

A STUDY OF THE ALKYLATION OF AROMATIC  
COMPOUNDS BY PHENYL CARBINOLS AND BY ETHERS  
PART I ALKYLATION BY PHENYL CARBINOLS AND  
THEIR SYMMETRICAL ETHERS  
PART II ALKYLATION BY  $\alpha$ -CHLOROETHYL METHYL  
ETHER

By  
Robert K. Preston

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of the requirements for the degree of  
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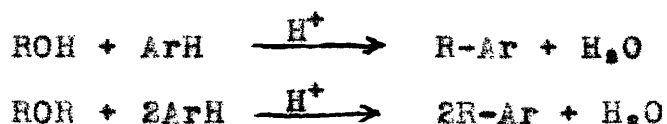
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## HISTORICAL INTRODUCTION

The objective of this investigation was to determine the applicability and scope of an azeotropic method for the alkylation of aromatic compounds by alcohols and ethers. The general reactions involved are shown in the following equations:

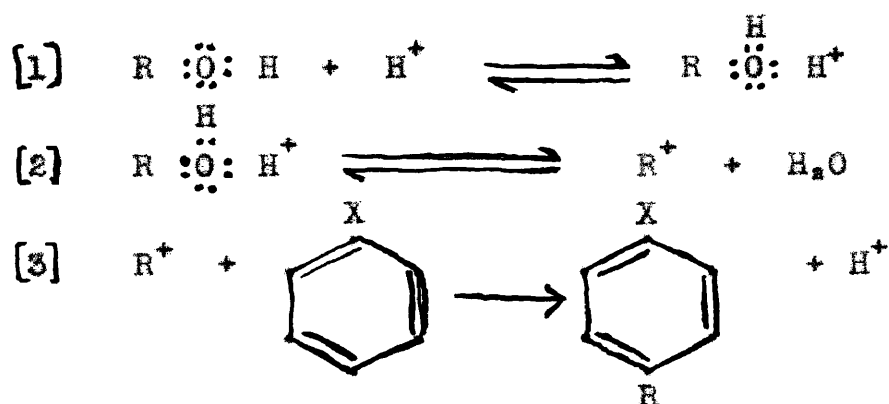


A collateral objective was the study of the effect of changes in structure of both the aromatic compound and the alcohol or ether on reactivity. By the azeotropic procedure, one should also be able to study the kinetics of the reactions and thus gain further insight into the mechanism of these alkylations. Improvement in the yields of Friedel and Crafts type reactions is likewise very desirable from a purely synthetic point of view.

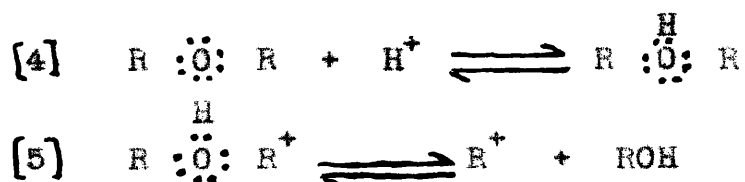
In the azeotropic method studied here the reactions were carried out in boiling benzene or a similar solvent in the presence of p-toluene sulfonic acid as a catalyst. The water formed in the reaction was distilled off with the solvent; the water was collected in an automatic liquid separator while the solvent was returned to the reaction mixture. By reading the increase in volume of water with time the reactions could be readily followed.

The current mechanism of Friedel and Crafts type alkylations using alcohols and ethers involves the forma-

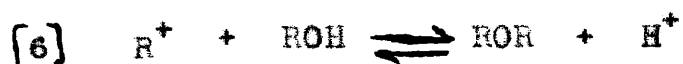
tion of a carbonium ion. The acid catalyst produces the carbonium ion which then attacks the point of highest electron density on the aromatic ring (1), (2), (3). Luder and Zuffanti (2) point out that the older theory of olefin formation as an essential part of the mechanism for alcohol alkylation is not satisfactory because of its inability to explain alkylations by benzyl alcohol which of course can not form an olefin. The preferred mechanism for an alcohol is as follows:



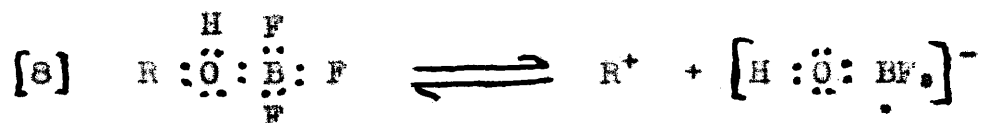
While that for an ether is:



In this case the  $\text{R}^+$  may react as shown in equation [3] while  $\text{R O H}$  may proceed as in equations [1], [2], and [3], or the  $\text{R O H}$  may react with  $\text{R}^+$  formed from another molecule of the alcohol as in equation [1] and [2] to regenerate a molecule of ether.



The most common acid catalysts are: aluminum chloride, aluminum bromide, stannic chloride, titanium chloride, zinc chloride, boron trifluoride, phosphorous pentoxide, hydrogen fluoride, phosphoric acid, and p-toluenesulfonic acid. Each of the salts and anhydrides has, like the protons from the acids, a strong tendency to accept a share in an unshared pair of electrons such as those found on the oxygen atoms of alcohols and ethers. With boron trifluoride for example the equations are:



Friedel and Crafts type alkylations of aromatic compounds by alcohols and ethers has been rather exhaustively reviewed by Thomas in his classic, "Anhydrous Aluminum Chloride in Organic Chemistry" (4). More recent reviews are given by Price (1) and by Groggins (5). Reviews by Calloway and one by Nightingale should also be consulted (6), (7). In the following discussion the alcohols will generally be considered in order of decreasing number of phenyl groups, i.e. first the triphenylcarbinols then diphenylcarbinols and monophenylcarbinols and finally the aliphatic alcohols. The important ethers will be discussed along with the corresponding alcohols.

Triphenylcarbinol has been condensed with phenols in yields of 80% to 90% in acetic acid with a trace of sulfuric



acid as the catalyst (8). Under these same conditions triphenylcarbinol was condensed with several cresols in excellent yields (9). Using similar conditions much poorer yields and multiple products have also been reported. With p-cresol the major product was triphenylmethane (10). Welsh and Drake were able to condense triphenylcarbinol with phenol in 95% yield by using aluminum chloride as the catalyst and an excess of the phenol as the solvent (11). Dimethylphenylcarbinol and diphenylmethylcarbinol were also condensed with phenol in 70% to 80% yields by this method. The reaction proceeded more readily as the aryl content of the carbinol increased. Triphenylcarbinol has also been condensed with aniline in acetic acid solution using hydrogen chloride as the catalyst (12).

Benzhydrol has been condensed with phenol using aluminum chloride as catalyst to give a 40% yield of p-hydroxy-triphenylmethane (13). Methyl- and ethylphenylcarbinols gave even lower yields under these conditions. When benzhydrol was reacted below  $10^{\circ}$  with benzene using aluminum chloride as the catalyst a 65% to 70% yield of triphenylmethane along with about 10% to 15% of diphenylmethane was found (14). Under these conditions methyl- and ethylphenylcarbinols gave mixtures containing diphenylmethanes in amounts corresponding to yields of 7% to 20%. Very excellent yields have been reported when benzhydrol was condensed with o- and p- cresol in acetic acid solution using sulfuric acid as the catalyst. With phenol under these conditions there was obtained a quantitative yield of 2,4,6-tribenzhydroyl-

phenol (10). Dibenzhydrylether has been used to alkylate benzene in 60% yields using phosphorous pentoxide as the catalyst at 0° (15).

Benzene has been alkylated with benzyl alcohol in 70% yields using hydrogen fluoride as a catalyst (16). With phosphorous pentoxide or aluminum chloride the yields were only about half as good (15). Huston and co-workers have done considerable work with aluminum chloride by the usual Friedel and Crafts procedure. When they condensed benzyl alcohol with benzene at 35°, poor yields of diphenylmethane, p-dibenzylbenzene, o-dibenzylbenzene, anthracene, and the usual tars and polymerized products were obtained (17). Phenol, anisole, and phenetole were alkylated by benzyl alcohol in 45% to 58% yields to give the corresponding p-benzyl product under these conditions. Cresols were also condensed with benzyl alcohol using petroleum ether as a solvent and aluminum chloride as the catalyst (19), (20), (21). The yields of the monoalkylation products ranged from 19% to 35%, as also did the yield of dialkylated product. Benzyl alcohol was condensed with 2,6-dichlorophenol to give a low yield of 3,5-dichloro-4-hydroxydiphenylmethane (22). Naphthalene has been alkylated with benzyl alcohol at 25° using boron trifluoride as catalyst (23). A 28% yield of  $\alpha$ -benzyl naphthalene and only a 2% yield of the beta isomer was obtained. There was also obtained a 15% yield of dibenzyl naphthalene and a 20% yield of tribenzyl naphthalene. When benzyl alcohol was replaced by cyclo-

hexyl, tertiary butyl, or isopropyl alcohol it was found that the beta isomer predominated. This was obtained in yields of 35% to 65%. Here again there was considerable di- and tri-alkylation of the naphthalene.

Benzyl alcohol has been condensed with benzene using beryllium chloride as the catalyst in yields of 35% to 80% (24). Toluene gave about 55% of p-benzyltoluene along with a trace of a dialkylated product. It has been recently reported that benzyl alcohol alkylated toluene in 28% yield using chlorosulfonic acid as a catalyst (25). There was also obtained a small yield of a disubstituted toluene. Benzene and toluene were alkylated in low yields with isopropyl alcohol and tertiary butyl alcohol (25).

When Russian workers (26) attempted to condense activated alcohols with benzene, toluene and phenol in the presence of ferric chloride, they obtained very poor yields. Benzyl alcohol gave a 58% yield of the monoalkylated product while allyl alcohol gave even lower yields.

Benzene has been alkylated with dibenzyl ether to give a 23% yield of diphenylmethane, a 26% yield of dibenzylbenzene and a 51% yield of polymerized products (27). The molar ratio of benzene to ether was two to one and the catalyst was boron trifluoride.

Benzyl n-propyl ether has been condensed with benzene, naphthalene, and phenol at 85° using boron trifluoride (28). With benzene the yield of diphenylmethane varied from 20% to 48% depending upon the ratio of boron trifluoride to benzene. Similar yields of dibenzylbenzene were also found.

Phenol gave a 48% yield of p-benzylphenol while naphthalene gave a 48% yield of  $\alpha$ -benzyl-naphthalene.

Tzukervanik and co-workers have condensed several tertiary aliphatic alcohols with benzene and toluene (29), (30). They used aluminum chloride as the catalyst and obtained yields of 50% to 70% in most cases. With other than tertiary alcohols poorer yields were usually obtained (31); but an excellent yield of p-cymene resulted from the condensation of isopropanol with toluene. These workers have also alkylated benzene and toluene with cyclohexanols, menthol, and borneol by this method (12), (32). The yields varied from 39% to 62%.

Cyclobutyl, cyclopentyl, and cyclohexyl carbinols have been condensed with benzene using aluminum chloride as the catalyst (33). The cyclopentylcarbinol gave the highest yield which was 45%.

Other alcohols have been used, such as allyl (34), (35); various tertiary aliphatic alcohols (36); primary and secondary alcohols (37), (38), (39); and xanthidrol (40); and borneol (31). In general yields with these alcohols were well below 50% and mixtures of products were obtained.

The use of a few dialkyl ethers has been reported in the literature (4). Diethyl ether has been used to alkylate benzene in 36% yield by condensing one-half mole of ether with three moles of benzene in the presence of one mole aluminum chloride. Reaction proceeded through intermediate formation of the molecular compound,  $(C_2H_5)_2O \cdot AlCl_3$ . Mono-

alkyl benzenes were obtained in 20% to 48% yields by condensing diisopropyl ether and di-n-butyl ether with benzene by means of aluminum chloride (4).

It is evident from the foregoing discussion that there is room for considerable improvement in the methods for the alkylation of aromatic compounds by alcohols and ethers. In particular none of the methods in the literature has been applied or are readily applicable to the accurate determination of reaction rates for use in kinetic studies and for use in studies of relative reactivities. Indeed the occurrence of side reactions such as polyalkylation and polymerization with the concomitant low yields of desired product would invalidate rate studies by many of these methods. So far as we have been able to determine the azeotropic method has not been previously applied.

## DISCUSSION

### PRELIMINARY STUDY OF THE APPLICABILITY AND SCOPE OF THE AZEOTROPIC METHOD

While studying the etherification of benzyl alcohol with n-butyl alcohol in benzene solution by an azeotropic method in these laboratories, Draper (41), found that almost as large a yield of benzylbenzene as of benzyl butyl ether was obtained. When he attempted to etherify benzyl alcohol with itself in benzene solution a 66% yield of diphenylmethane was obtained. An 83% yield of the same product was obtained when dibenzyl ether was reacted with benzene.

In the usual procedure for studying alkylation, one-eighth mole of the alcohol or one-sixteenth mole of the ether together with the catalyst and a suitable amount of the aromatic compound to be alkylated (if different from the solvent) is dissolved in sufficient benzene or similar solvent, to give a total volume of 500 ml. The rate of the reaction is determined by taking frequent readings of the volume of water produced as the reaction progresses. This is accomplished by refluxing the solution and allowing the water which is formed to azeotropically distill over and collect in a water separator. As the reaction mixture is refluxed one mole of water is carried into the water separator for each mole of mono-alkylated product formed (equations [1] to [3] of preceding section).

Since this appeared to be a very desirable method of effecting alkylations, a systematic study of its application

was inaugurated. A preliminary study of the types of compounds for alkylation and the types of alkylating agents suitable for reactions by this method was first made.

Using the general procedure, benzyl alcohol was reacted with phenol in benzene solution. When 0.125 mole of benzyl alcohol was reacted with 0.175 mole of phenol in the presence of 0.032 mole of p-toluene sulfonic acid as the catalyst a 50% yield of diphenylmethane and a 28% yield of p-benzylphenol was found. One-third of the starting phenol was recovered. It was apparent that even though phenol is much more easily alkylated than benzene, this alkylation could not be readily studied in benzene solution. Similar results were obtained using 100% phosphoric acid as the catalyst.

The reaction of benzyl alcohol with mesitylene under identical conditions except that the catalyst was twice as concentrated, likewise gave a mixture. Here a 64% yield of diphenylmethane was obtained with only a 21% yield of benzylmesitylene. This again demonstrated that the use of benzene as a solvent was undesirable unless benzene itself was the compound to be alkylated.

When benzyl alcohol was reacted with anisole in toluene solution in the presence of 100% phosphoric acid both the anisole and the toluene were alkylated. In this case the yield of p-benzylanisole was only 35%.

Thus it may be concluded from the foregoing experiments that since the solvent is present in such large excess it is alkylated to a large extent even though a small amount of a

second much more easily alkylated aromatic compound is present.

In one case, however, only slight alkylation of the solvent occurred. When triphenyl carbinol was reacted with a threefold excess of phenol in a benzene solution which was 0.0005 molar in p-toluene sulfonic acid, a 73% yield of p-triphenylmethyl phenol was obtained. In this case, however, only 75% of the theoretical amount of water was obtained and furthermore the product separated out of solution during the course of the reaction.

It was decided at this point to use the aromatic compound which was to be alkylated as the solvent and in this way avoid multiple products and yet be able to keep the product as well as the catalyst in solution. In comparison to most of Draper's etherifications (41), a considerably greater concentration of catalyst was necessary for these alkylations. p-Toluene sulfonic acid was chosen as the catalyst in preference to 100% phosphoric acid because of the ease with which the sulfonic acid is handled and because of its strong catalytic effect and its high solubility in aromatic compounds.

