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THE STUDY OF THE FACTORS WHICH DETERMINE THE RATE OF ETHERIFICATION OF PHENYLCARBINOLS

By

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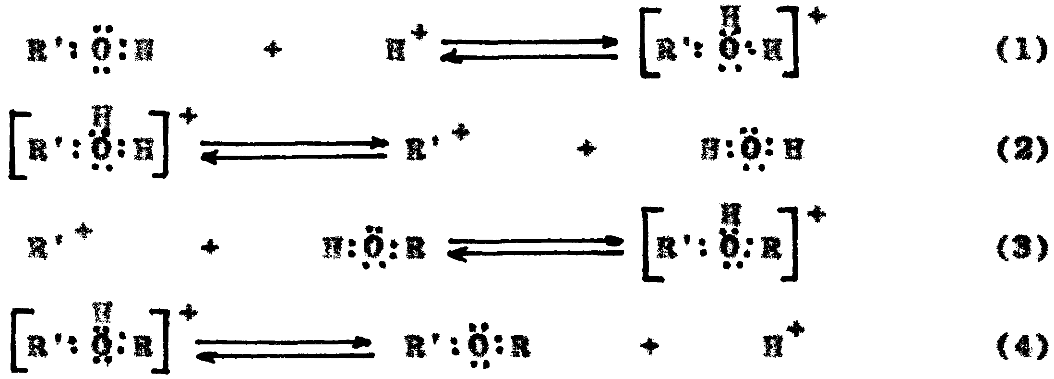
INTRODUCTION

It was found by Dr. J. D. Draper in these laboratories that triphenylcarbinol and benzhydrol could be readily etherified, with butyl alcohol for example, by a distillation method.[1] It was further found, by observing the rate at which the by-product water collected, that the reaction followed first order kinetics. These kinetic studies were extended in this investigation with emphases on increasing the accuracy of the data and on determining the effect of varying the reactant ratios. Other major objectives in this work were to determine whether the less highly activated benzyl alcohols could be etherified by the same method. If the benzyl alcohol etherifications proceeded satisfactorily, the effect on the rate of etherification of varying the *para* substituents in benzyl alcohols was to be investigated.

In addition to these etherifications, certain related reactions such as dehydration of alcohols to olefins, alkylation of the benzene solvent by the alcohols, rearrangement of a primary alkyl group to a secondary alkyl group, and polymerization were encountered. It seems desirable, therefore, to discuss the detailed mechanism of these reactions with emphases on their interrelations.

The currently proposed mechanism for the acid catalyzed etherification reaction requires a carbonium ion intermediate.[2] The mechanism is composed of the four equilibria:



$$R':\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \quad + \quad H^{+} \rightleftarrows \left[R':\overset{H}{\underset{\cdot\cdot}{O}}:H\right]^{+} \tag{1}$$

$$\left[R':\overset{H}{\underset{\cdot\cdot}{O}}:H\right]^{+} \rightleftarrows R'^{+} \quad + \quad H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \tag{2}$$

$$R'^{+} \quad + \quad H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:R \rightleftarrows \left[R':\overset{H}{\underset{\cdot\cdot}{O}}:R\right]^{+} \tag{3}$$

$$\left[R':\overset{H}{\underset{\cdot\cdot}{O}}:R\right]^{+} \rightleftarrows R':\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:R \quad + \quad H^{+} \tag{4}$$

If the reaction is to proceed successfully, R'OH must be an activated alcohol. This activation is usually supplied by an aromatic or olefinic bond on the carbon adjacent to the carbon atom holding the hydroxyl group.

Hammett states of the etherification reaction, "It is obviously a carbonium ion mechanism."[2] According to Alexander, "Reactions of this kind appear to be carbonium ion processes."[3] Remick states, "The well known synthesis of ethers by the action of sulfuric acid on alcohols is probably a carbonium ion reaction and it is not likely that ethylsulfuric acid is an intermediate in that reaction as previously supposed."[4] The mechanism for rearrangements of aryl alkyl ethers is closely related to the mechanism for the formation of ethers. In discussing these rearrangements, Wheland makes the following statement, "Some sort of organic cation is commonly assumed as an intermediate."[5] The words, obviously, appear, probably, and commonly assumed, used by the above investigators indicate that additional experimental data are needed. Hence the results of this investigation were to be analyzed to see whether they supported or controverted the carbonium ion mechanism.

The carbonium ion theory made its initial appearance less than forty years ago. Julius Steiglitz and Lauder W. Jones independently proposed the basic idea in 1913 to explain certain intramolecular rearrangements.[6] Whitmore, however was apparently the first investigator to realize the general applicability of the theory. He proposed in 1932 that the carbonium ion theory offered a common basis for explaining a number of intramolecular rearrangements.[6] Further broadening of the application of the theory has taken place since that time and it now offers the most reasonable explanation for a wide variety of reactions.

Textbooks on organic theories discuss at considerable length the essential features of the carbonium ion theory. In the simplest case, the fragment $:\underset{\cdot\cdot}{\ddot{C}}:\underset{\cdot\cdot}{\ddot{X}}:$, may be used to illustrate the formation of a carbonium ion. The two atoms, C (carbon) and X, (a negative atom or group such as chlorine or hydroxyl) are bound by a pair of electrons and each atom has a complete octet. This system is usually stable but remains so only as long as the octets are complete. It is postulated that when an ionic cleavage of the covalent bond between the two atoms occurs, X usurps both electrons of the bond and two ions result.

$$:\underset{\cdot\cdot}{\ddot{C}}:\underset{\cdot\cdot}{\ddot{X}}: \rightleftharpoons :\underset{\cdot\cdot}{\ddot{C}}^{+} \quad + \quad :\underset{\cdot\cdot}{\ddot{X}}:^{-} \qquad (5)$$

The carbon in this positive ion has only six electrons in its valence shell. This cation is called a carbonium ion.

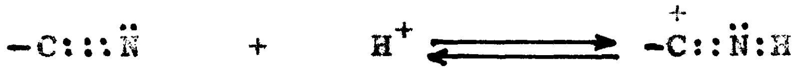
This cation is very reactive. It is often convenient to refer to the carbonium ion as being set free but its freedom is seldom, if ever, complete. Alexander states, "It is extremely improbable that an unsolvated open sextet of electrons ever exists on carbon other than momentarily."[7] The postulate of a free carbonium ion is, however, very useful in many organic processes.

Hammett gives a broader definition for a carbonium ion than the foregoing one. He states that in the absence of an electrophilic reagent, substances such as alkyl halides and toluenesulfonates react with nucleophilic reagents via a carbonium ion intermediate. To quote him, "These are the nucleophilic displacements on carbon and the driving force is the affinity of the unshared electron pairs of the reagent for the carbonium ion."[8] Equation 5 requires complete ionization whereas this extention of the definition does not. Apparently Hammett believes that the properties of a carbonium ion exist in a molecule in which there is unequal sharing of electrons of a covalent bond between carbon and some other strongly electronegative atom. This paper, however, is mainly concerned with the concept of the free carbonium ion as shown in Equation 5.

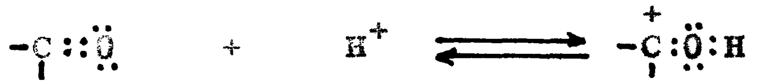
The generalization may be made that conditions favorable for carbonium ion formation exist whenever an acid is brought into the vicinity of a molecule which can furnish an electron pair. The electrons may be present as an unshared pair or they may be drawn out of a multiple bond by the action of the acid. The term, acid, is here used in accordance with the Lewis definition which states that any substance which can accept an electron pair is an acid. Besides the proton, such substances as the halides of aluminum and boron are included.

Several reactions in which carbonium ion formation is probable will now be considered. For the sake of completeness, reactions postulated to yield carbonium ions other than the ones encountered in this work will also be discussed briefly.

It is believed that an acid reagent causes a multiple bond to assume a more polarized form. This polarization is followed by coordination as is shown below.[9]



$$-C:::\ddot{N} \quad + \quad H^+ \rightleftharpoons -\overset{+}{C}::\ddot{N}:H \qquad (6)$$

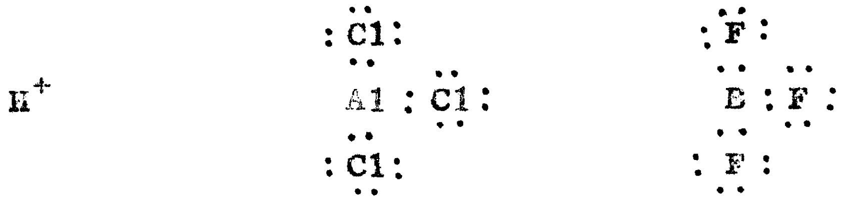


$$-\underset{|}{C}::\underset{..}{\ddot{O}} \quad + \quad H^+ \rightleftharpoons -\overset{+}{\underset{|}{C}}:\underset{..}{\ddot{O}}:H \qquad (7)$$

$$-\underset{|}{C}::\overset{|}{\underset{|}{C}} \quad + \quad H^+ \rightleftharpoons -\overset{+}{\underset{|}{C}}:\ \overset{|}{\underset{|}{C}}:H \qquad (8)$$

The product formed in each instance contains a carbon atom with an open sextet.

A Lewis acid such as boron fluoride or aluminum chloride could replace the proton in these equilibria. The strong tendency of the proton and of the boron and aluminum atoms in these halides to attain the stable rare gas electronic configurations accounts for the electrophilic properties of these acids.



$$H^+ \qquad \begin{array}{c} :\underset{..}{\ddot{Cl}}: \\ Al:\underset{..}{\ddot{Cl}}: \\ :\underset{..}{\ddot{Cl}}: \end{array} \qquad \begin{array}{c} :\underset{..}{\ddot{F}}: \\ B:\underset{..}{\ddot{F}}: \\ :\underset{..}{\ddot{F}}: \end{array} \qquad (9)$$

The acquisition of an electron pair by any of these acids would yield stable electronic configurations.

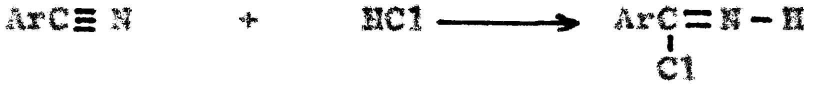
There is good evidence that the formula given for aluminum chloride is not correct. It is known to exist as a dimer. It is, however, reasonable to assume that an equilibrium exists between the two forms, especially in the presence of a Lewis base, so that at least a small amount of the monomer is present. The fact remains that aluminum chloride does act in the manner of an extremely strong acid in many reactions.

There is adequate evidence that the reactions indicated by Equations 6, 7 and 8 must take place. When dissolved in 100% sulfuric acid, most aldehydes, ketones, carboxylic acids, esters, and nitriles give a conducting solution and yield a molar freezing point depression twice that of a nonelectrolyte.[10] Since the starting materials may be recovered unchanged by the addition of water, the reaction can be only that indicated by Equation 10.

$$-\underset{|}{C}::\overset{..}{O}: \quad + \quad H_2SO_4 \rightleftharpoons -\overset{+}{\underset{|}{C}}:\underset{..}{\overset{..}{O}}:H \quad + \quad \left[HSO_4\right]^- \qquad (10)$$

Olefins undergo polymerization under these conditions. However, the fact that aromatic hydrocarbons are soluble in liquid hydrogen fluoride while saturated hydrocarbons are not is evidence for the existence of equilibria such as 8.

