

THE SYNTHESIS OF SOME DIARYL CYCLOPENTADIENES

BY

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Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy.

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both reactions being carried out in the presence of sodium ethoxide. Two derivatives of this substance have been prepared. These are the trinitrobenzolate and the maleic anhydride addition product.

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. Nathan L. Drake for the help and advice he has given during the course of this research.

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I. INTRODUCTION

The condensation of esters with methyl ketones in the presence of sodium ethoxide to form 1,3 diketones was discovered by Claisen and Ehrhardt¹. The reaction, known as the Claisen condensation has been used extensively with simple esters to effect the synthesis of 1,3 diketones. It was thought that

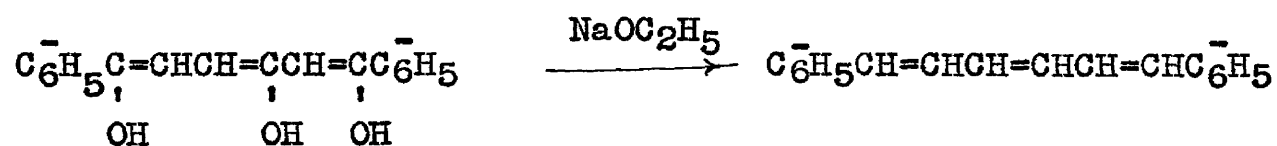
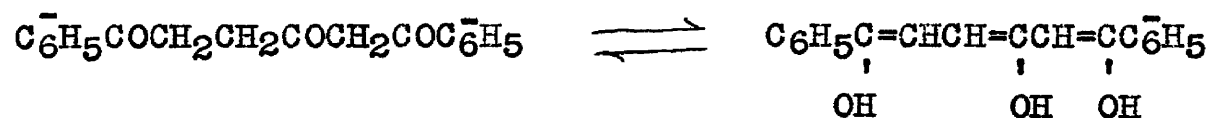
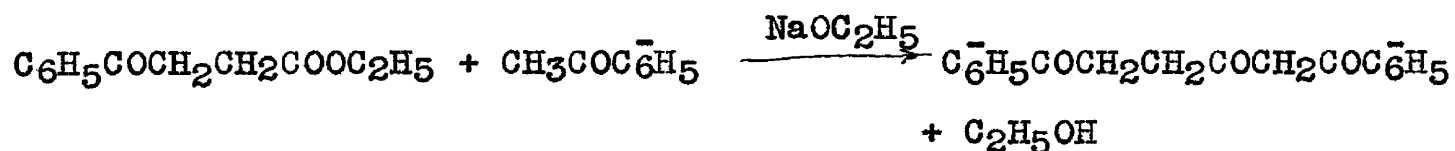


the extension of the reaction to keto-esters should offer a method of synthesis of triketones, and with this idea in mind attempts were made to react ethyl- β -benzoylpropionate with acetone and with acetophenone in the presence of sodium ethoxide².

Although the expected triketones were not obtained the reaction of acetophenone with the ester led to the formation of a rather interesting substance----- an unsaturated hydrocarbon whose solutions in the organic solvents and in concentrated sulfuric acid showed a pronounced fluorescence. It is the purpose of this thesis to describe the further investigation of this hydrocarbon as to its identity and the reaction by which it is formed.

II. DISCUSSION

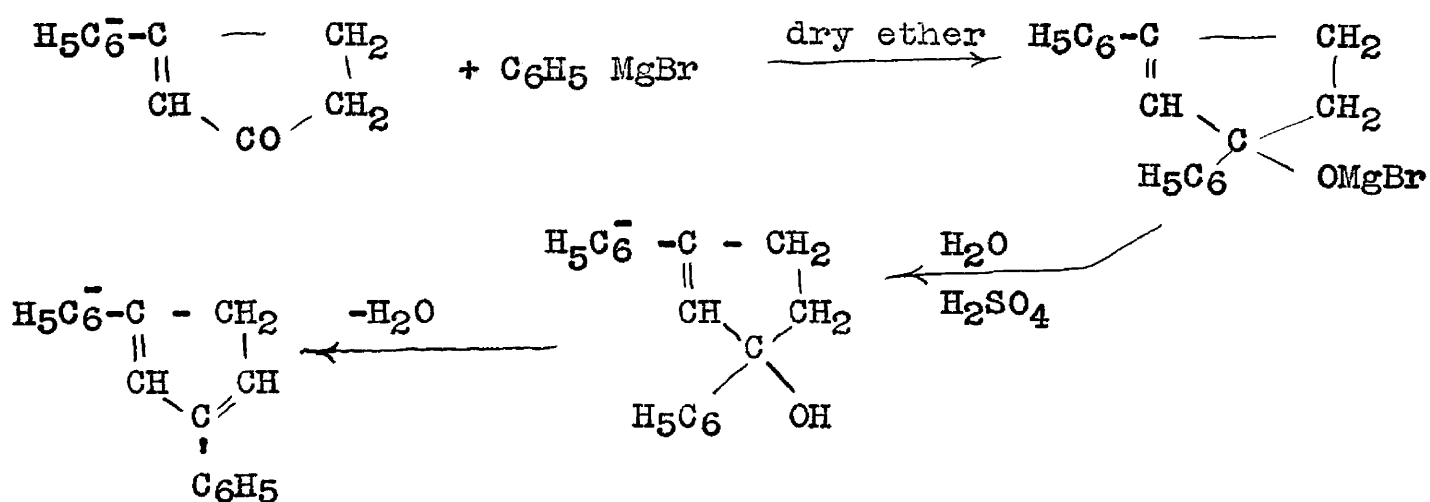
It was first thought that the hydrocarbon arising from the action of acetophenone on ethyl- β -benzoylpropionate in the presence of sodium ethoxide was a diphenylhexatriene because of the fluorescence of its solutions and because of the agreement with a carbon and hydrogen analysis. Such a substance might conceivably result from the reduction of the tri-enol of the triketone obtained through the Claisen condensation as indicated by the equations:



Kuhn and Winterstein³ made a substance of this structure (1,6-diphenyl-1,3,5-hexatriene) by ten different methods each of the products possessing the same melting point. Although the hydrocarbon in question had a different melting point than the diphenylhexatriene prepared by Kuhn and Winterstein, the possibility of its having the same

structure was not precluded because of the possible existence of six geometric isomers having this same structure.

Subsequent investigation of the hydrocarbon using samples purer than that first obtained, showed that the substance possessed the molecular formula $C_{17}H_{14}$ rather than $C_{18}H_{16}$ required by the diphenylhexatriene. This became evident as the result of carbon and hydrogen analyses, molecular weight determinations by the ebullioscopic and cryoscopic methods and by the determination of the neutralization equivalent of the picrate. Examination of the literature showed that a substance having the formula $C_{17}H_{14}$ closely answering the description of the hydrocarbon had been synthesized by Borsche and Menz⁴ who described it as 1,3 diphenyl-1,3-cyclopentadiene. Borsche's synthesis is indicated by the following equations:



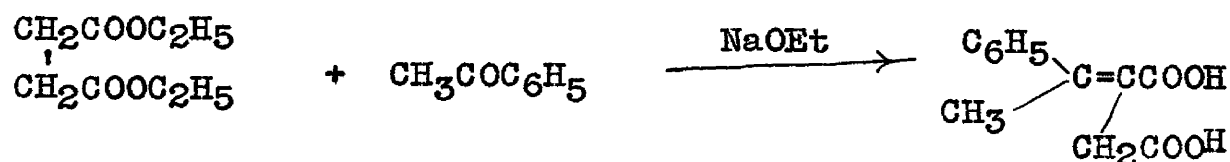
A melting point of a mixture of the "1,3-diphenyl-1,3-cyclopentadiene" obtained by Borsche's synthesis with the

hydrocarbon arising from the action of acetophenone on ethyl- -benzoylpropionate showed that the two substances were the same. The preparation of the trinitrobenzulates and picrates of the substances, examination of their properties, color and melting point, together with mixed melting point determinations offered further proof of the identity of these two substances. (It is interesting to note that Borsche states that his "1,3-diphenyl-1,3-cyclopentadiene" apparently does not form a picrate).