It was found that aliphatic alcohols did not react nearly so readily or cleanly as the phenyl carbinols. When an attempt was made to alkylate anisole with n-butyl alcohol using excess anisole as the solvent, some dehydration of the butyl alcohol occurred and only a 6% yield of p-n-butylanisole was obtained. A higher boiling fraction amounting to about five times the butyl anisole fraction was recovered, but it



has not yet been identified. It was surprising to find that this material contained only 55% of carbon. Reaction with the catalyst was ruled out as a possible cause of the low carbon content by the negative results obtained upon qualitative analysis for sulfur. Further work on the characterization of this material will be done in these laboratories.

When octanol-2 was reacted with anisole under these same conditions using 0.008 mole of p-toluene sulfonic acid, there was obtained an almost quantitative yield of octene.

On the basis of this preliminary work certain alkylating agents and compounds for alkylation were selected for more extensive and accurate investigation. Benzyl alcohol and benzhydrol and their symmetrical ethers appeared to be of particular interest. Triphenyl carbinol and several para substituted benzyl alcohols were to be studied also. Benzene, toluene, and anisole were selected as typical, important aromatic compounds to be alkylated but certain additional aromatic compounds were to be studied in order to better determine the scope of the method.

In order to facilitate this further study, a standard apparatus and procedure was adopted. The apparatus used was identical to that of Draper (41). It consisted of a one liter flask with two standard taper necks fitted with a thermometer well and a water separator which was calibrated in tenths of a milliliter. The top of the water separator held a reflux condenser equipped with a calcium chloride drying tube. This drying tube was used throughout the course of the

reaction. A "Glas-Col" heater was used with standard voltages for each substrate. This voltage was determined for each solvent and was the highest voltage which could conveniently be used without causing flooding. The "Variacs" used were calibrated against a voltmeter. These standard voltages were: 70 volts for benzene, 80 volts for toluene, 100 volts for anisole, and 105 volts for phenetole. Test runs were made to make sure that in all cases the water was removed as fast as it was produced. The thermometers used were checked against Bureau of Standards thermometers for each of the temperatures used. Barometer readings were taken, but usually variations in atmospheric pressure did not significantly effect the reflux temperature. Readings of the separated water volume were taken at every 0.1 ml. or more frequently as the case required.

This standard apparatus and the following standard procedure was used in all experiments except where noted otherwise. To 450 ml. of the dry substrate was added the necessary amount of p-toluene sulfonic acid monohydrate. The water separator was filled with solvent and the solution was then refluxed to remove the water from the catalyst. At the end of this period one-eighth of a mole of the alkylating alcohol or one-sixteenth of a mole of the ether was dissolved in sufficient substrate to give 50 ml. of solution and this was added to the hot solution of dehydrated catalyst. Upon renewed reflux the zero time was recorded. Reflux was continued until no more water appeared in the water separator over

several hours.

Upon completion of the refluxing, the solution was washed with a saturated aqueous solution of sodium bicarbonate to remove the acid and then with water until it became neutral. Most of the solvent was then distilled off at atmospheric pressure and the product was usually isolated by distillation under reduced pressure. All standard runs which gave good yields were checked at least once.

Standard amounts of catalyst were used. It was desired to use that concentration of catalyst which would give a rate of water elimination which could be conveniently followed. Whenever possible a concentration of catalyst was chosen which would enable a comparison with other reactions. The amount of the catalyst was varied according to the following progression:  $6.25 \times 10^{-5}$  mole,  $2(6.25 \times 10^{-5})$  mole,  $4(6.25 \times 10^{-5})$  mole, etc. up to and including  $4096(6.25 \times 10^{-5})$  mole. This highest concentration is close to the limit of solubility of p-toluene sulfonic acid in benzene. Eastman's white label p-toluene sulfonic acid monohydrate was shown to be of high purity and therefore was not further purified.

This method possesses certain limitations and sources of error which must be kept in mind. The solvent used must be sufficiently lighter than water so that the water separates readily and the solvent should dissolve very little water. The catalyst used must not react with the water so that it can not be removed as it is formed. It is interesting that p-toluene sulfonic acid fits this requirement so well.

The reactants and products must not be both highly volatile and water soluble so that they appear in the water layer and alter the volume readings. The alcohols must not dehydrate under these reaction conditions. The reflux temperature varies to a certain extent as the reaction progresses, but it was generally constant to within  $\pm 0.5^\circ$  over the 15% to 90% portion of the reaction and often the variation was not more than  $\pm 0.2^\circ$ . Solvents which boil between  $60^\circ$  and  $175^\circ$  may be used without a special condenser system.

There are numerous advantages to this method. The procedure avoids polymerization, polyalkylation, and mixtures of ortho and para products so that a single product is usually obtained in high yield. The constant removal of the water forces the reaction to completion and prevents inactivation of the catalyst. There is no time lag between taking a sample and analyzing it as there is in so many methods for determining reaction rates and the process is simple and rapid.

#### THE ALKYLATION OF BENZENE BY PHENYL CARBINOLS AND THEIR SYMMETRICAL ETHERS

Following the previously outlined standard procedure benzene was alkylated with benzyl alcohol in a 78% yield using 0.064 mole of catalyst (see Table I). A 6% yield of m-dibenzyl benzene was also isolated. Previous work (41) with twice as much catalyst gave a 66% yield of the expected diphenylmethane and a 17% yield of m-dibenzyl benzene. In all of the work reported in this section the reaction temperature was  $83.0 \pm 0.9^\circ$ . Within a given experiment the tempera-

TABLE I

Alkylating Agent	Catalyst (Moles)	Half-Time (Minutes)	Yield of Water (Percent)	Yield of Product (Percent)
$C_6H_5CH_2OH$	0.064	82	100	78
$(C_6H_5CH_2)_2O$	0.064	72	100	83
$(C_6H_5)_2CHOH^1$	0.064	--	71 <sup>2</sup>	9
$(C_6H_5)_2CHOH^3$	0.128	--	45	19
$(C_6H_5)_2CHOH^1$	0.256	--	85	52
$[(C_6H_5)_2CH]_2O$	0.128	--	78	54

1. These runs not checked.
2. 55% yield of sym-dibenzhydryl ether isolated.
3. 0.0625 mole of benzhydrol used instead of the standard 0.125 mole.

ture seldom varied more than  $0.4^{\circ}$  from its median value.

Examination of the rate curve obtained (see Figure I, Curve I) shows that the reaction rate gradually decreased from the beginning to a point near 50% completion. From here on the rate increased until the final flattening to the horizontal at 100% completion. Since it is possible for benzyl alcohol to etherify with itself under these conditions, Draper (41) repeated the reaction at a higher concentration of alcohol but stopped it when only one-fifth of the theoretical volume of water for etherification was given off. A 48% yield of the dibenzylether and about a 40% yield of diphenylmethane, based on the amount of water produced, was obtained. Draper also found (41), and his observation was confirmed in this investigation, (Table I and Curve II, Figure I) that under the standard conditions and with the same amount of catalyst used with benzyl alcohol, dibenzyl ether alkylated benzene to give an 83% yield of diphenylmethane. It is apparent from this work that a considerable part of the alkylation of benzene by benzyl alcohol proceeds via the intermediate formation of the ether.

Since both etherification and alkylation are occurring concurrently and in different proportions as the reactions proceed it is, perhaps, not surprising that the curves of Figure I do not show a constantly decreasing rate. Another factor, however, may be chiefly responsible for the inflection points in the rate curves. This factor is the variation in the "activity" of the catalyst as the reactions

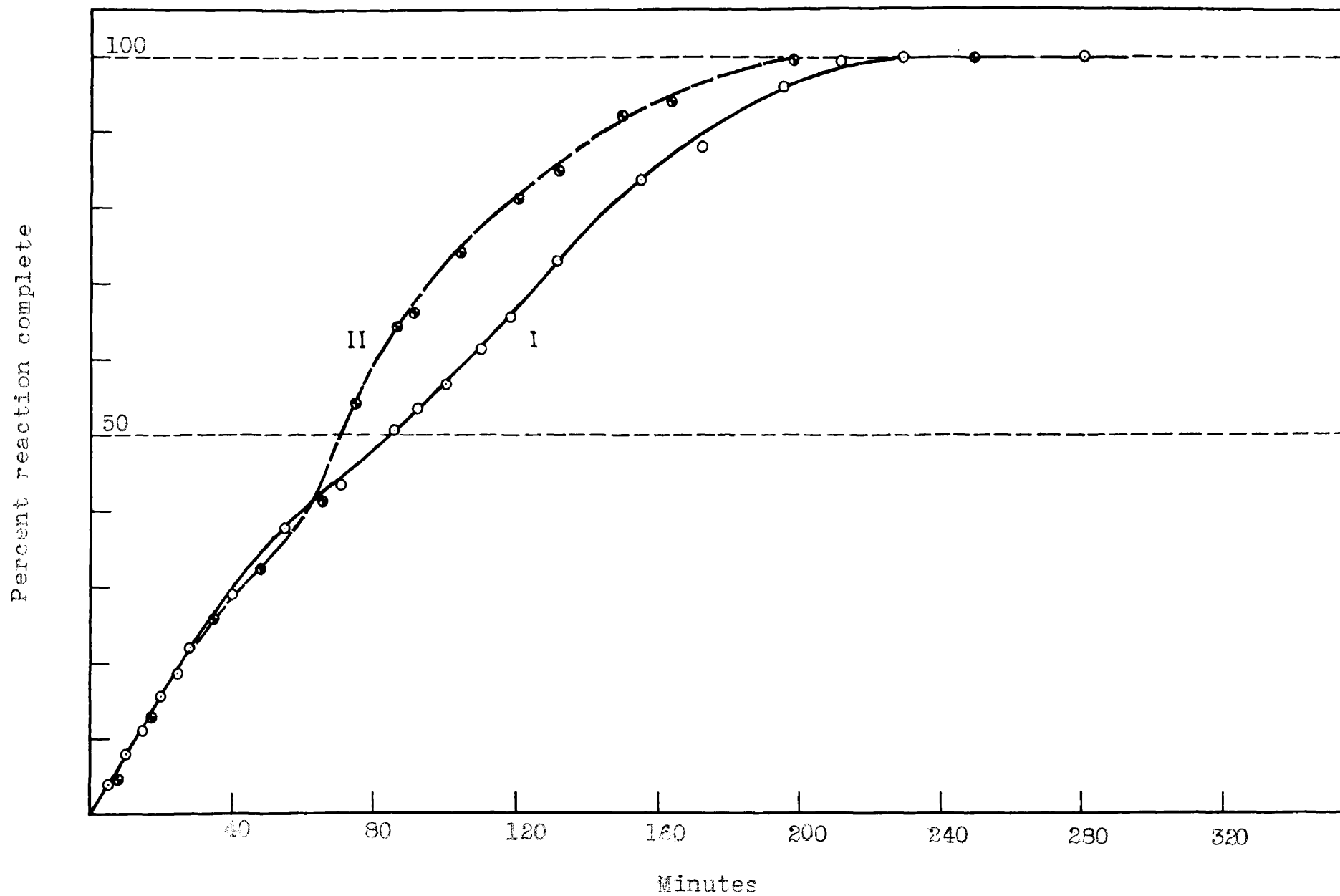


Figure I. Alkylation of benzene at catalyst conc. of 0.128 molar. I by benzyl alcohol, II by benzyl ether.

proceed. It is reasonable to assume that the protons from the catalyst coordinate with the unshared electron pairs of the oxygen atoms of the alcohol and ether to give  $C_6H_5CH_2OH_2^+$  and  $C_6H_5CH_2OCH_2C_6H_5^+$ . During the earlier part of the reaction more alcoholic and ethereal oxygen atoms than protons are present in the reaction mixture so that all of the protons can be coordinated with oxygen atoms; during the later part of the reaction, however, more protons (or molecules of unionized catalyst) than oxygen atoms are present. As a result the "activity" of the catalyst might be expected to increase and this in turn may cause the increase in reaction rate in spite of a decreasing concentration of reactants.

When benzhydrol was used in place of benzyl alcohol under these standard conditions using 0.064 mole of catalyst, the reaction came to a complete stop when only slightly more than 71% of the theoretical amount of water for alkylation had been obtained. A 9% yield of triphenylmethane and a 55% yield of dibenzhydrol ether was isolated (See Table I). When the reaction was repeated at twice the above catalyst concentration and one half the benzhydrol concentration there was obtained a 19% yield of triphenylmethane and a 50% crude yield of the symmetrical ether. These yields accounted for all of the water separated. A standard run was then made using 0.256 mole of catalyst and this gave a 52% yield of alkylated product along with 4% of p-dibenzhydrol benzene. There was no ether isolated at this high catalyst concentration. These runs are summarized in Table I.



A reasonable but not complete explanation of this increasing extent of alkylation with increasing catalyst concentrations is that all the benzhydrol formed by cleavage of its symmetrical ether becomes tied up as the oxonium ion  $\phi_2\text{CHOH}_2^+$  so that it cannot coordinate with any  $[\phi_2\text{CH}]^+$  ions and therefore alkylation is favored over etherification.

When dibenzhydrol ether was used with 0.128 mole of catalyst only 78% of the theoretical water for alkylation was obtained. A 54% yield of triphenylmethane and a 5.2% yield of p-dibenzhydrol benzene were found. These results compare favorably with the aforementioned alcohol run at twice this catalyst concentration. As yet a satisfactory explanation of why in two of the experiments with benzhydrol the reaction stopped completely even though a large amount of dibenzhydrol ether was present for further alkylation has not been obtained.

Since benzhydrol will rapidly form dibenzhydrol ether at a  $10^{-4}$  molar concentration of the catalyst in 90% yields (41), it is apparent that it is chiefly the ether that is doing the alkylating and that we never have a large proportion of the alcohol acting directly as the alkylating agent. When benzhydrol was used as alkylating agent (0.256 mole of catalyst) 50% of the water which is the amount for etherification, was given off in the first ten to fifteen minutes while the subsequent alkylation of the benzene by this ether proceeded much more slowly.

When triphenylcarbinol was reacted in benzene solution

using 0.064 mole of catalyst a 32% yield of triphenylmethane was found (41). A mixture of solids was also obtained which decomposed around  $250^{\circ}$ . It resisted separation and was in quantity of three times that of the triphenylmethane. The theoretical volume of water was evolved. The time for 50% completion of reaction was three hours.

#### THE ALKYLATION OF TOLUENE BY PHENYL CARBINOLS AND THEIR SYMMETRICAL ETHERS

Toluene was alkylated by the standard procedure with benzyl alcohol, using 0.032 mole of catalyst, to give a 90% yield of p-benzyltoluene (See Table II and Curve I of Figure II). The temperature of this and all of the other reactions of this section was  $113 \pm 0.5^{\circ}$  unless otherwise noted. Usually within a given experiment the temperature did not vary more than  $\pm 0.3^{\circ}$  from the median value.