Acid catalyzed addition reactions of olefins and carbonyl compounds have been postulated to be carbonium ion reactions. Nitriles appear to react similarly. Fieser suggests that the first step in the Stephen reaction is an addition reaction.[11]



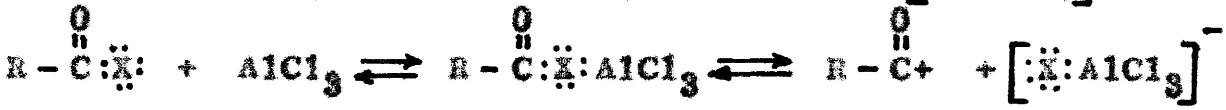
$$\mathrm{ArC{\equiv}N + HCl \longrightarrow Ar\underset{\displaystyle Cl}{\underset{|}{C}}{=}N-H} \qquad (11)$$

It is reasonable to assume that this reaction is initiated by a proton attack on one of the pairs of electrons of the triple bond to yield a carbonium ion (<u>cf</u>. Equation 6).

Organic halides constitute another important family of compounds that are postulated to react with acids to yield carbonium ions.[12]

$$\mathrm{R{:}\underset{..}{\ddot{X}}{:} + H^{+} \rightleftharpoons \left[R{:}\underset{..}{\ddot{X}}{:}H\right]^{+} \rightleftharpoons R^{+} + H{:}\underset{..}{\ddot{X}}{:}} \qquad (12)$$

$$\mathrm{R{:}\underset{..}{\ddot{X}}{:} + AlCl_3 \rightleftharpoons R{:}\underset{..}{\ddot{X}}{:}AlCl_3 \rightleftharpoons R^{+} + \left[{:}\underset{..}{\ddot{X}}{:}AlCl_3\right]^{-}} \qquad (13)$$

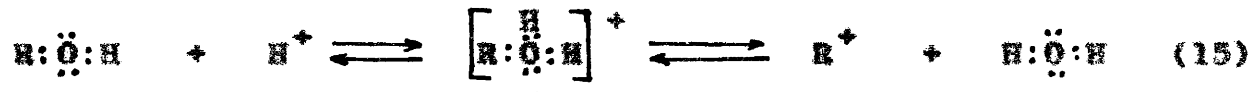


$$\mathrm{R-\overset{O}{\overset{\|}{C}}{:}\underset{..}{\ddot{X}}{:} + AlCl_3 \rightleftharpoons R-\overset{O}{\overset{\|}{C}}{:}\underset{..}{\ddot{X}}{:}AlCl_3 \rightleftharpoons R-\overset{O}{\overset{\|}{C}}{+} + \left[{:}\underset{..}{\ddot{X}}{:}AlCl_3\right]^{-}} \qquad (14)$$

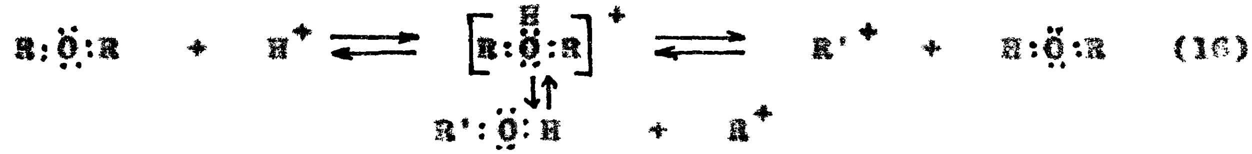
A solution of triphenylmethyl chloride in cresol shows a small but unmistakable conductance whereas cresol itself does not conduct.[13] This is evidence for Equation 12. The postulated equilibrium must therefore exist even though the proton is known to have a small affinity for the chloride ion. Transference experiments provide important evidence for the reaction indicated by Equation 13. Ethyl chloride and ethyl bromide are nonelectrolytes but when the corresponding aluminum halides are added, the resulting solutions can be electrolyzed. The anion has been shown to contain the aluminum.[14] There is also additional evidence for Equilibrium 13. It has been demonstrated that the hydrogen chloride produced in a

Friedel-Crafts condensation is in radioactive equilibrium with the aluminum chloride.[15] Equations 13 and 14 are currently proposed as the key steps in the Friedel-Crafts hydrocarbon and ketone syntheses respectively.

Compounds that contain singly bonded oxygen atoms apparently yield carbonium ions when treated with an acid. Alcohols and ethers are in this class.



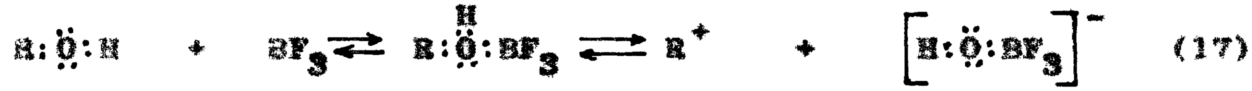
$$R:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \quad + \quad H^{+} \rightleftharpoons \left[R:\overset{H}{\underset{\cdot\cdot}{O}}:H\right]^{+} \rightleftharpoons R^{+} \quad + \quad H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \qquad (15)$$



$$R:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:R \quad + \quad H^{+} \rightleftharpoons \left[R:\overset{H}{\underset{\cdot\cdot}{O}}:R\right]^{+} \rightleftharpoons R'^{+} \quad + \quad R:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:R \qquad (16)$$

$$\downarrow\uparrow$$

$$R':\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \quad + \quad R^{+}$$



$$R:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H \quad + \quad BF_3 \rightleftharpoons R:\overset{H}{\underset{\cdot\cdot}{O}}:BF_3 \rightleftharpoons R^{+} \quad + \quad \left[H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:BF_3\right]^{-} \qquad (17)$$

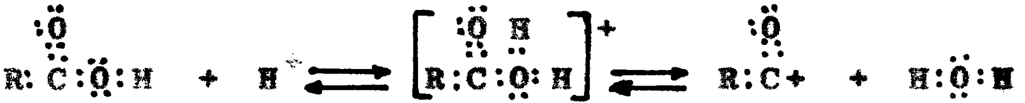
Cryoscopic measurements provide evidence for Equation 15. Triphenylcarbinol dissolved in 100% sulfuric acid gives a molar depression of the freezing point four times that of a nonelectrolyte.[16] The reaction can only be as indicated in Equation 18.

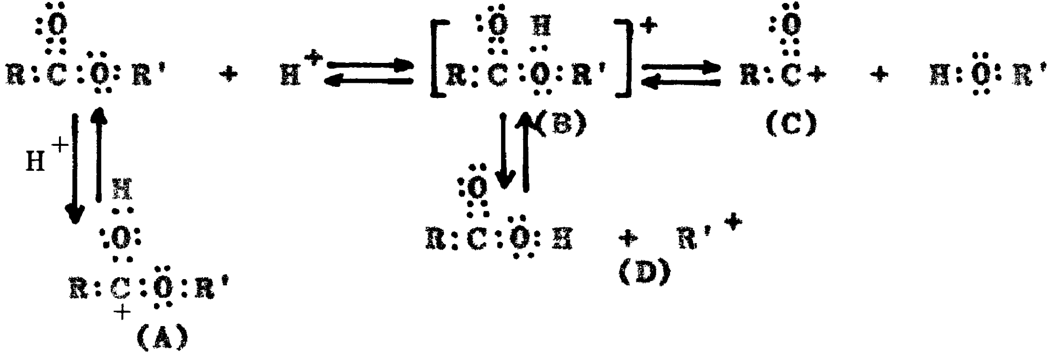
$$(C_6H_5)_3COH + 2H_2SO_4 \rightleftharpoons \left[(C_6H_5)_3C\right]^{+} + \left[H_3O\right]^{+} + 2\left[HSO_4\right]^{-} \qquad (18)$$

In addition to this evidence, colored anhydrous perchlorates of the type, $\left[(C_6H_5)_3C\right]^{+}\left[ClO_4\right]^{-}$ have been isolated and analyzed.[17] Cryoscopic data also indicate that the first equilibrium postulated in Equation 16 must exist. Most ethers give a molar freezing point depression twice that of a nonelectrolyte.[10]

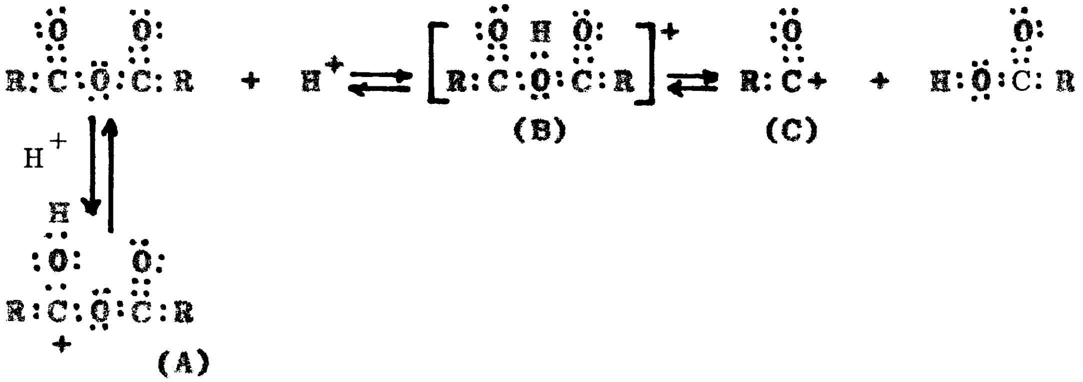
Inspection of Equations 15 and 16 reveals that acids catalyze the cleavage as well as the formation of ethers. The driving force in the reactions is the affinity of the acid for the unshared electron pairs of the oxygen. An unsymmetrical ether may yield two carbonium ions. Equation 17 shows why alcohols may be used to alkylate benzene under typical Friedel-Crafts conditions.[18]

There is evidence that considerably more complex equilibria exist when a Lewis acid reacts with an organic acid, ester or anhydride. These systems contain, in addition to the ethereal or hydroxyl oxygen, a carbonyl oxygen. Equations 19, 20, and 21 illustrate the possible courses of reaction.[19]


(19)



(20)

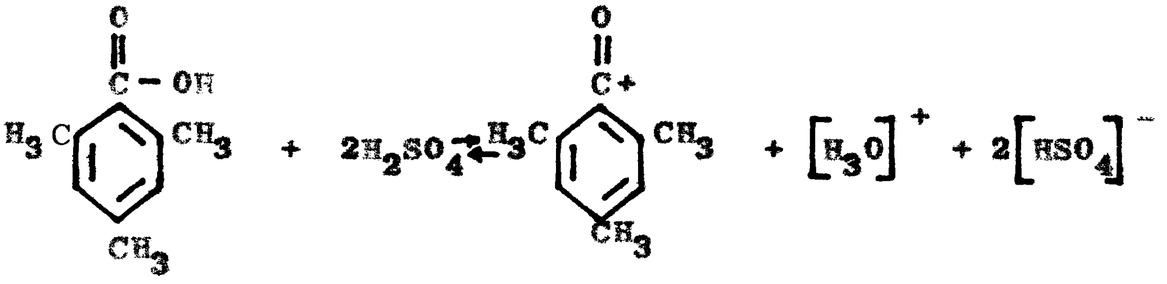


(21)

Hammett cites strong evidence for the equilibria indicated by Equation 19. Benzoic acid gives a molar depression of the freezing point twice that for a nonelectrolyte when dissolved in 100% sulfuric acid.[20] Equation 22 indicates the most probable course of the reaction.

$$C_6H_5COOH + H_2SO_4 \rightleftarrows [C_6H_5COOH_2]^+ + [HSO_4]^- \qquad (22)$$

Reversibility is indicated but it should be emphasized that in this solvent, the equilibrium must be preponderantly toward the right. Most derivatives of benzoic acid give a van't Hoff *i* factor of two under these conditions. 2, 4, 6-Trimethylbenzoic acid is, however, an exception and gives an *i* factor of four.[21] This is strong evidence for the acyl carbonium ion postulated in Equation 19. The probable course of reaction for this highly substituted benzoic acid is indicated by Equation 23.



