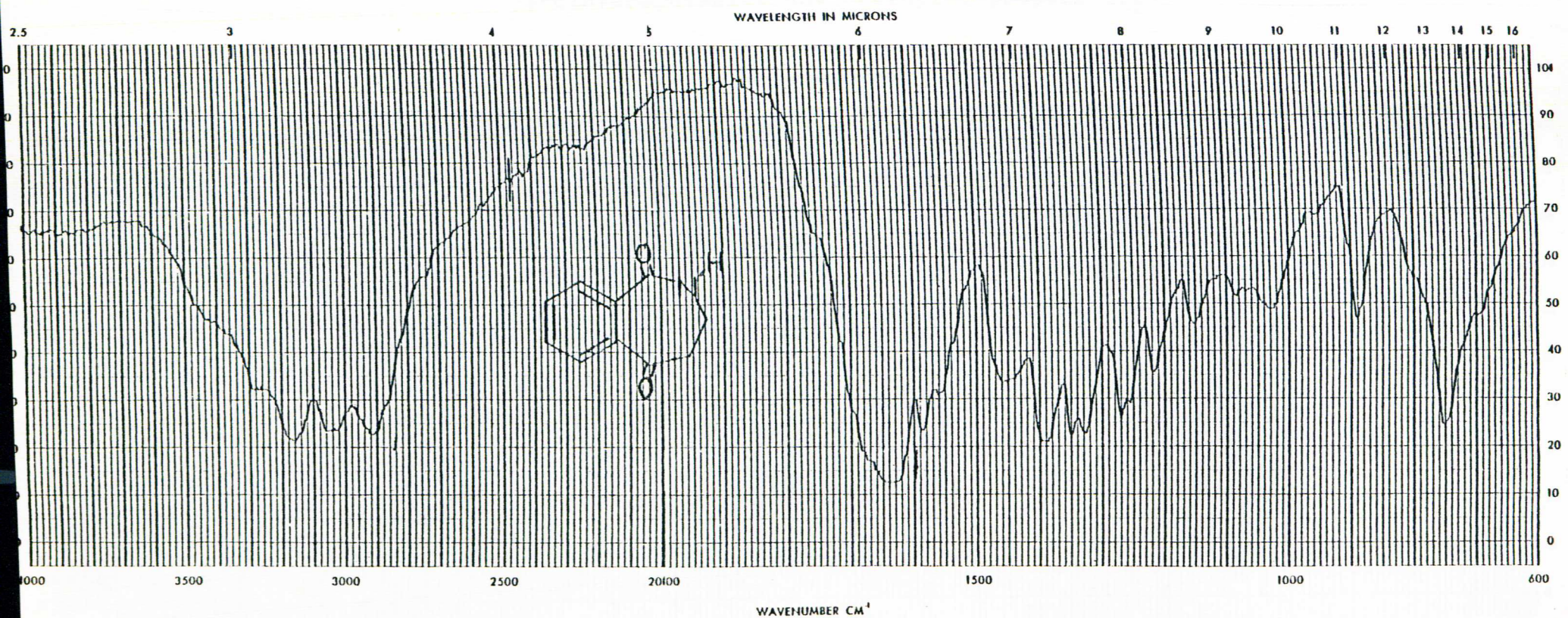
3-dihydrophthalimido-1-propene



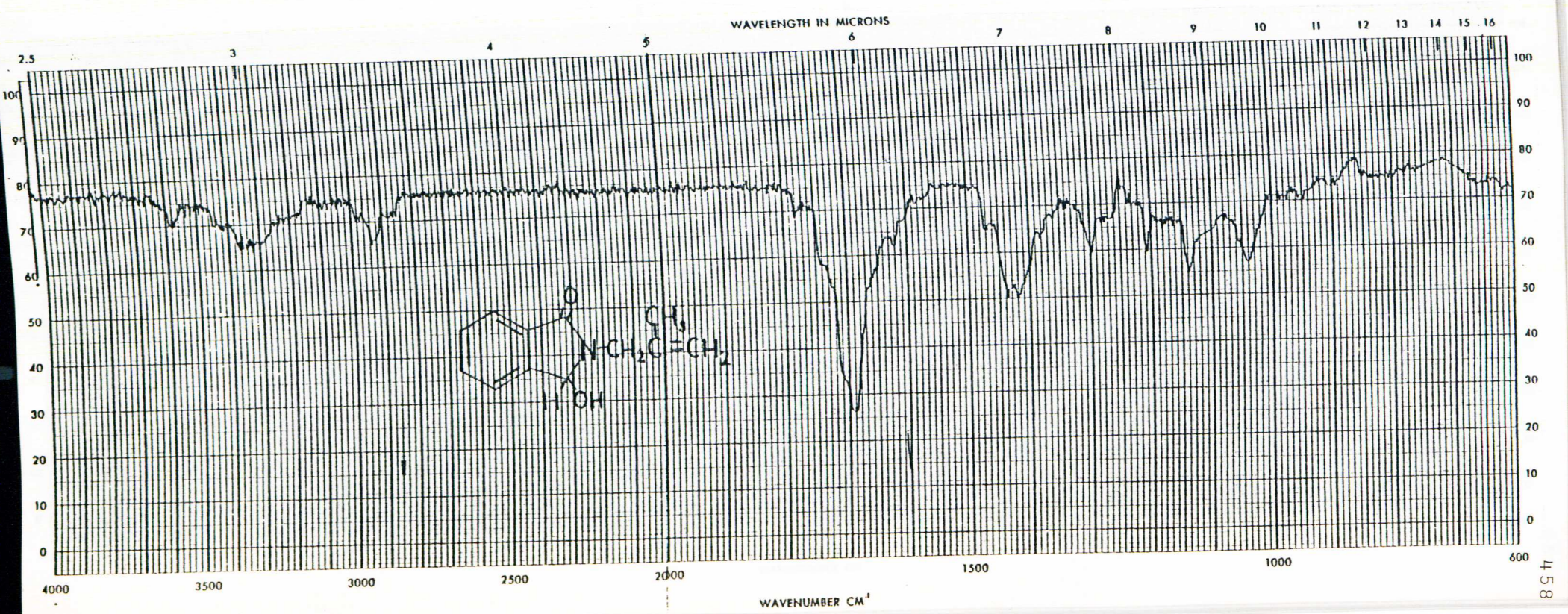
3,4-benzo-6,7-dihydro-6-methyl(1H)azepine-2,5-dione (36)



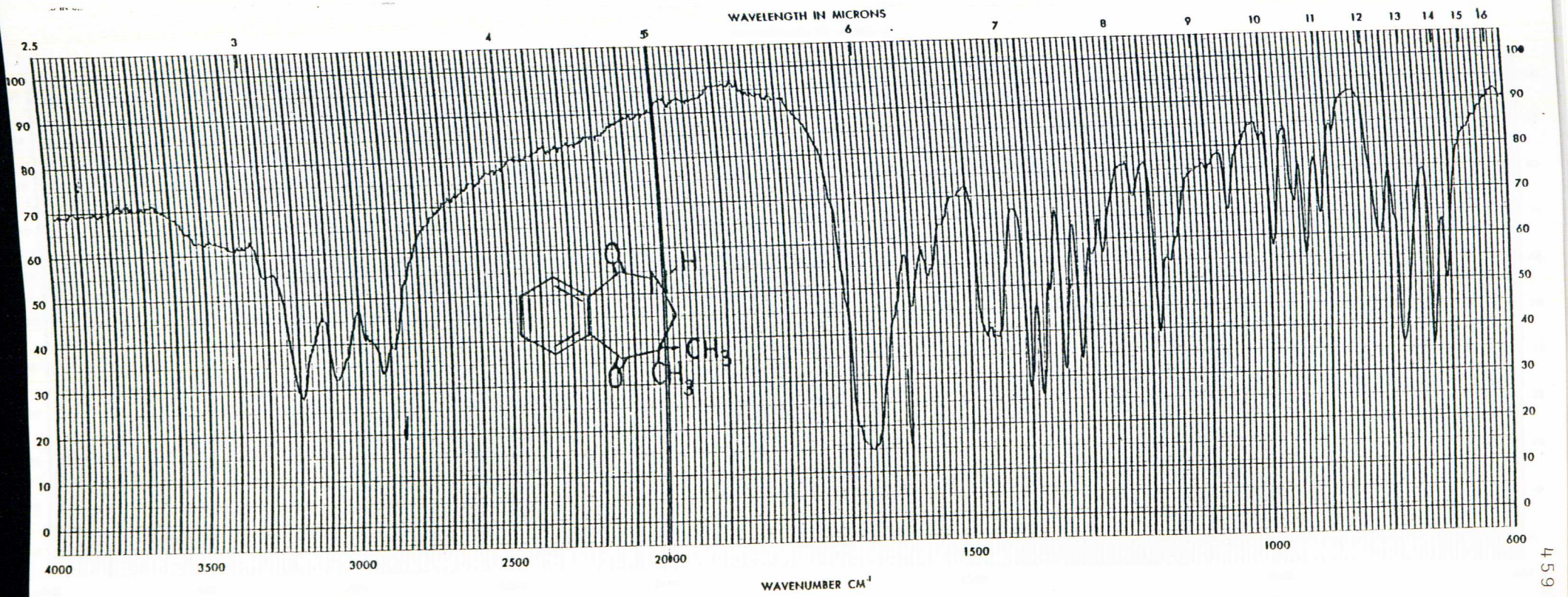
3,4-benzo-6,7-dihydro(1H)azepine-2,5-dione (37)



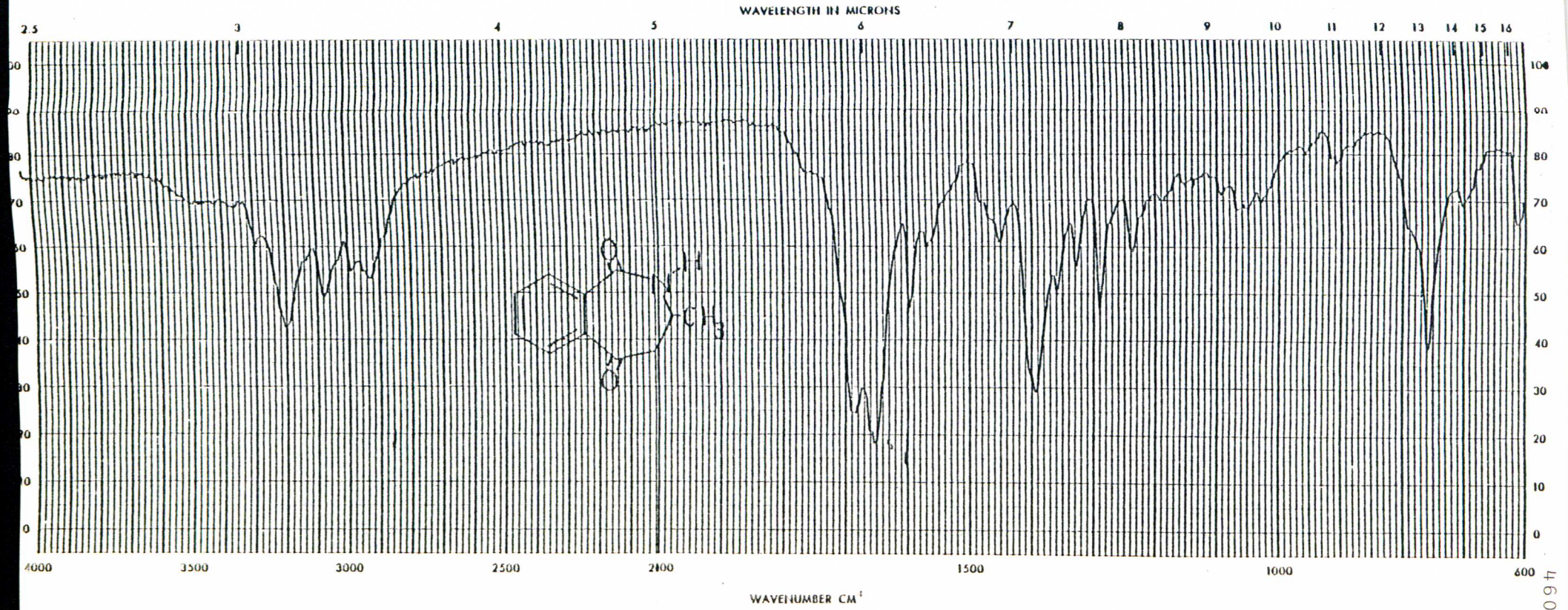
3-dihydrophthalimido-2-methyl-1-propene (38)