In order to compare the ease of alkylation of toluene and benzene, the foregoing run was repeated at a pressure (330 to 340 mm) which gave a reaction temperature of  $85.5^{\circ} \pm 0.5^{\circ}$ , which is close to the  $83^{\circ}$  found for benzene (See Table I). The same amount of catalyst (0.064 mole) was used for the two experiments. A 92% yield of product was isolated from the toluene reaction mixture. The half reaction time here was forty-two minutes which is only about half as long as that for the benzene experiment. It is apparent that toluene alkylates nearly twice as rapidly as benzene although fine comparisons are not valid since the influence of the self-etherification of the benzyl alcohol would not be

TABLE II

Alkylating Agent	Catalyst (Moles)	Half-Time (Minutes)	Yield of Water (Percent)	Yield of Product (Percent)
$C_6H_5CH_2OH$	0.032	82	100	90
$C_6H_5CH_2OH$	0.064	11	100	--
$C_6H_5CH_2OH$	0.064	42 <sup>1</sup>	99	92
$(C_6H_5CH_2)_2O$	0.032	80	98	90
$(C_6H_5)_3CHOH$	0.016	--	59	-- <sup>2</sup>
$(C_6H_5)_3CHOH$	0.032	--	100	89
$[(C_6H_5)_2CH]_2O$	0.032	525	99	90

1. Run under reduced pressure to give reaction temperature of  $85.5^{\circ} \pm 0.5^{\circ}$
2. One to two grams.

expected to be the same in both cases. This result demonstrates very pointedly the effect of the methyl group on the benzene ring in producing a center of high electron density in the para position.

A standard run of benzyl alcohol in toluene was also made using 0.064 mole of catalyst. Its rate is shown in Figure II, Curve III. By comparing Curve II to III one can see that by increasing the temperature  $28^{\circ}$  the half-reaction time was decreased from forty-two minutes to approximately eleven minutes. A comparison of Curves I and catalyst concentration the half-reaction time is decreased from eighty-two minutes to eleven minutes. The inflection points discussed for Figure I are found again in the curves of Figure II.

When toluene was alkylated with dibenzyl ether at the same catalyst concentration as was used for the benzyl alcohol (0.064 mole, Curve I, Figure II) a 90% yield of the expected product was obtained. The ordinate values of the rate curve did not vary at any point more than 10% from the curve for the benzyl alcohol and for the last 60% of the reaction this variation was less than 4%. The close similarity of the curves may indicate that the ether is the chief alkylating agent for the last part of the reaction in both cases.

When an attempt was made to alkylate toluene with benzhydrol in the presence of 0.0064 mole of catalyst only the theoretical amount of water for etherification was collected. When to the refluxing solution there was added 0.064 mole more catalyst the theoretical volume of water for alkylation ap-

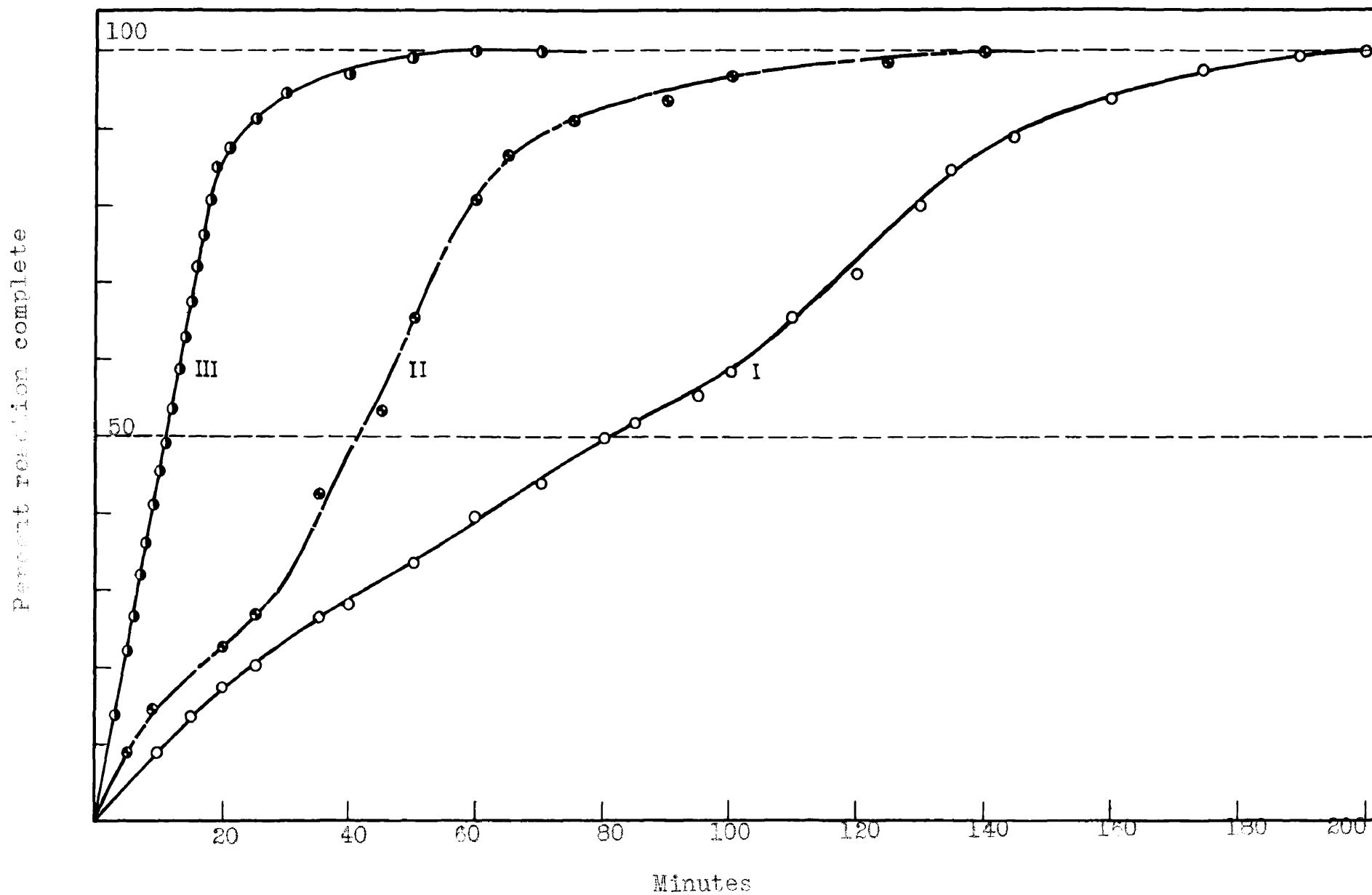


Figure II. Alkylation of toluene by benzyl alcohol. I at  $113^{\circ}$  with catalyst conc. 0.064 molar. II at  $85-86^{\circ}$  with catalyst conc. 0.128 molar. III at  $113^{\circ}$  with catalyst conc. 0.128 molar.

peared very rapidly. This final reaction mixture gave an 89% yield of p-dibenzhydryl toluene. When the reaction was repeated using 0.016 mole of catalyst (See Table II) a 91% yield of the dibenzhydryl ether and only one to two grams of alkylated products was obtained. This shows again the extreme tendency of benzhydrol to form the ether very rapidly in the presence of acid catalysts. When the catalyst concentration was doubled to 0.032 mole there was a very rapid elimination of the theoretical amount of water for ether formation and then a very slow production of water until the theoretical volume of water for alkylation had been obtained. Half-reaction times mean little here since the ether formation proceeds so rapidly, but the time for completed reaction was about thirty-two hours. Again the expected product was isolated in high yield (Table II).

It was found that dibenzhydryl ether alkylated toluene in 90% yield in the presence of 0.032 mole of catalyst. The rate curve is shown in Figure III. This curve demonstrates the effect of the changes in the activity of the catalyst as the reaction proceeds. Up to about the half-reaction point there is enough oxygen present for coordination with the protons of the catalyst but beyond that point the acid becomes successively more active and the rate increases until the reaction is almost complete. Fifteen hours were required for the complete reaction. It is difficult to understand why the changes in rate here should be so much greater than those found for dibenzyl ether with either benzene or toluene.

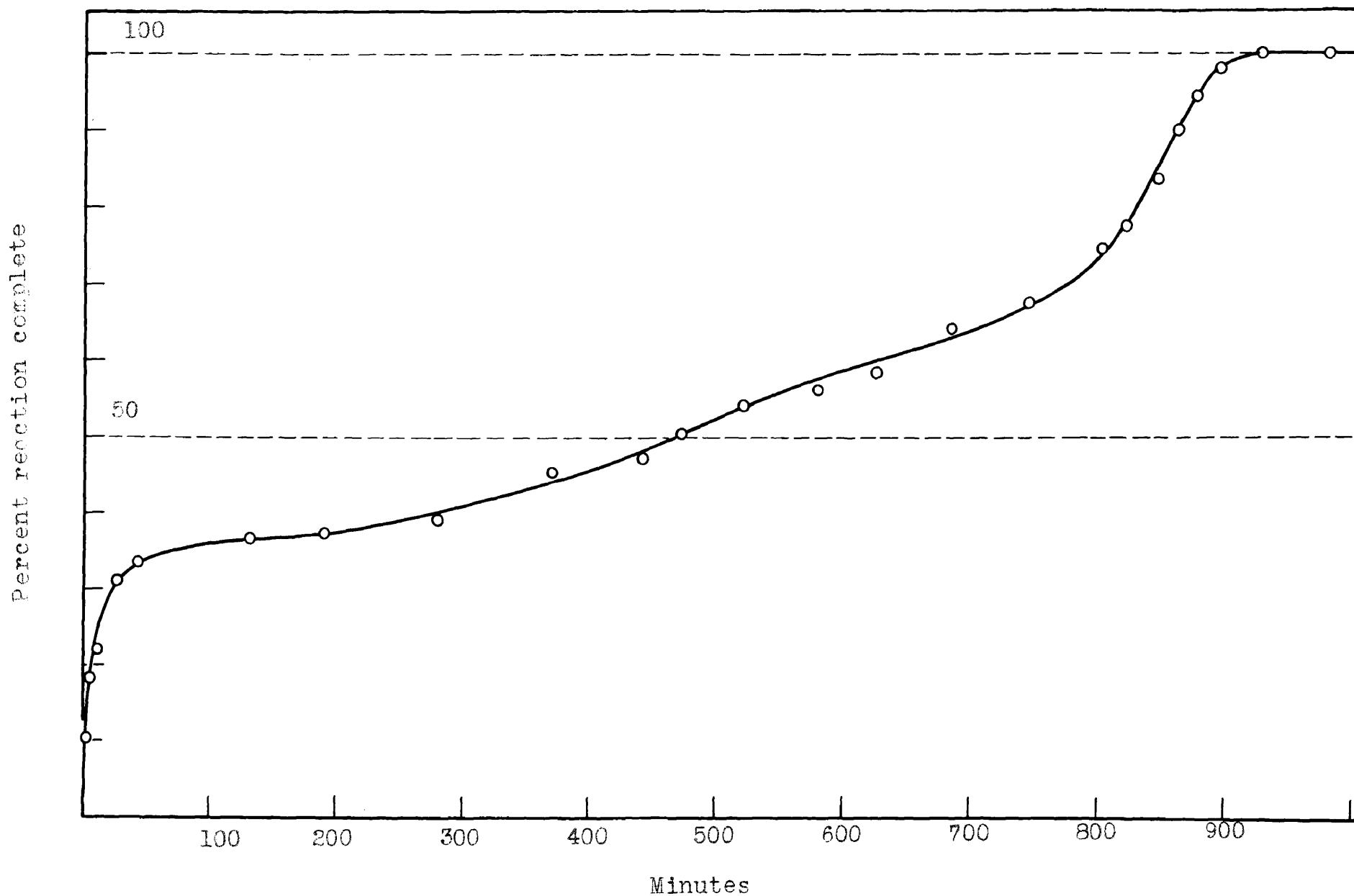


Figure III. Alkylation of toluene by dibenzhydryl ether at catalyst conc. of 0.064 molar.

Possibly steric hindrance is the complicating factor. When the catalyst concentration was doubled the water was formed faster than it could be completely removed and collected so the curve was meaningless.

Compared to benzene it is seen that toluene is much more readily alkylated. Even with toluene, however, most of the alkylation with benzhydrol proceeds through intermediate ether formation. Toluene is more readily alkylated and in far better yields by either benzhydrol or benzhydryl ether (Table II) than is benzene. Dibenzyl ether alkylated either benzene or toluene at about the same rate as does benzyl alcohol. Benzhydrol and its symmetrical ether might be expected on the basis of relative ease of carbonium ion formation to alkylate toluene more rapidly than benzyl alcohol or its ether, but the converse was found to be the case if the times for complete reaction are taken as the basis of comparison.

When an attempt was made to alkylate toluene with triphenyl carbinol, there was obtained a mixture of unidentified products and only 87% of the theoretical amount of water for alkylation was produced. More work is to be done in these laboratories on these products as well as on those from the alkylation of benzene by triphenyl carbinol.

#### THE ALKYLATION OF ANISOLE BY PHENYL CARBINOLS AND THEIR SYMMETRICAL ETHERS

Since anisole has two unshared pairs of electrons on the oxygen atom it is quite different from benzene or toluene. Thus if alkylations were carried out in anisole the large



changes in catalyst activity which were found above in toluene and benzene would not be expected to occur. This was shown to be the case.

Following the standard procedure anisole was reacted with benzyl alcohol using 0.016 mole of catalyst. An 89% yield of p-benzylanisole was obtained as the only product (Table III). The reaction gave good first order data over the 30% to 80% portion; the kinetics will be discussed in more detail in the next section. The reaction temperature for this and all the other experiments listed in Table III was within the range  $157.5^{\circ} \pm 0.5^{\circ}$ .

The alkylation of anisole with dibenzyl ether proceeded smoothly to give a 97% yield of product (Table III). The rate curve (Figure IV) does not follow first order kinetics which is, perhaps, not surprising since as was pointed out in the Historical Introduction, the mechanism for alkylation with ethers may be considerably more complicated than that for alkylation with alcohols. This may mean that in those cases where the alkylation with alcohols follows first order kinetics the process does not proceed with intermediate ether formation to any significant extent. This seems reasonable since apparently an alcohol molecule and an anisole molecule are competing for the carbonium ion



and it might be expected that the ease of alkylation of

TABLE III

Alkylating Agent	Catalyst (Moles)	Half-Time (Minutes)	Yield of Water (Percent)	Yield of Product (Percent)
$C_6H_5CH_2OH$	0.016	162	100	89
$(C_6H_5CH_2)_2O$	0.064	33	100	97
$(C_6H_5)_2CHOH$	0.0005	--	93	90
$[(C_6H_5)_2CH]_2O$	0.002	63	100	85 <sup>1</sup>