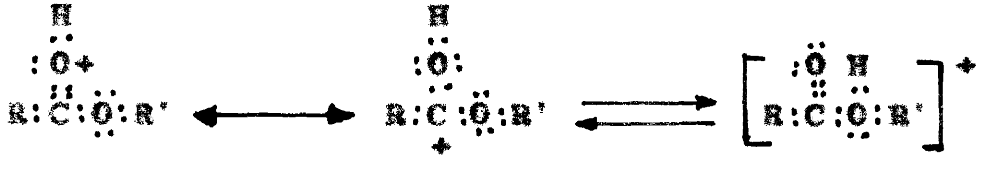
(23)

This observed anomalous behavior may be due to steric hindrance or to positive inductive effects or to both. The positive inductive effect of three methyl groups might increase the electron density at the carbonyl carbon to such an extent that the oxygen-carbon single bond is greatly weakened. This being true, the molecule would be expected to ionize like a base in 100% sulfuric acid. Whatever the explanation might be, the experimental data indicate the formation of an acyl carbonium ion. One more bit of evidence for acyl carbonium ion formation from an acid is the fact that a 73% yield of α-hydrindone can be obtained from hydrocinnamic acid using liquid hydrogen fluoride.[22]

An ester may yield three different species of carbonium ions. Most esters give a van't Hoff i factor of two when dissolved in 100% sulfuric acid.[23] Equation 24 is the proposed reaction.

$$RCOOR' + H_2SO_4 \rightleftharpoons [RCOOR'H]^+ + [HSO_4]^- \qquad (24)$$

Equation 24 makes no attempt to indicate to what part of the molecule the proton adds. Since double bonds are known to be readily polarizable, it is most reasonable to assume that the proton coordinates with the carbonyl oxygen to yield 20A. However, most investigators in their discussions of acid catalyzed esterification and ester hydrolysis prefer to show the proton as being associated with the ethereal oxygen. This view gives more logical intermediates for these reactions. Both 20A and 20B are probably correct since other equilibria may be postulated on the basis of resonance. The essential features of these equilibria are shown by Equation 25.


(25)

If these equilibria exist, then the view can be preserved that the initial attack of the proton is on the carbonyl oxygen and that the stage for reaction is set only after the proton is on the ethereal oxygen as in 20B. Equation 20 indicates that 20B may be the precursor of either an acyl or alkyl carbonium ion There is strong evidence that the equilibrium shown to exist between 20B and 20D lies almost completely on the side of 20B, especially, if R' is a primary or secondary alkyl group. Experiment has shown that the bond between the ethereal oxygen and the alkyl carbon remains intact in the process

Proofs for the acyl carbonium ion type fission of 20B are as follows:

(a) Complete optical activity is retained when optically active octanol-2 is esterified with acetic acid in the absence of mineral acid.[24]

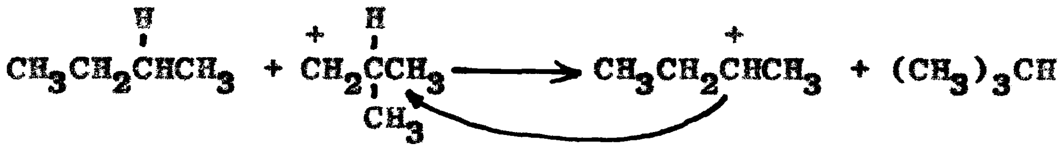
(b) No rearranged products are isolated in the formation or hydrolysis of neopentyl acetate.[25] It has been demonstrated in other experiments that a neopentyl carbonium ion ordinarily rearranges.

(c) If benzoic acid is esterified with methyl alcohol containing the isotope O^{18}, only normal water is obtained indicating that the carbon-oxygen bond in methanol remains intact.[26]

The anhydride system is quite analogous to the ester system since it contains both carbonyl and ethereal oxygen atoms The anhydride system is, however, capable of even more complex equilibria especially in the case of an unsymmetrical anhydride. This system will not be discussed further than to mention that anhydrides are frequently reactants in the Friedel-Crafts reactions.[27]

The decomposition of certain diazonium salts indicates that carbonium ion intermediates are probable. The diazotization of n-butylamine yields 25% of n-butyl alcohol, 5.2% of n-butyl chloride and traces of n-butyl nitrate.[28] Other reactions of diazonium salts however appear to be free radical processes.

The commercial isomerization of n-butane to isobutane has been postulated to proceed by way of a carbonium ion attack on n-butane to yield a new carbonium ion. Equation 26 indicates one of the proposed steps of the process.[29]

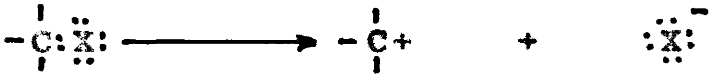


$$CH_3CH_2\overset{H}{C}HCH_3 + \overset{+}{C}H_2\underset{CH_3}{\overset{H}{C}}CH_3 \longrightarrow CH_3CH_2\overset{+}{C}HCH_3 + (CH_3)_3CH \qquad (26)$$

(A)

The foregoing discussion indicates that a wide variety of compounds are capable of producing carbonium ions. Some compounds apparently yield carbonium ions easily while others require the most powerful electrophilic reagents available. Even in a given family of compounds, there is often a large difference in the ease with which carbonium ion formation occurs. Triphenylcarbinol apparently yields carbonium ions very readily whereas ethanol does not. The ease of formation of carbonium ions and their stability are so intimately related that they will be discussed together.

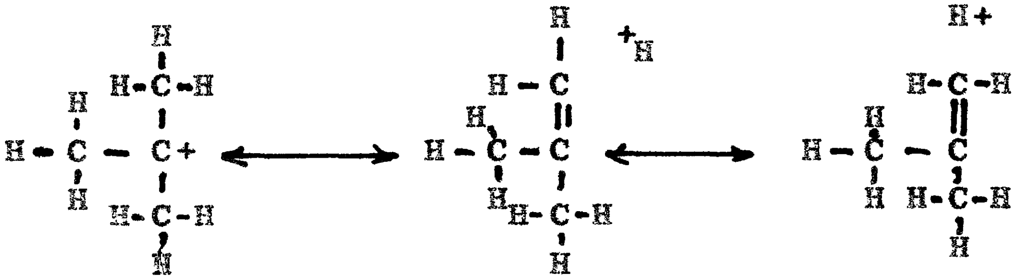
As previously pointed out carbonium ions may form via the following reaction.



$$-\overset{|}{\underset{|}{C}}:\overset{..}{\underset{..}{X}}: \longrightarrow -\overset{|}{\underset{|}{C}}+ \quad + \quad :\overset{..}{\underset{..}{X}}:^{-} \qquad (27)$$

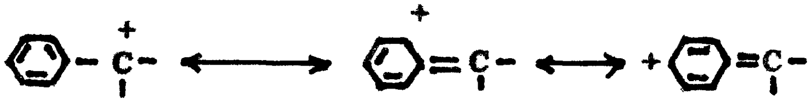
Any structural feature in the molecule that feeds electrons on to this carbon should favor the fission. The resultant higher electron density on the carbon would cause the shared pair to shift toward X, thereby weakening the bond. This same tendency would also have the effect of distributing the positive charge throughout the carbonium ion structure thereby lowering its tendency to recombine.

Experimentally, it has been found that the ease of formation of alkyl carbonium ions decreases in the following order: tertiary, secondary, primary. The positive inductive effect of alkyl groups has been commonly proposed as an explanation. There is much data to indicate that a methyl group does release electrons. More recently the hyperconjugation effect has been proposed in the place of the inductive effect as offering a better explanation for the observed order. This theory assumes that an electron pair constituting a carbon-hydrogen bond may momentarily shift into a carbon-carbon linkage to produce a double bond. This is also known as _no bond resonance_ or the Baker-Nathan effect.[30] On the basis of hyperconjugation, there may be written for the t-butyl carbonium ion a total of ten structures, nine of which are resonance hyperconjugation forms. Equation 28 indicates a few of these structures.[31]


(28)

There can be written a total of seven and four structures respectively for the i-propyl and ethyl carbonium ions. The overall result, assuming this theory to operate, is also a general increase of electron density on the carbonium carbon and a greater distribution of the positive charge throughout the structure. Berliner and Bondhus suggest that hyperconjugation and the positive inductive effect may be one and the same.[32]

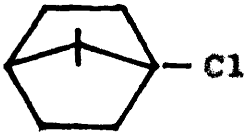
Benzyl and allyl carbonium ions form readily except when their double bonds are conjugated with the double bonds of electron withdrawing groups. These facts have been explained in terms of the resonance theory. The existence of resonance in these systems would lead to a higher electron density on carbon and to a general distribution of the positive charge throughout the structure. The first factor would favor the ionization and the second would increase the stability of the resulting carbonium ion. Equations 29 and 30 indicate the operation of resonance in these ions.


(29)

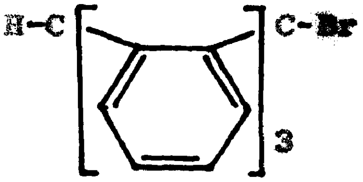
$$-\underset{|}{C}=\underset{|}{C}-\underset{|}{\overset{+}{C}}-\longleftrightarrow-\underset{|}{\overset{+}{C}}-\underset{|}{C}=\underset{|}{C}- \qquad (30)$$

A *para* nitro or carbethoxy group on the structure shown in Equation 29 would create a new resonance system that would oppose ionization. Under these conditions, carbonium ion formation is unlikely.

Experimental data indicate that if a carbonium ion is to be formed, the resulting structure must be able to attain a planar configuration. As a rule, tertiary halides readily yield carbonium ions under mild conditions. Bartlett, however, showed that the tertiary chloride, 1-chloroapocamphane (formula below) is inert to boiling aqueous alcoholic silver nitrate.[33]

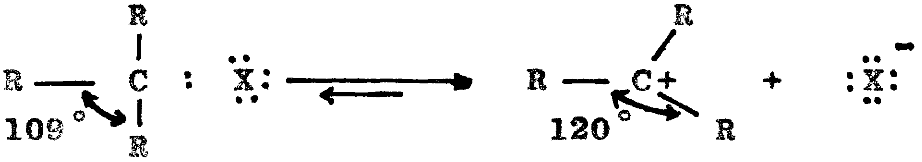


The structure is sterically unable to attain a planar configuration at the carbon which is bound to the halide atom. 1-Bromotriptycene (formula below) is a non-conductor in liquid sulphur dioxide while the tertiary halide, triphenylmethyl chloride is an excellent conductor.[34]



Again it is presumed that the cage structure of the former makes impossible a planar configuration at the seat of the reaction.