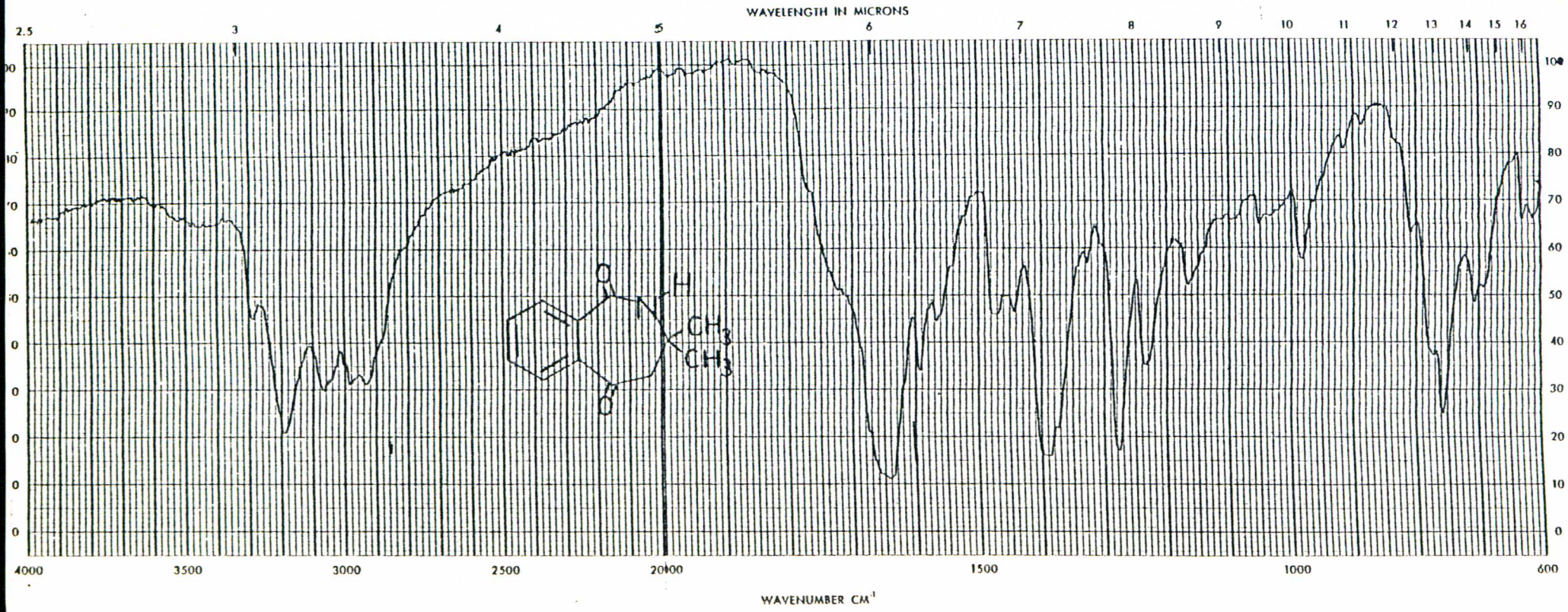
3,4-benzo-6,7-dihydro-6,6-dimethyl(1H)azepine-2,5-dione (39)



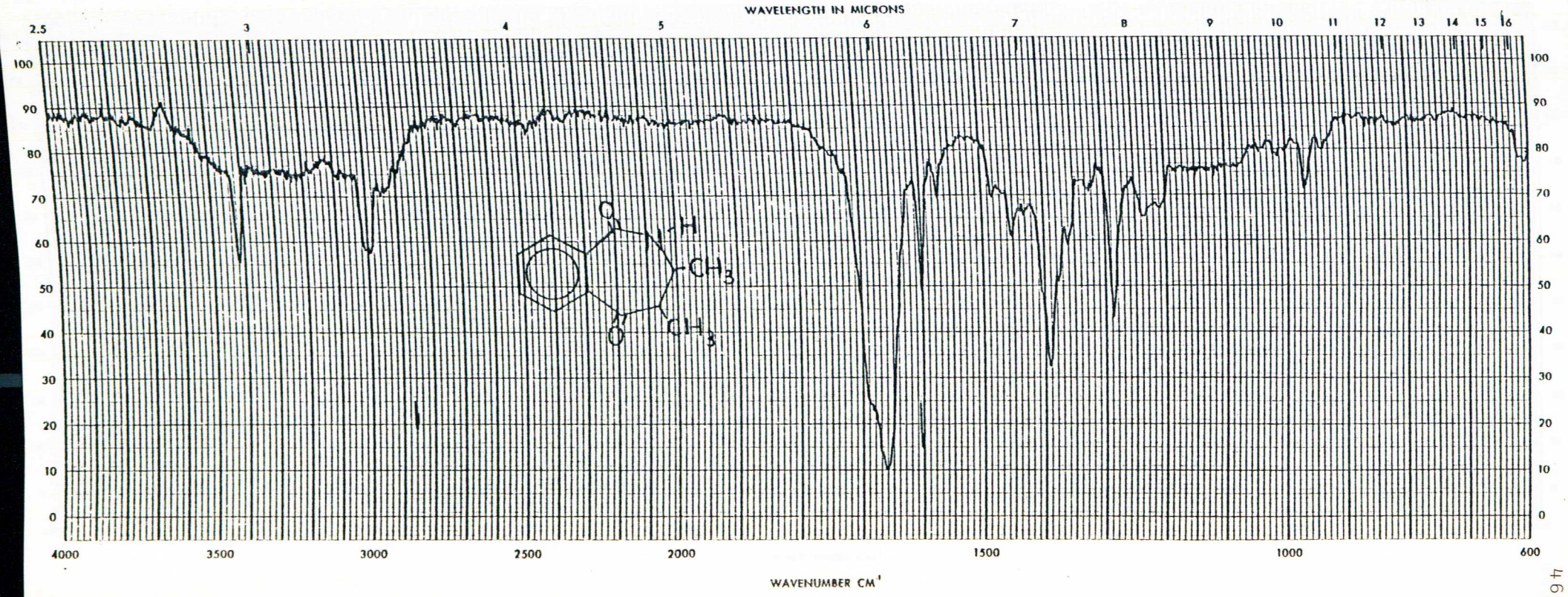
3,4-benzo-6,7-dihydro-7-methyl(1H)azepine-2,5-dione (40)



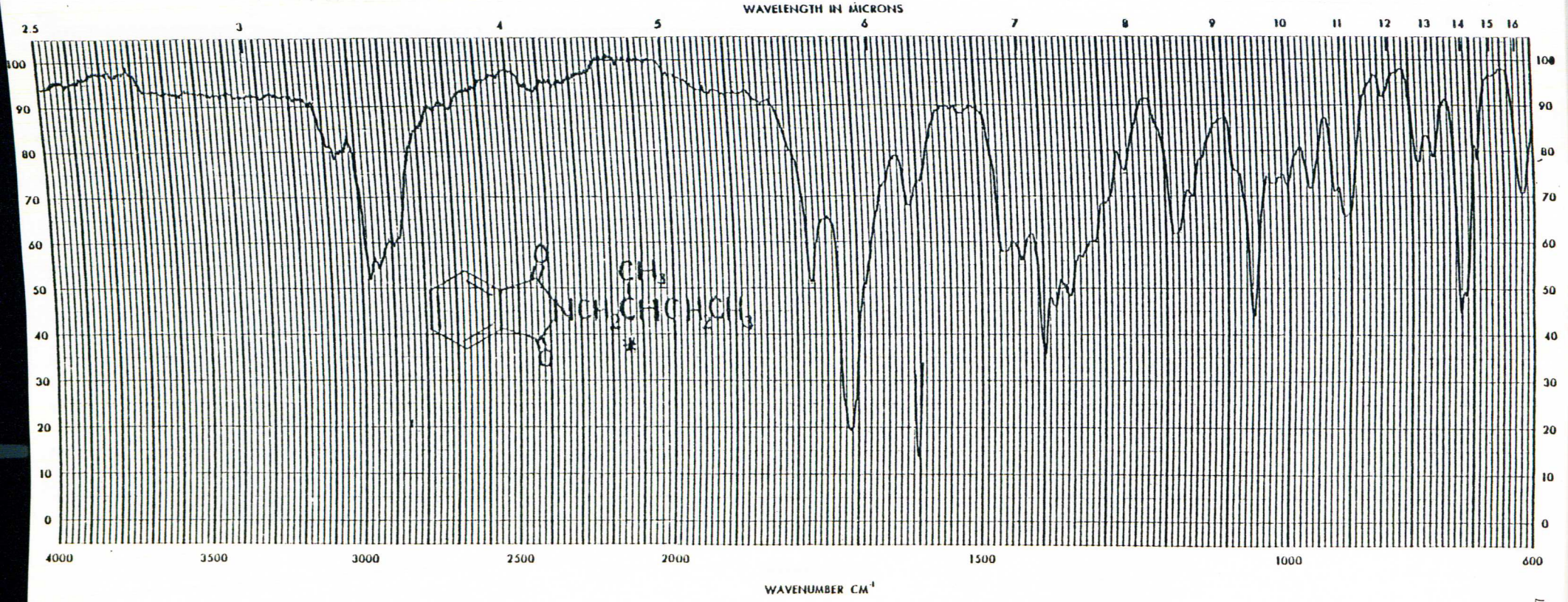
3,4-benzo-6,7-dihydro-7,7-dimethyl(1H)azepine-2,5-dione (41)



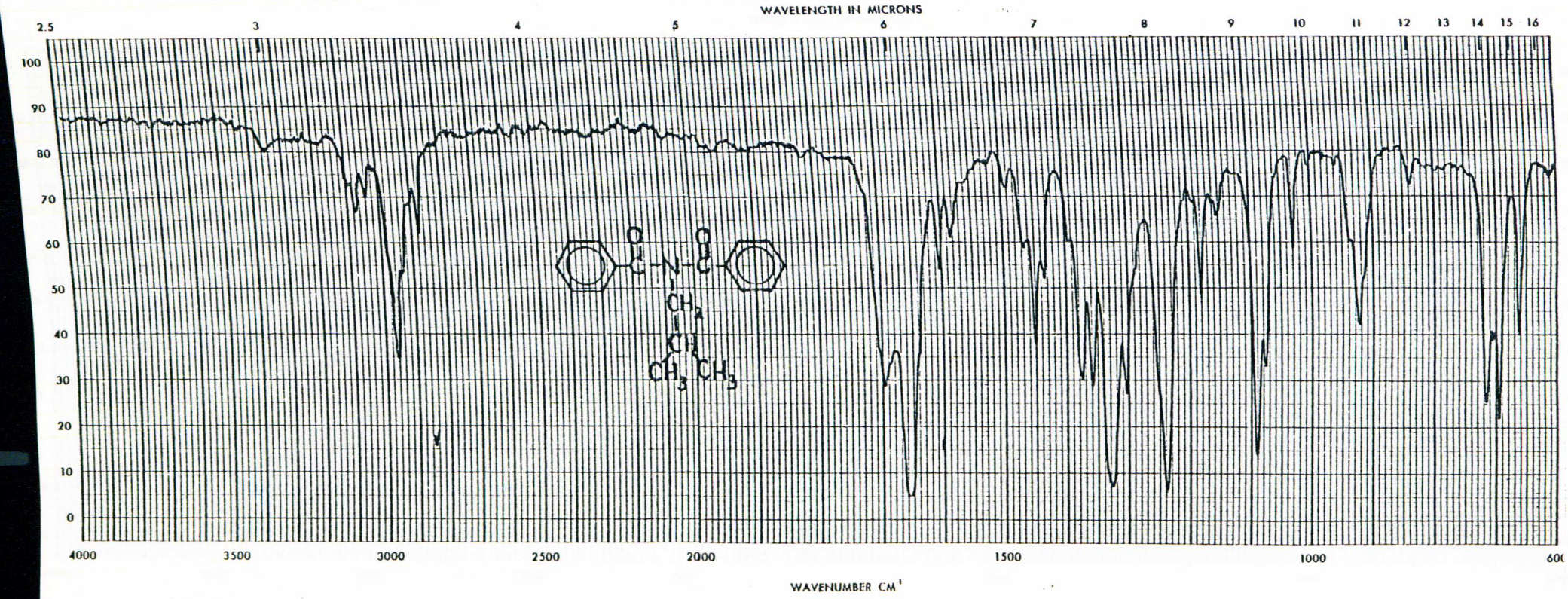
cis and trans-3,4-benzo-6,7-dihydro-6,7-dimethyl(1H)azepine-2,5-dione (43)