1. Crude yield was 93.5%

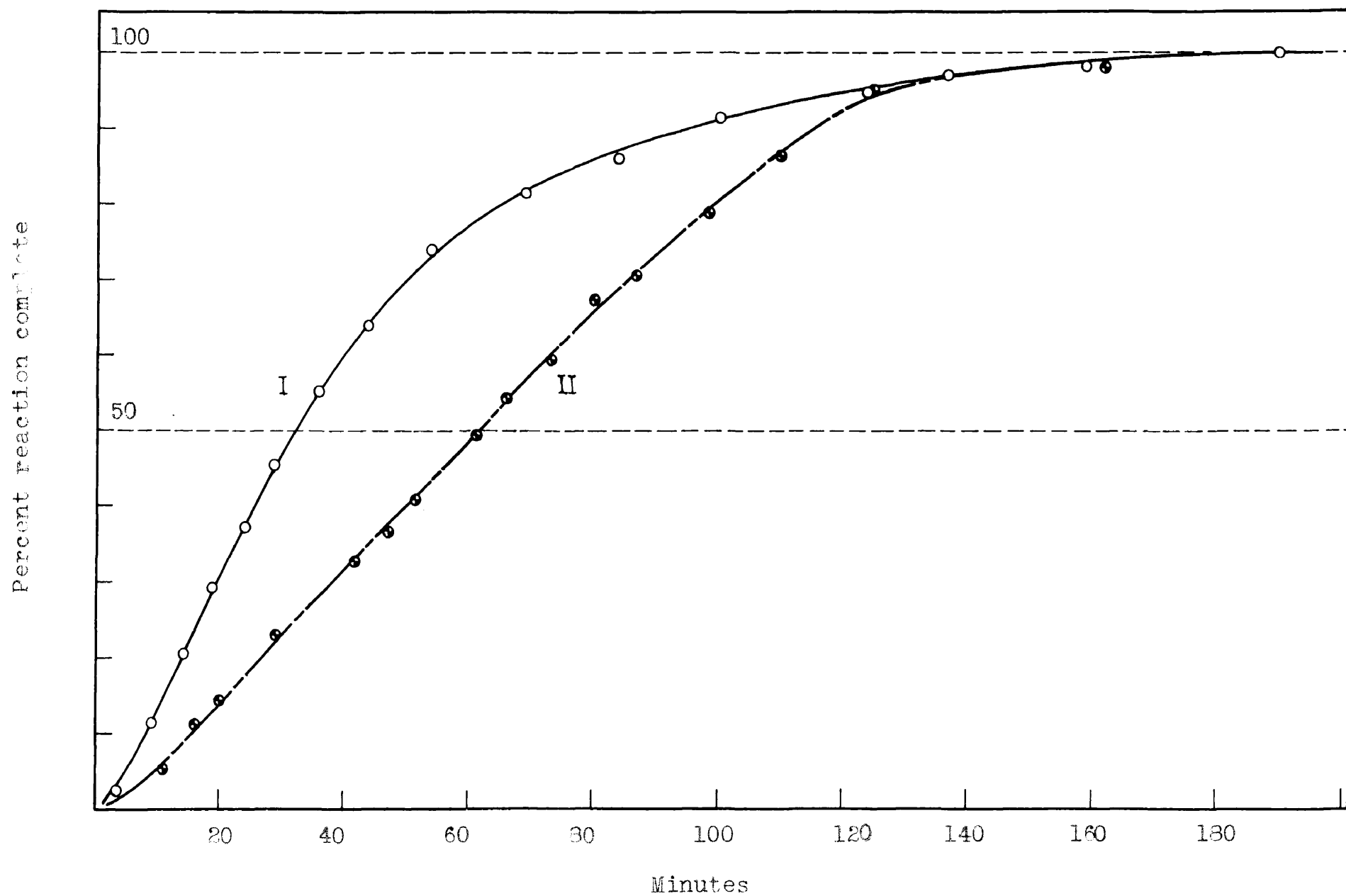


Figure IV. Alkylation of anisole. I by dibenzyl ether at catalyst conc. of 0.128 molar. II by dibenzhydriyl ether at catalyst conc. of 0.004 molar.

anisole together with the fact that the anisole is present in such large excess would cause reaction [10] to predominate over reaction [9].

When benzhydrol was reacted in this solvent in the presence of 0.0005 mole of catalyst, a 90% yield of p-methoxytriphenylmethane was obtained (Table III). The percent reaction versus time curve (Figure V) is interesting. There was a very fast reaction for the first 50% which indicated, as in the case of benzene and toluene, a rapid formation of dibenzhydryl ether. The curve then gradually increased to completion. In contrast to toluene there was no sudden increase in rate due to changes in the activity of the catalyst. This again clearly demonstrates the "leveling effect" of the anisole. As in the case of toluene there was a long reaction time required beyond the 50% point and obviously the curve does not correspond to one which would satisfy the equation for any integral order.

When anisole was alkylated with dibenzhydryl ether at four times (0.002 mole) the catalyst concentration required for benzhydrol, there was obtained a 93.5% crude yield (Table III) of the p-dibenzhydrylanisole. The reaction time required in this case was three hours while with benzhydrol the alkylation of anisole required almost twenty-five hours (See Figure IV, Curve II and see also Figure V). The rate curve has the shape of an elongated "S" which obviously does not represent a reaction of any integral order. These curves for alkylation of anisole with dibenzyl and dibenz-

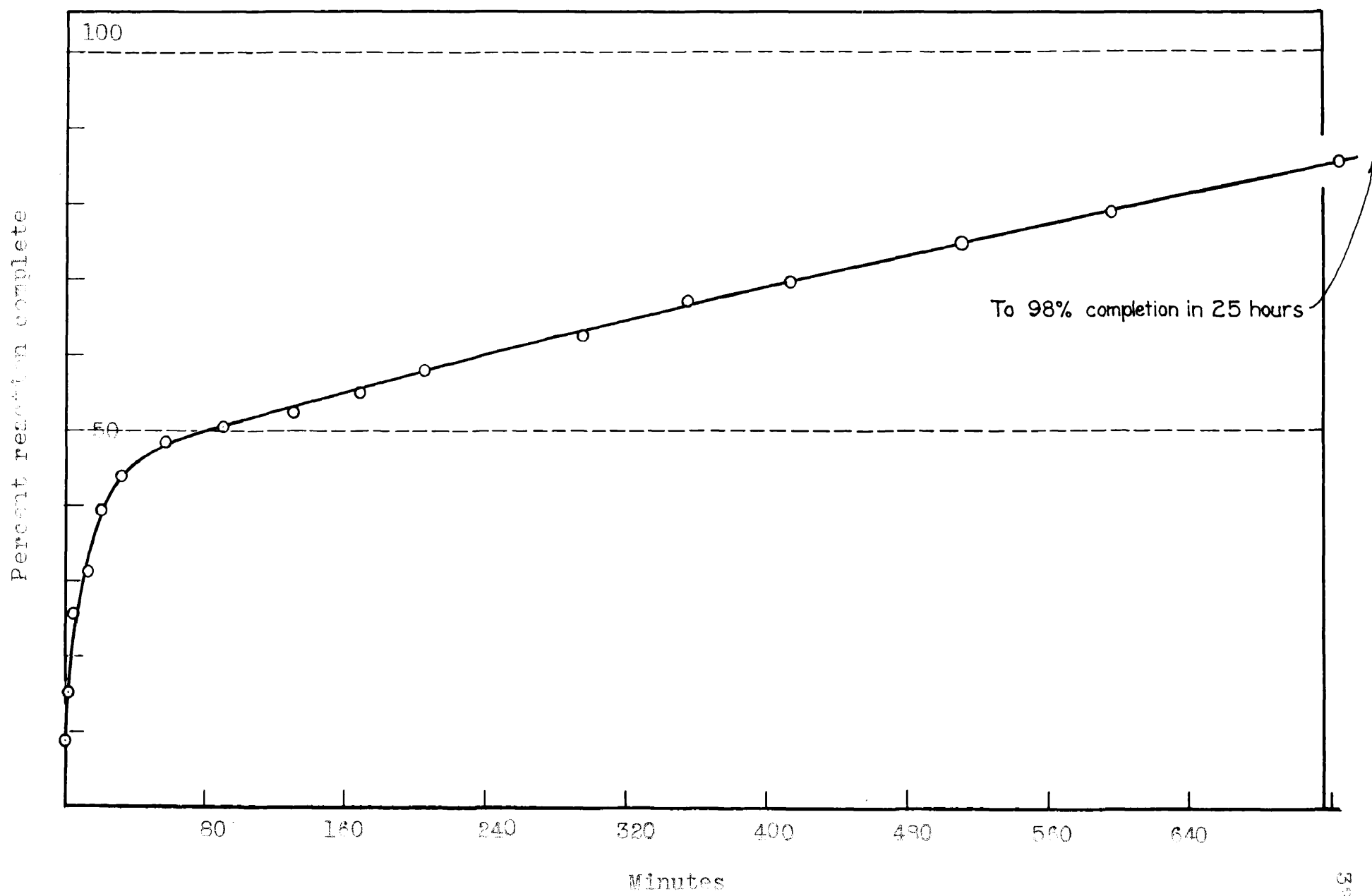


Figure V Alkylation of anisole by benzhydrol at catalyst conc. of 0.010 molar.

hydryl ethers have considerable resemblance to the curves obtained by Draper (41) for the transesterification of di-benzhydryl ether with butyl and benzyl alcohols.

It is apparent that in contrast to the experiments with benzene and toluene much lower catalyst concentrations are required for benzhydrol and its ether than for benzyl alcohol and its ether.

When an attempt was made to alkylate anisole with triphenylcarbinol there was obtained several products and further rate studies were discontinued.

The difficulties encountered in attempting to alkylate benzene, toluene, or anisole with triphenyl carbinol and the similar difficulties found in attempting to alkylate benzene with benzhydrol may be related to the poor results obtained by Draper (41) in attempting to etherify triphenyl carbinol with itself or with benzhydrol.

#### THE ALKYLATION OF ANISOLE BY PARA SUBSTITUTED BENZYL ALCOHOLS

It was of interest to determine the effect on the rate of alkylation of anisole of substituting a chlorine atom or a methyl, methoxy, or nitro group in the para position of benzyl alcohol.

The p-chlorobenzyl alcohol was the only one which could be conveniently run at the catalyst concentration used with benzyl alcohol (0.016 mole). A 91.5% yield of p-chlorophenyl-p-methoxyphenylmethane was isolated. The very satisfactory rate constants are shown in Table IV. When benzyl

alcohol was used under these conditions the average value of  $k$  was  $5.54 \times 10^{-3}$  reciprocal minutes with an average deviation of  $0.06 \times 10^{-3}$ .

All the values used in calculations were read from the experimental curve. Zero time was taken when the reaction was 15% complete in order to give the system time to establish complete equilibrium. Calculations were not extended beyond the 80% point because marked deviations appear during the last stages of the reaction.

The constant found for the *p*-chlorobenzyl alcohol run at the same catalyst concentration as with benzyl alcohol (0.016 mole), was  $2.35 \times 10^{-3}$  reciprocal minutes with an average deviation of  $0.04 \times 10^{-3}$ .

When benzyl alcohol was run at twice this catalyst concentration (Table IV), fairly satisfactory first order constants were obtained. The constant in this case was  $23.9 \times 10^{-3}$  reciprocal minutes with an average deviation of  $1.7 \times 10^{-3}$ . Thus doubling the catalyst concentration in this system increases the reaction rate by approximately four times. A similar effect in toluene was mentioned in the preceding section. In solvents of this type increasing the concentration of an acid catalyst usually produces a greater than proportional increase in the reaction rate (42). On the basis of these results with benzyl alcohol and with *p*-chlorobenzyl alcohol reaction rate constants could be predicted for the para methyl, methoxy, and nitro groups (run at the same catalyst concentration) by Hammetts method (42). The calcu-

TABLE IV

ALKYLATING AGENT	CATALYST (MOLES)	YIELD OF WATER PRODUCT (PERCENT)	YIELD OF HALF-TIME PRODUCT (MINUTES)	FIRST ORDER REACTION RATE CONSTANTS ( $\times 10^{-3} \text{ Min}^{-1}$ )							Ave. Const.
				30%	40%	50%	60%	70%	80%		
$\text{C}_2\text{H}_5\text{CH}_2\text{OH}$	0.016	100	89	164	5.49	5.50	5.45	5.51	5.65	5.60	5.54
$\text{C}_2\text{H}_5\text{CH}_2\text{OH}$	0.032	100	--	34	22.4	22.0	22.1	23.3	24.9	27.0	23.9
$p\text{-ClC}_2\text{H}_4\text{CH}_2\text{OH}$	0.016	95	92	296	2.38	2.38	2.33	2.39	2.38	2.24	2.35
$p\text{-CH}_3\text{C}_2\text{H}_4\text{CH}_2\text{OH}$	0.008	98	77	39	22.0	22.0	22.0	23.2	24.6	26.0	23.3
$p\text{-CH}_3\text{OC}_2\text{H}_4\text{CH}_2\text{OH}$	0.000125	100	85	27	26.4	26.2	26.6	26.4	24.3	21.7	25.3



lated half-time are seventy-seven, fifty-three, and nineteen hundred and twenty minutes respectively but the actual values found were far from these.

Since the alkylation with p-methylbenzyl alcohol proceeded too rapidly in the presence of 0.016 moles of catalyst to measure it was run with one-half this amount of catalyst. The half-time in this case was thirty-nine minutes. These conditions gave quite satisfactory first order constants which averaged  $23.3 \times 10^{-3}$  reciprocal minutes with an average deviation of  $1.3 \times 10^{-3}$ . This reaction gave a 77% yield of p-tolylanisole (Table IV).

It was also found that p-methoxybenzyl alcohol alkylated entirely too rapidly at this catalyst concentration. It was necessary to use only one hundredth as much catalyst (0.000125 mole) and even under these conditions the half-time was only twenty seven minutes. The first order constant is  $25.3 \times 10^{-3}$  reciprocal minutes with an average deviation of  $1.5 \times 10^{-3}$ . This reaction gave an 85% yield of di-(p-methoxyphenyl)methane. Difficulty was experienced in getting reproducible rate curves in this case for some as yet not established reason.

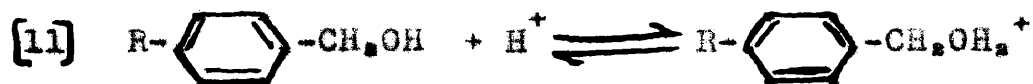
It will be noted that several of the rate constants shown in Table IV for the later stages of the reactions show an appreciable variation from those for the earlier stages. The cause of this is not yet known, but much of it may be due to unavoidable experimental errors.

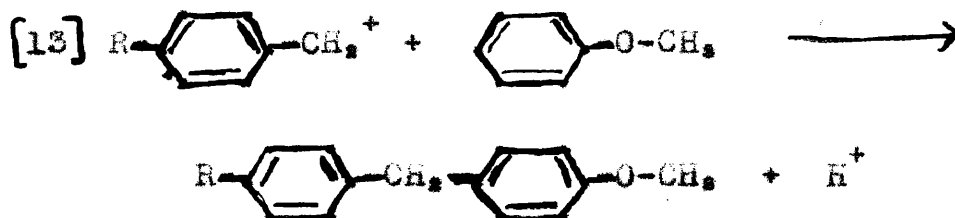
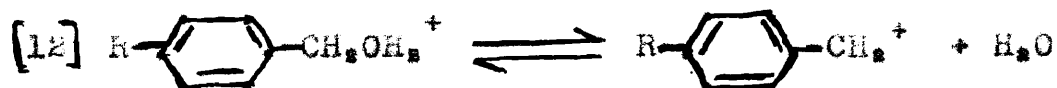
The predicted half-time for the p-nitrobenzyl alcohol

was nineteen-hundred and twenty minutes; however, the reaction would only proceed at four times the catalyst concentration required for benzyl alcohol and the half-time was three hundred minutes. The reaction mixture turned very black and gave a small yield of an unidentifiable product which did not contain nitrogen. Thus any kinetic studies would have little value.

From the study of these five systems we can see that although the results did not fit in with Hammett's theory, they do show very pointedly the effect of altering the para substituents on the rate of the reaction. When arranged in the order of decreasing rates we have:  $\text{CH}_3\text{O}-$ ,  $\text{CH}_3-$ ,  $\text{H}-$ ,  $\text{Cl}-$ ,  $\text{NO}_2-$ . Here the methoxy group has the greatest electron releasing ability so that the electrons on the hydroxylic oxygen have greater attraction for the proton of the catalyst. As a result the carbonium ion is formed more rapidly and the rate of reaction is increased. The methyl, hydrogen, and chlorine are close together but very definitely in that order as to relative electron releasing abilities which of course means the relative rate of carbonium ion formation and in turn the relative rate of alkylation.

The fact that the reaction is first order with respect to the benzyl alcohols is in agreement with the postulated mechanism:





It is apparent that either equations [11] or equation [12] could be rate controlling on the basis of these first order kinetics. A choice between these two steps cannot be definitely made but equation [12] might be expected to require the greater absorption of energy and hence it would be the favored choice.