I. MECHANISM

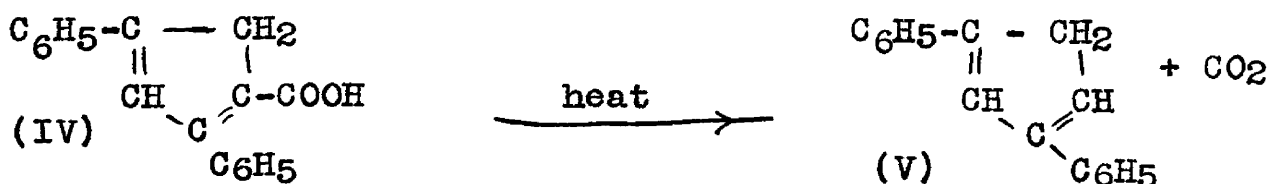
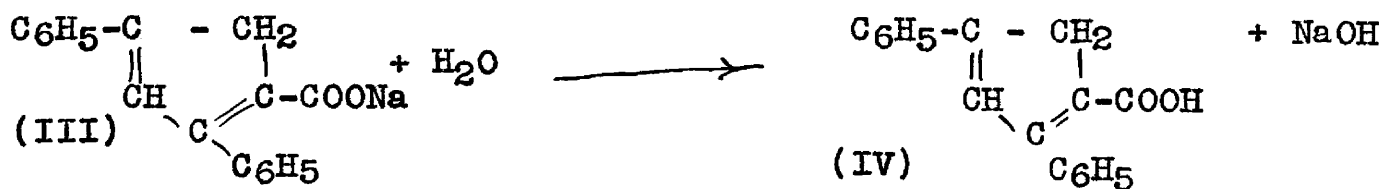
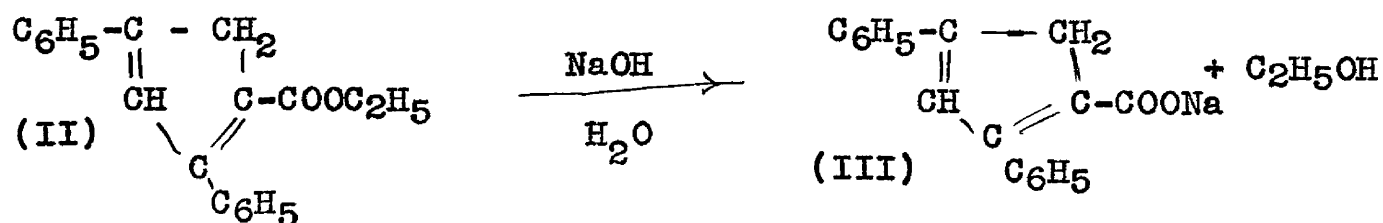
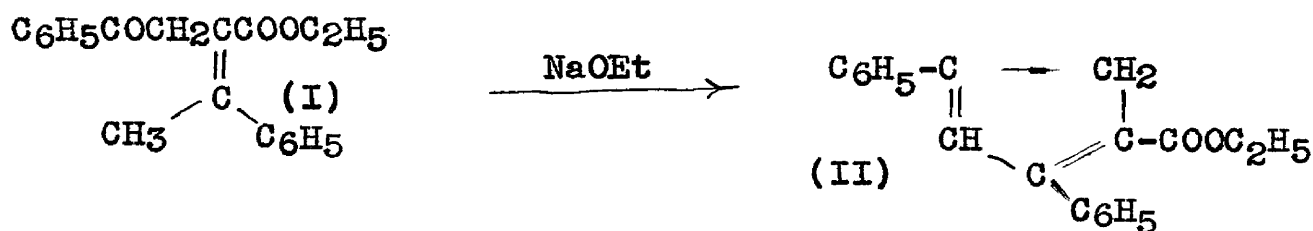
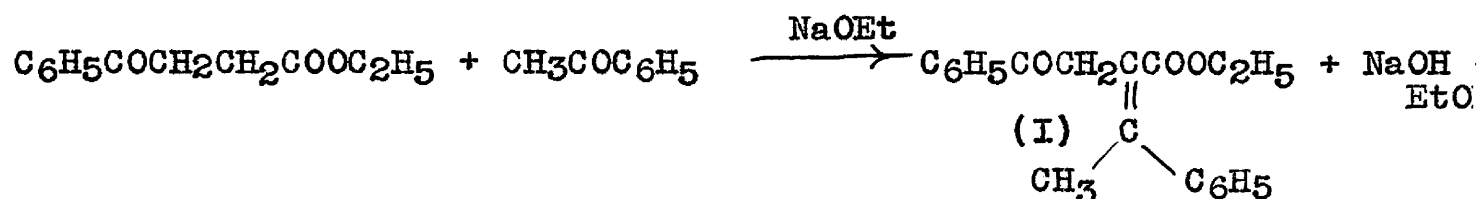
Any mechanism showing the formation of diphenylcyclopentadiene from acetophenone and ethyl- β -benzoylpropionate must show the loss of one carbon atom other than those of the ethyl group. This loss of carbon might well be explained by decarboxylation. Inasmuch as the Claisen reaction eliminates the potential carboxyl group without the loss of carbon it was necessary to postulate some other sort of reaction between the ketone and ester.

It is known that ketones in the presence of sodium alkoxide will condense with esters with the elimination of water from the alpha hydrogens and the carbonyl oxygen. For example, Stobbe⁵ has prepared γ -methyl- γ -phenylitaconic acid from the action of acetophenone on ethyl succinate in the presence of sodium ethoxide.

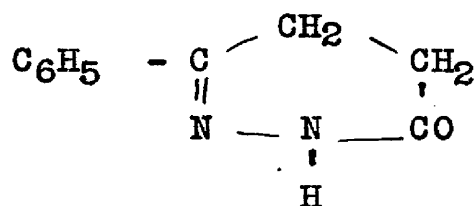


If acetophenone should condense in the same way with ethyl- β -benzoylpropionate an unsaturated keto-ester (I) would result. This substance would readily undergo an intramolecular reaction to split out a second molecule of water forming an unsaturated cyclic ester (II). The latter reaction would take place because of the activation of the methyl group by the carbethoxyl group through the vinyl residue and because

of the proximity of the methyl and carbonyl groups. The cyclic ester (II) should be saponified by the water and sodium hydroxide now present in the reaction mixture resulting in the formation of the sodium salt (III). On the addition of water the salt (III) should go to the aqueous layer where it should yield the cyclic carboxylic acid (IV) on hydrolysis. If the acid (IV) lost carbon dioxide on heating the hydrocarbon 1,3-diphenyl-1,3-cyclopentadiene (V) should result. This proposed mechanism is summed up in the following equations:



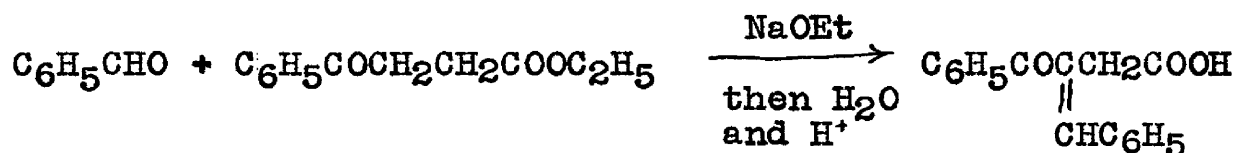
If diphenylcyclopentadiene results from this series of reactions then it should be possible to isolate the first intermediate by blocking the carbonyl group of the ester as one of its derivatives and subsequently hydrolyzing the condensation product. With this idea in mind attempts were made to prepare and purify the oxime of ethyl- β -benzoyl-propionate. Because of the instability of the substance to heat and because of its reluctance to crystallize it was not obtained in the pure state. The semicarbazone of the ester was then made and subjected to conditions under which condensation with acetophenone should have occurred. The product obtained from this reaction was identified as 3-phenyl-pyridazin-one-6.