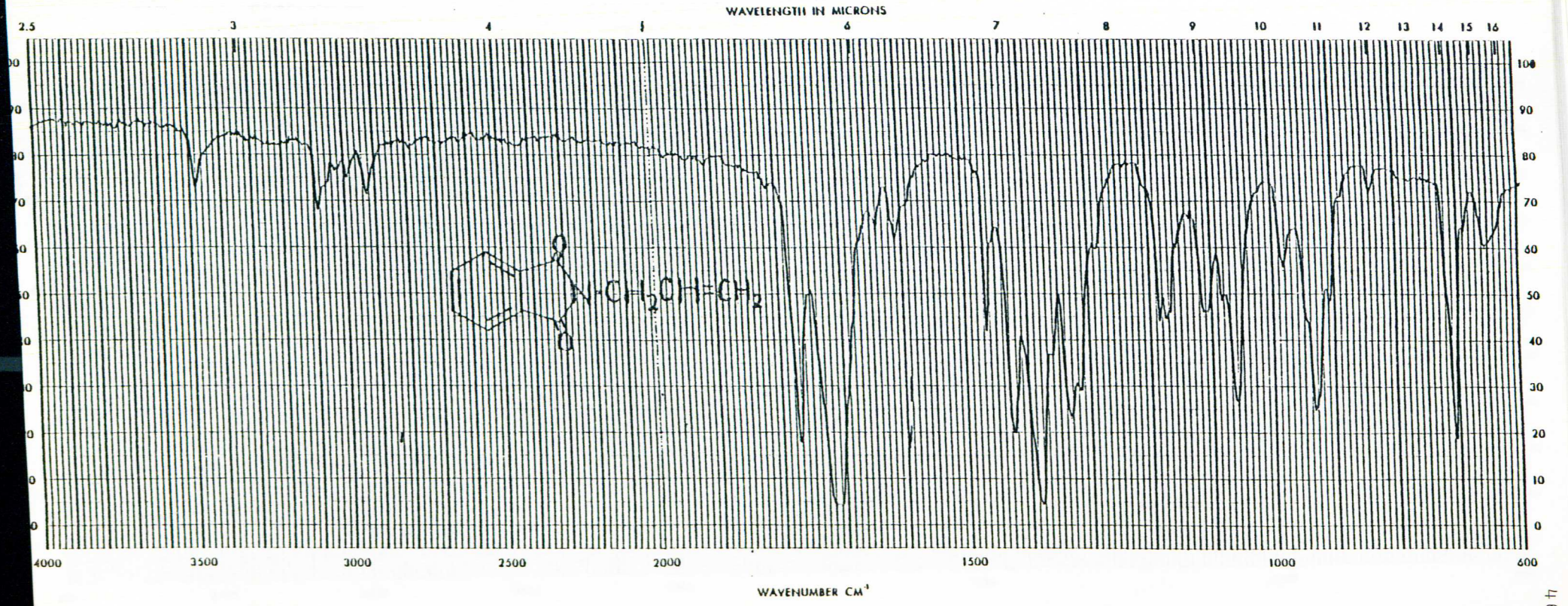
(2S)-(+)-2-methylbutylphthalimide



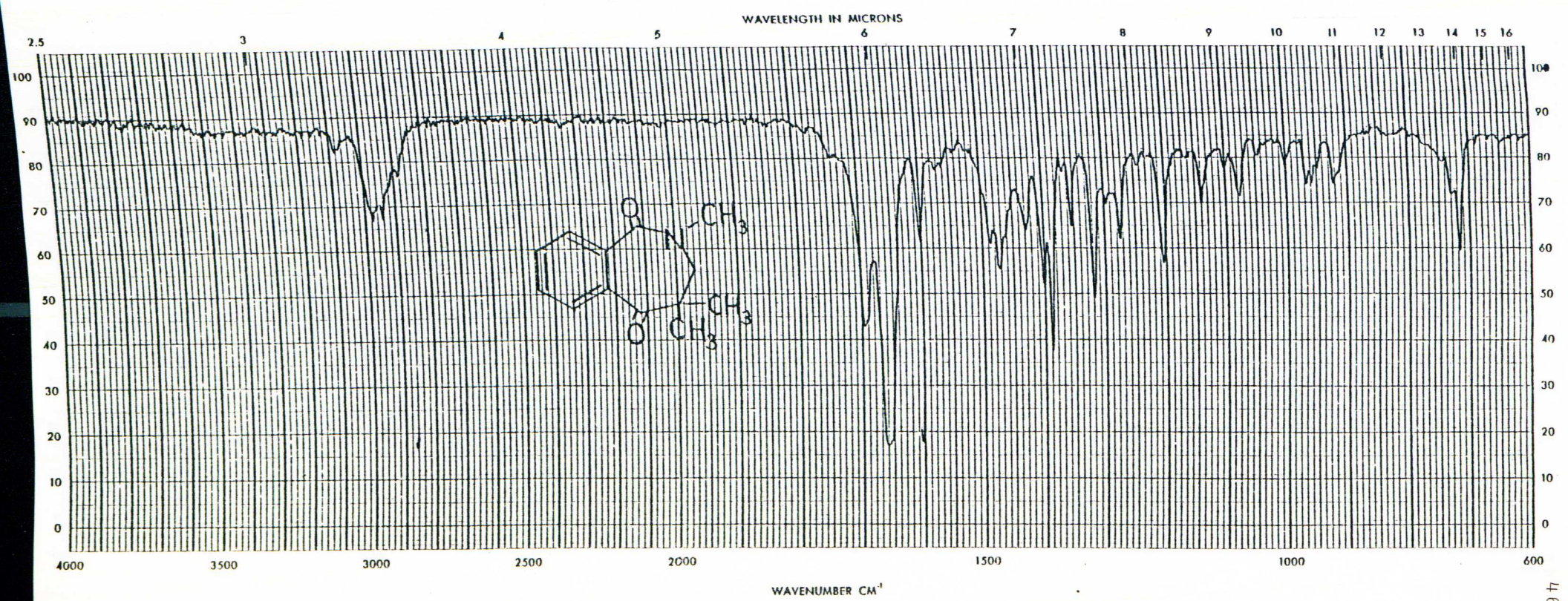
N,N-dibenzoylisobutylamine



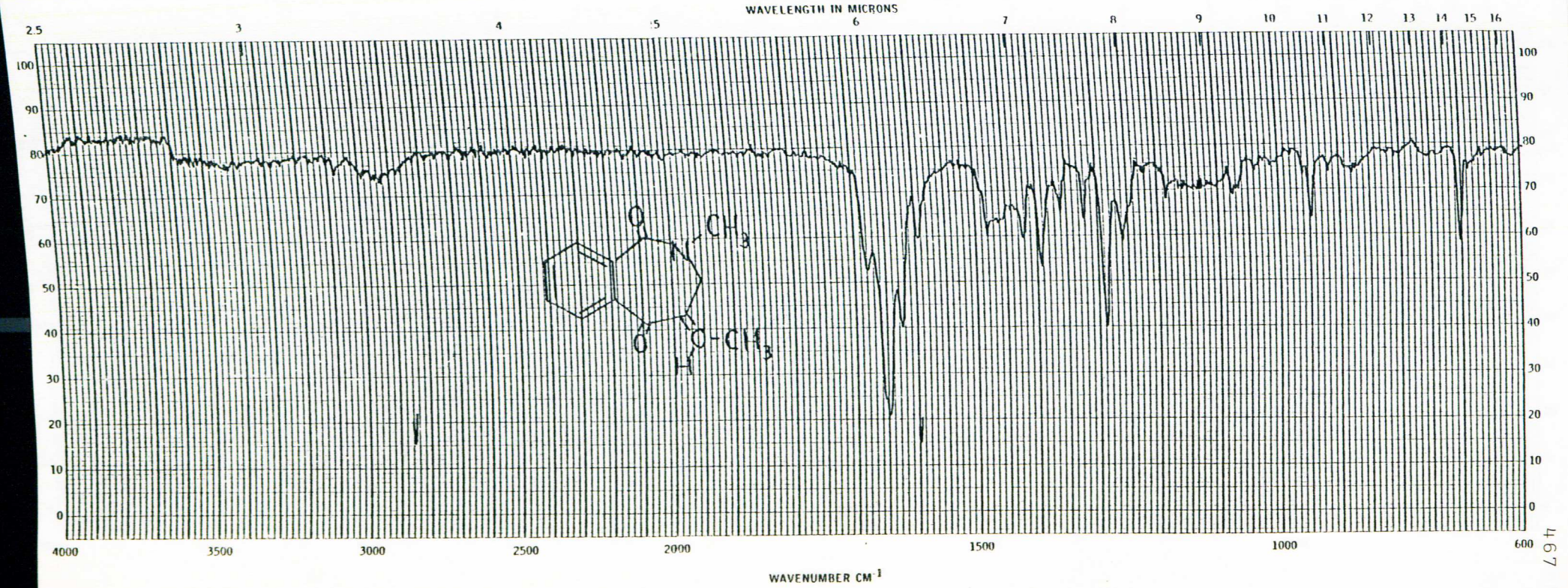
N-2-propenylphthalimide



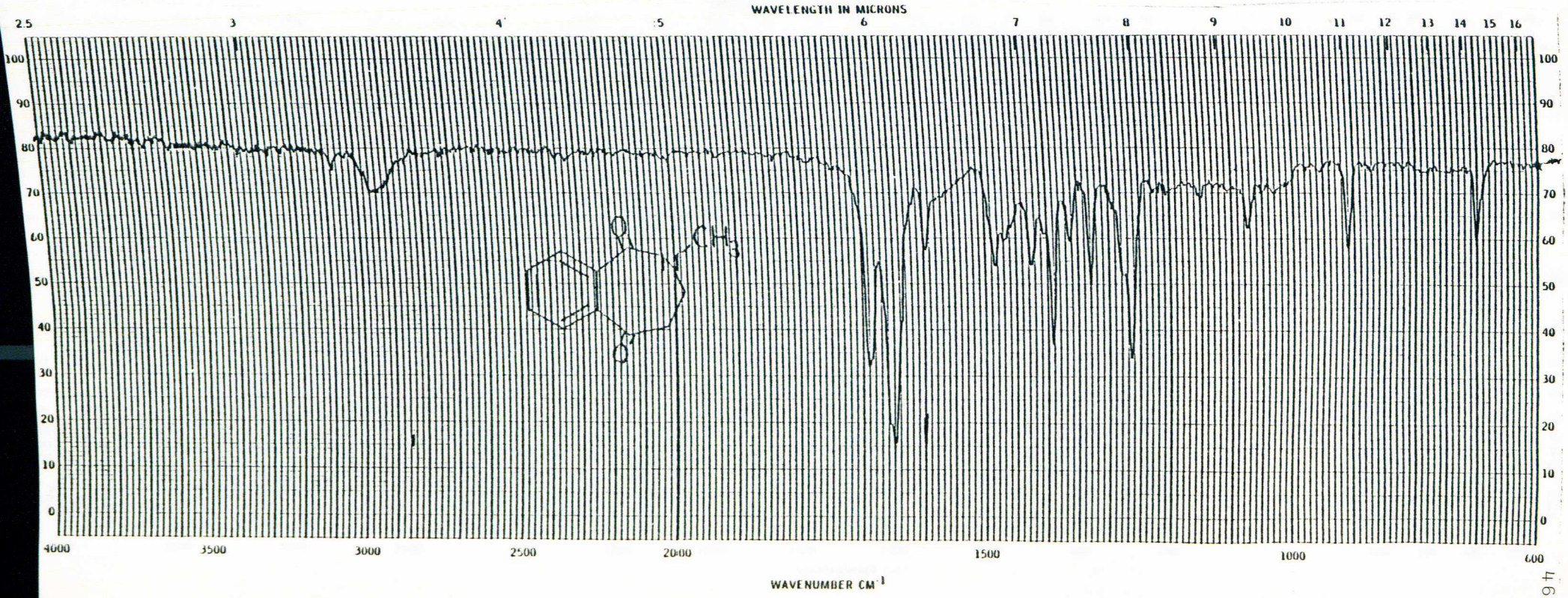
3,4-benzo-6,7-dihydro-1,6,6-trimethylazepine-2,5-dione (56)