The proton shown in equation [11] most probably actually exists in coordination with the oxygen atoms of the benzyl alcohols or with the oxygen atoms of the anisole. Since the alcoholic hydroxyls are all removed when the reaction is complete we may have significant changes in catalyst activity during about the last 10% to 20% of the reaction.

The kinetics of equation [13] is not amenable to study by this method. In order for equation [13] to be rate controlling, however, it would have to proceed at a much lower rate than the rate at which the water was found to be produced. This would require that a high concentration of the  $\text{p-RC}_6\text{H}_4\text{CH}_2^+$  ions be built up. This in itself seems unlikely since carbonium ions are in general so reactive. It would be

expected, furthermore, that when the reaction mixture is washed with water any  $p\text{-RC}_6\text{H}_4\text{CH}_2^+$  remaining would be converted back to the starting alcohol and the yield of product would be considerable lower than that actually obtained. It was hoped that it could be shown whether variations in structure of the compound to be alkylated had any effect on the rate of reaction by alkylating phenetole at a pressure reduced sufficiently to give the same reflux temperature as anisole. This was not possible because of the anomalous behavior of phenetole as described in the next section.

It is felt that this kinetics work offers considerable support for the proposed mechanism, but that further work will be required before it can be considered that the mechanism has been proved. It is planned to do further work in these laboratories in an attempt to find a suitable inert solvent for carrying out the reaction so that the effect of varying the ratio of reactants can be determined. In any case it appears that the alkylation of anisole by these various benzyl alcohols proceeds by the same mechanism and therefore the determination of their relative reactivity rests on a sound foundation.

It must be emphasized that the reaction order for the alkylation of benzene and toluene has not been determined. As mentioned above under the conditions used here toluene alkylates much more readily than benzene and hence in these cases the compound to be alkylated appears to be involved in the rate controlling step or steps.

The author wishes to thank Dr. William J. Svirbely for helpful discussions on the kinetic aspects of this investigation.

THE ALKYLATION OF PARA XYLENE,  
MESITYLENE, AND PHENETOLE BY BENZYL ALCOHOL

In order to study the scope of this method of alkylation more completely, p-xylene, mesitylene and phenetole were alkylated by benzyl alcohol.

Following the standard procedure p-xylene was alkylated by benzyl alcohol in 84% yield using 0.032 mole of catalyst (Table V). The reaction temperature in this case was  $140^{\circ} \pm 0.2$ . The half-reaction time was sixteen minutes. When this reaction was repeated at  $86^{\circ} \pm 2^{\circ}$  under 125 to 135 mm pressure, a 77% yield of benzyl-p-xylene was obtained. (See Table V). Since in this case some of the water was lost in the reduced pressure system, the rate curve is not given.

Since p-xylene has four equivalent positions for alkylation while toluene was alkylated only in the one para position, close comparison may not be justifiable. Intermediate ether formation may also be involved to different extents here. It may, nevertheless, be pointed out that in the alkylation of p-xylene at  $86^{\circ}$  the time for complete reaction was approximately the same as required for complete alkylation of toluene under the same general conditions.

The rate curve for the alkylation at atmospheric pressure had the same general shape as Curve I, Figure I. As in the case of benzene and toluene there was a definite inflection point near the 50% reaction complete point due to the change

TABLE V

ALKYLATED COMPOUND	CATALYST (MOLES)	HALF-TIME (MINUTES)	YIELD OF WATER (PERCENT)	YIELD OF PRODUCT (PERCENT)
p-Xylene	0.032	--	--- <sup>1</sup>	77
p-Xylene	0.032	16	100	84
Mesitylene	0.032	--	100	89
Phenetole	0.000	33	100	87
Phenetole	0.000125	49	100	--

1. Run at  $86^{+2}_{-2}^{\circ}$  under reduced pressure.

in catalyst activity as the benzyl alcohol was used up in the reaction.

Mesitylene was alkylated with benzyl alcohol using 0.032 mole of catalyst. The reaction temperature was  $165.5^{\circ} \pm 1.5^{\circ}$ . The reaction went so fast at this catalyst concentration that the rate measurements made had little significance. A 98% crude yield (89% pure) of the benzyl mesitylene was found (Table IV). Here the three methyl groups reinforce each other and the alkylation is there-by facilitated.

Phenetole was alkylated by benzyl alcohol in 87% yield. The half reaction time was 33 minutes (Table V). The alkylation of this particular substrate uncovered some very interesting anomalies. First the alkylation proceeded with no catalyst at all; secondly it did not give good order data as did anisole; thirdly there was a very noticable induction period with and without "catalyst"; and fourthly the addition of "catalyst" appeared to slow the reaction. There is no ready explanation for all of this and more work is to be done on this reaction in these laboratories. The curves obtained are shown on Figure VI and some data for these experiments are summarized in Table V. The reaction temperature here was  $173 \pm 0.5^{\circ}$ . It is noteworthy that even at this high temperature the water formed, condensed and collected in the liquid separator satisfactorily.

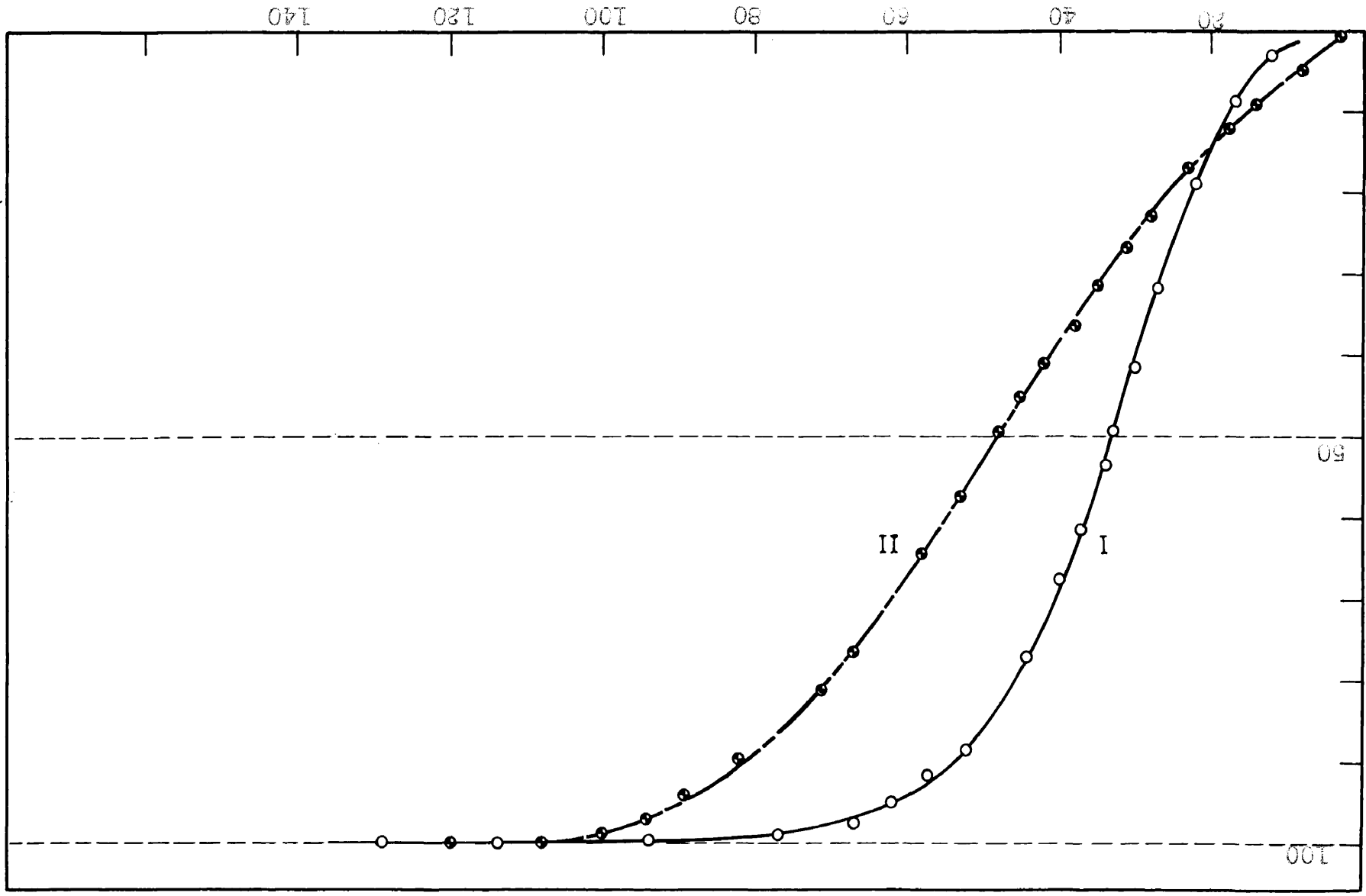


Figure VI. Alkylation of phenetole by benzyl alcohol. I with no *p*-toluene sulfonic acid present. II at *p*-toluene sulfonic acid conc. of 0.000250 molar.



EXPERIMENTAL<sup>1</sup>PRELIMINARY STUDY OF THE APPLICABILITY AND  
SCOPE OF THE AZEOTROPIC METHOD

Alkylation of phenol in benzene. One-half mole of benzyl alcohol, 0.75 mole of phenol, and 250 ml. of benzene were placed in a 500 ml. two-neck flask fitted with an automatic liquid separator which in turn held a reflux condenser. Heat was applied by a "Glas-Col" mantle and controlled by a variac. The above mixture was heated to boiling and 0.15 mole of 100% phosphoric acid was added. This mixture was refluxed for twenty-four hours at which time the water volume was constant. The solution was washed with saturated sodium bicarbonate solution and then with water until neutral. Approximately 90% of the benzene was removed by distillation at atmospheric pressure. The residue was then vacuum distilled at 20 to 30 mm pressure. A phenol fraction boiling at 85° to 87° was collected. It weighed 40.0 grams. A second fraction, collected at 1 mm pressure, boiled over a large range and weighed 46 grams. This material was washed with 20% aqueous sodium hydroxide. The non-phenolic portion proved to be benzyl alcohol and weighed 11.0 grams. The phenolic layer amounted to 34 grams and boiled at 140-148° at 1 mm pressure and was assumed to be benzyl phenol. The literature gives

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<sup>1</sup>Microanalyses were by Mrs. Mary Aldridge, Mr. Byron Baer and Miss Eleanor Werble.

the boiling point as  $143^{\circ}$  at 4 mm. pressure. This represents a 37% yield. The remaining fractions were not worked up.

The reaction was repeated in 450 ml. of benzene using 0.32 mole (8.08 g.) of p-toluene sulfonic acid monohydrate as a catalyst. The water in the catalyst was removed by preliminary refluxing. To this benzene solution was then added 0.125 mole of benzyl alcohol and 0.125 mole of phenol both dissolved in 50 ml. of benzene solution. This total mixture was then refluxed nine hours until no more water appeared in the water separator. The reaction mixture was washed with saturated aqueous sodium bicarbonate and then with water until neutral. Most of the solvent was distilled off at atmospheric pressure and the residue was distilled under vacuum. There was obtained 3.7 g. of phenol (31.4%) boiling at  $90^{\circ}$  at 22 mm. pressure. A second fraction, which boiled at  $124-125^{\circ}$  at 1.0 mm. pressure was diphenylmethane. This represented a 50% yield. A third fraction which boiled at  $191-193^{\circ}$  under the same pressure amounted to 6.5 grams (28%). This proved to be benzyl phenol. The theoretical amount of water was produced in both of these reactions.

Alkylation of anisole in toluene. When 0.5 mole of benzyl alcohol and 0.75 mole of anisole were reacted in 250 ml. of toluene using 0.15 mole of 100% phosphoric acid catalyst the theoretical volume of water was collected. Upon working up the reaction mixture in the general fashion described above, a 35% yield (34 g.) of p-benzyl anisole was found along with some p-benzyl toluene.

Alkylation of mesitylene in benzene. When 0.064 mole of p-toluenesulfonic acid monohydrate was dissolved and dehydrated in 400 ml. of benzene and 0.125 mole of mesitylene along with 0.125 mole of benzyl alcohol (both dissolved in 100 ml. of benzene solution) were added and the total solution was refluxed, the theoretical amount of water for alkylation was obtained in six hours. Upon working up as described above two fractions were obtained. One fraction boiled at 153°-154° under 25 mm. pressure. This was diphenylmethane and amounted to 11.5 g. (64%),  $n_D^{23}$  1.5706 (lit.,  $n_D^{20}$  1.5768). The second fraction (4.0 g.) boiling at 115°-116° at 1 mm. was benzylmesitylene, m.p. 34°-35° (lit., 35°-36°).

Alkylation of phenol by triphenyl carbinol in benzene. When 0.07 mole of triphenyl carbinol (m.p. 161°-162°; lit., m.p. 162.5°) was reacted with 0.20 mole of phenol in 250 ml. of benzene using 0.00025 mole of p-toluene sulfonic acid as a catalyst, a considerable quantity of solid material separated during the refluxing which was continued for twenty-four hours. Sufficient benzene to dissolve the solid was added and then the total solution was extracted with saturated aqueous sodium bicarbonate and then with water until neutral. The benzene was removed under vacuum and the residue dissolved in and recrystallized three times from 95% ethanol. The product was p-triphenylmethyl phenol and it amounted to 17.1 g. (73%); m.p. 281-282° (lit., m.p. 282°). The rate data are given below:

TIME (Min)	VOLUME H <sub>2</sub> O (ml.)	TIME (Min)	VOLUME H <sub>2</sub> O (ml.)
5	0.10	120	0.60
20	0.20	150	0.69
30	0.30	180	0.78
60	0.39	1440	0.90
90	0.49		

Alkylation of anisole by n-butyl alcohol. When 0.125 mole of n-butyl alcohol was reacted in 500 ml. of anisole solution in the presence of 0.128 mole of p-toluene sulfonic acid there was obtained 73% of the theoretical volume of water for complete alkylation. A dry ice trap was placed between the system and the atmosphere and there was condensed therein 20% of the starting butyl alcohol as butene. Upon working up the product after washing with sodium bicarbonate and then distilling, there was obtained 2.7 g. of p-n-butyl anisole, b.p. 70-72° at 1.1 mm. pressure,  $n_D^{25}$  1.5005 (lit.,  $n_D^{15}$  1.5027).

Anal. Calcd. for C<sub>11</sub>H<sub>14</sub>O: C, 80.25; H, 9.82; Found: C, 80.34; H, 9.84. There was also obtained 18.0 g. of a higher boiling fraction, b.p. 135-138° at 1.5 mm. pressure,  $n_D^{20}$  1.5089.

Anal. Found: C, 55.69; H, 6.61.

Alkylation of anisole with octanol-2. The octanol-2 used here had b.p. 177-178° at 764 mm. pressure (lit., b.p. 178°-179°). When 0.0625 mole of octanol-2 was reacted in 250 ml. of anisole solution in the presence of 0.064 mole of catalyst there was obtained upon working up, as in the case of n-butyl alcohol-anisole reaction, 10 to 12 ml. of octene,

b.p. 126-134° (lit., b.p. 123°), and no other product except anisole. The product decolorized a twelvefold volume of bromine water.

#### THE ALKYLATION OF BENZENE BY PHENYL CARBINOLS AND THEIR SYMMETRICAL ETHERS

The standard procedure described in the discussion was used for this and all subsequent experiments unless otherwise noted.