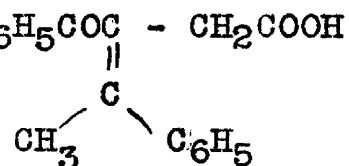
The desired semicarbazone of the first intermediate was not obtained. Finally the oxime methyl ether of the ester was prepared and distilled. The product obtained although not analytically pure was reacted with acetophenone in the presence of sodium ethoxide in the usual way. The only product isolated from the reaction was a small quantity of diphenylcyclopentadiene, probably formed from unchanged ester present in the oxime ether as an impurity.

The failure to obtain carbonyl derivatives of the first intermediate by such condensations seemed to indicate that the

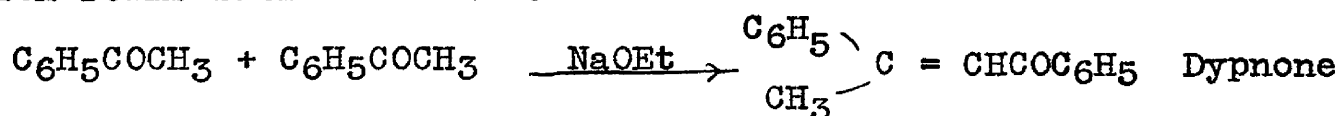
above mechanism is not correct. This view is corroborated by a consideration of the work of Borsche⁶ who condensed benzaldehyde with ethyl- β -benzoylpropionate in the presence of sodium ethoxide. The ultimate product of this reaction was β -benzal- β -benzoylpropionic acid. This would indicate that the hydrogens of the



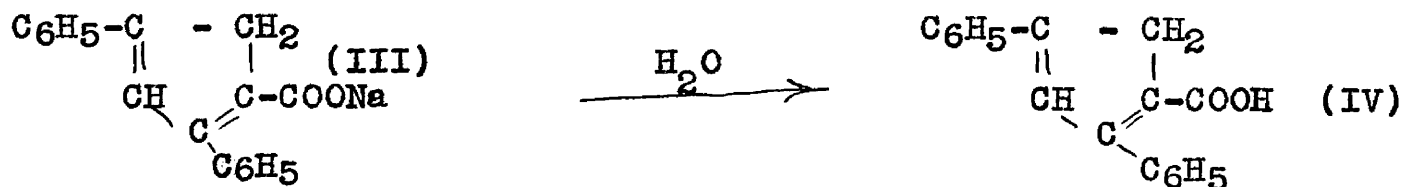
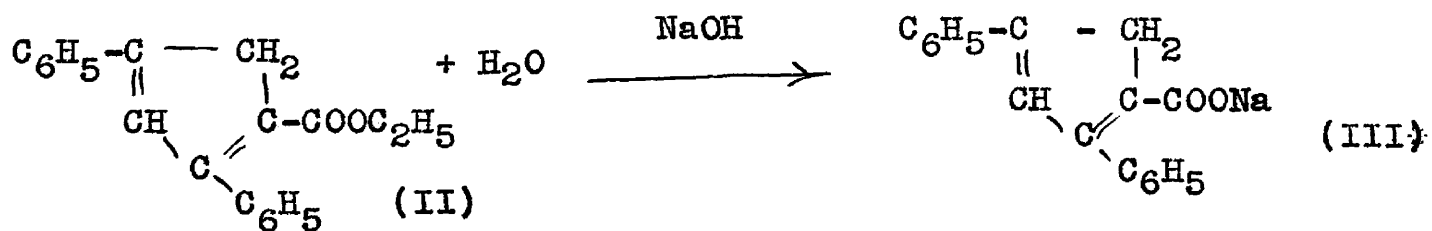
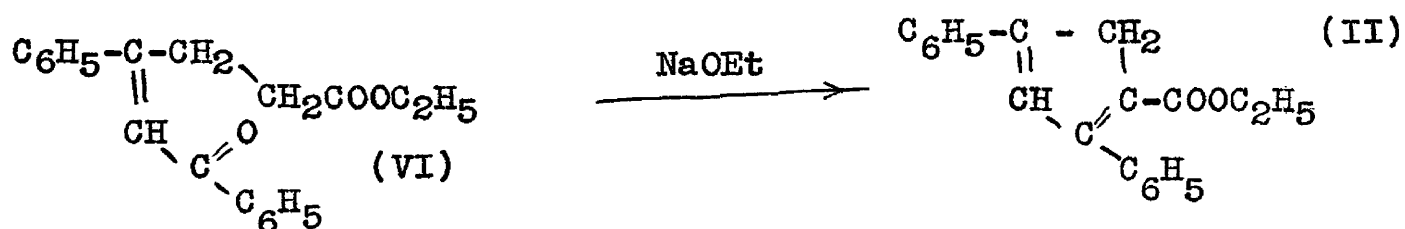
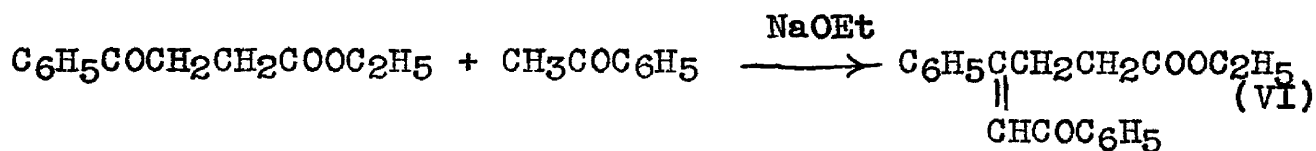
methylene group activated by the carbonyl group are more active than those on the methylene group activated by the carbethoxyl group. Hence acetophenone like benzaldehyde should condense on the β carbon of the ester yielding a substance which could not be an intermediate in the formation of diphenylcyclopentadiene --

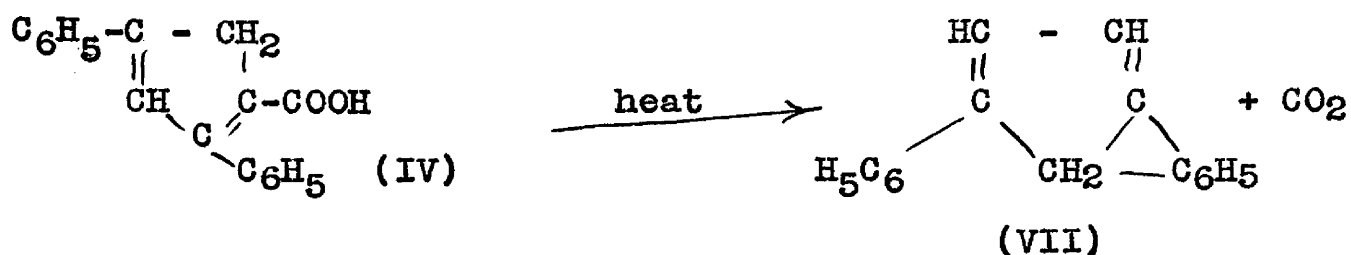


Another mechanism involving a series of reactions similar to those of the first mechanism is not open to the same objection. The first reaction is a condensation in which water is eliminated from the hydrogens of the methyl group of the ketone and the carbonyl oxygen of the keto-ester. This is analagous to the preparation of dyphone from acetophenone and sodium ethoxide⁷. The unsaturated keto-ester (VI) which forms from this first



reaction cyclizes to form the unsaturated cyclic ester (II) because of the proximity of the carbonyl group and the methylene group activated by the carbethoxyl group. The ester (II) is then saponified by the water and sodium hydroxide now present in the reaction mixture to form the salt (III) which on the addition of water dissolves in the aqueous layer. The salt then hydrolyzes to form the corresponding acid (IV) which decarboxylates on heating to form diphenylcyclopentadiene (VII). The proposed mechanism is summed up in the following equations:





The reactions above seem to represent the most logical mechanism for the formation of this hydrocarbon. It will be noted that the last reaction assumes not only decarboxylation but also a shift of double bonds to a position of conjugation with the phenyl groups. The reason for this assumption is explained in the discussion of the proof of the structure of diphenylcyclopentadiene. Of all the intermediates in the reaction only one -- the acid (IV) has been isolated. Attempts were first made to obtain from the salt, esters of the acid such as the methyl ester, the p-nitrobenzyl ester, and the p-phenylphenacyl ester, but without success. The acid itself was obtained by careful acidification with acetic acid of the aqueous solution containing the sodium salt (III). This is described in detail in the experimental part of this work. The acid unlike the hydrocarbon dissolves readily in aqueous sodium hydroxide solution. On warming it melts at the same temperature as the hydrocarbon, and mixed melting points show no depression. Unlike the hydrocarbon the acid shows no fluorescence in benzene, chloroform, amyl ether, or glacial acetic acid solutions even on warming. For this reason it is

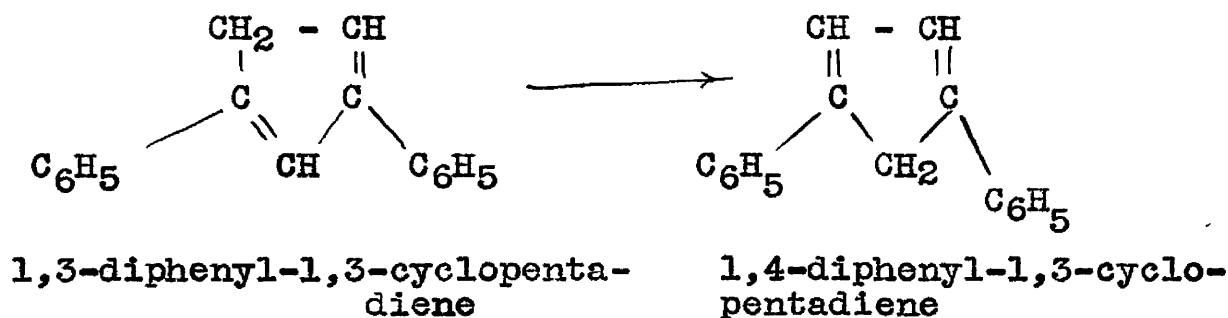
assumed that the double bonds in the acid molecule have not shifted to a position of conjugation with the two phenyl groups. Ethyl and amyl alcohol solutions of the acid, however, on warming take on a fluorescence similar to that of the solutions of the hydrocarbon probably because of the breakdown of the esterification intermediate to form hydrocarbon with the simultaneous shift of double bonds to the position of conjugation. The acid has been converted to the hydrocarbon by crystallization from ethyl alcohol and by warming with aqueous sodium hydroxide.

Attempts to obtain other intermediates have been unsuccessful probably because of the rapidity with which the first reaction takes place, a small amount of diphenylcyclopentadiene being obtained from a condensation allowed to run only ten minutes. The mechanism outlined above is believed to represent the method of formation of diphenylcyclopentadiene from acetophenone and ethyl- β -benzoylpropionate. It appears to be more logical and to be more in agreement with the facts than any other mechanism.

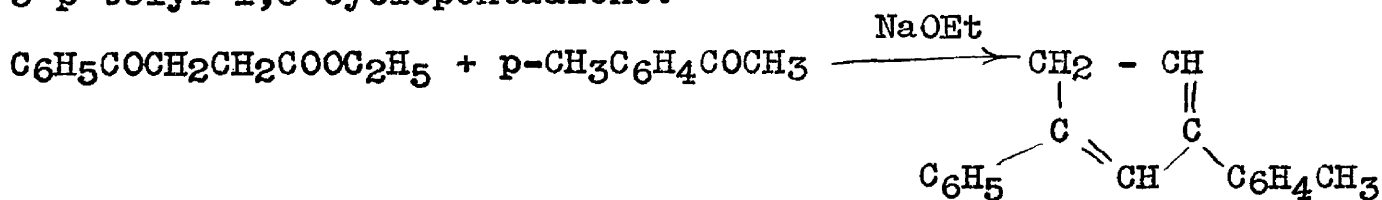
Proof of the Structure of Diphenylcyclopentadiene

Although diphenylcyclopentadiene was prepared by Borsche and Menz⁴ long before the present work was undertaken, these investigators failed to prove the structure of the hydrocarbon. Aside from the straightforwardness of the reaction employed the only evidence for the structure was a carbon and hydrogen analysis. From this work they concluded that the substance was 1,3-diphenyl-1,3-cyclopentadiene. As mentioned before, molecular weight determinations have corroborated their assumption. The fact that catalytic reduction leads to the formation of a substance which analyzes for diphenylcyclopentane adds further support to the proposed structure. None of this work, however, aside from the reaction first used in its preparation, gives

any clue as to the position of the double bonds. Because of the fluorescence of the substance in most of the common solvents it was suspected that the double bonds might have shifted to a position of conjugation with the phenyl groups. The result of such a shift would be 1,4-diphenyl-1,3-cyclopentadiene. It should be possible to get some indication as

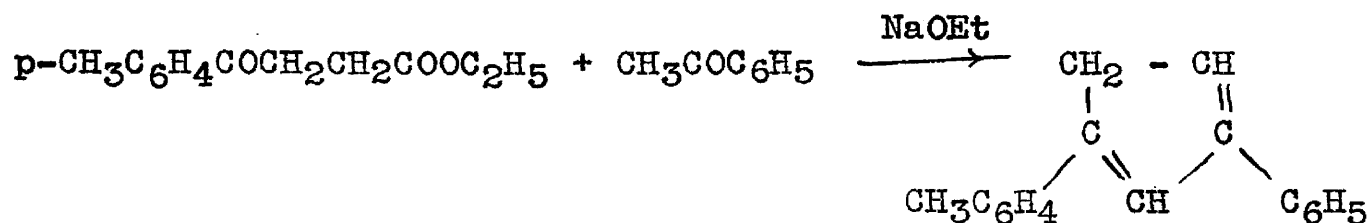


to whether a shift has occurred by the preparation of two diaryl cyclopentadienes with the same unlike aryl groups -- in which the same aryl group in the one compound was derived from the ester and in the other compound from the ketone. If a shift of double bonds has not occurred the compounds should be different. If a shift has occurred they will be the same. To be specific --- if ethyl- β -benzoylpropionate is reacted with methyl-p-tolyl ketone in the presence of sodium ethoxide the resulting hydrocarbon should be 1-phenyl-3-p-tolyl-1,3-cyclopentadiene.

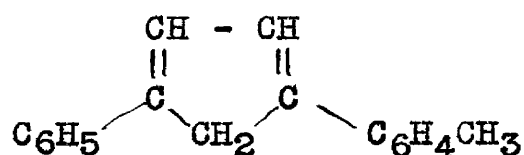


And if ethyl- β -p-toluypropionate is reacted with acetophenone in the presence of sodium ethoxide the resulting

hydrocarbon should be 1-p-tolyl-3-phenyl-1,3-cyclopentadiene. This is true only if a



shift of double bonds has not occurred. If the double bonds have shifted to a position of conjugation with the aryl groups the same compound 1-phenyl-4-p-tolyl-1,3-cyclopentadiene should result from both reactions.