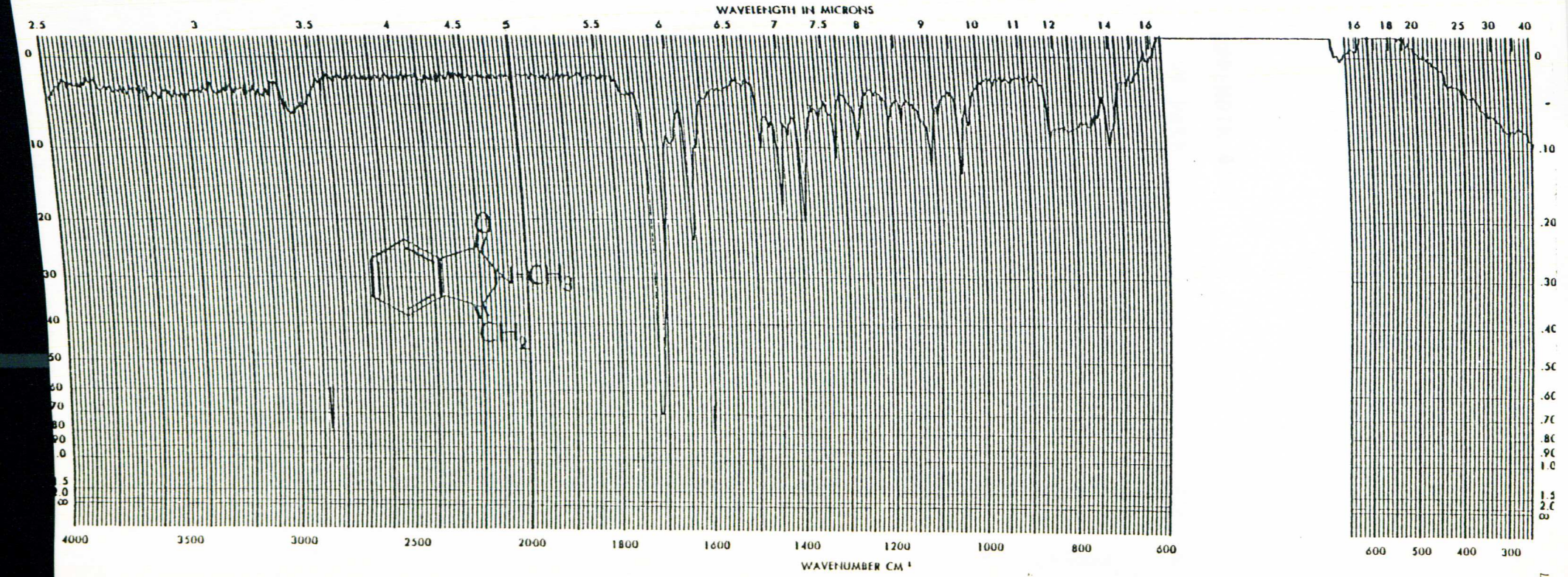
anti-3,4-benzo-6,7-dihydro-6-ethylidene-1-methylazepine-2,5-dione (58)



3,4-benzo-6,7-dihydro-1-methylazepine-2,5-dione (62)

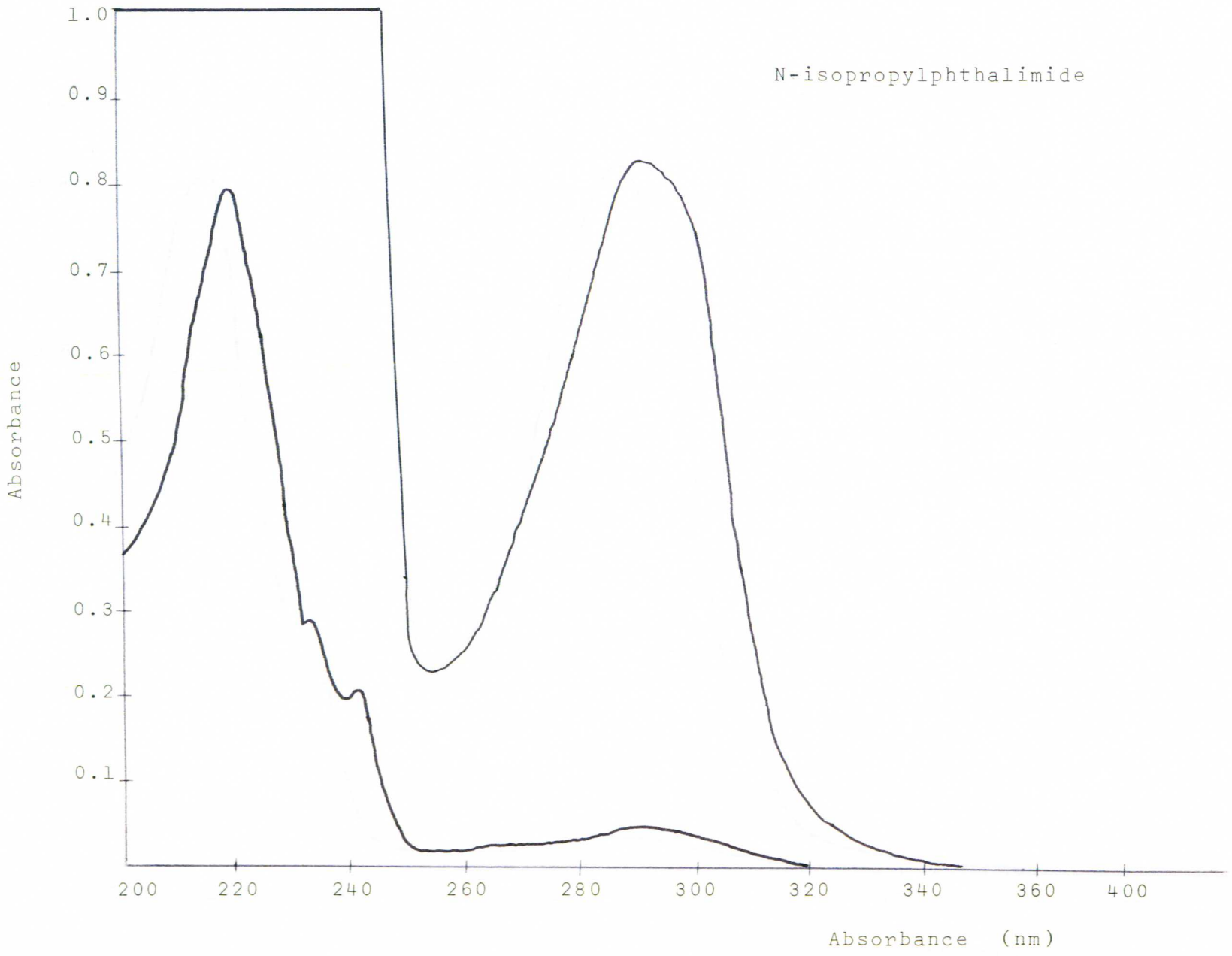


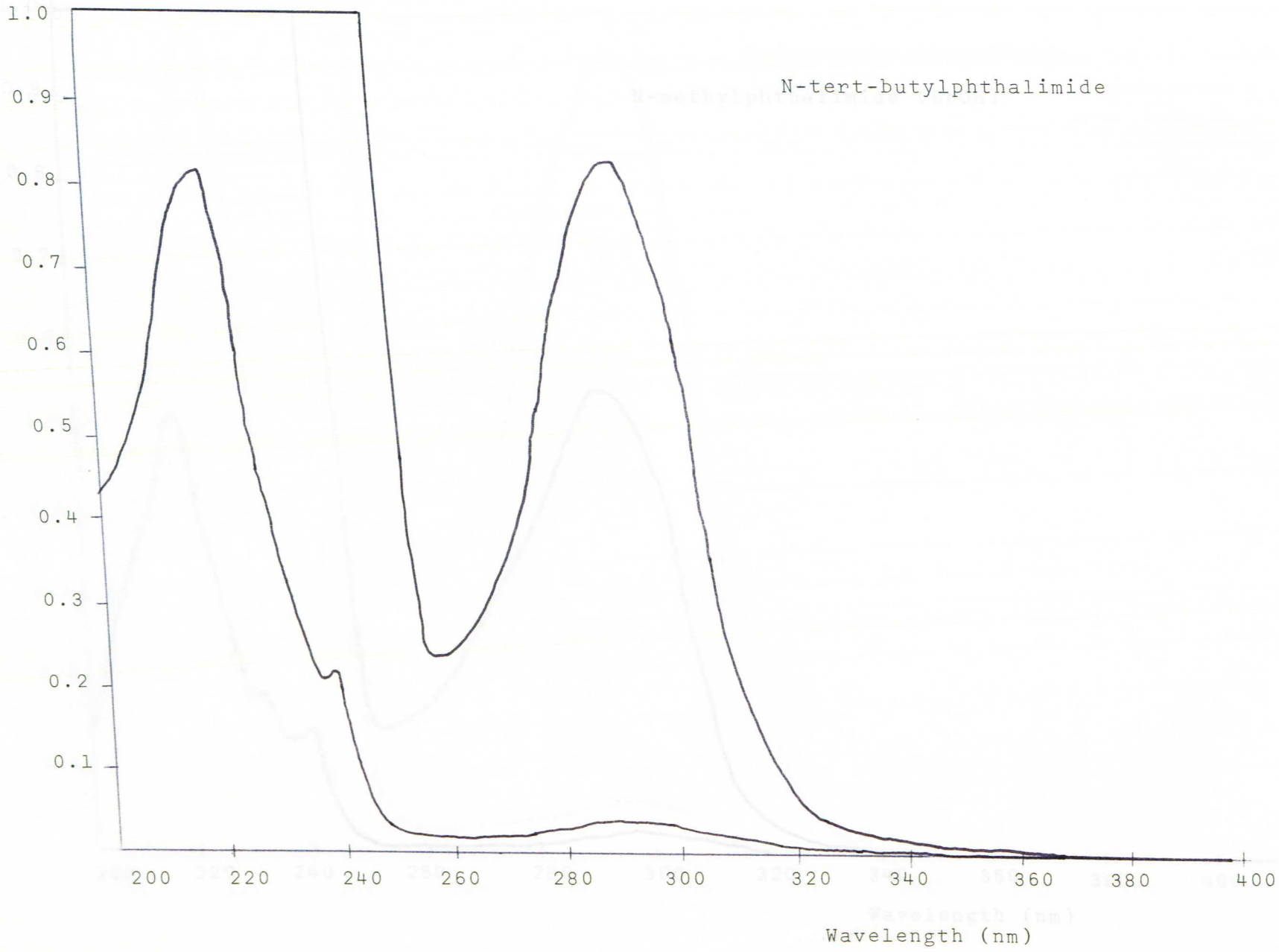
3-methylene-2-methyl-2-azaindanone (63)