Certain generalizations can be made regarding the ease of formation of tertiary carbonium ions. Apparently the larger the group attached to the carbonium carbon, the easier the reaction proceeds. This is attributed to the operation of the principle known as "B" strain.[35, 36] Alexander states, "It is assumed to arise as a result of the fact that large groups have a pressure on each other when the valence bonds of carbon have a tetrahedral configuration. This strain can be relieved when the carbonium ion is formed and consequently the equilibrium below is forced to the right."[37]



(31)

The data in the following table furnish good evidence for the operation of this principle.

TABLE I

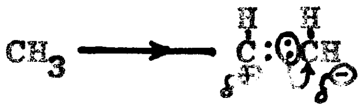
Relative Rates of Ionization of Tertiary Chlorides in 1 to 3 Acetone-Water Solution at 25°.[38]

A.	t-Butyl Chloride	1.00
B.	Dimethylethylmethyl Chloride	2.06
C.	Dimethylisopropylmethyl Chloride	1.75
D.	Dimethyl-t-butylmethyl Chloride	2.43
E.	Triisopropylmethyl Chloride	6.91

Dimethylisopropylmethyl chloride appears to be an exception in this series.

On the basis of hyperconjugative effects alone, it would be expected that t-butyl chloride would ionize most rapidly. The number of hyperconjugation resonance forms possible decreases in going from compound A to compound E. This is an instance where two factors work in opposition. With respect to favoring carbonium ion formation and stability, it is concluded that "B" strain is a more important factor in this series of compounds than resonance hyperconjugation.

The action of an acid on an unsaturated compound is also postulated to lead to carbonium ion formation (cf. Equation 8). Certain structural features in olefins are known to facilitate addition reactions. Ethylene gas is not absorbed by concentrated hydrochloric acid but the higher homologs usually react under these conditions.[39] These reactions are greatly favored by an accumulation of methyl groups on one of the olefinic carbons. Propylene adds hydrogen fluoride under considerably milder conditions than ethylene and the yield is also better.[40] The usual explanation is that the positive inductive effect of the methyl group aids the polarization of the double bond with the result that the i-propyl carbonium ion forms more readily than the ethyl carbonium ion. Operation of this positive inductive effect is shown in Equation 32.



$$CH_3 \longrightarrow \underset{\delta+}{\overset{H}{C}}:\overset{H}{C}\underset{\delta-}{H} \qquad (32)$$

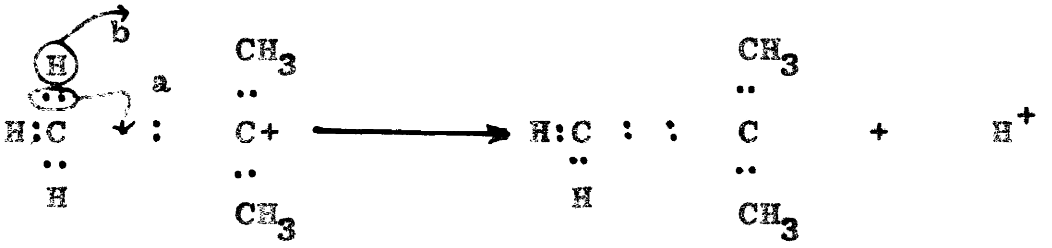
Once a carbonium ion has been formed, there are several ways in which it may react. The final product of the reaction is seldom determined by the source of the ion. An open sextet on carbon constitutes a system that is exceedingly reactive. In order to satisfy this electron deficiency on carbon, the carbonium ion will in general react with any reagent at hand that is able to supply electrons. This would account for the wide variety of by-products and the low yields obtained in many reactions. The course of reaction of a carbonium ion will as a rule be determined jointly by its structure and environment.

If any of the procedures calculated to produce a carbonium ion are carried out in the presence of water, an alcohol is almost certain to be one of the products. The acid hydrolysis of an alkyl halide, the action of a strong aqueous acid on an ether or an olefin, or the acid catalyzed decomposition of an aliphatic diazonium salt all yield alcohols. The common driving force in all these reactions could be the affinity of the carbonium ion for the unshared electron pairs on the oxygen atom of water to produce the conjugate acid of the alcohol. An aqueous environment must therefore be avoided if this course of reaction is to be entirely blocked.

The action of an acid upon alcohols often leads to etherification or dehydration. The electrophilic reagents, sulfuric acid, boron fluoride, zinc chloride and various sulfonic acids all act upon ethyl alcohol under specified conditions to yield diethyl ether. Similarly benzhydrol is readily converted to its ethyl ether by the action of a dilute solution of hydrogen chloride in ethanol. Dibenzhydryl ether is also formed in this reaction.[41] A plausible explanation for the presence of two products is that the benzhydryl carbonium ion coordinates to the unshared electron pairs on both alcohols present to produce the conjugate acids of the corresponding ethers (cf. Equation 3). Ethyl t-butyl ether may be prepared in 95% yield by heating to 70° a mixture of t-butyl and ethyl alcohols containing 15% of sulfuric acid.[42] This high yield of unsymmetrical ether indicates that the t-butyl carbonium ion is unable to coordinate successfully with the unshared electron pairs on the oxygen of the sterically hindered t-butyl alcohol. This reaction suggests that the principle of steric hindrance may be usefully employed to predict what types of alcohols must be paired to yield a successful unsymmetrical ether synthesis.

Dehydration of alcohols to olefins is familiar both as a main reaction and as a side reaction. The carbonium ion intermediate is first believed to undergo an internal electronic rearrangement which is followed by the expulsion of a hydrogen. It is assumed that the electron deficiency of the carbonium carbon is relieved by the capture of an electron pair which constitutes a covalent bond between the adjacent carbon atom and its hydrogen. Equation 33 indicates the steps leading to olefin formation by a t-butyl carbonium ion.

Step a precedes Step b.



$$\mathrm{H{:}\underset{\underset{H}{..}}{C}{:}\overset{\overset{CH_3}{..}}{\underset{\underset{CH_3}{..}}{C+}}} \longrightarrow \mathrm{H{:}\underset{\underset{H}{..}}{C}{::}\overset{\overset{CH_3}{..}}{\underset{\underset{CH_3}{..}}{C}}} + H^+ \qquad (33)$$

It should be noted that this reaction can go by either of two mechanisms depending upon the environment. The yield of olefin in the hydrolysis of 2-octyl bromide in aqueous ethanol solutions is a function of pH. The olefin yield varies from 10% to 55% in going from an acid to an alkaline solution.[43] An acid medium favors the solvolytic (carbonium ion) mechanism whereas a basic medium favors a displacement reaction. Olefin formation is impossible for carbonium ions that have no hydrogens attached to the carbon adjacent to the carbonium carbon. Benzyl, benzhydryl or triphenylmethyl carbonium ions can yield no olefins.

A carbonium ion may also attack an olefin to yield a new carbonium ion. This new carbonium ion may react in various ways some of which have been considered before. A continuation of the original process whereby each succeeding new carbonium ion reacted with an olefin molecule would eventually lead to a long chain polymer.[44]

It was mentioned earlier that a carbonium ion is assumed to be capable of abstracting a hydride ion from an alkane to yield a new carbonium ion (cf. Equation 26). A carbonium ion is an exceedingly electrophilic particle apparently successfully seeking out electrons where none would seem available.

Another very important general reaction supposed to be a carbonium ion type is the Friedel-Crafts reaction.

$$R_3C+ \quad + \quad C_6H_6 \longrightarrow R_3CC_6H_5 \quad + \quad H^+ \qquad (34)$$

There are examples of Friedel-Crafts reactions where no special catalysts are needed In the presence of excess phenol at 90°, t-butyl and triphenylmethyl bromides react readily to yield the alkylated products.[45] Apparently phenol is acidic enough to promote carbonium ion formation in instances where carbonium ion formation occurs easily. In both of these reactions, the alkyl groups go to the nuclear carbon rather than to the phenolic oxygen.

It has been emphasized earlier that it makes little difference what the source of the carbonium might be with reference to a particular product. With sufficiently powerful electrophilic reagents, alkylation of benzene and naphthalene is achieved with alcohols, olefins, ethers and esters as well as with the classically used alkyl halides.[46]

A most important variation of the Friedel-Crafts reaction is the acylation reaction. This reaction is most commonly carried out with acid chlorides but acids and anhydrides are also frequently employed. The mechanism of the reaction is essentially the same as that for alkylations except that the reaction intermediate is an acyl rather than an alkyl carbonium ion.

The carbonium ion theory was originally proposed as a general theory to account for a variety of rearrangements which had been observed up to 1932. The phenomena termed "allylic shift" may be reasonably explained by assuming the existence of a resonating carbonium ion intermediate. The action of hydrobromic acid on α-phenylallyl alcohol produces the corresponding derivative of cinnamyl alcohol.[48] A resonating carbonium ion is believed to be the intermediate.

$$C_6H_5-\underset{+}{\overset{H}{C}}-\overset{H}{C}=\underset{H}{\overset{H}{C}} \longleftrightarrow C_6H_5-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}+ \qquad (35)$$

The fact that cinnamyl alcohol is converted wholly to cinnamyl bromide under these conditions indicates that the resonance equilibrium in Equation 35 must be preponderantly to the right. There are analogous systems where both products are obtained indicating a more balanced resonance equilibrium. α-Methylallyl alcohol gives 80% of rearranged product and 15% of normal product with hydrobromic acid. The same relative proportions of the same products are obtained if crotol alcohol instead of α-methylallyl alcohol is used.[49] These results are very reasonably explained by assuming that both these reactions have a common resonating carbonium ion intermediate.

$$CH_3-\overset{H}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}{}^{+} \longleftrightarrow CH_3-\underset{+}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}-H \qquad (36)$$

A second important type of rearrangement involves a change in the carbon skeleton. Whitmore proposed that the essential step was the formation of a carbonium ion.[6] He postulated that the carbonium carbon could capture from an adjacent carbon an alkyl group *together with its bonding electron pair*. This shift was assumed to produce a more stable carbonium ion. Experiment has shown that the direction of shift is usually such that the *new* carbonium carbon holds more alkyl groups than the original carbonium carbon.

As an illustration of this principle, neopentyl alcohol is converted exclusively to dimethylethylmethyl bromide by the action of hydrobromic acid.[50] A new method has recently been reported in which a neopentyl alcohol derivative was converted *directly* to the corresponding halide.[51] This one piece of work does not however disprove the apparent fact that a neopentyl carbonium ion always rearranges. A review of this work reveals that the experimental conditions selected and the neopentyl alcohol derivatives chosen constituted a system that could be considered unfavorable to a carbonium ion mechanism. In the Wagner-Meerwein rearrangement the carbon skeleton also changes. There is excellent reason to believe that the reaction proceeds *via* a carbonium ion intermediate. The well known conversion of camphene to isobornyl chloride is the classical example of this rearrangement.