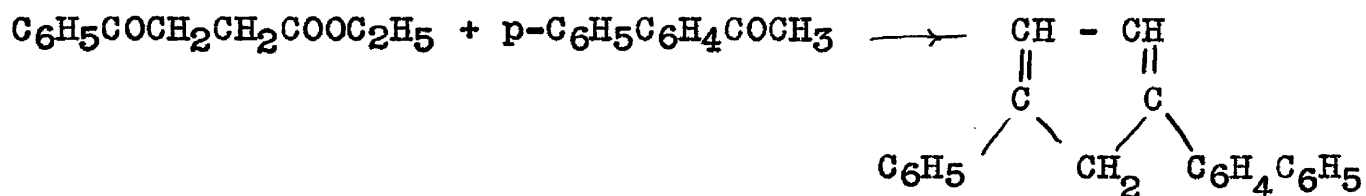


The two reactions described above were actually carried out and the products of these reactions were identical. This was proved not only by a mixed melting point taken on the hydrocarbons themselves but also by a mixed melting point taken on the maleic anhydride addition products of the two hydrocarbon products. Moreover, trinitrobenzolates made from the two samples had the same melting point and the same appearance. It would seem, then, from this work that the double bonds do shift to a position of conjugation with the aryl groups, that both hydrocarbon samples are 1-phenyl-4-p-tolyl-1,3-cyclopentadiene, and that correspondingly the other hydrocarbon must be 1,4-diphenyl-1,3-cyclopentadiene.

In order to prove definitely the structure of diphenylcyclopentadiene the substance was subjected to ozonization. If the substance were 1,3-diphenyl-1,3-cyclopentadiene the products resulting from decomposition of the ozonide should be benzoylformic and benzoylacetic acids. On the other hand, if the substance were 1,4-diphenyl-1,3-cyclopentadiene the products should be dibenzoylmethane and glyoxal. Actually the ozonide yielded dibenzoylmethane (proved by mixed melting point) and glyoxal as a derivative the p-nitrophenylosazone (proved by analysis and melting point). This work definitely proves the substance to be 1,4-diphenyl-1,3-cyclopentadiene and the other hydrocarbon to be 1-phenyl-4-p-tolyl-1,3-cyclopentadiene.

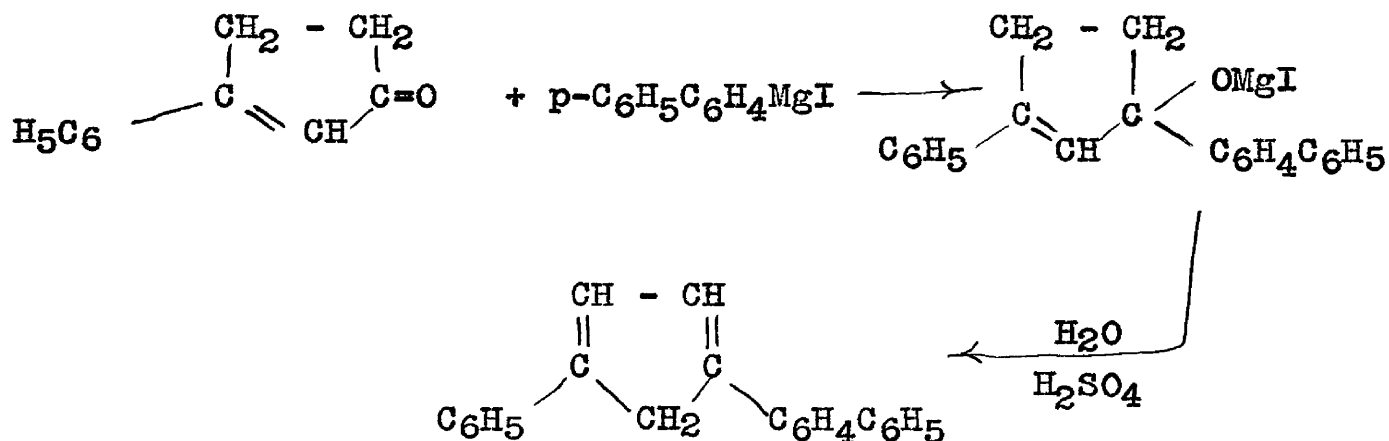
Preparation of 1-phenyl-4-p-xenyl-1,3-cyclopentadiene

Besides the two hydrocarbons previously described a third one, 1-phenyl-4-p-xenyl-1,3-cyclopentadiene has been made. This was synthesized from ethyl-β-benzoylpropionate and methyl-p-xenyl ketone. The reaction was carried out in the presence of sodium ethoxide.



It was also prepared by the method of Borsche and Menz from 1-phenyl-3-keto-1-cyclopentene and xenyl magnesium iodide.

By analogy to the



other hydrocarbons and because of the fluorescence of its solutions the substances are given the structure indicated above with the double bonds conjugated with the aryl groups. Neither the picrate nor the trinitrobenzolate of the substance could be prepared probably because of its insolubility in the usual solvents.

III. EXPERIMENTAL

Preparation of 1,4-Diphenyl-1,3-Cyclopentadiene

1. The most satisfactory method from the standpoint of yield and purity of product obtained.

In a 1000 ml. round bottom flask 5.36 grams (0.233 gram atom) of sodium was dissolved in about 120 ml. of absolute ethyl alcohol. The excess alcohol was removed by distillation in vacuo on the water pump. The residue was covered with 200 ml. of dry benzene. Twenty-four grams (0.116 mole) of ethyl- β -benzoylpropionate was added to the mixture and the mixture allowed to stand with occasional shaking for about ten minutes. During this time most of the sodium ethoxide dissolved, and the mixture took on a red color. Fourteen grams (0.116 mole) of acetophenone was added after which the mixture turned almost black and became slightly warm. The flask was stoppered and placed in a constant temperature bath and allowed to stand for 24 hours at 40°. The mixture was then cooled in an ice bath and poured into a mixture of ice and water (about 1000 ml.) and shaken well in a separatory funnel. After the two layers had separated the aqueous layer was drawn off and warmed with stirring on a steam bath to a temperature of about 60°. After several minutes crystals separated. The aqueous mixture was

cooled and filtered. The crystals were washed well on the filter with water. White crystals - M.P. 158°-158.5°. Yield 8.5 grams (33.5%). Recrystallized from alcohol or benzene-petroleum ether mixture. M.P. 158°-158.5°.

Analysis. Calcd. for C₁₇H₁₄: C, 93.58; H, 6.48

Found: C, 93.69, 93.64; H, 6.64, 6.60

(This procedure has been carried out several times using 6 grams (0.029 mole) of ethyl-β-benzoylpropionate and correspondingly smaller amounts of the other reactants, and the yields are consistently 33%).

Several runs were made using 6 grams of ester for different lengths of time. Temperature 40°.

<u>Time</u>	<u>% Yield</u>
10 minutes	trace
1 hour	4 %
20 hours	32 %
24 hours	33 %
30 hours	16 %
42 hours	16 %
48 hours	17 %

It appears that the optimum time is about 24 hours.

Several runs were made in which xylene was used as a solvent and in which the mixture was heated on the steam cone for 3 hours instead of in the constant temperature bath for a longer period. The same procedure was used with

benzene as a solvent. In every case the yields were very poor (approximately 5%).

One run made by allowing the mixture to stand in the ice-box for 48 hours gave no yield. Another run made by using ordinary alcohol in the preparation of the sodium ethoxide gave only a trace of hydrocarbon. A run made by allowing the mixture to stand at room temperature (30°) for 43 hours and by allowing the aqueous solution to stand over night without heating gave a yield of 25%. Runs made with one atom of sodium to one molecule of ester and with four atoms of sodium to one molecule of ester gave only a trace of hydrocarbon.

II. 1,4-Diphenyl-1,3-cyclopentadiene was made by the method of Borsche and Menz⁴.

Intermediates:

1. Phenacyl bromide was made by the method described by Rather and Reid⁸.
2. Ethyl- α -phenacylacetoacetate was made by method described by Borsche and Fels⁹.
3. 1-Phenyl-3-keto-1-cyclopentene was made by the method described by Borsche and Menz¹⁰.

M.P. 157.5°-158.0°.

Mixed melting point of mixture of the products of I and II. 157.5°-158.5°.

Molecular Weight Determinations on 1,4-Diphenyl-1,
3-cyclopentadiene

I. Ebullioscopic (Benzene as solvent $K = 2.95$ obtained from running naphthalene)

<u>Wt. of hydrocarbon</u>	<u>Wt. of benzene</u>	<u>ΔT_B</u>	<u>M. W.</u>
0.145 grams	33.64 grams	0.055	231
0.304	33.64	0.120	222
0.413	33.64	0.160	227
0.492	33.64	0.205	211
0.606	33.64	0.257	207

Average M. W. = 220
Theor. M. W. = 218

II. Neutralization equivalent of the Picrate

(2X Neut. Eq. of picrate) - (2X M.W. of picric acid) =
M.W. of hydrocarbon.