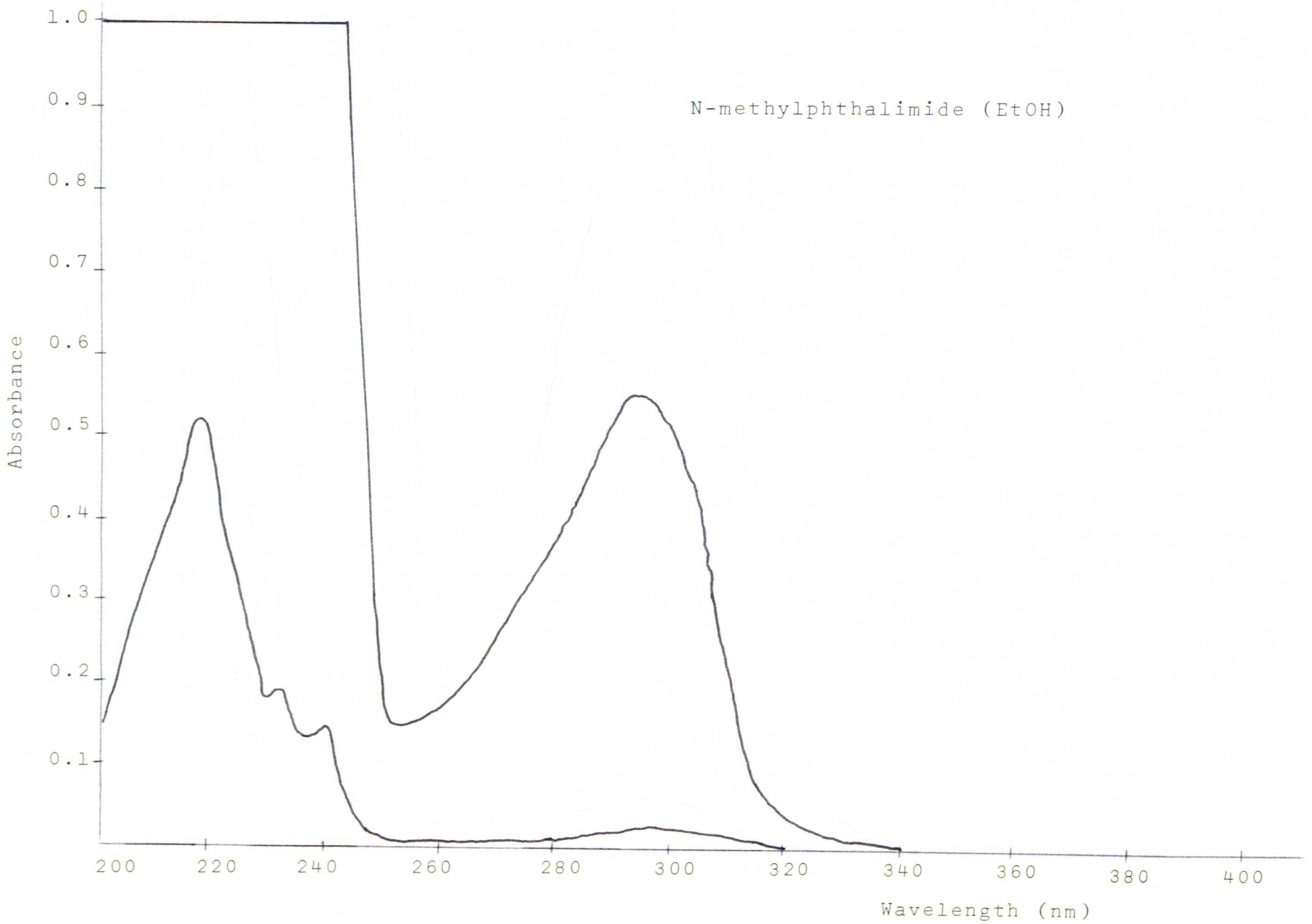


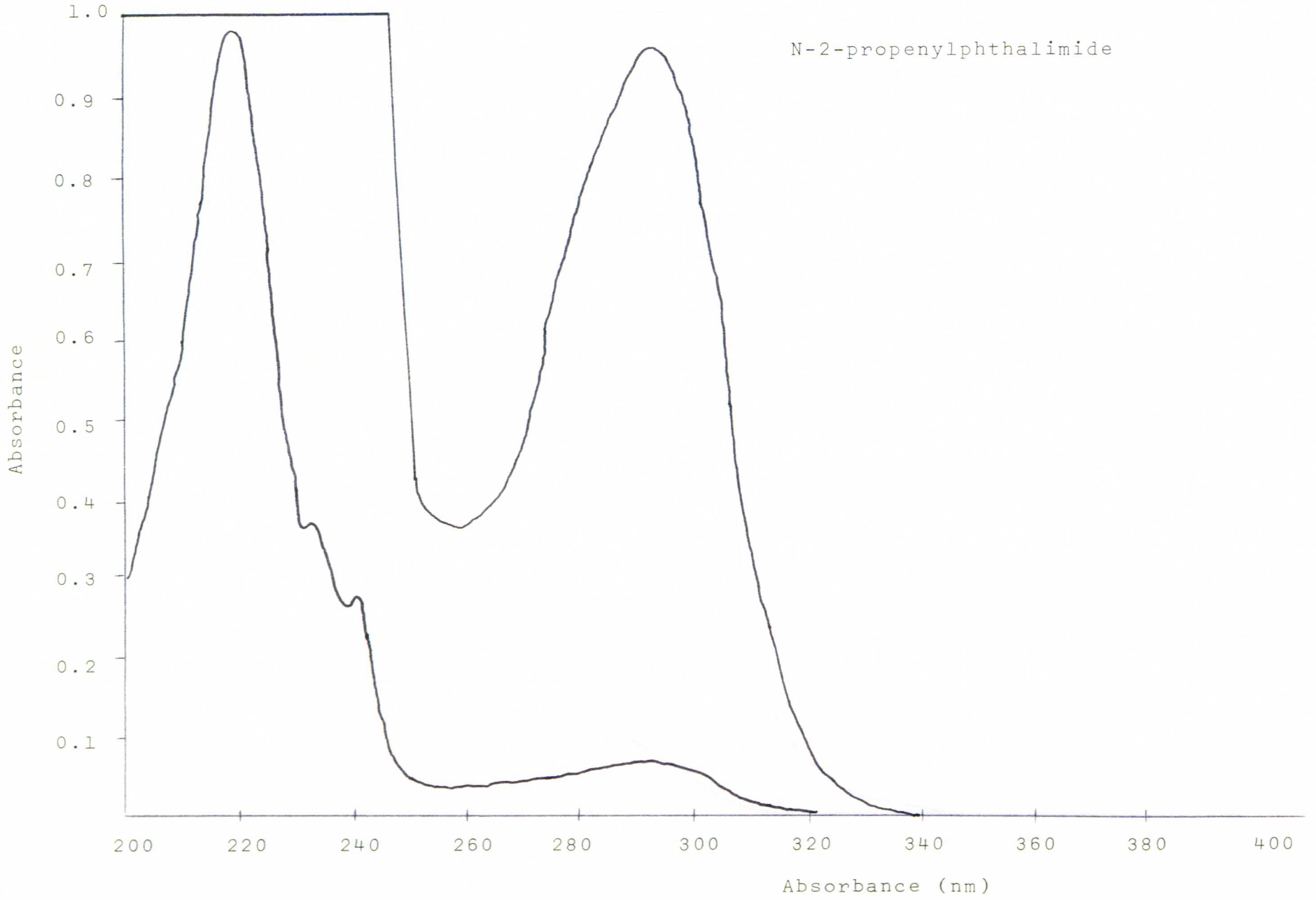
APPENDIX 4

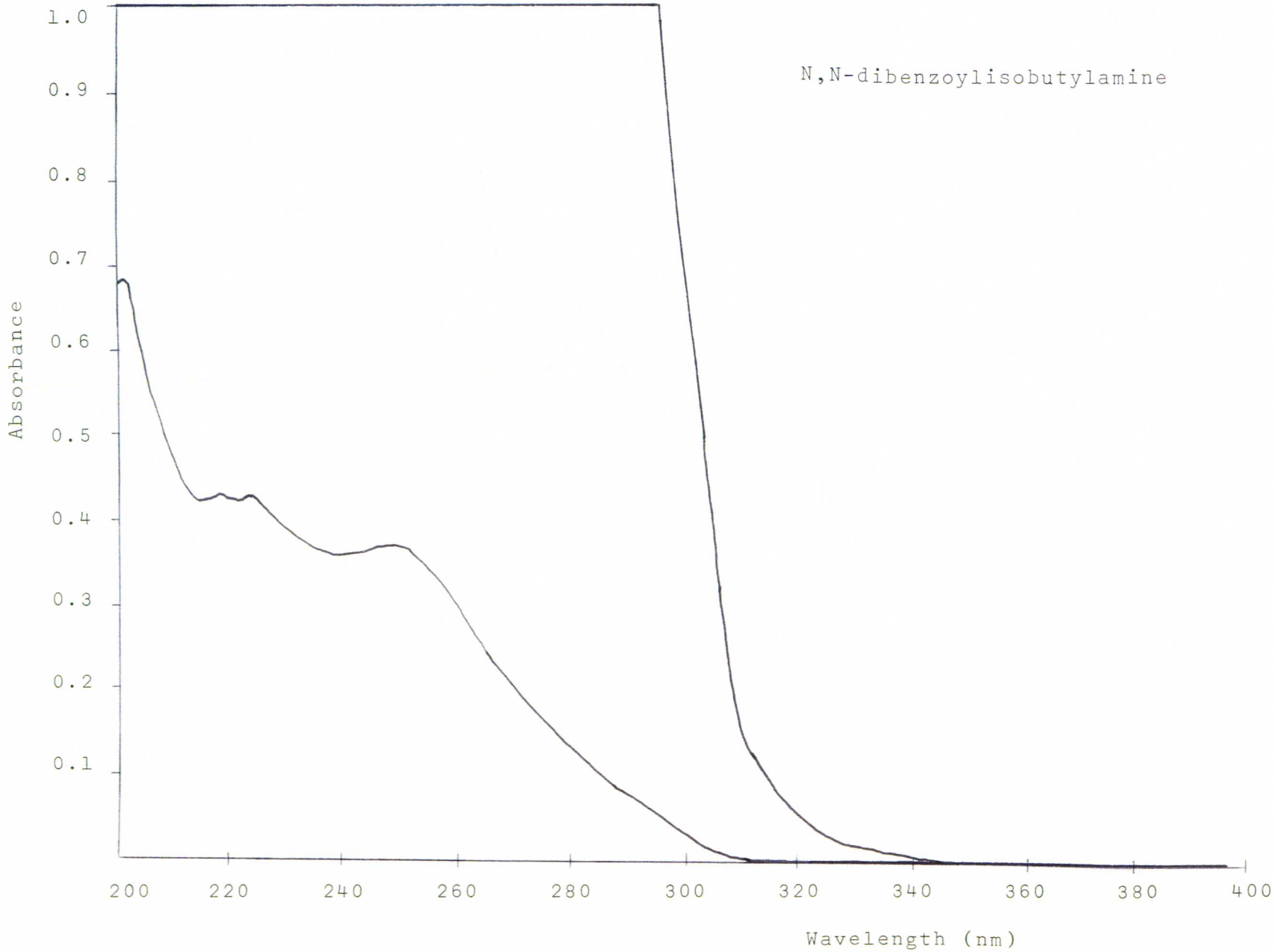
UV Data

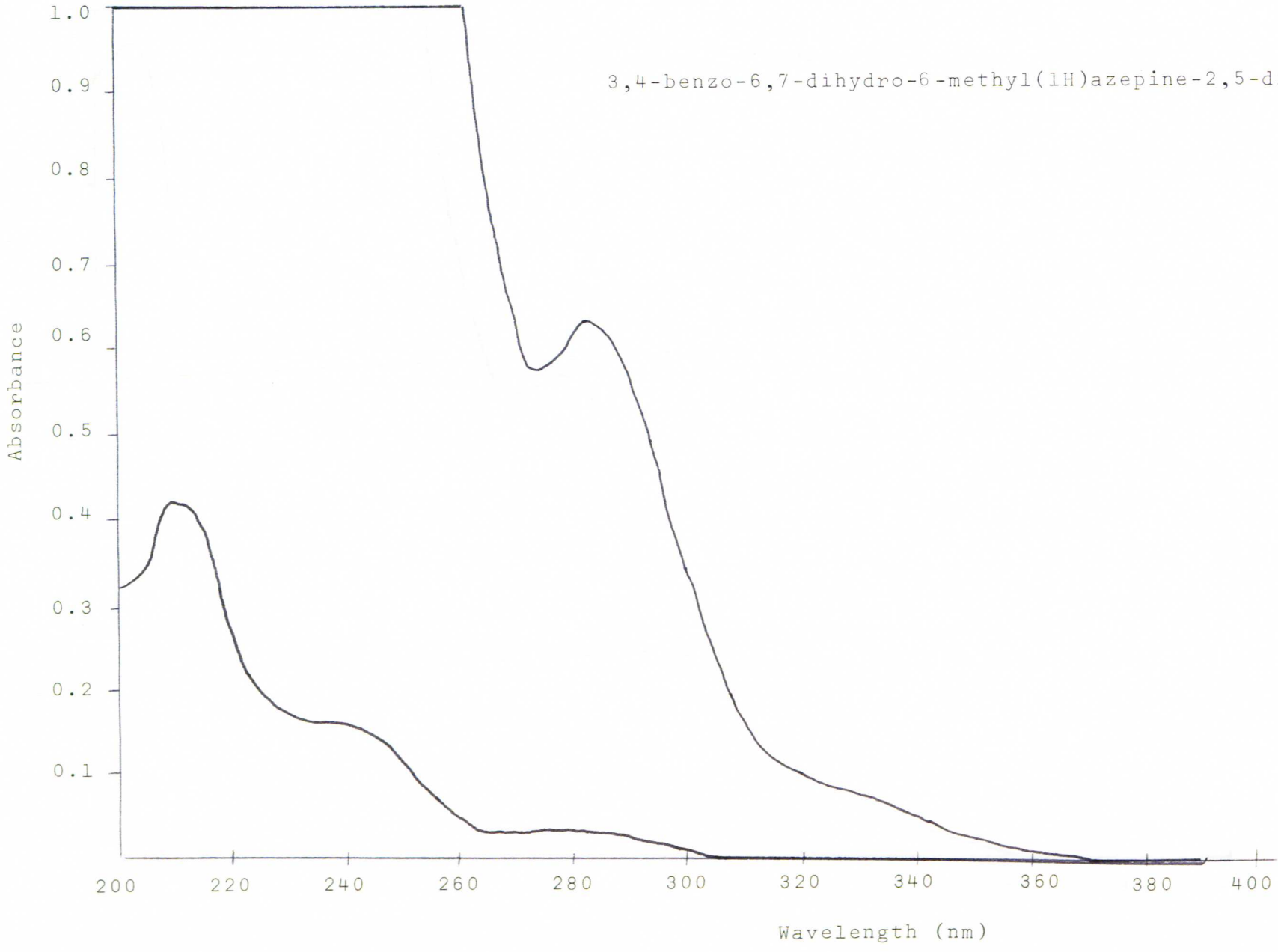

N-isopropylphthalimide
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
400
Absorbance (nm)