This reaction is almost instantaneous in liquid sulfur dioxode or cresol.[52, 53] These are the same solvents in which triphenylmethyl chloride ionizes most extensively.[13]

Another common type of shift encountered in many rearrangements is the hydride ion shift. Once a normyl alkyl carbonium ion has been formed, it apparently rearranges to become a more stable carbonium ion by capturing from the adjacent carbon a hydrogen atom together with its bonding electrons. This is in agreement with the principle previously cited that the new carbonium carbon carries a greater number of alkyl groups than its precursor. Thus n-propyl alcohol is readily isomerized to i-propyl alcohol by aqueous sulfuric acid. In the Friedel-Crafts hydrocarbon synthesis, normal alkyl halides with longer carbon chains than the ethyl derivatives invariably yield at least some of the secondary alkyl aromatic products.[54]

The hypothesis of carbonium ion intermediates in many acid catalyzed reactions is a reasonable and attractive one. Since the intermediate cannot be isolated, evidence for its existence must be of an indirect nature. There is, however, much evidence in favor of the existence of carbonium ions. Carbonium ions are very useful in the postulation of a reasonable mechanism for many important reactions.

DISCUSSION

THE KINETICS OF THE ETHERIFICATION OF POLYPHENYLCARBINOLS

Dr. J. D. Draper, in these laboratories, investigated in a preliminary fashion the kinetics of the etherification of triphenylcarbinol by n-butyl alcohol by the distillation method.[55]

$$(C_6H_5)_3COH + CH_3(CH_2)_3OH \longrightarrow (C_6H_5)_3CO(CH_2)_3CH_3 + H_2O$$

He found that the reaction went smoothly and that it was first order with respect to the concentration of one of the alcohols. In the present research, the kinetics of this reaction were investigated more completely with emphases on determining the effect of varying the ratio of reactants and catalyst concentration and on increasing the accuracy of the method.

A major improvement in accuracy was obtained by increasing the volume of the reaction mixture four-fold. With the larger volume, the temperature variation within an experiment was not more than $\pm 0.10^\circ$ in the typical case since the concentration of the reaction mixture varied less as the reaction progressed. A second important modification was the use of twice as much of the reactants (i.e. ordinarily at least 0.250 mole of each reactant) so that 4.50 ml. instead of 2.25 ml. of water was evolved. As a result the relative error on each reading of the volume of water was cut in half. Further improvement in accuracy was obtained by selecting a catalyst concentration low enough to keep the half reaction time over two hours in the vast majority of the experiments. With these slower rates, it was doubly certain that the water was being removed as fast as it was formed and the volumes of water and the time intervals could be determined more accurately.

In the original procedure, the catalyst which was p-toluenesulfonic acid had been weighed out into small beakers on an analytical balance. The solid catalyst is however quite hygroscopic. To eliminate variations among experiments due to this difficulty, a standard solution of the catalyst in benzene was made up for this whole series of experiments. The desired volume of this solution was added to the refluxing reaction mixture. The errors arising from weighing out quantities of catalyst as low as about 25 mg. were also avoided in this way and time was saved.

A further refinement was the use of extra large graph paper for plotting the rate data. Other minor modifications in Draper's procedure will be discussed in the Experimental.

The improved procedure was as follows: The desired amounts of the polyphenylcarbinol and n-butyl alcohol were weighed out and dissolved in about 800 ml. of benzene. By adding more benzene, this solution was brought to a total volume of 1888 ± 5 ml. at 25°, less the volume of catalyst solution to be added later. This volume of dry benzene expanded to two liters at the reflux temperature.

The solution was quickly transferred from the thermostat bath to a three-liter, round-bottomed flask fitted with a thermometer well and having a small second neck for introducing the catalyst solution. The Dean-Stark water collector was then fitted on to the larger neck and filled with benzene. About one-fifth ml. of water was placed in the Dean-Stark tube in order to get a more accurate "zero" reading. A steel shot was also added. Prior to taking readings of the volume of water, this shot was raised through the meniscus by means of an external magnet. This gave smooth reproducible menisci. A condenser was fitted to the water collector and a calcium chloride drying tube was attached to the top of the condenser. Standard taper ground glass joints were used throughout. A large hemispherical "Glas-Col" heating mantle supplied the heat.

Boiling chips were added and the current was turned on. A "Variac" was used to adjust the voltage which was 67 for all these experiments. The reaction mixture was permitted to reflux for about one hour to remove any water present in the reactants or adsorbed on the apparatus. The catalyst was added from either a 10 ml. or 50 ml. buret depending on the volume needed. The volume of catalyst solution varied in these experiments from 1.25 ml. to 40.0 ml. The time and temperature were noted when the catalyst was added. A long "Chromel" wire with a loop on the end was inserted through the top of the condenser and used to loosen and knock down any droplets of water adhering to the tip of the condenser before each reading of the volume of water was taken.

Percentage completion of the reaction was plotted against time in minutes on the large size graph paper. A smooth curve was drawn through these points. From the curve, the time for 20% completion was accurately determined. Due to unavoidable fluctuations in the early observations, the first 20% of the reaction was discarded in the kinetic treatment. This was done by recalculating the concentrations of the reactants for a new zero time at the 20% completion point.

From the curve, the times for 30%, 40%, 50%, 60%, 70%, and 80% completion of the reaction were read. These values were then substituted into the following integrated form of the first order equation.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

The terms used in this equation are defined as follows: $\underline{k}$ is the first order reaction rate constant; $\underline{t}$ is the time elapsed since the <u>new</u> zero time; $\underline{a}$ is the molar concentration at the new zero time of the species which controls the rate; and $(a-x)$ is the concentration of this species at time $\underline{t}$.

The rate constants, calculated by letting $\underline{a}$ be the concentration of triphenylcarbinol are given in Table II. An examination of the average deviations shows that the $\underline{k}$ values are satisfactorily constant for the 20 to 80% portion of a given experiment except for Experiment 2 which is discussed below.

TABLE II

THE KINETICS OF TRIPHENYLMETHYL n-BUTYL ETHER FORMATION

Expt. No.	% excess BuOH	Cat. Concn., m./l. x 10^{-4}	t 1/2, min.[b]	k, 10^{-4} min.$^{-1}$							
				30%	40%	50%	60%	70%	80%	Av.	Av. dev.[c]
1	___[a]	0.625	39.9	61.5	61.0	61.6	63.0	63.8	65.2	62.7	1.33
2	0	0.625	120	50.4	52.4	55.0	57.5	59.7	63.2	___[d]	___[d]
3	100	0.625	189	37.1	36.2	36.6	36.6	36.2	36.7	36.6	0.26
4	200	0.625	200	34.1	34.5	34.3	34.6	34.6	34.3	34.4	0.20
5	300	0.625	241	28.9	29.1	28.8	28.7	28.0	28.2	28.6	0.30
6	200	2(0.625)	104	67.1	67.8	67.3	66.4	66.2	64.8	66.6	0.80
7	200	0.5(0.625)	451	15.1	15.3	15.5	15.4	15.1	14.7	15.2	0.23

a. A 100% excess (total of 0.50 mole) of triphenylcarbinol was used here.

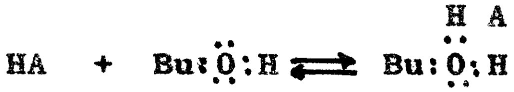
b. These values were read from the graph.

c. The average deviation ($\pm$) of a single k value from the average.

d. Values here would have little meaning.

Many of these experiments were repeated and on this basis it was estimated that the rate constants were reproducible to within ± 1.5%. The excellent results of Experiments 3, 4, and 5 emphasize the improved precision of the modified procedure.

It was of considerable interest to find that an excess of n-butyl alcohol retards the reaction. To explain this, an acid-base neutralization equilibrium may be assumed to exist between the catalyst and the butyl alcohol.[56]



$$HA \;+\; Bu:\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}:H \rightleftharpoons Bu:\underset{\cdot\cdot}{\overset{H\ A}{\overset{\cdot\cdot}{O}}}:H$$

Any increase in the concentration of the base, n-butyl alcohol, would drive the above equilibrium to the right and effectively reduce the concentration of the acid.

A comparison of the rate constants for Experiments 2 to 5 shows that there is less drift when an excess of butyl alcohol is used. It can be predicted that triphenylmethyl n-butyl ether is significantly less basic than n-butyl alcohol.[56] The effective catalyst concentration in Experiment 2 would therefore be expected to rise as the reaction proceeds so that the rate constants would drift upward. An excess of n-butyl alcohol should decrease this change in catalyst activity and hence diminish or eliminate this upward drift of the constants.

If the butyl alcohol were involved in the rate controlling step, its influence could be eliminated by using a large excess of it. One might attempt to explain on this basis the better first order kinetics obtained under these conditions. If the butyl alcohol were involved in the slow step, however, the kinetics would be expected to improve further as the excess of butyl alcohol is increased from 100% to 200% to 300%, but such was not the case. Furthermore, the rate decreases rather than increases as the excess of butyl alcohol is increased. In addition, the upward drift in constants as the reaction progressed with the one to one ratio of reactants (Expt. 2), shows a tendency toward zero order rather than second order kinetics. It seems evident, therefore, that the butyl alcohol is not involved in the rate controlling step.

Comparison of the rate constants for Experiments 1 and 2 suggests that an excess of triphenylcarbinol results in better kinetics. The apparently improved kinetics, however, may be primarily due to the fact that the calculations are less sensitive under these conditions.

Experiments 4, 6, and 7 show that the rate is approximately proportional to the catalyst concentration. An experiment like Experiment 2 except at four times the catalyst concentration gave a rate about four times as fast. (See Experimental.)

The average yield of water for the experiments of Table II was 95%. The results of preliminary isolation experiments showed that the yield of ether was over 90%.

Dr. Draper's preliminary data for related experiments were available and a number of experiments preliminary to those tabulated were also performed. The results of these were consistent with the results of Table II.

The etherification of benzhydrol and n-butyl alcohol was investigated in an analogous manner. The same standard procedure was used. A thirty-two fold increase in catalyst concentration was necessary however, in order to get reaction rates suitable for accurate kinetic study.

The rate constants calculated on the assumption that the first power of the concentration of benzhydrol determined the overall rate for this series of experiments, are given in Table III. The average yield of diphenylmethyl n-butyl ether was 89% and the average yield of water was 94%.

An examination of the average deviations shows that the k values are fairly satisfactorily constant except for Experiment 8. The downward drift in constants here may be mainly due to the fact that diphenylmethyl n-butyl ether is less basic than n-butyl alcohol.[56] As in the analogous triphenylcarbinol experiment, increased catalyst activity would therefore be expected as the reaction proceeds.

There is a definite but not large downward drift in the rate constants for the slower reactions, e.g. Experiments 12 and 14. It has been found that esterification of the catalyst does take place very slowly at considerably higher catalyst concentrations than used here. In these unusually slow re-

TABLE III

THE KINETICS OF DIPHENYLMETHYL n-BUTYL ETHER FORMATION

				k, 10^{-4} min.$^{-1}$						
Expt. No.	% excess BuOH	Cat. Concn., m./l.	t 1/2, min.[a]	30%	40%	50%	60%	70%	Av.	Av. dev.[b]
8	0	0.002	102	56.8	58.6	64.0	67.9	71.1	—[c]	—[c]
9	100	0.002	295	21.9	22.4	23.2	23.5	23.6	22.9	0.62
10	200	0.002	518	13.9	13.5	13.5	13.4	13.2	13.5	0.16
11	300	0.002	707	10.2	10.2	10.0	9.81	9.52	9.95	0.22
12	500	0.002	908	8.14	7.97	7.81	7.63	7.40	7.79	0.16
13	200	0.004	181	37.1	37.4	38.1	38.3	38.5	37.9	0.50
14	200	0.001	1348	5.40	5.22	5.13	5.14	5.03	5.18	0.10

a. These values were read from the graph.

b. The average deviation ($\pm$) of a single $\underline{k}$ value from the average.

c. Values here would have little meaning.

actions, it is not impossible that a small but significant reduction in catalyst concentration may occur in this way.