Alkylation by benzyl alcohol. The benzyl alcohol used boiled at 100° at 20 mm. pressure,  $n_D^{20}$  1.5402 (lit.,  $n_D^{20}$  1.5400). The benzene was dried by azeotropic distillation. The first 15% of the water and benzene mixture was discarded, the next 70% of the distillate was collected for use, and the last 15% discarded ( $n_D^{27}$  1.4969; lit.,  $n_D^{25}$  1.4981). For this alkylation 0.064 mole of catalyst was used. The reaction mixture was refluxed for approximately five hours and the reaction temperature was 83°±0.2°. By working up the product in the usual fashion there was obtained a 77% yield (16.2 g.) of diphenylmethane. This product boiled at 115° to 118° at 4.5 mm. pressure; f.p. 23-24°,  $n_D^{23}$  1.5764 (lit.,  $n_D^{20}$  1.5768). In the residue there was found 2.1 g. (6% to 7%) of m-dibenzyl benzene (41). The rate data for this run are given in Table VI. A repeat run gave a rate curve for which the ordinate values were always within ±0.5% of those for the original run (See Curve I of Figure I).

TABLE VI

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
10	0.17	118	1.47
15	0.26	131	1.64
20	0.34	143	1.85
25	0.41	155	1.88
35	0.57	172	1.97
40	0.65	183	2.05
55	0.84	195	2.15
70	0.97	230	2.25
85	1.13	290	2.25
100	1.27	350	2.25

Alkylation by dibenzyl ether. The dibenzyl ether had the following physical constants: b.p. 159-160° at 11 mm. pressure (lit., b.p. 160° at 11 mm pressure),  $n_D^{25}$  1.5592 (lit.,  $n_D^{25}$  1.5597). When 0.0625 mole of dibenzyl ether was refluxed with 0.064 mole of catalyst the following rate data were found (The product was not isolated (41)): (See Curve II of Figure I)

TABLE VII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
8	0.05	91	0.74
17	0.14	104	0.83
28	0.24	120	0.91
37	0.29	132	0.95
48	0.36	150	1.03
63	0.46	164	1.05
74	0.60	177	1.06
76	0.62	199	1.12
86	0.72	250	1.13

Alkylation by benzhydrol. The benzhydrol melted at 66-67° (lit., m.p. 67-68°). Here 0.064 mole of catalyst was used; only 71% of the theoretical water for alkylation was obtained when the reaction stopped after twelve hours

of refluxing. The rate data are given in Table VIII. Upon working up the product, there was obtained 2.7 g. (3.9%) of triphenylmethane; b.p. 123-126° at 2 mm. pressure; crystallization twice from 95% ethanol gave m.p. 95.5-96° (lit., m.p. 93-94°). There was also found 1.3 g. (55%) of dibenzhydryl ether (crystallized three times from 95% ethanol) m.p. 103-109° (lit., m.p. 109-110°).

TABLE VIII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
5	0.69	45	1.49
10	1.09	70	1.54
15	1.28	109	1.57
20	1.34	293	1.59
30	1.44	533	1.59

When the reaction was repeated using one-half this concentration of benzhydrol (0.0625 mole) and using twice as much catalyst (0.128 mole) there was found a 19% yield of triphenylmethane. By crystallizing the residues from 95% ethanol a 50% yield of dibenzyl ether was isolated. A third run (standard procedure) using 0.256 mole of catalyst gave 15.8 g. (52%) of triphenylmethane (See Table I). (See Table IX for rate data). By adding acetone to the residue from the distillation and allowing the solution to stand for several days there was obtained 1.3 g. (4%) of *p*-dibenzhydryl benzene, m.p. 167-169°. (lit., m.p. 170-171°). There was no dibenzhydryl ether isolated from this reaction.

TABLE IX

Time (Min.)	Volume (H <sub>2</sub> O ml.)	Time (Min.)	Volume (H <sub>2</sub> O ml.)
5	0.02	40	1.40
10	0.15	46	1.50
15	0.49	55	1.60
18	0.68	70	1.70
20	0.79	100	1.80
22	0.91	120	1.82
25	1.00	240	1.89
30	1.17	270	1.90
35	1.29	1170	1.90

Alkylation by dibenzhydryl ether. The ether used melted at 109.5-110.5° (lit., m.p. 109-110°). It was reacted with benzene in the presence of 0.128 mole of catalyst. Only 76% of the theoretical amount of water for alkylation was collected. After recrystallizing the crude distillate a 54% yield of triphenylmethane was obtained (m.p. 92°-93°). By working the residue as in the above run with benzhydryl there was obtained 2.0 g. (5.2%) of p-dibenzhydryl benzene, m.p. 167-169°.

TABLE X

Time (Min.)	Volume (H <sub>2</sub> O ml.)	Time (Min.)	Volume (H <sub>2</sub> O ml.)
5	0.20	20	0.68
7	0.30	30	0.77
10	0.43	45	0.79
12	0.49	135	0.80
15	0.58	1155	0.87

#### THE ALKYLATION OF TOLUENE BY PHENYL CARBINOLS AND THEIR SYMMETRICAL ETHERS

Alkylation by benzyl alcohol. The toluene was azeotropically dried by exactly the same procedure as was des-



cribed for benzene ( $n_D^{27}$  1.4926; lit.,  $n_D^{25}$  1.4939). The benzyl alcohol was reacted in toluene with 0.032 mole of catalyst to give a 90% yield of p-benzyltoluene; b.p. 157-158° at 22 mm pressure,  $n_D^{20}$  1.5686, (lit.,  $n_D^{15}$  1.5692). The reaction temperature of all toluene runs was 113° $\pm$ 0.5° unless otherwise noted. The rate data are given in Table XI. (See Table II and Curve I of Figure II). A repeat run gave a curve for which the ordinate values were always within  $\pm 0.5\%$  of those for the original run.

TABLE XI

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
5	0.06	100	1.31
10	0.20	110	1.47
15	0.30	120	1.60
20	0.39	130	1.80
25	0.45	135	1.90
35	0.60	140	1.98
50	0.76	160	2.11
60	0.89	175	2.19
70	0.99	190	2.24
85	1.12	250	2.26
95	1.24		

Benzyl alcohol was also run in toluene using 0.064 mole of catalyst (See Curve III of Figure II). The product was not isolated but the rate data are given in Table XII. Possibly this reaction went too fast for high accuracy, but a smooth curve was obtained.

TABLE XII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
3	0.31	16	1.62
5	0.50	17	1.71
6	0.60	18	1.81
7	0.71	19	1.91
8	0.82	20	1.93
9	0.92	22	2.02
10	1.02	25	2.05
11	1.10	30	2.12
12	1.21	40	2.19
13	1.32	50	2.22
14	1.41	100	2.24
15	1.52	150	2.25

Benzyl alcohol was also run in toluene under reduced pressure in the presence of 0.064 mole of catalyst. Here the water separator was replaced by a two foot asbestos wrapped tube (1 cm. i.d.) fitted with a female ball joint. To this was fitted one end of an arch shaped tube eight inches wide fitted with male ball joints. This was connected at the other end to the top of a condenser. The lower end of the condenser entered a water separator which returned the toluene to the reaction mixture through the second neck. Between this circulating system and an oil pump was placed in sequence from the pump, a dry ice trap, manometer, and a five liter flask to serve as a reservoir in order to smooth out fluctuations in the pressure. A 92% yield of p-benzyltoluene was obtained;  $n_D^{26}$  1.5690 (lit.,  $n_D^{21}$  1.5711). The rate data is given in Table XIII, (See Curve II of Figure II).

TABLE XIII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
5	0.19	65	1.95
10	0.32	75	2.05
20	0.50	90	2.10
25	0.60	95	2.15
35	0.95	100	2.18
45	1.20	110	2.20
50	1.48	125	2.22
60	1.82	155	2.22

Alkylation by dibenzyl ether. When this ether was reacted with toluene using 0.032 mole of catalyst following the standard procedure, a 90% yield of p-benzyltoluene was obtained; b.p. 109-111° at 1.2 mm. pressure. The rate data are given in Table XIV. (See Table II). A repeat run gave a curve for which the ordinate values were always within  $\pm 2\%$  of those for the original run.

TABLE XIV

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
20	0.05	121	0.82
37	0.20	136	0.90
49	0.30	151	0.95
54	0.36	166	1.00
69	0.43	181	1.04
81	0.53	201	1.09
91	0.62	216	1.11
101	0.71	231	1.12
111	0.79	251	1.12

Alkylation by benzhydrol. When benzhydrol was used with 0.0064 mole of catalyst, only half of the theoretical water for alkylation was obtained; this indicating ether formation. At this point there was added 0.064 mole more of

the catalyst and the reflux was continued until no more water separated. This took only ten to fifteen minutes. Upon distillation 23.5 g. of p-benzhydryl toluene was obtained. This represents an 89% yield of material boiling at 193-194° at 2 mm. pressure. This solidified and was recrystallized from 95% ethanol to give a product of m.p. 70-71°, (lit., m.p. 70-71°). When this experiment was repeated in the presence of 0.016 mole of catalyst there was found one to two grams of the above alkylated product and 20 g. of dibenzhydryl ether, m.p. 109-111°, (lit., 109-110°). A third run with 0.032 mole of catalyst gave a 90% yield of the same para substituted toluene. The rate data for these last two runs are given in Table XV and XVI respectively (See also Table II).

TABLE XV

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
3	0.68
8	1.16
13	1.20
28	1.27
88	1.29
238	1.33
538	1.33

TABLE XVI

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
5	0.27
15	1.37
25	1.47
55	1.59
310	1.63
445	1.67
1880	2.20
2720	2.26

Alkylation by dibenzhydrylether. This ether was reacted with toluene in the presence of 0.032 mole of catalyst to give a 90% yield of p-benzhydryl toluene, m.p. 70-71°. The rate data are given in Table XVII. (See also Table II). This rate curve is plotted in Figure III. A repeat run gave a rate curve for which the ordinate values were always within ±1% of those for the original run.

TABLE XVII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
3	0.12	640	0.69
5	0.21	745	0.76
10	0.27	760	0.81
25	0.35	805	0.84
40	0.38	820	0.87
130	0.41	845	0.94
190	0.42	860	1.01
280	0.44	875	1.06
330	0.50	895	1.09
440	0.53	910	1.10
480	0.57	980	1.12
580	0.63		

Alkylation by triphenylcarbinol. The triphenyl carbinol used had a m.p. of 161-162°, (lit., m.p. 162.5°). When this carbinol was reacted with toluene in the presence of 0.016 mole of catalyst following the aforementioned procedure, there was obtained a fraction boiling at 170-189° at 2.5 mm. pressure. A second fraction boiling at 193-220° at this pressure and a third fraction boiling at 220-224° were obtained. Attempts at recrystallization were unsuccessful. Further work with triphenyl carbinol and toluene was abandoned. The rate data found are given in Table XVIII.

TABLE XVIII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
20	0.16	135	1.68
35	0.38	145	1.68
40	0.46	155	1.77
45	0.55	165	1.83
50	0.64	205	1.90
65	0.86	295	1.97
75	0.96	325	1.97
95	1.16	715	1.97
106	1.33	1435	1.97
125	1.48		

THE ALKYLATION OF ANISOLE BY PHENYL CARBINOLS  
AND THEIR SYMMETRICAL ETHERS

Alkylation by benzyl alcohol. The anisole used in all cases was freshly distilled b.p. 153-154°, (lit., 153-154°);  $n_D^{24}$  1.5176 (lit.,  $n_D^{20}$  1.5179). The anisole was alkylated by benzyl alcohol in the presence of 0.016 mole of catalyst to give an 89% yield of p-benzyl anisole (See Table III) b.p. 121-123° at 1.5 mm pressure,  $n_D^{28}$  1.5723; the reaction temperature was 157.5°±0.5°.

Anal. Calcd. for  $C_{11}H_{14}O$ : C, 84.81; H, 7.12. Found: C, 84.70; H, 7.45.

First order constants calculated from the data in Table XIX are given in Table IV. A repeat run gave a curve for which the ordinate values were always within ±1% of those for the original run.

TABLE XIX

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
10	0.05	120	0.99	231	1.73
25	0.14	135	1.09	340	1.89
35	0.24	150	1.18	380	1.97
60	0.47	165	1.29	420	2.00
65	0.52	185	1.38	520	2.10
73	0.60	211	1.50	620	2.16
83	0.72	241	1.61	800	2.20
101	0.83	251	1.67	1460	2.25

Alkylation by dibenzyl ether. This ether was condensed with anisole in the presence of 0.064 mole of catalyst. There was obtained 24.0 grams (97%) of p-benzyl anisole, b.p. 128°-130° at 2 mm pressure. The rate data are given in Table XX. A repeat run gave a rate curve for which the ordinate values

were always within  $\pm 2\%$  of those for the original run.

TABLE XX

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
3	0.03	29	0.51	84	0.97
8	0.12	38	0.63	100	1.03
14	0.23	44	0.72	124	1.06
19	0.33	54	0.82	159	1.11
24	0.42	69	0.92	190	1.12

Alkylation by benzhydrol. This alcohol was reacted in the presence of 0.0005 mole of catalyst in the standard procedure to give a 96% (33 g.) crude yield of p-benzhydryl anisole, b.p. 230-245° at 10 mm pressure. Upon recrystallization twice from 95% ethanol, there was obtained a 90% yield (30 g.) m.p. 62-63°, (lit., m.p. 64-65°) (See Table III). The rate data are given in Table XXI. A repeat run gave a curve for which the ordinate values were always within  $\pm 0.5\%$  of those for the original run.

TABLE XXI

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
5	0.29	99	1.09	415	1.56
10	0.50	130	1.11	480	1.66
15	0.69	165	1.18	540	1.75
20	0.79	265	1.22	655	1.89
31	0.89	220	1.28	715	1.98
42	0.97	265	1.31	765	2.02
52	0.99	280	1.38	790	2.04
77	1.06	340	1.47	1495	2.20

Alkylation by dibenzhydryl ether. This ether was reacted with anisole in the presence of 0.002 mole of the catalyst to give an 85% yield of p-benzhydryl anisole, m.p. 62-63°. The rate data are given in Table XXII. A repeat run gave a rate curve for which the ordinate values were always within

$\pm 0.8\%$  of those for the original run.

TABLE XXII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
5	0.01	42	0.37	80	0.75
11	0.06	47	0.41	98	0.89
16	0.13	51	0.46	110	0.97
20	0.16	61	0.56	125	1.07
29	0.26	66	0.61	162	1.10
37	0.35	73	0.67	190	1.11

Alkylation by triphenylcarbinol. This alcohol was reacted in anisole in the presence of 0.008 mole of catalyst. Upon working up the reaction mixture there was obtained several fractions and further work on this reaction was discontinued. The rate data are given in Table XXIII.