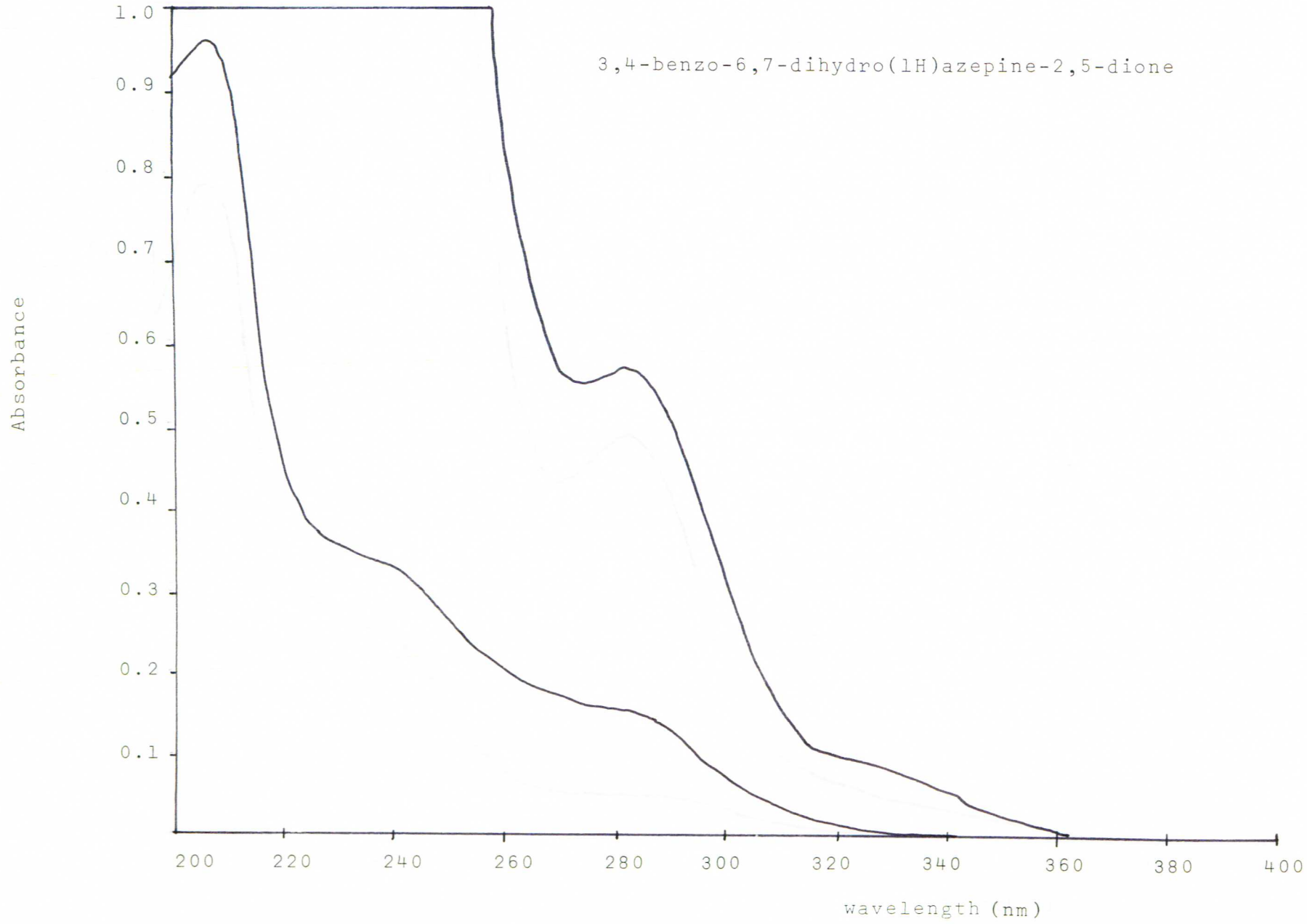

N-tert-butylphthalimide
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

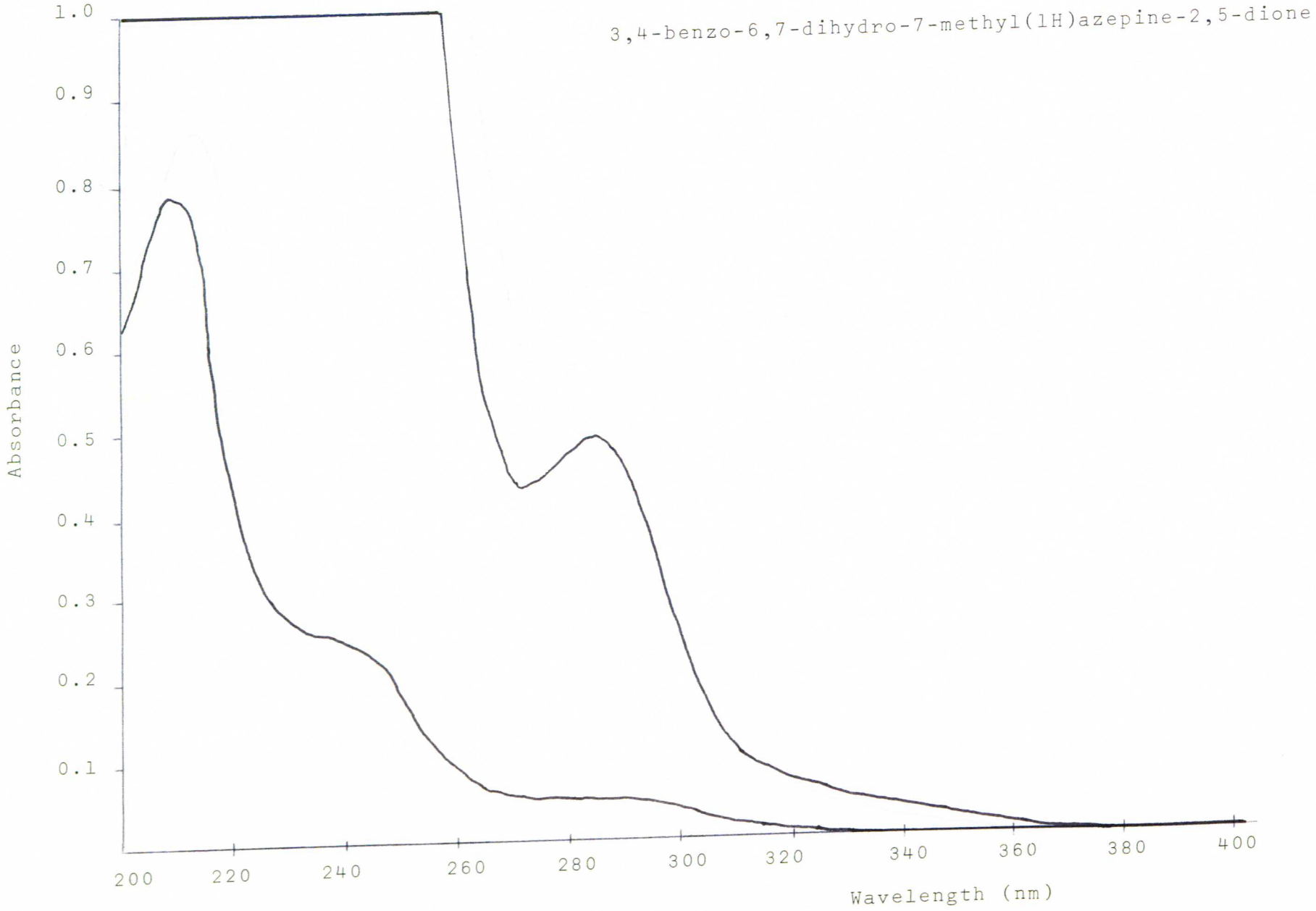

N-methylphthalimide (EtOH)
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

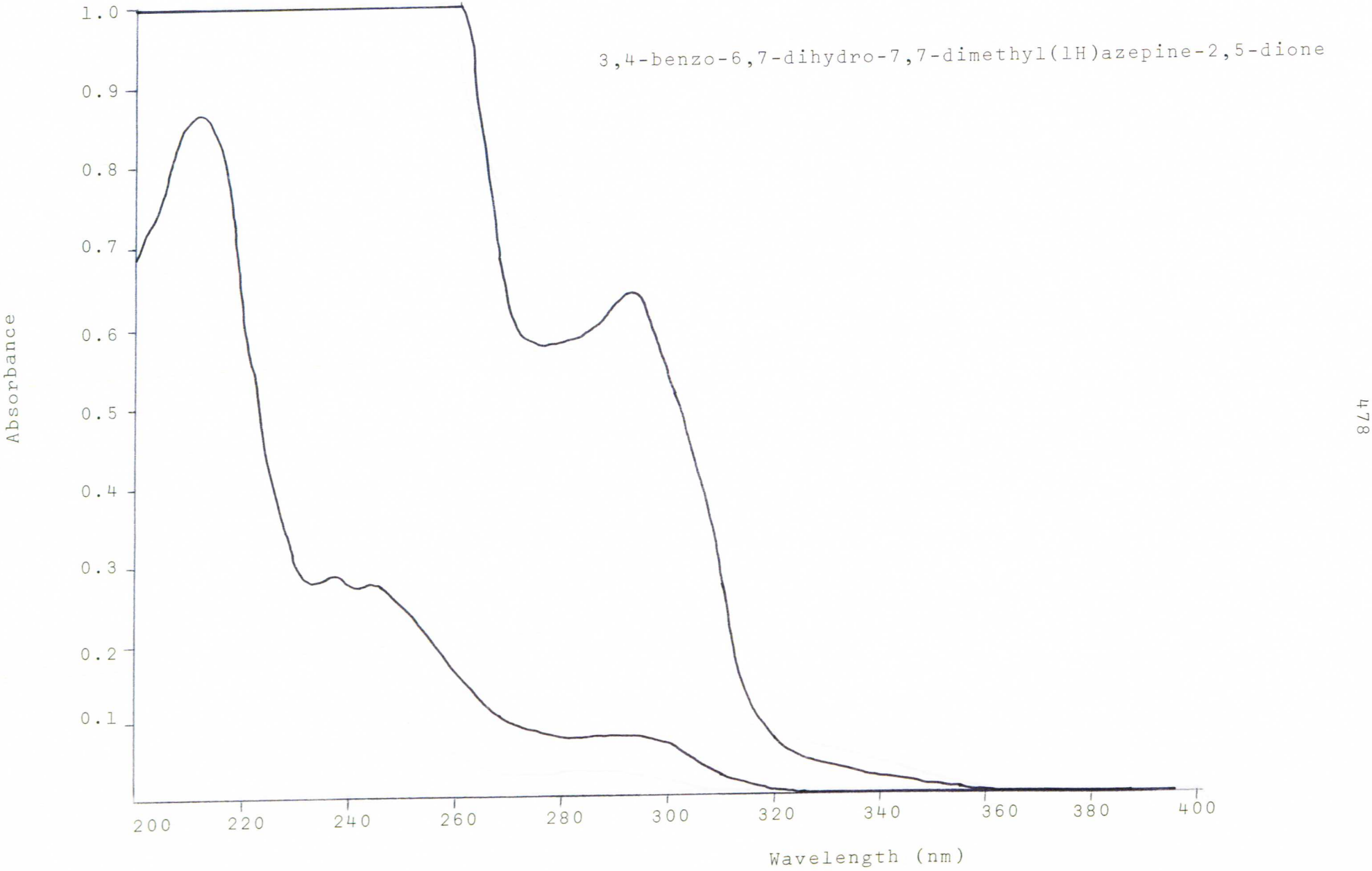

N-2-propenylphthalimide
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Absorbance (nm)