In order to test this, the catalyst from Experiment 12 was recovered by several water extractions and titrated with standard base. The results showed a 99% recovery of catalyst. It appears, therefore, that the catalyst concentration was essentially constant throughout the reaction. It is still possible, however, that small amounts of the sulfonate ester were present and that they were hydrolyzed in the process of extraction and titration.

An excess of n-butyl alcohol retarded the reaction in much the same way as for the experiments of Table II. The retardation resulting from the addition of succeeding given amounts of butyl alcohol decreased as the total amount of this alcohol increased. It is reasonable to assume here, as in the previous case, that butyl alcohol functioning as a base deactivates the catalyst. The rate decreases due to this are larger here than they were with triphenylcarbinol. This may be related to the fact that doubling the catalyst concentration approximately triples the rate. (See below.)

The data show that the use of an excess of n-butyl alcohol improves the kinetics. As in the triphenylcarbinol experiments, the excess of n-butyl alcohol may aid in maintaining constant catalytic activity as the concentration of the diphenylmethyl n-butyl ether increases.

The kinetics do not improve further as larger and larger excesses of n-butyl alcohol are used. Therefore in these reactions, as well as with those in Table II, n-butyl alcohol must not be involved in the rate controlling step. Further, as before, the rate decreases as the excess of n-butyl alcohol is increased.

The effect of catalyst concentration was studied using a 200% excess of n-butyl alcohol. The data in Experiments 10, 13, and 14 indicate that doubling the catalyst concentration approximately triples the rate. Similar results of a preliminary nature were obtained by Dr. Draper. Assuming no change in the activity coefficient of the catalyst upon doubling its concentration, a doubled rate would be expected. A two-fold increase in concentration, at these relatively high catalyst concentratinns, could conceivably raise the dielectric constant of the solution enough to significantly aid the ionization postulated in the rate controlling step. Rate studies on other reactions using benzene as solvent show that a non-linear relationship between catalyst concentration and reaction rate is not uncommon.[57]

Good constants were obtained for a smaller portion of the reaction in this series of experiments. Thus in Table III, no data are given after 70% reaction while the 80% point was included in Table II. This may be largely due to dibenzhydryl ether formation. This product was isolated in all experiments in about 5% yields. This may also account for the slightly lower yields of water and product as compared with the experiments in Table II. The larger excesses of n-butyl alcohol did not appear to reduce this side reaction significantly. Any uncharacterized residues were negligible in amount in all experiments in both Tables II and III.

An experiment analogous to Experiment 1 in Table II was performed but the rapid concurrent formation of dibenzhydryl ether precluded any satisfactory kinetic study of the reaction. Triphenylcarbinol being more sterically hindered than benzhydrol shows little if any tendency to self-etherify under the conditions of the distillation method.[55]

THE ETHERIFICATION OF BENZYL ALCOHOLS

The primary objective of this study of the etherification of benzyl alcohols was to determine if the distillation method could be used to synthesize benzyl ethers in good yields. Several self-etherifications of phenyl alkyl carbinols using p-toluenesulfonic acid as the catalyst but not using the distillation method are reported by Vernimmen, but in no instance were the yields good.[58] If successful, the formation of benzyl ethers by the distillation method would find wider use than the previously reported syntheses of tri- and diphenylmethyl ethers.[1] If these reactions did proceed satisfactorily, a further objective was to determine the effect of different _para_ substituents on the rate of reaction.

Since the etherification of a large number of benzyl alcohols was to be attempted, certain modifications were made in the experimental procedure. The realization of the above objectives did not require as precise kinetic data as obtained in the polyphenylcarbinol etherification studies. Since many of the starting materials were difficult to obtain, only half as much of each alcohol was used for an experiment. The total volume of solution was also cut from two liters to one liter. For the majority of the experiments, solid catalyst was used instead of aliquot amounts of a standard catalyst solution. In spite of the unfavorable effect of these modifications on the accuracy of the kinetic data, it was found when several of the experiments listed in the tables in this section were duplicated, that the average value of the <u>k</u> could be reproduced to within ± 6%. The yield data also checked satisfactorily.

A major change in the standard experimental procedure was necessary when catalyst concentrations in excess of 0.004 moles per liter were used. In these cases, a solution of the solid catalyst in benzene was dehydrated azeotropically prior to being mixed with the reactants.

The maximum temperature variation among the experiments listed in the tables of this section (excluding Expt. 29) was ± 1.4°, this being about twice that observed among the polyphenylcarbinol etherifications. The maximum temperature variation within a given experiment was ± 0.1° but in 80% of the experiments this was 0.05° or less. All reaction temperatures (which are corrected) are listed in the Experimental.

The data for the etherification of several <u>para</u> substituted benzyl alcohols with n-butyl alcohol are given in Table IV. A 200% excess of n-butyl alcohol was used throughout. It is apparent that good yields of the desired products were obtained except that p-chlorobenzyl alcohol gave only a 40% yield. When attempts were made to etherify p-nitrobenzyl alcohol by this method, none of the desired ether was obtained. On the basis of the resonance theory, carbonium ion formation by this latter alcohol is unlikely.[59]

TABLE IV

ETHERIFICATION OF PARA SUBSTITUTED BENZYL ALCOHOLS WITH n-BUTYL ALCOHOL

Expt No	Benzyl Alcohol	Cat Concn , m /1	Yield, %	t 1/2, min
15	$p\text{-}(CH_3)_2NC_6H_4CH_2OH$	0.000125	76	158
16	$p\text{-}CH_3OC_6H_4CH_2OH$	0.002	87	184
17	$p\text{-}CH_3C_6H_4CH_2OH$	0.064	72	254
18	$C_6H_5CH_2OH$	0.128	59[a]	1210
19	$p\text{-}ClC_6H_4CH_2OH$	0.256	40[b]	347
20[c]	$p\text{-}ClC_6H_4CH_2OH$	0.256	40[d]	279

[a] A 9% yield of diphenylmethane was also obtained.

[b] A 30% yield of p-chlorodiphenylmethane was also obtained.

[c] A 1 to 3 mixture of nitrobenzene and cyclohexane was used as solvent in place of benzene. This solvent was first used by Mr. Segrave in these laboratories.

[d] A 11% yield of bis-(4-chlorobenzyl) ether was also isolated.

In Experiments 16, 17, 18, and 19 the yield of ether generally became lower as the *para* substituent became a poorer electron donor. Concurrent with lower yields of ether, however, were found increased yields of alkylation product The solvent used in Experiment 20 precluded alkylation taking place but only a 40% yield of the unsymmetrical ether was again obtained

The trend away from etherification and toward alkylation in Experiments 16, 17, 18, and 19 is paralleled by an expected decreasing stability of the corresponding carbonium ions. The p-chlorobenzyl carbonium ion would be expected to be considerably more reactive than the benzyl carbonium ion, for example, with the result that the former would react more readily when it collided with a molecule of solvent while the latter would tend to bump from solvent molecule to solvent molecule until it found a butyl alcohol molecule to react with. There is evidence that a relatively stable carbonium ion such as expected from anisyl or p-methylbenzyl alcohol cannot be made to alkylate benzene under these conditions.[60] However, carbonium ion stability, attractive as it may seem, probably is not the only factor which determines the proportion of etherification to alkylation. Studies on variation of catalyst concentration (see below) have shown that this factor also markedly affects the course of these reactions and might have an influence in the direction found here.

The yield of water from a typical experiment in this table was 99%. The amount of uncharacterized residue was about 6% of the weight of the starting benzyl alcohol.

To get practical rates of reaction with n-butyl alcohol as the <u>para</u> substituents were varied from $(CH_3)_2N$- through CH_3O-, CH_3-, and H- to Cl-, a 2048 fold increase in catalyst concentration was necessary. The order of decreasing reactivity of these benzyl alcohols is therefore the same as the order of decreasing electron releasing ability of the para substituents. (A comparison of Experiment 31 in Table VII with Experiment 19 in Table IV shows clearly that p-chlorobenzyl alcohol is less reactive than benzyl alcohol.)

In spite of the presence of excess n-butyl alcohol, there were serious drifts in the first order k values as the reaction progressed for most of these experiments. The actual values are given in the Experimental. p-Dimethylaminobenzyl alcohol gave by far the largest downward drift. The downward drift was smaller with anisyl alcohol. Upward drifts were observed for the other benzyl alcohols. The upward drifts may be due to changes in the activity of the catalyst as the reaction progressed as discussed for Tables II and III. The cause of the downward drift is not known. Experiments 16 and 18 were duplicated except that no excess of n-butyl alcohol was used and the drifts approximately doubled in magnitude. Therefore here, as in the reactions of Tables II and III, an excess of n-butyl alcohol tends to improve the kinetic data.

In view of these drifts, rate constants were calculated for Experiments 15 and 20 and for a duplicate of Experiment 19 on the assumption that the reaction was first order with respect to both the benzyl and butyl alcohol. The k values thus obtained for Experiment 15 did have a slightly smaller maximum deviation than the first order values but for the other two experiments, the first order k values were much superior to the second order values.

Mr. Harold Segrave has found in his studies on the alkylation of aromatic compounds by alcohols using the distillation method that at extremely high catalyst concentration, the rate of water evolution does not necessarily indicate the rate of alkylation.[60] At a catalyst concentration of 0.256 moles per liter and with only one molecule of benzyl alcohol present per three molecules of catalyst, he isolated a 91% yield of diphenylmethane after stopping the reaction when only a 25% yield of water had been evolved. He further found that under these conditions, the water was evolved according to the first order law (calculated on the basis of the benzyl alcohol) but that constant $\underline{k}$ values were obtained only when the concentration of the catalyst was at least 0.128 moles per liter and there was not less than a 200% excess of the catalyst with respect to the benzyl alcohol present. At high concentrations of catalyst, he also found that doubling its concentration actually slowed down the rate of water evolution. He concluded that the first order removal of water under these conditions was due merely to dehydration of the catalyst monohydrate which was rapidly formed in the reaction mixture.

On the basis of the Mr. Segrave's findings, it is conceivable that the rate of water evolution in Experiments 18, 19, and 20 could have been dependent upon the rate of dehydration of the catalyst monohydrate. It appears, however, that such was not the case probably because of the excess of n-butyl alcohol which is postulated to form a complex with the catalyst as discussed above. In all cases in this work, an increase in the concentration of the catalyst increased the rate of water evolution.

The data for the etherification of anisyl alcohol with para substituted benzyl alcohols are given in Table V. A 200% excess of the benzyl alcohol listed in the second column of the table was used in the first four experiments while a 200% excess of anisyl alcohol was used in Experiment 25. The unique character of the latter experiment is explained below.