TABLE XXIII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
22	0.17	99	1.36	162	1.98
47	0.62	109	1.45	178	2.02
52	0.72	114	1.55	192	2.04
62	0.87	127	1.65	290	2.06
72	1.07	142	1.77	350	2.09
87	1.17	152	1.90	410	2.09

#### THE ALKYLATION OF ANISOLE BY PARA SUBSTITUTED BENZYL ALCOHOLS

The para chloro-, methoxy-, methyl-, and nitrobenzyl alcohols were each condensed with anisole according to the standard procedure. The kinetic data, moles of catalyst, and percent yield are given in the discussion (See Table IV). The physical data of both starting material and product as well as analyses for new products are summarized in Table XXIV. In Table XXV are given the observed rate data. Repeat runs for



TABLE XXIV

ALKYLATING AGENT	PHYSICAL CONSTANTS OF THE ALKYLATING AGENT	PHYSICAL CONSTANTS OF THE PRODUCT	ANALYSIS
p-Cl C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	m.p. 70-71° (lit., m.p. 70-71°)	b.p. 170-175° at 5 mm pressure n <sub>D</sub> <sup>25</sup> 1.5820	Calcd. for C <sub>11</sub> H <sub>11</sub> ClO: C, 72.26; H, 5.26. Found: C, 72.26; H, 5.71
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	b.p. 107-8° at 1.5 mm pressure n <sub>D</sub> <sup>25</sup> 1.5414 (lit., n <sub>D</sub> <sup>25</sup> 1.5422)	b.p. 166-167° at 0.9 mm pressure m.p. 49.5- 50.5° (lit., m.p. 50- 51°) (from 95% etha- nol)	
p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	m.p. 59-60° (lit., m.p. 59-60°)	b.p. 140-143° at 2.7 mm pressure n <sub>D</sub> <sup>25</sup> 1.5671	Calcd for C <sub>11</sub> H <sub>12</sub> O: C, 84.86; H, 7.60. Found: C, 84.85; H, 7.68
p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH	m.p. 97-98° (lit., m.p. 93-94°)	b.p. 109-111° at 0.5 mm pressure n <sub>D</sub> <sup>25</sup> 1.5219	Calcd for C <sub>11</sub> H <sub>10</sub> O <sub>2</sub> N: C, 69.14; H, 5.35. Found: C, 53.44; H, 5.73

1. Contained no nitrogen

TABLE XXV

(p-CH <sub>3</sub> O-)		(p-Cl-)		(p-CH <sub>3</sub> -)		(p-NO <sub>2</sub> -)	
Min.	Ml.-H <sub>2</sub> O	Min.	Ml.-H <sub>2</sub> O	Min.	Ml.-H <sub>2</sub> O	Min.	Ml.-H <sub>2</sub> O
5	0.19	20	0.07	5	0.07	10	0.08
9	0.38	40	0.14	10	0.17	20	0.10
13	0.59	60	0.20	12	0.20	50	0.16
17	0.76	80	0.29	14	0.36	80	0.22
20	0.88	110	0.46	17	0.47	125	0.36
23	0.99	130	0.54	21	0.58	200	0.47
26	1.10	150	0.62	24	0.68	245	0.51
29	1.19	170	0.70	25	0.72	320	0.59
34	1.31	200	0.81	28	0.85	410	0.65
39	1.40	230	0.91	33	0.98	530	0.72
44	1.48	260	1.00	37	1.07	590	0.78
50	1.54	305	1.13	40	1.17	650	0.80
60	1.68	335	1.22	43	1.27	1310	0.96
70	1.76	380	1.31	46	1.36	1370	0.99
80	1.80	450	1.48	50	1.42	1440	1.00
90	1.87	530	1.59	55	1.56	1620	1.02
105	1.91	620	1.69	62	1.67	2790	1.20
120	2.00	730	1.79	65	1.74		
155	2.10	825	1.87	75	1.87		
195	2.17	860	1.89	85	1.97		
235	2.20	1010	1.94	95	2.03		
265	2.22	1105	1.99	115	2.11		
		1345	2.00	130	2.13		

the p-chlorobenzyl alcohol gave a rate curve for which the ordinate values were always within  $\pm 0.2\%$  of those for the original run while a repeat run for the p-methylbenzyl alcohol gave a rate curve for which the ordinate values were within  $\pm 0.5\%$  of those for the original run. The reaction temperature in all of these runs was  $157.5^\circ \pm 0.5^\circ$ .

In Table XXVI are given the kinetic data which were obtained from the alkylation of anisole by benzyl alcohol in the presence of 0.032 mole of catalyst (See also Table IV).

TABLE XXVI

Min.	Ml. H <sub>2</sub> O	Min.	Ml. H <sub>2</sub> O	Min.	Ml. H <sub>2</sub> O
4	0.07	26	0.90	53	1.61
7	0.25	28	0.95	60	1.77
10	0.36	31	1.02	63	1.80
13	0.48	33	1.10	68	1.90
15	0.51	36	1.20	77	2.00
18	0.66	38	1.25	82	2.06
20	0.70	41	1.33	87	2.10
22	0.79	44	1.40	99	2.16
123	0.80	48	1.50	112	2.22

THE ALKYLATION OF PARA XYLENE,  
MESITYLENE, AND PHENETOLE BY BENZYL ALCOHOL

Alkylation of p-xylene. The xylene used had b.p. 136-137°, (lit., b.p. 138.5°) It was alkylated by benzyl alcohol in the presence of 0.032 mole of catalyst to give an 84% yield of benzyl xylene, b.p. 124-125° at 1 mm pressure  $n_D^{22}$  1.5694.

Anal. Calcd. for C<sub>11</sub>H<sub>14</sub>: C, 91.84; H, 8.16. Found: C, 91.91; H, 8.30.

The reaction temperature was 140°±0.1° (See Table V)  
The rate data for this run are given in Table XXVII

TABLE XXVII

TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)	TIME (Min.)	VOLUME (H <sub>2</sub> O ml.)
1	0.15	14	1.00	28	1.91
2	0.29	16	1.13	30	2.00
4	0.41	18	1.27	35	2.09
6	0.54	20	1.39	40	2.14
8	0.69	22	1.51	50	2.20
10	0.79	24	1.68	60	2.22
12	0.86	26	1.81	75	2.22

This reaction was repeated at 85-86° using the previously mentioned reduced pressure system. The pressure required was 125-135 mm. Since water was lost in the system there was no measure of the rate. It took approximately three hours for complete reaction. This gave a 77% yield, b.p. 165-168° at 24 mm pressure,  $n_D^{20}$  1.5710 (See Table V).

Alkylation of mesitylene. Mesitylene was alkylated with benzyl alcohol using 0.032 mole of catalyst to give 12.8 g. (98% crude yield) of product, b.p. 126-127° at 5 mm. pressure. The reaction temperature was 165.5°±1.5°. Upon recrystallization from 95% ethanol there was obtained an 89% (11.6 g.) yield of benzyl mesitylene, m.p. 34-35° (lit., m.p. 36-37°).

Alkylation of phenetole. This aromatic ether was alkylated in usual manner with benzyl alcohol but using no catalyst. There was obtained 23 grams (87%), (The reaction temperature was 173°±0.5°), p-benzyl phenetole, b.p. 126° at 1.5 mm pressure,  $n_D^{24}$  1.5654.

Anal. Calcd. for  $C_{11}H_{12}O$ : C, 84.86; H, 7.60. Found: C, 84.81; H, 7.61.

The rate data are given in Table XXVIII. In Table XXIX there are given the kinetic data for the run made using 0.000125 mole of catalyst. A repeat run gave a rate curve for which the ordinate values were always within ±4% of those for the original run.

TABLE XXVIII

TIME (MIN.)	VOLUME (H <sub>2</sub> O ml.)	TIME (MIN.)	VOLUME (H <sub>2</sub> O ml.)
12	0.07	42	1.61
17	0.20	44	1.72
22	0.42	47	1.85
27	0.71	52	1.98
30	0.93	57	2.05
32	1.02	62	2.12
33	1.10	67	2.19
34	1.20	77	2.21
36	1.29	111	2.25
37	1.36	160	2.25
40	1.52		

TABLE XXIX

TIME (MIN.)	VOLUME (H <sub>2</sub> O ml.)	TIME (MIN.)	VOLUME (H <sub>2</sub> O ml.)
4	0.03	45	1.01
5	0.07	48	1.11
6	0.10	53	1.29
8	0.11	58	1.44
14	0.20	67	1.71
18	0.27	71	1.81
21	0.31	76	1.91
23	0.38	82	2.01
28	0.50	89	2.11
31	0.60	94	2.17
35	0.71	100	2.21
36	0.81	113	2.25
42	0.91		

## PART II

ALKYLATION BY  $\alpha$ -CHLOROETHYL METHYL ETHERHISTORICAL INTRODUCTION

It was the objective of this investigation to study the  $\alpha$ -chloroethylation of aromatic nuclei using  $\alpha$ -chloroethyl methyl ether. By carrying out the chloroethylation with this chloroether it was hoped that the use of strong acid catalysts could be avoided and consequently the formation of the unsymmetrical diaryl ethanes and resinous by-product could be decreased; in the analogous reaction with chloromethyl ether no strong acid catalyst is required (43).

The  $\alpha$ -chloroethylation of many aromatic nuclei has been reported in the literature (4), (5), (43). In all of these cases some form of acetaldehyde and an acid catalyst was used (44)-(49). Quelet reacted anisole, paraldehyde, and hydrogen chloride at 5°, using anhydrous zinc chloride as the catalyst, to give a 50% yield of the p- $\alpha$ -chloroethyl anisole. He reported that a large proportion of the by-product 1-di-(p-methoxyphenyl)ethane was formed (44). The  $\alpha$ -chloro derivative dehydrohalogenated upon vacuum distillation to give the corresponding p-vinyl anisole. Various cresols when reacted under these conditions gave 40% to 60% yields of the vinyl derivatives (45), (46). Homologues of anisole have also been reacted to give similar yields of the p-vinyl compounds (49). Anisole has also been  $\alpha$ -chloropropy-

lated and  $\alpha$ -chlorobutylated by this procedure using respectively propionaldehyde and butyraldehyde in place of paraldehyde. These yields were reported to be around 30% (47), (48), (49). Phosphoric acid has also been used as a catalyst in these condensations (48), (49). Recent workers have reported reactions of various cresols by this procedure to give the corresponding styrenes (50).

Chloroethylation via acetaldehyde or its homologues has proved to be more limited in scope than chloromethylation by the Blanc and related methods (43). The attempted  $\alpha$ -chloroethylation of o-, m-, and p-chloroanisole; m-, and p-bromoanisole; dimethylaniline; and p-dimethoxybenzene was unsuccessful (50). The following styrenes have been prepared in 34% to 49% yields by this method: 4-methoxy-3-methylstyrene, 2-methoxy-5-methylstyrene, and 5-isopropyl-4-methoxy-2-methylstyrene.

Chloromethyl ether has been used to chloromethylate aromatic rings in good yields (51)-(54). Vavon, Bolle, and Calin (55) were able to introduce the chloromethyl group by using chloromethyl ether in acetic acid as the solvent without any strong acid catalysts. They followed the reaction by hydrolyzing the remaining chloromethyl ether and titrating the free hydrochloric acid. The rate, as would be expected, varied greatly as the groups substituted on the aromatic ring were varied (43). Alkyl and alkoxy groups facilitated the condensation, while halogen atoms, and halomethyl and carboxylic groups inhibited it. Vavon, Bolle, and Calin

give the following order of decreasing reactivity of the substrates: anisole, mesitylene, m-xylene, toluene, benzene, nitrobenzene. It was found that bromomethyl ether reacted ten times faster than the chloromethyl ether. Variations of the solvents produced variations of the reaction rate; nitrobenzene, sym-tetrachloroethane, and 1,2-dichloroethane gave slow rate of reaction where as might have been predicted 30% formic acid in acetic acid or dichloroacetic acid gave a much increased rate of reaction (58).

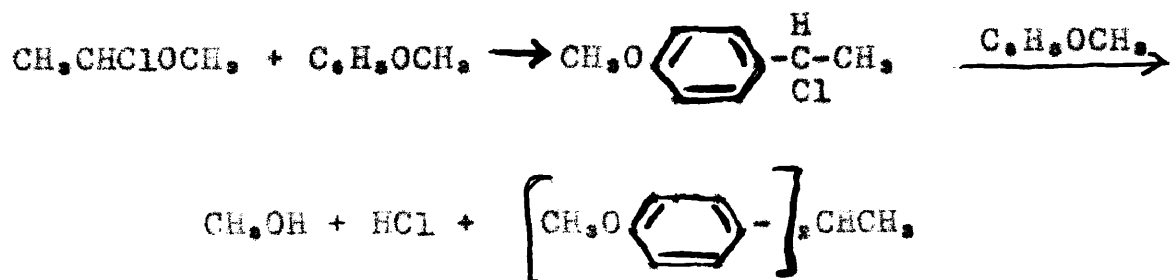


## DISCUSSION

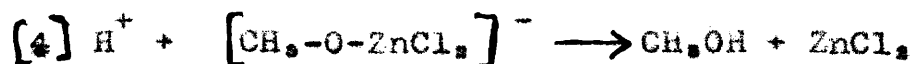
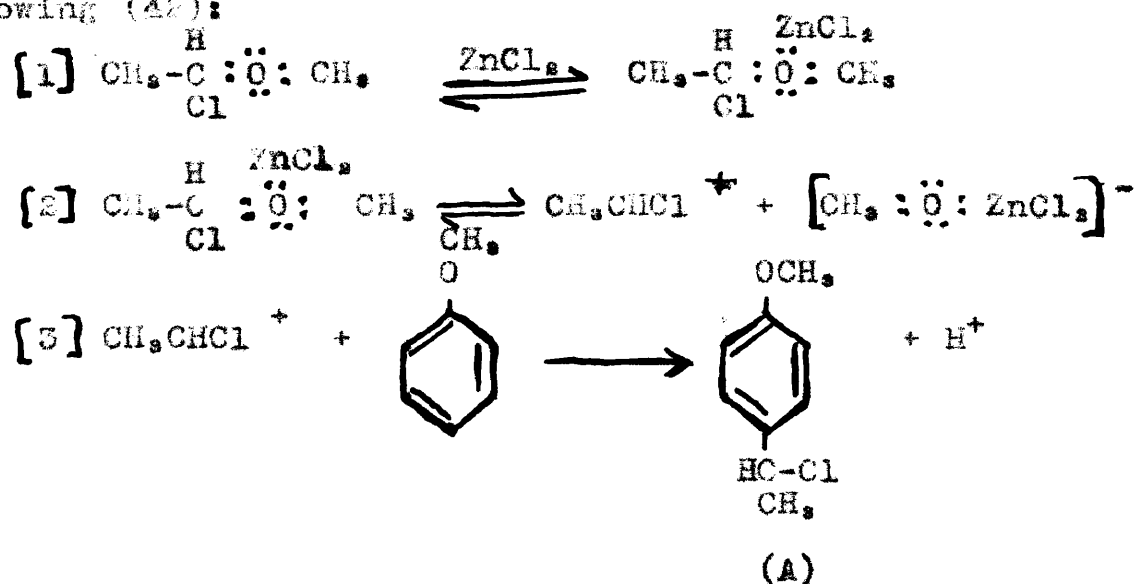
When benzene, toluene, or mesitylene was treated at 0° to 15° with  $\alpha$ -chloroethyl methyl ether in the absence of a catalyst, the starting materials were recovered quantitatively. There was no reaction even with anisole in the presence of glacial acetic acid; under these conditions the chloromethyl ether reacted readily (55).

A preliminary study of possible catalysts showed that many of them dehydrohalogenated and polymerized the chloro-ether. A semi-quantitative study of this dehydrohalogenation at 0° showed that the activity decreased in the following order: stannic chloride, aluminum chloride, aluminum bromide, sulfuric acid, phosphorous pentoxide, zinc chloride, 100% phosphoric acid. The last two catalysts were the only ones which did not convert the chloro-ether to a black tar almost immediately (57). The stannic chloride reacted with almost explosive violence.

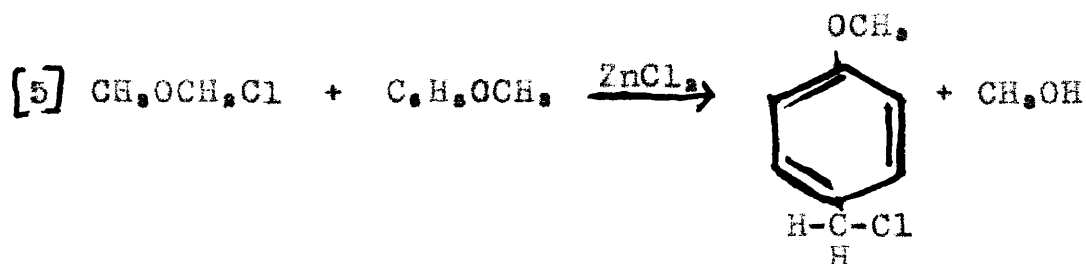
Phosphoric acid was ineffective as a catalyst for the condensation of anisole and the chloro-ether, but zinc chloride was quite active. The chief product was the unsymmetrically disubstituted ethane, however, instead of the intermediate chloroethylated compound. A 67% yield of this ethane was obtained when equimolecular amounts of anisole and  $\alpha$ -chloroethyl methyl ether were reacted at 0 to +5° and the same yield resulted when the proportion of anisole was doubled.