<u>Wt. of Picrate</u>	<u>mls. of NaOH</u>	<u>Neut. Eq. of Picrate</u>	<u>M.W. of Hydrocarbon</u>
0.0568 gms.	7.40 (.0229 N)	336	214
0.0682	3.85 (.0531 N)	334	210
0.0809	4.55 (.0531 N)	335	212
0.0659	3.65 (.0531 N)	340	222

<u>Wt. of Picrate</u>	<u>mls. of NaOEt</u>	<u>Neut. Eq. of Picrate</u>	<u>M.W. of Hydrocarbon</u>
0.0317 gms.	4.15 (.0338 N)	336	214
0.0740	9.60 (.0228 N)	338	218
0.0548	7.25 (.0226 N)	335	212
0.0368	4.75 (.023 N)	337	216
0.0207	2.90 (.021 N)	339	220

Average M. W. = 216
Theor. M. W. = 218

III. Cryoscopic (Camphor as solvent $K = 33.4$)

<u>Wt. of Hydrocarbon</u>	<u>Wt. of Camphor</u>	<u>ΔT_F</u>	<u>M.W.</u>
0.341 mg.	2.950 mg.	18.8	206
0.484	5.640	13.2	218

Theor. M. W. = 218

Fluorescence of Solutions of 1,4-Diphenyl-1,3-cyclopentadiene

1,4-diphenyl-1,3-cyclopentadiene dissolves in most of the organic solvents to form solutions which show a pronounced purple fluorescence. Solvents tried were benzene, ethyl alcohol, methyl alcohol, chloroform, acetic acid, dioxane, acetic anhydride, acetone, pyridine, ethyl acetate, and carbon tetrachloride. Of these solutions only the solution in carbon tetrachloride shows no fluorescence. It is interesting to note that a drop or two of carbon tetrachloride added to any of the other solutions causes the fluorescence of the solution to disappear. The hydrocarbon dissolves in concentrated sulfuric acid to form a solution which fluoresces blue. This fluorescence differs from that observed in the solutions in the organic solvents in that the solution is not transparent although it is translucent and is red to transmitted light.

Color Test on 1,4-Diphenyl-1,3-cyclopentadiene

A small amount (about 2 to 3 mg.) of 1,4-diphenyl-1,3-cyclopentadiene was dissolved in a mixture of 1 ml. of

chloroform and 1 ml. of glacial acetic acid. Three or four drops of concentrated sulfuric acid were added. The solution took on a yellow color which slowly turned to green.

Cyclopentadiene takes on a violet color on similar treatment¹¹.

Picrate of 1,4-Diphenyl-1,3-cyclopentadiene

A small amount of a hot concentrated alcoholic solution of 1,4-diphenyl-1,3-cyclopentadiene was added to a hot concentrated alcoholic solution of picric acid and the mixture warmed several minutes. The solution was cooled in an ice bath and the picrate filtered. It was crystallized from alcohol containing an excess of picric acid. Dark purple crystals resembling iodine. M.P. 145°-146°d.

Analysis. Calcd. for $C_{29}H_{20}O_{14}N_6$: C, 51.48; H, 2.98

Found: C, 51.54, 51.25; H, 3.19, 3.02

Picrate of 1,4-diphenyl-1,3-cyclopentadiene made by the method of Borsche and Menz was made in the same way. M.P. 145°-146°d. Mixed M.P. 145°-146°d.

Trinitrobenzolate of 1,4-Diphenyl-1,3-cyclopentadiene

A small amount of hot concentrated alcoholic solution of 1,4-diphenyl-1,3-cyclopentadiene was added to a hot concentrated alcoholic solution of trinitrobenzene and the mixture warmed several minutes. The solution was cooled in

an ice bath and the trinitrobenzolate filtered. It was crystallized from alcohol. Brilliant red crystals.

M. P. 151° - 152° d.

Analysis. Calcd. for $C_{29}H_{20}O_{12}N_6$: C, 54.04; H, 3.11

Found: C, 53.73, 53.56; H, 3.03, 3.17

Trinitrobenzolate of 1,4-diphenyl-1,3-cyclopentadiene made by the method of Borsche and Menz was made in the same way. M.P. 151.5° - 152.5° d. Mixed melting point M.P. 151° - 152° d.

1,3-Diphenylcyclopentane

Five grams of 1,4-diphenyl-1,3-cyclopentadiene was mixed with 100 ml. of absolute alcohol. To this mixture was added 0.5 gram of palladium on charcoal. The mixture was then shaken in an atmosphere of hydrogen for several hours until hydrogen was no longer taken up. It was then filtered to remove the catalyst and alcohol removed from the filtrate by distillation. Ether was added to the residue, and the resulting solution dried over calcium chloride. After removing the ether the residue was distilled. It boiled at 140° - 141° at 3 m.m. pressure. The yield was 4 grams. Colorless liquid (possessing fluorescence due to the presence of the unsaturated hydrocarbon).

Analysis. Calcd. for : $C_{17}H_{18}$ C, 91.89; H, 8.17

Found: C, 91.95, 92.10; H, 8.39, 8.09

(Attempts to remove fluorescence of 1,3-diphenylcyclopentane were not successful. The substance was reduced again and redistilled but was still fluorescent. Removal of unsaturates by washing with concentrated sulfuric acid gave a non-fluorescent liquid which on distillation gave a fluorescent liquid.)

Density at 25° = 1.0196

Refractive Index at 25° = 1.56965

Molecular Refraction (observed) = 71.50

Molecular Refraction (calc'd) = 71.68

Exaltation = -0.18

1,4-Diphenyl-1,4-endomethylene-2-cyclohexene-5,6-dicarboxylic acid anhydride

One gram of 1,4-diphenyl-1,3-cyclopentadiene was dissolved in benzene with 0.5 gram (theory 0.45 grams of maleic anhydride). The solution was warmed on a steam bath for about an hour and then cooled. Crystals of addition product were filtered. Yield 1.2 grams (83%). Recrystallized from benzene. White crystals - M.P. 154°. (Mixed melting point with 1,4-diphenyl-1,3-cyclopentadiene gives marked depression.)

Analysis. Calcd. for C₂₁H₁₆O₃: C, 79.75; H, 5.10

Found: C, 79.77, 79.79; H, 5.34, 5.34

(The addition product gives no fluorescence in benzene unless the solution is warmed. In concentrated sulfuric

acid it gives the same fluorescence as 1,4-diphenyl-1,3-cyclopentadiene. The fluorescence in both cases is probably the result of dissociation of the addition product).

Preparation of 1,3(?) -Diphenyl-4^(?)Carboxy-1,3-Cyclopentadiene

In a 200 ml. round bottom flask 1.34 grams (0.058 gram atom) of sodium was dissolved in about 30 ml. of absolute alcohol. The excess alcohol was removed by distillation in vacuo on the water pump. The residue was covered with 50 ml. of dry benzene. Six grams (0.029 mole) of ethyl- α -benzoylpropionate was added to the mixture and the mixture allowed to stand with occasional shaking for about 10 minutes. During this time most of the sodium ethoxide dissolved, and the mixture took on a red color. Acetophenone (3.5 gms.-0.029 mole) was added after which the mixture turned almost black and became slightly warm. The flask was stoppered and placed in a constant temperature bath and allowed to stand for 24 hours at 40°. The mixture was then cooled in an ice bath and poured into a mixture of ice and water (about 300 ml.) and shaken well in a separatory funnel. After the two layers separated the aqueous layer was drawn off and cooled in an ice bath. Glacial acetic acid was added drop by drop until no more precipitate formed. The aqueous suspension containing a

flocculent precipitate was centrifuged and the supernatant liquid decanted off. The moist precipitate was crystallized from benzene. The yield was 0.8 to 1.0 gram (10.5-13.1 %). After three recrystallizations from benzene the melting point became constant. White crystals. M.P. 157°-158°.