TABLE V

ETHERIFICATION OF ANISYL ALCOHOL WITH PARA SUBSTITUTED BENZYL ALCOHOLS

Expt. No.	Benzyl Alcohol	Cat. Concn., m./l.	Yield, %	t 1/2, min.
21	p-$CH_3C_6H_4CH_2OH$	0.001	73	181
22	$C_6H_5CH_2OH$	0.001	93	98.0
23	p-$ClC_6H_4CH_2OH$	0.001	94	43.3
24	p-$O_2NC_6H_4CH_2OH$	0.001	87	14.0
25[a]	p-$(CH_3)_2NC_6H_4CH_2OH$	0.000125	74	73.0
26	p-$CH_3OC_6H_4CH_2OH$ [b]	0.001	80	120

a. A 200% excess of anisyl alcohol was used here.

b. The total starting concentration was 0.250 moles/l.

The yields of product were uniformly good and averaged 83%. No by-products were isolated but uncharacterized residues weighing about 8% as much as the starting anisyl alcohol were obtained. The average yield of water was 95.5%.

In order to determine the effect of variation in the *para* substituent on the rate of reaction, the first four experiments were run at a constant catalyst concentration. The rates of reaction increased as the *para* substituents were varied in the following order; CH_3-, H-, Cl-, O_2N-. The half reaction time values differed by a factor of 13 overall. These different rates can be explained in terms of current theory. The relative strengths of *para* substituted benzoic acids have been explained on the basis that the substituent group can transmit its inductive effect through the aromatic nucleus.[61] Assuming that analogous electron displacements accur in similarly substituted benzyl alcohols, it would be predicted that the basicities of the alcohols would decrease in the same order that the etherification rates increased. It appears reasonable, therefore, to ascribe the different rates to different degrees of catalyst deactivation rather than to fundamental differences in the reactivities of these alcohols.[56] This explanation is based on the carbonium ion mechanism for etherification which is discussed in the Introduction and in the following section.

Experiment 25 was fundamentally different from the first four experiments in that anisyl alcohol was the reactant in excess. On the basis of Experiments 15 and 16 (*cf*. Table IV), it could be predicted that p-dimethylaminobenzyl alcohol should give a carbonium ion much more readily than anisyl alcohol. It might be noted that Green[62] also found that a dimethylamino group releases electrons more readily than a methoxy group, but according to Hammett, the methoxy group releases electrons the more readily.[63] In order to hold self-etherification of anisyl alcohol to a minimum, a catalyst concentration one eighth that used in the other experiments in this table was chosen. That this self-etherification was effectively suppressed was shown by the fact that a 74% yield of the unsymmetrical ether was obtained. No bis-(dimethylaminobenzyl) ether was isolated but a larger than usual residue was obtained. It can be predicted that this latter product would be very unstable toward distillation.[64] At higher catalyst concentration, a mixture of the three possible ethers would be expected. By the distillation method however, the minimum catalyst concentration needed to give the p-dimethylaminobenzyl carbonium ion is readily ascertained since one need only add catalyst portionwise until water evolution begins. If this low catalyst concentration is used, there is no appreciable formation of the p-methoxybenzyl carbonium ion, hence no dianisyl ether. The excess of anisyl alcohol effectively diminishes the formation of bis-(p-dimethylaminobenzyl) ether so that an excellent yield of the unsymmetrical ether is obtained.

The expected deactivation of the catalyst by the basic amino group of p-dimethylaminobenzyl alcohol was not apparent in either Experiment 15 or 25 probably because of the extreme reactivity of this alcohol.

In Experiment 26 anisyl alcohol was self-etherified. This ether has been made in good yield by the action of concentrated hydrochloric acid on anisyl alcohol dissolved in diethyl ether.[65] Since this reaction went so readily, it was believed in the early part of this study that this ether might be an intermediate in the formation of at least part of the anisyl n-butyl ether (cf. Expt. 16, Table IV). To test this assumption, an experiment was carried out in which dianisyl ether was reacted with n-butyl alcohol under the conditions used in Experiment 16. Little if any transetherification took place at a catalyst concentration of 0.002 moles per liter. This transetherification did however go smoothly to give a 94% yield of product when the catalyst concentration was doubled.

The kinetic data for the experiments of Table V are given in the Experimental. The rate constants in all these experiments, except Experiment 25, are calculated on the assumption that the first power of the concentration of anisyl alcohol determined the overall rate of reaction. In Experiment 25, the concentration of p-dimethylaminobenzyl alcohol was used in the rate equation in place of the concentration of anisyl alcohol since the amino alcohol would be expected to form carbonium ions more readily (see above).

The best kinetic data were obtained for Experiments 23 and 24. The k values generally drifted downward except in Experiment 24 where a definite maximum value was reached at the 60% reaction point. These downward drifts appear to be characteristic for almost all etherifications of anisyl alcohol.

It was noted in the preceding section that the formation of dibenzhydryl ether probably caused drifts in the rate constants as the etherification of benzhydrol by n-butyl alcohol progressed. Benzyl alcohols, of course, have even less steric hindrance toward self-etherification than benzhydrol. Self-etherification of benzyl alcohols, therefore, may have interfered with the kinetic studies in all cases where the formation of benzyl butyl ethers was being studied even though the symmetrical ethers were seldom isolated in significant amounts. Perhaps, in certain cases, part of the symmetrical ether was transetherified which would also interfere with the kinetics. The yields obtained in these etherifications were in general very good but not nearly quantitative enough to exclude the possibility of side reactions occurring to an extent sufficient to interfere with the kinetic calculations.

The data for the etherification of anisyl alcohol with primary, secondary, and tertiary butyl alcohol are given in Table VI. A 200% excess of the butyl alcohol was used in each case.

TABLE VI

ETHERIFICATION OF ANISYL ALCOHOL WITH PRIMARY, SECONDARY, AND TERTIARY BUTYL ALCOHOL

Expt. No.	Butyl Alcohol	Cat. Concn., m./l.	Yield, %	t 1/2, min.
27	$CH_3CH_2CH_2CH_2OH$	0.002	87	184
28	$CH_{3_3}CH_{2_2}CH_2CH_{2_3}OH_{OH}$	0.002	84	287
29	$(CH_3)_3COH$	0.002	48[a]	426

a. Dianisyl ether also isolated in 29% yield.

The yields of expected product were good for both primary and secondary butyl alcohols but poor for the tertiary alcohol. In the last case, a slight evolution of isobutylene was noted and, in addition, a 29% yield of dianisyl ether was obtained. One possible explanation for the low yield of unsymmetrical ether and the presence of dianisyl ether is that the steric hindrance in the t-butyl alcohol molecule, to a certain extent, shields the oxygen from attack by the postulated p-methoxybenzyl carbonium ion. In fact, it would be expected that an anisyl carbonium ion should encounter less steric hindrance in reacting with an anisyl alcohol molecule than with a t-butyl alcohol molecule. Without an excess of the tertiary alcohol, dianisyl ether would doubtlessly have been the chief product. The presence of isobutylene indicates that t-butyl alcohol undergoes carbonium ion formation even at this low catalyst concentration. Since evolution of isobutylene was slight, and, since tertiary butyl alcohol was present in large excess, it is very improbable that this side reaction contributed significantly to the reduction in the yield of the desired product.

The rate of water evolution for the primary alcohol was more than twice that for the tertiary alcohol. The rate for the secondary alcohol was intermediate being a little closer to that for primary butyl alcohol. On the basis of the electron releasing ability of alkyl groups, it would be expected that the basicities of these alcohols would decrease in the order, tertiary, secondary, primary. These widely different rates can, therefore, be ascribed to different degrees of deactivation of the catalyst.

The first order k values, obtained by assuming that the first power of the concentration of anisyl alcohol determined the rate, are given in the Experimental. These kinetic results were fair becoming progressively poorer as the alcohol became more highly branched. Of course with the tertiary alcohol, the low yield invalidates the calculations. The constants drifted downward in a manner characteristic of other etherifications of anisyl alcohol.

The investigation of the effects of varying the ratio of reactants in the etherification of benzyl alcohols was done only with those most readily available. The data are given in Table VII. In all cases, reaction was continued until one mole of water was evolved per mole of the benzyl alcohol.

TABLE VII

THE EFFECTS OF VARYING THE RATIO OF THE n-BUTYL ALCOHOL TO THE BENZYL ALCOHOL

Expt. No.	$p\text{-}RC_6H_4CH_2OH$	Cat. Concn., m./l.	t 1/2, min.	Ratio of BuOH to $p\text{-}RC_6H_4CH_2OH$	Yield Ether, %	Yield Alk.,[a] %
30	$C_6H_5CH_2OH$	0.256	21.5	1/1	0	74
31	$C_6H_5CH_2OH$	0.256	193	3/1	47	32
32	$C_6H_5CH_2OH$	0.256	2160[b]	9/1	80	0
33	$C_6H_5CH_2OH$	0.128	207	1/1	23	57
34	$C_6H_5CH_2OH$	0.128	1210	3/1	59	9
35	$p\text{-}CH_3OC_6H_4CH_2OH$	0.002	96.0	1/1	47	0[c]
36	$p\text{-}CH_3OC_6H_4CH_2OH$	0.002	184	3/1	87	0

a. This is the yield of alkylated benzene.

b. This is approximate only.

c. 3.3 grams of an unidentified crystalline solid was also obtained.

At a catalyst concentration of 0.256 moles per liter, the yield of ether increased regularly as the ratio of n-butyl to benzyl alcohol was increased (cf. Expts. 30, 31, and 32). The absence of any ether in Experiment 30 is consistent with the carbonium ion mechanism. The third step of this mechanism requires free n-butyl alcohol.

$$R'^{+} \quad + \quad \mathrm{Bu}:\underset{\cdot\cdot}{\ddot{O}}:H \rightleftarrows \left[R':\underset{\cdot\cdot}{\overset{H}{O}}:\mathrm{Bu}\right]^{+}$$

A large excess of catalyst with respect to the n-butyl alcohol, as in Experiment 30, would be expected to convert essentially all the alcohol to the complex, $\mathrm{Bu}:\underset{\cdot\cdot}{\overset{H}{\ddot{O}}}:\overset{A}{H}$ and thus block this third step. It is noteworthy, as would be expected on the basis of this explanation, that decreasing the amount of catalyst has much the same effect as increasing the amount of n-butyl alcohol. Thus with less catalyst, more ether and less alkylation product is obtained. (Compare Expt. 33 with 30 and 34 with 31.) This appears to be an interesting new method for controlling the course of a reaction.

Increasing the ratio of n-butyl to anisyl alcohol from one to one to three to one nearly doubled the yield of the ether (cf. Expts. 35 and 36) and no alkylation product was isolated in either experiment. The amount of catalyst here, relative to the amount of n-butyl alcohol, precluded any important blocking action such as just discussed. As was discussed above, lack of alkylation product might also indicate that the relatively stable (low energy) anisyl carbonium ion is unable to muster the necessary energy to alkylate benzene under these conditions.