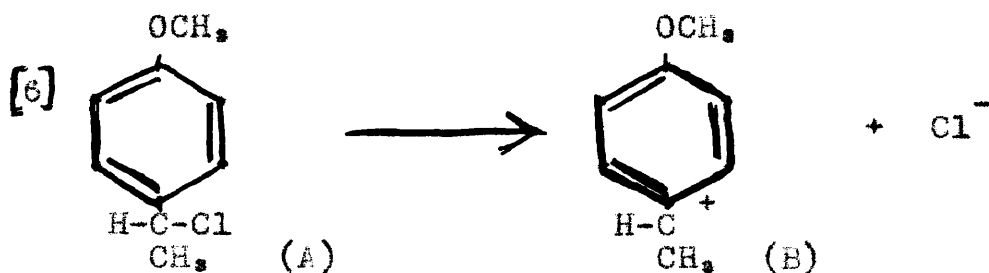
None of the intermediate p- $\alpha$ -chloroethyl anisole was isolated in either case. When this reaction was allowed to proceed for only one-third of the reaction time of the above condensation, there was obtained a 15% yield of the disubstituted ethane as the only product. A reasonable mechanism is the following (48):



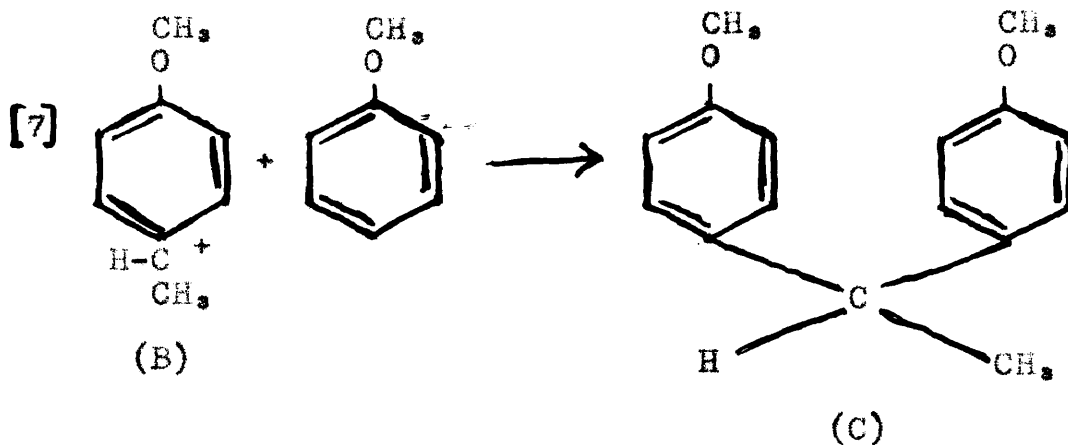
The compound (A) is the expected  $\alpha$ -chloroethyl derivative reported by other workers (49). When compared to the chloromethyl derivative prepared via the monochloromethyl ether (51), the essential difference is the presence of the methyl group in place of a hydrogen atom.



The fact that this methyl group has a greater tendency to release electrons than the hydrogen atom facilitates the conversion of (A) to (B).



The natural consequence is that conversion of (A) to (C) will more readily occur. This is shown in equation [7].





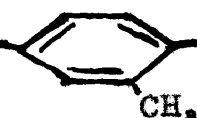
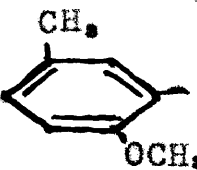
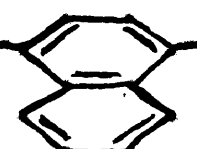
Several other phenolic ethers were condensed with the  $\alpha$ -chloroethylmethyl ether in a similar fashion. These results are summarized in Table XXX. A 55% yield was obtained in the condensation with phenetole. The p-cresylmethyl ether

gave a 62% yield while the m-cresyl ether gave only a 19% yield of its diarylethane derivative. A very small yield of crystalline product was obtained when the condensation was run with  $\alpha$ -naphthyl methyl ether. The few crystals separated out of a black tarry mass after standing for several weeks in the refrigerator.

The structures proposed in Table XXX are based upon information and analogues in the literature. The product from anisole has been previously prepared by related methods and its structure established (50), (58). p-Methyl anisole would be expected to alkylate ortho to the methoxy group and the corresponding chloromethyl and chloroethyl compounds have been prepared (45), (49), (50). The crystalline product obtained in this investigation was prepared as a liquid by Meldrum and Lonkar (62) by condensation of p-methyl anisole with chloral followed by hydrogenation. The other three compounds are new. Phenetole would be expected to react like anisole especially since the chloromethylation of phenetole occurs chiefly at the para position (54). The structure proposed for the product from m-methyl anisole is based upon the closely related chloroethyl and chloromethyl compounds prepared by Quelet (45), (49). The para alkylation of  $\alpha$ -naphthyl methyl ether is proposed since para substitution predominates with the monocyclic ethers. It is not improbable, however, that both ortho and para substitution occurred, for only a small fraction of the total crude product was obtained as crystals.

TABLE XXX

R,CHCH<sub>3</sub> COMPOUNDS PREPARED

R	Yield, %	M.P., °C. <sup>a</sup>	Analyses <sup>b</sup>			
			Calculated		Found	
			C	H	C	H
CH <sub>3</sub> O- 	67	71.2-71.5	79.31	7.49	79.40	7.82
C <sub>2</sub> H <sub>5</sub> O- 	55	30.9-32.4	79.96	8.02	79.92	8.26
CH <sub>3</sub> O- 	20	Below 25	79.96	8.02	79.69	8.06
	70	39.4-39.9	79.96	8.02	79.75	8.06
CH <sub>3</sub> O- 	-- <sup>c</sup>	126.8-128.3	84.18	6.48	84.41	6.49

a All melting points corrected.

b Microanalyses by Eleanor Werble.

c Only a small amount of solid crystallized from crude product corresponding to an 86% yield.

Attempts to condense the chloroether with mesitylene or benzene in the presence of zinc chloride were unsuccessful.

## EXPERIMENTAL

$\alpha$ -Chloroethyl methyl ether. Attempts to prepare this ether in yields as high as those previously reported (59) were unsuccessful. The procedure below was found, however, to give 70% yields of distilled ether consistently.

Dry hydrogen chloride was forced through a sintered glass disk into a one to three molar mixture of paraldehyde and methanol cooled in an ice-salt bath. The hydrogen chloride was introduced slowly over four to five days while keeping the temperature below  $10^{\circ}$ . It is essential that the mixture be kept cold and that enough hydrogen chloride be added for thorough saturation. After separating the colorless layers the lower layer was extracted with ether; calcium chloride was used as a salting-out agent. The original upper layer was added to the ether extract and the solution was dried over calcium chloride. Upon distillation at 155-160 mm. pressure the product was collected at  $32-34^{\circ}$ . It should be stored in the refrigerator.

Attempted condensation with anisole in acetic acid.

Sixty milliliters of glacial acetic acid was added to a mixture of 0.09 mole of the chloroether and 0.075 mole of anisole while holding the temperature at  $10^{\circ}$ . The mixture was then placed in a constant temperature bath and held at  $35^{\circ}$  for about twenty hours. The clear, homogeneous solution was poured into ice water and the acid formed was neutralized

with dilute potassium hydroxide. Upon extraction and distillation at 13 mm. pressure 75% of the starting anisole was recovered (b.p. 43-45°,  $n_D^{20}$  1.512). No other products were isolated.

Relative dehydrochlorination activity of possible catalysts. Dry air was passed at a constant rate over a mixture of 0.033 mole of  $\alpha$ -chloroethyl methyl ether and 0.008 mole of catalyst at 0° C. The air containing only hydrogen chloride and traces of the chloroether was absorbed in a gas washing bottle containing 100 ml. of 0.01 N. sodium hydroxide (60). A piece of congo red paper placed in the solution of alkali served as the indicator. In a control run with no catalyst added the time required to change the color of the indicator was 2.93 minutes. With catalysts present the times varied as follows: 100%  $H_3PO_4$ , 1.8 min.;  $ZnCl_2$ , 1.8 min.;  $PCl_5$ , 1.2 min.;  $H_2SO_4$ , 1.1 min.;  $AlBr_3$ , 0.8 min.;  $AlCl_3$ , 0.2 min.

1,1-Di-(p-methoxyphenyl) ethane. A suspension of 0.2 mole of pulverized anhydrous zinc chloride in 0.33 mole of anisole was well stirred with cooling in an ice bath while 0.33 mole of  $\alpha$ -chloroethyl methyl ether was added drop-wise at such a rate as to hold the temperature below 5°. As the addition proceeded over a period of two hours the color changed from yellow through pink and red to dark brown or black. After stirring for an additional half hour the reaction mixture was poured into ice water. The product was isolated by extraction with ether and recrystallized from 95% ethyl alcohol. A 67% yield of colorless crystals, which melted at



71.2-71.5°, was obtained (reported 70-72° (58)).

When this reaction was repeated but only allowed to run for one-third of the reaction time of the above condensation, there was obtained only a 15% yield of the same product.

In a similar experiment, in which 0.4 mole anisole, 0.2 mole chloroether, and 0.2 mole zinc chloride was used, the same yield of the same product was obtained.

In another similar run the reactants were used in 0.15 molar amounts and the catalyst was 0.09 mole of 100% phosphoric acid (61). There was no apparent change as the chloroether was added except a slight yellowing of the catalyst. Seventy-five per cent of the anisole was recovered.

1,1-Di-(p-ethoxyphenyl) ethane. This reaction was carried out in the general manner just described. One-fifth mole of each of the reactants and 0.07 mole of zinc chloride was used. Upon distillation at 2 mm. pressure 26 g. of crude product was collected at 170-180°. The distillate, which crystallized upon cooling, was recrystallized from glacial acetic acid to give 14.9 g. of colorless crystals; m.p. 30.9-32.4°.

1,1-Di-(p-methoxy-o-methyl-phenyl)ethane. The reactants were used in 0.25 molar amounts with 0.025 mole of zinc chloride and the condensation was carried out as described above for anisole. The product was isolated as a slightly yellow, viscous liquid by distillation at 178-180° at a pressure of 3.5 mm. Attempts at crystallization were unsuccessful.

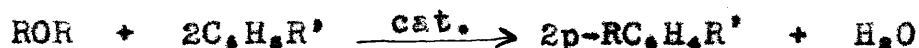
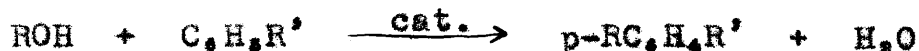
1,1-Di-(o-methoxy-m-methyl-phenyl) ethane. This com-

pound was prepared as just described except that the methyl ether of p-cresol was used in place of the methyl ether of o-cresol. The product distilled at 185-8° at 3 mm- pressure. (reported 185° at 10 mm. (62)). This compound was obtained as white crystals from glacial acetic acid; m.p. 39.4-39.p°.

1,1-Di-( $\alpha$ -p-methoxy-naphthyl) ethane. In this preparation 0.25 mole of  $\alpha$ -naphthyl methyl ether, 0.13 mole of  $\alpha$ -chloroethyl methyl ether, and 0.025 mole of anhydrous zinc chloride were used. The chloroether was added over a one and one-half hour period. Upon distillation in a von Braun flask at 1-2 mm. pressure, 36.5 g. of a dark amber, viscous liquid was obtained. After standing in the refrigerator several weeks a small amount of solid separated. Colorless crystals were obtained for analysis by recrystallizing the solid twice from glacial acetic acid and three times from acetone; m.p. 126.8-128.3°.

## SUMMARY

An azeotropic method for the alkylation of aromatic rings by phenyl carbinols and their symmetrical ethers has been investigated:



In this study, the aromatic compound was used in excess as the solvent and the catalyst was p-toluene sulfonic acid. The reactions were followed by measuring the rate at which the water collected when the solution was refluxed in an apparatus equipped with an automatic water separator.

Mono- or diphenylcarbinol or their symmetrical ethers were found to alkylate toluene and anisole in yields of about 90%. Benzyl alcohol and its symmetrical ether alkylated benzene in about 80% yield, but benzhydrol and its ether gave only 50% to 55% yields. Very little dialkylation or alkylation at other than the para position occurred.

Alkylation of benzene and toluene by benzyl alcohol was found to proceed, at least in part, via the formation of the symmetrical ethers as intermediate. There was, however, little if any ether formation in the alkylation of anisole by benzyl alcohol and various para substituted benzyl alcohols. In every case the benzhydrol appeared to be rapidly converted to the dibenzhydryl ether which then acted as the alkylating agent. An interesting but as yet not completely explained

"S" shaped rate curve was obtained for the alkylation of toluene by dibenzhydriyl ether.

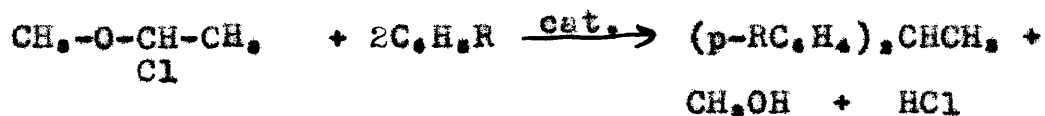
Phenetole, mesitylene, and p-xylene were readily alkylated in yields of 80% to 90% by benzyl alcohol. No catalyst was required with phenetole and there was an induction period, the cause of which is as yet unknown. With n-butyl alcohol and anisole there was found only a 6% yield of p-n-butylanisole along with a fair yield of unidentified product with a surprising low carbon content. This material will be further investigated in these laboratories.

A study was made of the kinetics of the alkylation of anisole by benzyl alcohols substituted in the para position by hydrogen and chlorine atoms and by methoxy, methyl, and nitro groups. Satisfactory first order constants were obtained in all cases except that of the p-nitrobenzyl alcohol. The order of increasing rate of reaction was p-nitro, p-chloro, p-hydrogen, p-methyl and p-methoxy as would be predicted on the basis of the relative electron-releasing ability of these groups. These results on the kinetics and relative reactivities are shown to be in agreement with the carbonium ion mechanism which has been proposed for this reaction. Except for p-nitrobenzyl alcohol the yields of alkylation products were 80% to 90%. Concurrent etherification and alkylation and changes in the activity of the catalyst as the reaction proceeded made it impossible to obtain valid kinetic data when an aromatic hydrocarbon is alkylated.

The method discussed here would be the preferred one

for preparing most compounds of the types described because of the generally high yields and the simplicity of the procedure.

The condensation of  $\alpha$ -chloroethylmethyl ether with aromatic rings was also investigated.



The alkylation of aromatic rings by this chloroether has been shown to give 1,1-diaryl ethanes in every case. In the presence of anhydrous zinc chloride at zero degrees the condensation with anisole, phenetole, m-cresyl methylether, p-cresyl methylether, and with  $\alpha$ -naphthyl methyl ether occurred readily to give the corresponding diarylethanes in 20% to 70% yields. No condensations were effected with benzene or mesitylene under these conditions.

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