Analysis. Calcd. for $C_{18}H_{14}O_2$: C, 82.44; H, 5.39

Found C, 82.34*, 82.29; H, 5.57*, 5.51

(Mixed melting point with 1,4-diphenyl-1,3-cyclopentadiene shows no depression. The acid differs from the hydrocarbon in that it dissolves in dilute sodium hydroxide, in sodium bicarbonate solution, in benzene without fluorescence, and in sulfuric acid to form a yellow solution with a slightly greenish fluorescence.)

Conversion of 1,3(?) -Diphenyl-4(?) carboxy-1,3-cyclopentadiene into 1,4-Diphenyl-1,3-cyclopentadiene by Way of the Sodium Salt

1,3(?) Diphenyl-4(?) -carboxy-1,3-cyclopentadiene (0.3 gm.) was suspended in a dilute solution of sodium hydroxide. The mixture was warmed for an hour on the steam bath. Crystals which separated were filtered. The amount of hydrocarbon obtained was 0.25 gram (yield practically quantitative). Recrystallized from a benzene-petroleum ether mixture, the hydrocarbon was obtained in long white needles. M.P. 159°.

* The author is indebted to J. K. Wolfe for this analysis.

(Insoluble in sodium hydroxide or sodium bicarbonate solution; benzene solution fluorescent.)

Analysis. Calcd. for $C_{17}H_{14}$: C, 93.58; H, 6.48

Found: C, 93.84; H, 6.62

Conversion of 1,3-(?)-Diphenyl-4(?)-carboxy-1,3-cyclopentadiene into 1,4-Diphenyl-1,3-cyclopentadiene by Crystallization from Alcohol

1,3(?) -diphenyl-4(?) -carboxy-1,3-cyclopentadiene (0.3 gram) was dissolved in alcohol by warming on the steam bath. On cooling the solution 0.125 gram of 1,4-diphenyl-1,3-cyclopentadiene separated. White crystals. M.P. 159° . (Insoluble in sodium hydroxide or sodium bicarbonate solution; benzene solution fluorescent).

Analysis. Calcd. for $C_{17}H_{14}$: C, 93.58; H, 6.48

Found: C, 93.44, H, 6.57

Preparation of 1-Phenyl-4-p-Tolyl-1,3-Cyclopentadiene

I. (From ethyl- β -benzoylpropionate and methyl-p-tolyl ketone).

In a 200 ml. round bottom flask 1.34 grams (0.058 gram atom) of sodium was dissolved in about 30 ml. of absolute ethyl alcohol. The excess alcohol was removed by distillation in vacuo on the water pump. The residue was covered with 50 ml. of dry benzene. Six grams (0.029 mole) of ethyl- β -benzoylpropionate was added and

the mixture allowed to stand with occasional shaking. During this time most of the sodium ethoxide dissolved, and the mixture took on a red color. After about ten minutes 3.9 grams (0.029 mole) of methyl-p-tolyl ketone was added to the mixture. The flask was stoppered and placed in a constant temperature bath and allowed to stand for 24 hours at 40°. The mixture was then cooled in an ice bath and poured into a mixture of ice and water (about 300 ml.) and shaken well in a separatory funnel. After the two layers separated the aqueous layer was drawn off and warmed with stirring on a steam bath to about 60°. After several minutes crystals separated. The aqueous mixture was cooled and filtered. The crystals were washed well on the filter with water. White crystals. Yield 2.3 grams (34%). Recrystallized from ethyl alcohol. White crystals. M.P. 153°-153.5°.

Analysis. Calcd. for C₁₈H₁₆: C, 93.06; H, 6.94

Found: C, 92.80, 93.24; H, 7.03, 7.16

II. (From ethyl-β -p-toluypropionate and acetophenone)

In a 200 ml. round bottom flask 1.34 grams (0.058 gram atom) of sodium was dissolved in about 30 ml. of absolute ethyl alcohol. The excess alcohol was removed by distillation in vacuo on the water pump. The residue was covered with 50 ml. of dry benzene.

Ethyl-β -p-toluypropionate (6.5 grams-0.029 mole) was added to the mixture. After about five minutes 3.5

grams (0.029 mole) of acetophenone was added. The flask was stoppered and placed in a constant temperature bath and allowed to stand for 24 hours at 40°. The mixture was then cooled in an ice bath and poured into a mixture of ice and water (about 300 ml.) and shaken well in a separatory funnel. After the two layers separated the aqueous layer was drawn off and warmed with stirring on a steam bath to 60°. After several minutes crystals separated. The aqueous mixture was cooled and filtered. The crystals were washed well on the filter with water. White crystals. Yield 1.9 grams (27.7%). Recrystallized from ethylalcohol. White crystals. M.P. 153°-153.5°.

Mixed melting point of 1-phenyl-4-p-tolyl-1,3-cyclopentadiene by methods I and II. M.P. 153°-153.5°.

Fluorescence of Solutions of 1-Phenyl-4-p-tolyl-1,
3-cyclopentadiene

1-Phenyl-4-p-tolyl-1,3-cyclopentadiene dissolves in the usual organic solvents to form solutions which fluoresce blue. In concentrated sulfuric acid it forms a solution which fluoresces dark green. This solution is not transparent but is translucent and is red to transmitted light.

1-Phenyl-4-p-tolyl-1,4-endomethylene-2-cyclohexene-5,
6-dicarboxylic acid anhydride

a. (using phenyltolylcyclopentadiene from procedure I)

1-phenyl-4-p-tolyl-1,3-cyclopentadiene (0.413 gram) was dissolved with 0.175 gram of maleic anhydride in benzene. The solution was boiled for about 3 hours, cooled and the crystals filtered. Recrystallized from benzene. M.P. 145.5° - 146° .

b. (using phenyltolylcyclopentadiene from procedure II)

1-phenyl-4-p-tolyl-1,3-cyclopentadiene (0.443 gram) was dissolved with 0.188 gram of maleic anhydride in benzene. The solution was boiled for about 3 hours, cooled, and the crystals filtered. Recrystallized from benzene. M.P. 146° - 146.5° .

Mixed melting point of the two samples described above. M.P. 145.5° - 146° .

Analysis. Calcd. for $C_{22}H_{18}O_3$: C, 79.96; H, 5.49

Found: C, 80.07, 80.04; H, 5.45; 5.67

Trihitrobenzolate of 1-Phenyl-4-p-tolyl-1,3-cyclopentadiene

a. (using phenyltolylcyclopentadiene from procedure I)

1-phenyl-4-p-tolyl-1,3-cyclopentadiene (0.1 gram) was mixed with a little more than the theoretical amount

of trinitrobenzene (2 moles per 1 mole of hydrocarbon). The mixture was dissolved in hot alcohol. On cooling crystals of the trinitrobenzolate separated out. The filtered crystals were red. Recrystallized from alcohol. M.P. 144° - 145° d.

b. (using phenyltolylcyclopentadiene from procedure II)

Carried out in the same way as procedure a.

Red crystals. M. P. 144° - 145° d.

Analysis. Calcd. for $C_{30}H_{22}O_{12}N_6$: C, 54.69; H, 3.37

Found: C, 54.92, 54.73; H, 3.29, 3.52

Preparation of 1-phenyl-4-p-xenyl-1,3-cyclopentadiene

I. In a 200 ml. round bottom flask 1.34 gram (0.058 gram atom) of sodium was dissolved in 30 ml. of absolute ethyl alcohol. The excess alcohol was removed by distillation in vacuo on a water pump. The residue was covered with 50 ml. of dry benzene. Six grams (0.029 mole) of ethyl- β -benzoylpropionate was added and the mixture allowed to stand for five minutes during which time most of the sodium ethoxide dissolved. Then 5.7 grams (0.029 mole) of methyl-p-xenyl ketone was added. The flask was stoppered and placed in a constant temperature bath where it was kept at 40° for 24 hours. The mixture was then cooled and added to a mixture of ice and water (about 300 ml.) with which it was well shaken. The mixture was allowed

to stand for 24 hours at about 40°. The aqueous layer was then drawn off and the crystals of 1-phenyl-4-p-xenyl-1,3-cyclopentadiene obtained by filtering.