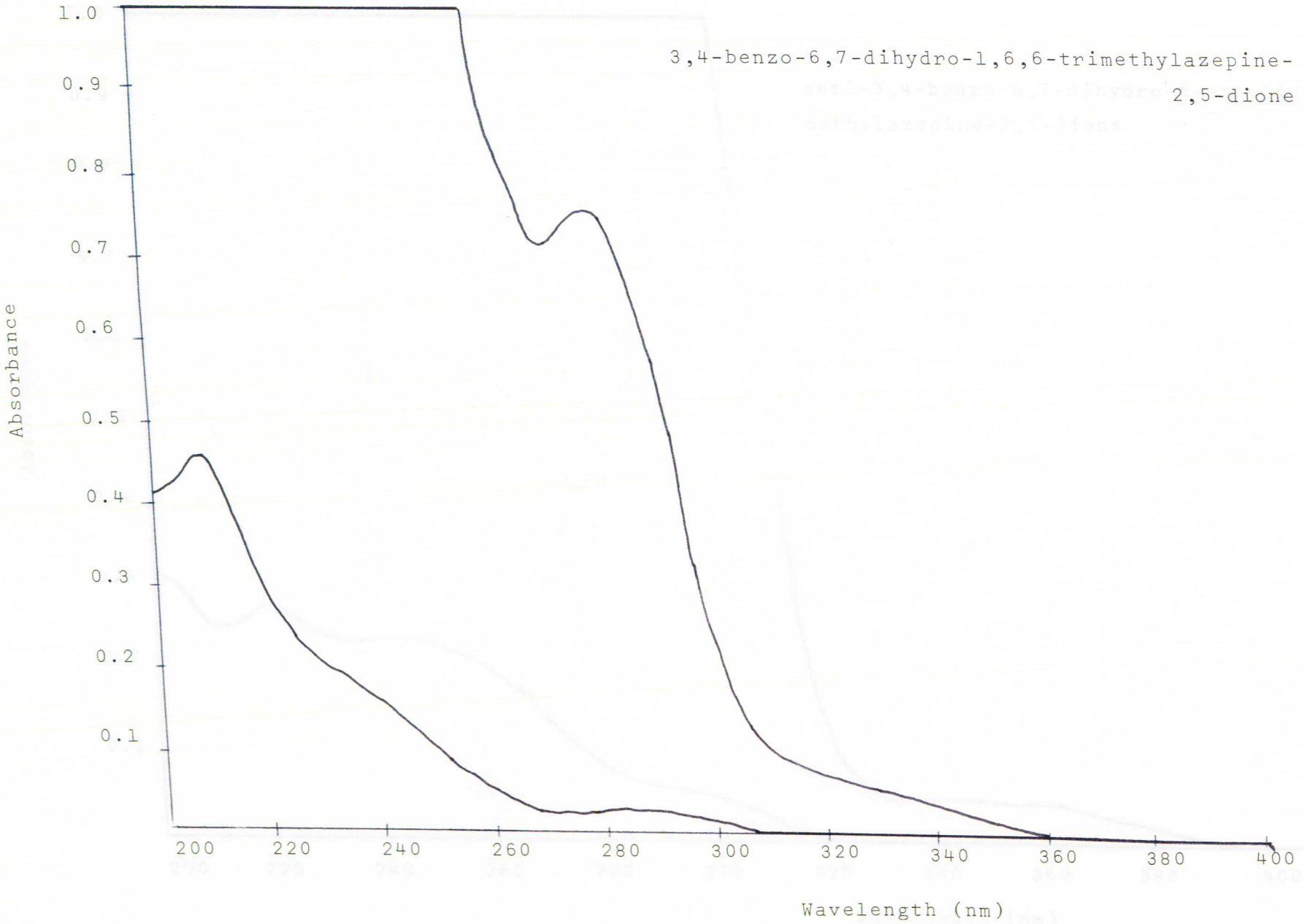

N,N-dibenzoylisobutylamine
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

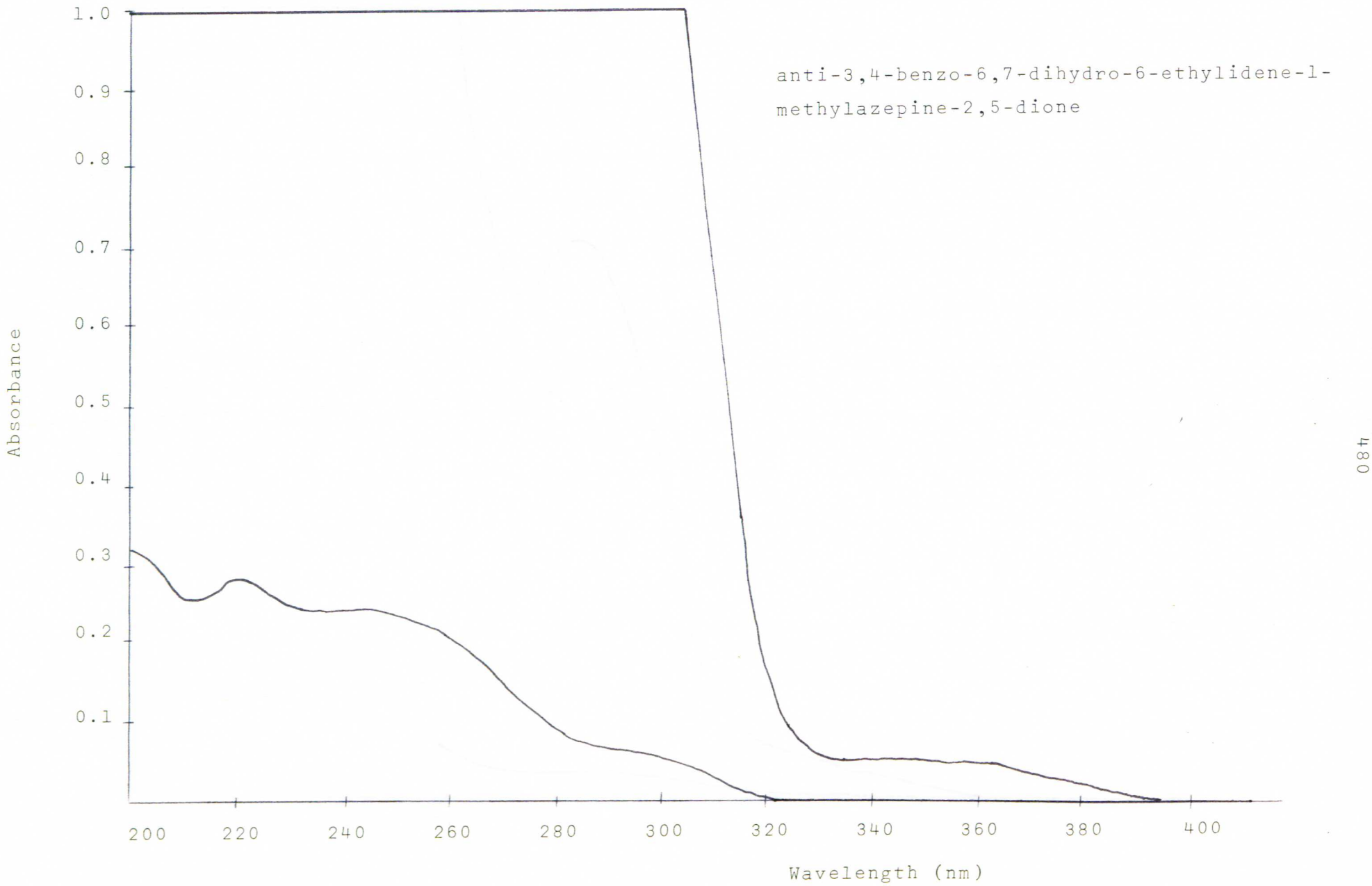

3,4-benzo-6,7-dihydro-6-methyl(1H)azepine-2,5-dione
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

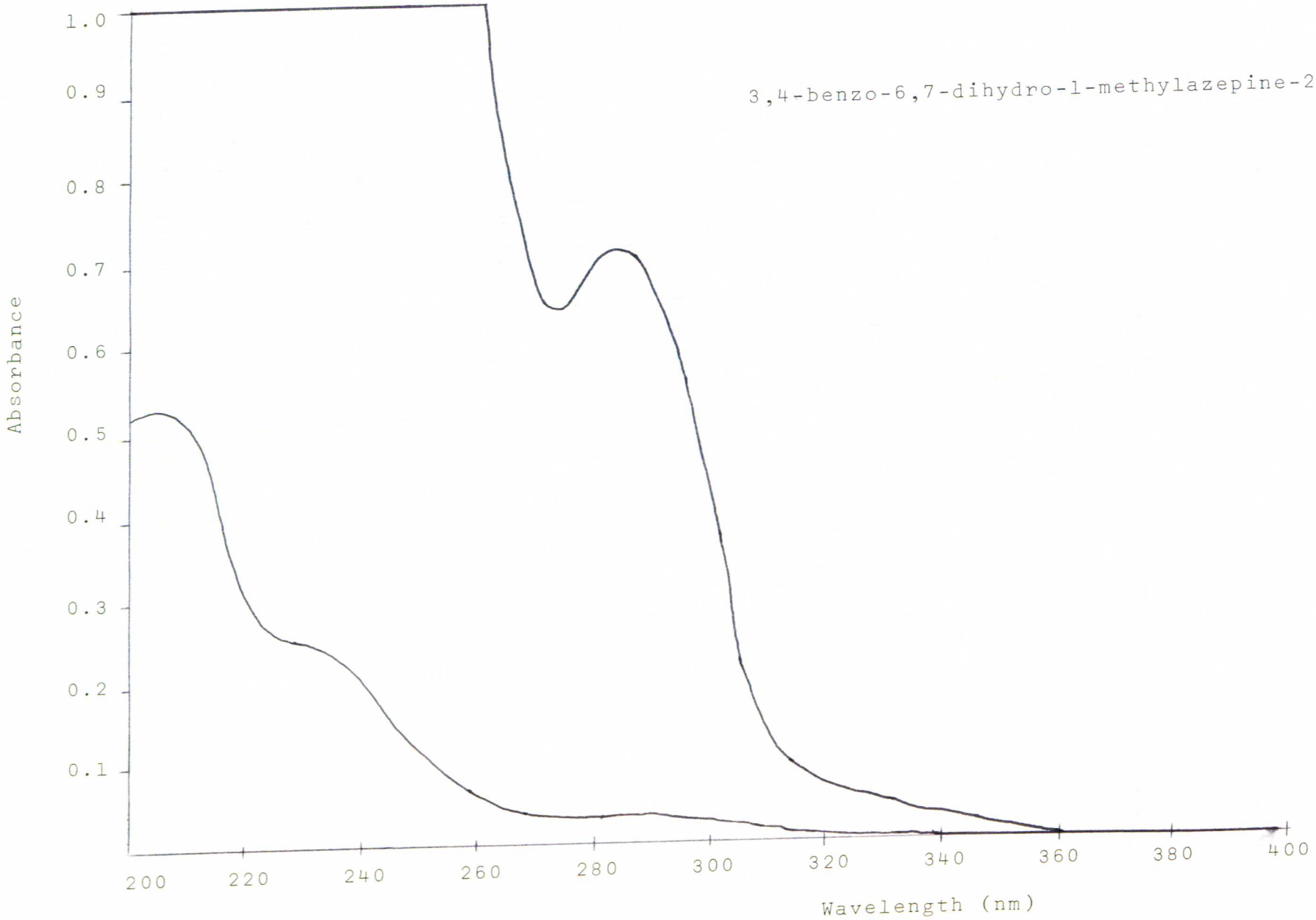

3,4-benzo-6,7-dihydro(1H)azepine-2,5-dione
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
wavelength (nm)


3,4-benzo-6,7-dihydro-7-methyl(1H)azepine-2,5-dione
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)


3,4-benzo-6,7-dihydro-7,7-dimethyl(1H)azepine-2,5-dione
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)


3,4-benzo-6,7-dihydro-1,6,6-trimethylazepine-2,5-dione
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)


anti-3,4-benzo-6,7-dihydro-6-ethylidene-1-methylazepine-2,5-dione
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
480


3,4-benzo-6,7-dihydro-1-methylazepine-2,5-dione
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)