Recrystallized from benzene. Yield 2.1 grams (24.7%)
Yellow crystals. M. P. 217°-218°d.

Analysis. Calcd. for $C_{23}H_{18}$: C, 93.88; H, 6.12

Found: 93.49, 94.18; H, 6.28, 6.36

II. p-Xenyl iodide (5.5 gms.) was added slowly to 0.9 gram of magnesium turnings covered with dry ether. The mixture was refluxed for one hour. It was then cooled in a cold water bath and an ethereal solution (150 ml.) containing 3 grams of 1-phenyl-3-keto-1-cyclopentene was added slowly. After this addition the mixture was refluxed for an hour and allowed to stand over night. It was then decomposed by pouring on a mixture of ice and sulfuric acid. The ethereal layer was removed, the aqueous layer extracted with ether, and the combined ether layers washed with water and dried over sodium sulfate. The ether volume was reduced by distillation and the hydrocarbon crystallized. M. P. 208°-210°d. Recrystallized from benzene. M. P. 216°-217°d. Mixed M. P. with product from procedure I. M.P. 216.5°-218°d.

Fluorescence of Solutions of 1-Phenyl-4-p-xenyl-1,
3-cyclopentadiene

Like the other hydrocarbons of this series, 1-phenyl-4-p-xenyl-1,3-cyclopentadiene dissolves in the organic

solvents to form fluorescent solutions. It is considerably less soluble in these solvents than are the other two hydrocarbons. It dissolves in concentrated sulfuric acid to form a solution that fluoresces with a brilliant green color. This solution is not transparent but is translucent and is red to transmitted light.

Color Test on 1-Phenyl-4-p-xenyl-1,3-cyclopentadiene

Two to three mg. of 1-phenyl-4-p-xenyl-1,3-cyclopentadiene was dissolved in a mixture of 1 ml. of chloroform and 1 ml. of glacial acetic acid. Three or four drops of concentrated sulfuric acid was added. The solution took on a red to violet color.

(Attempts to make picrate and trinitrobenzolate of 1-phenyl-4-p-xenyl-1,3-cyclopentadiene were not successful. Although solutions of the hydrocarbon and nitro compound deepened in color on warming the color disappeared on cooling. By evaporating a solution of hydrocarbon and picric acid to dryness a residue was obtained which resembled the picrate of 1,4-diphenyl-1,3-cyclopentadiene. This could not be recrystallized.)

Ozonization of 1,4-Diphenyl-1,3-CyclopentadienePreparation of Dibenzoylmethane

a. One gram of 1,4-diphenyl-1,3-cyclopentadiene was dissolved in chloroform. The theoretical amount of ozone made from air was passed through the solution at -30° . The solution was added to water and the chloroform removed by distillation. The water was decanted off and the residue dissolved in ether. The ethereal solution was extracted with water. The ether was evaporated off and the residue treated with an absolute alcoholic solution of cupric acetate. A yellowish precipitate of crude copper salt of dibenzoylmethane formed immediately. The copper salt was filtered and recrystallized from benzene. Yield 45%. M. P. 296° - 302° d. Literature value 294° - 307° d. The copper derivative was treated with dilute hydrochloric acid and the dibenzoylmethane liberated was crystallized from alcohol. M. P. 79° - 80° .

b. One gram of sodium was powdered in xylene and reacted under reflux with 2 grams of absolute alcohol. After a while a slight excess of alcohol was added. To this was added 6.5 grams of ethyl benzoate. Acetophenone (5.2 grams) was then added very slowly and the mixture refluxed for three hours. On cooling it was extracted

with water, the aqueous solution acidified with glacial acetic acid and extracted with ether. The ether was evaporated off and the residue treated with alcoholic cupric acetate. The copper derivative was obtained by filtration, placed in dilute hydrochloric acid and warmed. On cooling crude dibenzoylmethane was filtered off and crystallized from alcohol. M. P. 79° - 80° .

Mixed melting point of dibenzoylmethane obtained by procedures a and b. M. P. 70° - 80° .

Preparation of p-Nitrophenylosazone of Glyoxal

One gram of 1,4-diphenyl-1,3-cyclopentadiene was ozonized in chloroform and the ozonide decomposed by adding the chloroform solution to sodium bisulfite solution and distilling off the chloroform. The aqueous solution was extracted with ether and then treated with 1.4 grams of p-nitrophenylhydrazine and about 3 or 4 ml. of glacial acetic acid. As the mixture was warmed gently a flocculent precipitate came out which gradually took on a red color. The mixture was centrifuged and the aqueous solution poured off. The flocculent precipitate was mixed with water and again centrifuged. The precipitate was then heated in alcohol but complete solution not effected. After cooling the alcoholic mixture was centrifuged, the alcohol poured off and the precipitate allowed

to dry. Crystallized from pyridine. M. P. 306° - 307° d.

Recrystallized from pyridine. M. P. 306° - 307° d.

Analysis. Calcd. for $C_{14}H_{12}O_4N_6$: C, 51.20; H, 3.69

Found: C, 51.30; H, 3.71.

Attempt to Condense Carbonyl Derivatives of Ethyl- β -Benzoylpropionate with Acetophenone

Preparation of ethyl- β -benzoylpropionate semicarbazone

Ethyl- β -benzoylpropionate (1.1 grams) was dissolved in 10 ml. of alcohol. Water was added until the mixture became just turbid. Turbidity was removed by the addition of alcohol. One gram of semicarbazide hydrochloride and 1.5 grams of sodium acetate were added. The mixture was heated by placing in a beaker of boiling water and allowed to cool slowly. The precipitated semicarbazone was recrystallized three times from an aqueous alcohol solution. M. P. 141° - 142° .

Analysis. Calcd. for $C_{13}H_{17}O_3N_3$: C, 59.32; H, 6.52

Found: C, 59.43, 59.18; H, 6.58, 6.58

Preparation of 3-Phenyl-pyridazinone-6 - (Attempt to condense ethyl- β -benzoylpropionate semicarbazone with acetophenone).

In a 200 ml. round bottom flask 0.45 gram of sodium was dissolved in about 30 ml. of absolute ethyl alcohol.

The excess alcohol was removed by distillation in vacuo, The residue was covered by 40 ml. of dry benzene. Five grams of ethyl- β -benzoylpropionate semicarbazone was then added. The mixture was allowed to stand at room temperature for six days. The benzene layer contained crystals which were filtered off and twice recrystallized from alcohol. M. P. 151° - 152° . Mixed melting point with known 3-phenyl-pyridazinone-6 was 151° - 152° .

Analysis. Calcd. for $C_{10}H_{10}ON_2$: C, 68.93; H, 5.79

Found: C, 68.83, 68.87, 68.72; H, 5.78, 5.86,
5.85.

(The desired semicarbazone of the first intermediate in the proposed mechanism was not obtained.)

(Attempt to prepare the oxime methyl ether of ethyl- β -benzoylpropionate led to a substance which analyses indicated to be impure. This substance was subjected to treatment which should have effected condensation with acetophenone but which yielded only a small amount of 1,4-diphenyl-1,3-cyclopentadiene.)

(Attempts to prepare pure ethyl- β -benzoylpropionate oxime were completely unsuccessful.)

IV. SUMMARY

1. The synthesis of three diarylcyclopentadienes has been effected by the action of methyl-aryl ketones on α -aroylpropionic esters in the presence of sodium ethoxide.
2. A mechanism for this synthesis has been proposed and one of the intermediates isolated.
3. Several derivatives of these diarylcyclopentadienes have been made.
4. The structure of these hydrocarbons has been proved by both analytical and synthetic methods.

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