BIBLIOGRAPHY

1. Guillet, "Symposium on Polymers and Ecological Problems", Plenum Press, New York (1972).

2. Booth and Norrish, J. Chem. Soc., 168(1952).

3. B.C. Spall and E.W.R. Steacie, Proc. Roy. Soc. (London), A239, 1(1957).

4. A.F. Trottman-Dickenson, and E.W.R. Steacie, J. Chem. Phys., 18, 1097(1950).

5. Rideal and Mitchell, Proc. Roy. Soc. (London), A159, 206(1937).

6. D. Carpenter, J. Amer. Chem. Soc., 62, 289(1940).

7. W.H. Sharkey and W.E. Mochel, J. Amer. Chem. Soc., 81, 3000(1959).

8. M. Lock and F. Sagar, Proc. Chem. Soc. (London), 358(1960).

9. R.F. Moore, Polymer, 4, 493(1963).

10. T. Cottrell, "The Strengths of Chemical Bonds", Butterworths, London (1958).

11. P. Mazzocchi and J. Thomas, unpublished results.

12. C.H. Nicholls and P.A. Leermakers, J. Org. Chem., 35, 2754(1970).

13. P. J. Wagner, Accts. Chem. Res., 4, 168(1971).

14. N.C. Yang and S.P. Elliot, and B. Kim, J. Amer. Chem. Soc., 91, 7551(1969).

15. J. Calvert and J.N. Pitts, "Photochemistry", Wiley and Sons, New York, p. 382 (1966).

16. J.L. Michael and W.H. Noyes, J. Amer. Chem. Soc., 85, 1027(1963).

17. R.P. Borkowski and P. Ausloos, J. Phys. Chem., 65, 2257(1961).

18. N. Yang and D. Yang, J. Amer. Chem. Soc., 80, 2913(1958).

19. A. Scala and G. Hussey, J. Amer. Chem. Soc., 96, 4069(1974).

20. P. Ausloos, Can. J. Chem., 36, 383(1958).

21. M.H. Wijnen, Can. J. Chem., 36, 691(1958).

22. J.E. Gano, Mol. Photochem., 3, 79(1971).

23. J.E. Gano, Tet. Letters, 2549(1969).

24. J.T. Gruver and J.G. Calvert, J. Amer. Chem. Soc., 78, 5208(1956).

25. J. Kerr and A. Trotman-Dickenson, J. Chem. Soc., 1602(1960).

26. C.H. Bamford and R.G.W. Norrish, J. Chem. Soc., 1504(1935).

27. P. Ausloos, Can. J. Chem., 34, 1709(1956).

28. W. Davis, and W.A. Noyes, Jr., J. Amer. Chem. Soc., 69 2153(1947).

29. V. Brunet and W. Noyes, Bull. Soc. Chem. France, 121(1958).

30. N.C. Yang and R. Dusenbery, J. Amer. Chem. Soc., 90, 5900(1968).

31. P.J. Wagner and A. Kemppainen, J. Amer. Chem. Soc., 5896(1968).

32. N.C. Yang, D. McClure, S. Murov, J. Houser and R.Dusenbery, J. Amer. Chem. Soc., 89, 5466(1967).

33. P.J. Wagner, A.E. Kemppainen and H.N. Schott, J. Amer. Chem. Soc., 95, 5604(1973).

34. P.J. Wagner, and A.E. Kemppainen, J. Amer. Chem. Soc., 94, 7495(1972).

35. C. Walling and M.J. Gibian, J. Amer. Chem. Soc., 87, 3361(1965).

36. H.E. Zimmerman and D.I. Schuster, J. Amer. Chem. Soc., 84, 4527(1962).

37. P. Beak, F. Fry, J. Lee, and F. Steels, J. Amer. Chem. Soc., 98, 171(1976).

38. H. Specker and H. Gawrosch, Ber., 75, 1338(1942).

39. L. Pauling, "Symposium on Protein Structure", A. Newberger, Ed. Wiley, New York, p. 17 (1958).

40. J. Idoux and R. Zarrillo, J. Org. Chem., 40, 1519(1975).

41. S. Nakagura, Mol. Phys., 3, 105(1960).

42. D. Peterson and W. Simpson, J. Amer. Chem. Soc., 79, 2375(1957).

43. M.B. Robin, F.A. Bovey, and H. Basch, "The Chemistry of Amides", J. Zabicky and S. Patai, Ed., Interscience, New York, p. 45 (1970).

44. Robin, Bovey and Basch, ibid., p. 50.

45. J. Schellman and E. Neilson, J. Phys. Chem., 71, 3914 (1967).

46. R. Johnson and R. Greene, J. Org.Chem., 40, 2186(1975).

47. Y. Chow and T. Joseph, Chem. Comm., 490(1969).

48. R. Ditchfield, J. Del Bene and J. Pople, J. Amer. Chem. Soc., 94, 703(1972).

49. A. Padwa, Accts. Chem. Res., 4, 48(1971).

50. A. Padwa and D. Eastman, J. Amer. Chem. Soc., 91, 462(1969).

51. P.J. Wagner, P.A. Kelso, A. Kemppainen and R. Zepp, J. Amer. Chem. Soc., 94, 7500(1972).

52. R.H. Hess, Ad. Free Rad. Chem., 1, 83(1969).

53. L.A. LaPlanche and M.T. Rogers, J. Amer. Chem. Soc., 86, 337(1964).

54. A. J. Bourn, D. Gillies, and E. Randall, Tetrahedron, 20, 1811(1964).

55. L.A. LaPlanche and M. Rogers, J. Amer. Chem. Soc., 85, 3728(1963).

56. A. Haigler, L. Leiserowitz, and M. Tuval, J. Amer. Chem. Soc., 98, 4600(1976).

57. R. Hammaker and B. Gugler, J. Mol. Spectry, 17, 356(1965).

58. K. Pfordte, Justus Leibigs, Ann. Chem., 625, 30(1959).

59. K. Shima and S. Tsutsumi, Bull. Chem. Soc. Jap., 36, 121(1963).

60. G.O. Schenck, H.D. Becker, K.H. Schulte-Elte and C.H. Krauch, Chem. Ber., 96, 509(1963).

61. W. Droste, H.D. Scharf, F. Korte, Justus Leibigs, Ann. Chem., 724, 71(1969).

62. A. Watterson and S. Shama, J. of Chem., 40, 19(1975).

63. J. A. Hyatt, J. Org.Chem., 37, 1254(1972).

64. P.H. Mazzocchi and E. Bodurgil, unpublished results.

65. N.C. Yang, D.P. Tang, D.M. Thap, and J.S. Sallo, J. Amer. Chem. Soc., 88, 2851(1966).

66. R. Srinivasan, J. Amer. Chem. Soc., 84, 2475(1962).

67. P. Pfeffer, L. Silbert, E. Kinsel, Tet. Letters, 14, 1163(1973).

68. F. Lewis and H. Heine, J. Org Chem., 40, 488(1975).

69. I. Rosenthal and D. Elad, J. Org Chem., 33, 805(1968).

70. J. Frank and E. Rabinowitsch, Trans. Far. Soc., 30, 120(1934).

71. A. Beckett and G. Porter, Trans. Far. Soc., 59, 2038 (1963).

72. P.H. Mazzocchi and C.W. Jameson, unpublished results.

73. Y. Kanaoka and Y. Hatanaka, J. of Chem., 41, 400(1976).

74. K. Heyns and W. Pyrus, Chem. Ber., 88, 678(1955).

75. R. Morrison and R. Boyd,"Organic Chemistry",2nd Ed., Allyn and Bacon, Boston, p. 805 (1966).

76. O. L. Chapman, "Organic Photochemistry", Marcel Dekker, New York (1967).

77. Y. Kanaoka and Y. Hatanaka, Heterocycles, 2, 423(1974).

78. D. Elad, D. Rao, and V. Stenberg, J. Org Chem., 30, 3252(1965).

79. M. Fischer, Tet. Letters, 2281(1969).

80. R. Okan and R. Furey, Tet. Letters, 2573(1966).

81. Y. Katsuhara, H. Maruyama, Y. Shigemitsu, and Y. Odaira, Tet. Letters, 1323(1973).

82. E. Noe and M. Raban, J. Amer. Chem. Soc., 97, 5811(1975).

83. N. Pellissier, Ph.D. Thesis, Claude Bernard University, (Lyon), 1974.

84. Y. Kanaoka, Y. Migita, K. Koyama, Y. Sato, H. Nakai, and T. Mizoguchi, Tet. Letters, 1193(1973).

85. Y. Sato, H. Nakai, T. Mizoguchi, M. Kawanishi, and Y. Kanaoka, Chem. Pharm. Bull., 21, 1164(1973).

86. Y. Kanaoka and K. Koyama, Tet. Letters, 4517(1972).

87. Y. Kanaoka, Y. Migita, Y. Sato, and H. Nakai, Tet. Letters, 51(1973).

88. Y. Sato, H. Nakai, H. Ogiwara, T. Mizoguchi, Y. Migita, and Y. Kanaoka, Tet. Letters, 4565(1973).

89. Y. Kanaoka, J. Amer. Chem. Soc., 98, 2349(1976).

90. H. J. Roth and D. Schwarz, Arch. Pharm., 308, 218(1975).

91. H. J. Roth, D. Schwarz and G. Hundeshagen, Arch. Pharm., 309, 48(1976).

92. G. Scharf and B. Fuchs, Chem. Comm., 244(1975).

93. H. Nakai, Y. Sato, H. Ogiwara, T. Mizoguchi, and Y. Kanaoka, Heterocyles 2, 621(1974).

94. Y. Kanaoka, K. Koyama, J. Flippen, I. Karle, and B. Witkop, J. Amer. Chem. Soc., 96, 4719(1974).

95. Y. Kanaoka and Y. Migita, Tet. Letters, 3693(1974).

96. Y. Kanaoka, C. Nagasawa, H. Nakai, Y. Sato, H. Ogiwara, and T. Mizoguchi, Heterocycles, 3, 553(1975).

97. M. Tanabe, R. Dehn, and R. Bramhall, J. Agr. Food Chem., 22, 54(1974).

98. H. Roth and D. Schwarz, Arch. Pharm., 309, 52(1976).

99. H. Roth and G. Hundeshagen, Arch. Pharm., 309, 58(1976).

100. Y. Kanaoka and Y. Hatanaka, Chem. Pharm. Bull., 22, 2205(1974).

101. Y. Kanaoka, K. Sakai, R. Murata, and Y. Hatanaka, Heterocycles, 3, 719(1975).

102. E. Horning, Ed.,"Organic Synthesis", Vol. III, J. Wiley New York, p. 151 (1955).

103. K. Howard and T. Koch, J. Amer. Chem. Soc., 97, 7288 (1975).

104. A. Kjaer and P. Friis, Acta Chem. Scand., 16, 936(1962).

105. P. Dunion and C. Trumbore, J. Amer. Chem. Soc., 87, 4211(1965).

106. A. Blades, Can. J. Chem., 48, 2269(1970).

107. C. Hatchard, and C. Parker, Proc. Roy. Soc. (London), A235, 518(1956).

108. J.J. Thomas, Ph.D. Thesis, University of Md. (1977).

109. P.J. Wagner, J. Amer. Chem. Soc., 89, 5898(1967).

110. P.J. Wagner, P. Kelso, and R. Zepp, J. Amer. Chem. Soc., 94, 7480(1972).

111. N.C. Yang and S. Elliot, J. Amer. Chem. Soc., 91, 7550 (1969).

112. P.H. Mazzocchi, J.J. Thomas, and F. Danisi, Polymer Letters Ed., 13, 737(1975).

113. L. Caswell, L. Soo, D. Lee, R. Fowler, and J. Campbell, J.ORG.Chem., 39, 1527(1974).

114. C. Lee and W. Kumler, J. Amer. Chem. Soc., 83, 4586(1961).

115. N. Turro, "Molecular Photochemistry", W.A. Benjamin, Reading, Mass. (1965).

116. J. Hemperly, S. Wolff, and W. Agosta, J. Org.Chem., 40, 3315(1975).

117. N. Yang and D. Thap, Tet. Letters, 3671(1966).

118. N. Yang and A. Morduchowitz, J.Org.Chem., 29, 1654(1964).

119. P. Leermakers, P. Warren, and G. Vesley, J. Amer. Chem. Soc., 86, 1768(1964).

120. W. Urry and D. Trecker, J. Amer. Chem. Soc., 84, 118(1962).

121. T. Evans and P. Leermakers, J. Amer. Chem. Soc., 90, 1840(1968).

122. P. Wagner, R. Zepp, K. Liu, M. Thomas, T. Lee, and N. Turro, J. Amer. Chem. Soc., 98, 8125(1976).

123. F. Lewis, R. Lauterbach, H. Heine, W. Hartman, and H. Rudolph, J. Amer. Chem. Soc., 1519(1975).

124. P. Mazzocchi and N. Narain, unpublished paper.

125. Agosta, private consultation.

126. D. Elad and J. Rokach, J. Org. Chem., 29, 1855(1964).

127. J. Meinwald and A. Hamner, Chem. Comm., 1302(1969).

128. O. Chapman and W. Adams, J. Amer. Chem. Soc., 89, 4243 (1967) and 90, 2333(1968).

129. D. Elad, Fortsch Chem. Forsch, 7, 528(1967).

130. D. Elad and J. Sinnreich, unpublished results.

131. J. Sinnreich and D. Elad, Tetrahedron, 24, 4509(1968).

132. L. Paquette, T. Barton, and E. Whipple, J. Amer. Chem. Soc., 89, 5481(1967).

133. L. Paquette and J. Malpass, J. Amer. Chem. Soc., 90, 7151(1968).

134. L. Paquette and G. Krow, J. Amer. Chem. Soc., 90, 7149 (1968).

135. L. Paquette, J. Malpass, and G. Krow, J. Amer. Chem. Soc., 92, 1980(1970).

136. R. Odum and B. Schmall, Chem. Comm., 1299(1969).

137. T. Koch and D. Brown, J. Org. Chem., 36, 1934(1971).

138. T. Koch, M. Geigel, and C. Tsai, J. Org. Chem., 38, 1090(1973).

139. T. Koch, J. Olesen, and J. DeNiro, J. Amer. Chem. Soc., 97, 7285(1975).

140. R. Rodehorst and T. Koch, J. Amer. Chem. Soc., 97, 7298 (1975).

141. N. Turro, Accts. Chem. Res., 5, 92(1972).

142. N. Turro and V. Ramamurthy, Tet. Letters, 2423(1976).

143. P. Mazzocchi and N. Narain, unpublished results.

144. J. Sheehan and W. Bolhofer, J. Amer. Chem. Soc., 72, 2786(1950).