An excess of n-butyl alcohol very markedly retards the rate of water evolution in a manner analogous to that observed in the experiments of Tables II and III. The nine to one and three to one ratios of n-butyl to benzyl alcohol yielded rates only about 1% and 10% of that observed for the corresponding one to one ratio (cf. Expts. 30, 31, and 32). The three to one ratio of n-butyl to anisyl alcohol gave a rate of water evolution 48% of that observed for the corresponding one to one ratio (cf. Expts. 35 and 36). These data indicate that a given excess of n-butyl alcohol appears to be less effective in retarding the rate as the catalyst concentration decreases. Of course the different proportions of products obtained must be considered, but in spite of this, it is reasonable to assume here as in previous cases, that these excesses of n-butyl alcohol retard the rate through deactivation of the catalyst.

The kinetic data for the experiments of Table VII are given in the Experimental. The k values were calculated on the assumption that the first power of the concentration of the benzyl alcohol determined the overall rate. As observed before, the kinetics were uniformly poor in the absence of an excess of n-butyl alcohol. Since there never was a two to one ratio of catalyst to total alcohol present in any of these experiments, the anomalous effects found by Mr. Segrave would not be expected here. The k values generally drifted upward in the reactions with benzyl alcohol suggesting increased catalytic activity as the reaction proceeded. As usual, the k values drifted downward in the anisyl alcohol experiments.

The data pertinent to the study of the effect of variation of the catalyst concentration on the rate of water evolution for the reaction of benzyl alcohol with n-butyl alcohol are found in Table VII. At a one to one ratio of n-butyl alcohol to benzyl alcohol, doubling the catalyst concentration increased the rate nine-fold (cf. Expts. 33 and 30). At the three to one ratio of these same alcohols, the corresponding increase was six-fold (cf. Expts. 34 and 31).

The data for the etherifications of triphenylcarbinol (cf. Expts. 4 and 6, Table II) and diphenylcarbinol (cf. Expts. 10 and 13, Table III) with n-butyl alcohol (which were analogous to Expts. 34 and 31 above) showed that doubling the catalyst concentration doubled and tripled respectively the rates of water evolution. One possible explanation for the unexpected increase in rate associated with a doubling of the catalyst concentration, as the number of phenyl groups in the carbinol decreases from three to two to one, is that the increasingly larger amounts of catalyst needed to get a practical reaction rate changes the medium in a manner that favors the reaction. This view is also supported by the fact that the effect of catalyst concentration on the rate of etherification of anisyl alcohol with n-butyl alcohol is almost identical with that observed for the corresponding etherification of diphenylcarbinol. Since these reactions were all carried out in the same range of catalyst concentration, it appears that the total catalyst concentration and not the number of phenyl groups in the carbinol determines the effect of variation of catalyst concentration on the rate of reaction.

In benzene solvent, the kinetic order of the reaction of diazoacetic ester with formic or picric acid is approximately two with respect to the acid.[57] Other reactions also give orders between one and two. Bell's assumption, that the catalyst functions as a base as well as an acid in these reactions, would account for orders with respect to the catalyst up to a maximum of two. If hydrogen bonding between the oxonium ion from Step 2 of the mechanism (page 2) and the free catalyst is assumed (which would aid the dissociation), then it would follow that the reaction should be of some order greater than one but less than two with respect to the catalyst. This theory does not, however, satisfactorily explain why orders higher than two are observed. One possible cause of these high values is that the large amounts of catalyst increase the dielectric constant of the medium sufficiently to increase the rate of Step 2.

At a one to one ratio of n-butyl alcohol to anisyl alcohol, raising the catalyst concentration from 0.002 to 0.004 moles per liter cut the half reaction time from 96.0 minutes to 24.7 minutes and raised the yield from 47% to 71%. There was no evidence of the alkylation product in either of these experiments. At a three to one ratio of these alcohols, raising the catalyst concentration from 0.002 to 0.008 moles per liter decreased the half reaction time from 184 minutes to 19.3 minutes but had no effect on the yield.

Certain additional etherifications of benzyl alcohol with itself and with n-hexyl alcohol were attempted. The results are of only secondary importance and therefore are given only in the Experimental.

The self-etherification of diethylene glycol in benzene was also attempted but no reaction took place. Polymeric ethers of decamethylene glycol, xylylene glycol, and methyl substituted xylylene glycols have been made by heating these with sulfonic acid.[66] Diethylene glycol was, however, etherified with benzhydrol in benzene using p-toluenesulfonic acid as catalyst. This product which was a new compound was isolated in 63% yield.

In view of the good results for the etherification of benzyl alcohols summarized in the foregoing tables, an attempt was made to etherify an even less active alcohol, e.g. a normal aliphatic alcohol. Mrs. Gloria Weiss, in this laboratory, had previously obtained a dihexyl ether in fair yield in an attempted esterification of p-toluenesulfonic acid with n-hexyl alcohol.[67]

Four moles of n-hexyl alcohol at a catalyst concentration of 0.250 moles per liter (the alcohol served as its own solvent) was reacted in the standard azeotropic apparatus. At 25, 50, 75, and 100% completion of reaction, one fourth of the original weight of the reaction mixture was removed and quickly cooled and neutralized. Each fraction was worked up separately, care being taken to recover small amounts of by-products as well as the unreacted alcohol. On the basis of water evolved, the yield of hexyl ether was 86, 85, 94, and 75%. Since the primary hexyl carbonium ion would be expected to rearrange to the secondary, it is believed that the product is n-hexyl sec-hexyl ether. It is remarkable that so little hexene was formed and such good yields of ether were obtained. The absence of solvent probably allowed the hexyl carbonium ion to react with a molecule of hexyl alcohol before it had time to be converted to hexene. It is pertinent to note that Preston got large yields of butene when attempts were made to react n-butyl alcohol in an inert solvent.[68]

ANALYSIS OF THE RESULTS IN TERMS OF THE CARBONIUM ION MECHANISM OF ETHERIFICATION

One of the objectives of this research was to determine whether the foregoing results substantiated or controverted the carbonium ion mechanism of etherification as given on page 2. It may be noted in this connection that Hammett states, ".... the study of the rates of reaction is the most useful tool available for the investigation of reaction mechanism.... ."[69]

It has been assumed in the discussion which follows that Step 2 of this mechanism is most probably the slowest and therefore rate determining. In reactions proceeding via carbonium ions, the formation of these ions is often found to be the high energy process and hence the slowest step. On the basis of this assumption, the rate of water formation is a direct measure of the overall rate of etherification. It is pertinent to note that in the work on the self-etherification of n-hexyl alcohol, it was found that the yield of water at different points in the course of reaction was a reliable measure of the amount of etherification.

In the first place, it is evident that Step 1 of the mechanism is a reasonable explanation of the function of the acid catalyst in these etherifications. The same step is involved in other well known reactions, e.g. Friedel-Crafts alkylation with alcohols.[18] Further evidence for the first step is that with triphenylcarbinol (Table II), the rate was linearly proportional to the catalyst concentration. Of course with diphenylcarbinol and benzyl alcohols (Tables III and VII), doubling the catalyst concentration more than doubled the rate. This effect is not well enough understood to decide whether it offers any significant argument against the carbonium ion mechanism. Since the first order k values obtained were dependent upon catalyst concentration, they are actually pseudo first order constants.

The triphenylcarbinol etherifications furnish good evidence for Step 2 of the mechanism because of the excellent kinetics obtained on the assumption that the first power of the concentration of triphenylcarbinol alone determined the rate of reaction. It has been well established that the triphenylcarbinol would tend to form carbonium ions much more readily than the n-butyl alcohol. Cryoscopic data, for example, indicate that triphenylcarbinol produces the corresponding carbonium ion in 100% sulfuric acid while n-butyl alcohol does not.[16] Further, it has been shown by both conductance and absorption experiments that the formation of the triphenylmethyl carbonium ion is extremely probable when triphenylmethyl chloride is dissolved in cresol.[13] n-Butyl chloride very probably does not give carbonium ions under these conditions. Since cresol has also a low dielectric constant, it being only twice that for benzene, it is not unreasonable to consider that the oxonium ion dissociates to give the triphenylmethyl carbonium ion as required by

Step 2 of the mechanism.

The etherifications of diphenylcarbinol (Table III) gave kinetic results which strongly supported the foregoing interpretations. On the basis of similarity of structure, it is reasonable to assume that if triphenylcarbinol can give a carbonium ion, diphenylcarbinol should do likewise.

The etherification of benzyl alcohols also provided important support for this mechanism. The data of Table V on the etherification of anisyl alcohol by benzyl alcohols with a para CH_3-, H-, or Cl- substituent gave an especially interesting type of support for the carbonium ion mechanism. The same catalyst concentration was used throughout here while it was necessary to vary the catalyst concentration over two thousand fold when n-butyl alcohol was etherified with the various para substituted benzyl alcohols (Table IV). This strongly indicates, as predicted by this theory, that in the former cases anisyl alcohol was the carbonium ion former throughout while in the latter cases the substituted benzyl alcohols were the carbonium ion formers. It is of especial interest that the somewhat surprising fact, that anisyl alcohol etherifies p-nitrobenzyl alcohol thirteen times as fast as it etherifies p-methylbenzyl alcohol can be readily explained in terms of the carbonium ion theory. (See discussion in preceding section on catalyst deactivation by these alcohols.)

The effect of para substituents in benzyl alcohols on rate of etherification of butyl alcohol (Table IV) is significant. Electron releasing groups in the para position should favor the dissociation postulated in Step 2 and this was found to be true. It will be recalled that the rate decreased consistently as the para substitutent was varied from $(CH_3)_2N$- through CH_3O-, CH_3-, and H- to Cl-.

The kinetic results obtained with benzyl alcohols seem to be closer to first order than any other order and hence furnish at least as much evidence for this mechanism as against it. Of course the mechanism might change as the para substitutent is changed but there is no strong evidence that it does. It is not inconceivable that the deviations from first order kinetics were not due to the fact that the reaction was fundamentally of a different order but were due to side-reactions, medium effects, or other secondary influences.

The shift, discussed above, from a good yield of benzyl butyl ether to a good yield of diphenylmethane, as the amount of n-butyl alcohol was decreased, gives evidence in favor of Step 3 of the mechanism.

The analysis of these results in terms of the proposed mechanism of etherification have in general resulted in its support. This support of the mechanism is based chiefly on finding much evidence in its favor and at the same time uncovering no strong evidence against it.

EXPERIMENTAL

THE KINETICS OF THE ETHERIFICATION OF POLYPHENYLCARBINOLS

General Considerations

Starting Materials.--The benzene used in these experiments was supplied by Jones and Laughlin in 55 gallon drums. It was purified and dried by distillation in 10 l. lots. The middle 70% portion, which distilled at a constant temperature, was collected and stored in tightly stoppered gallon jugs. Upon removal from storage, these jugs were fitted with a stopper having a pouring spout and an air inlet to which was attached a calcium chloride drying tube. This arrangement prevented excessive moisture absorption. The physical constants of this benzene are listed in Table X.

The catalyst used was Eastman white label p-toluenesulfonic acid monohydrate. It was used without further purification since previous workers had shown that it was of high purity and entirely satisfactory for this type of work.[55, 62] Its purity was, however, indirectly checked by titration of the recovered catalyst from Experiment 12. Better than 99% purity was indicated. One lot of catalyst served for all the experiments in this section. To assure uniformity, the solid catalyst was thoroughly mixed in its container with a glass rod.

A standard solution of catalyst sufficient in amount to serve for all the triphenylcarbinol experiments was made up in the following manner. A 4.756 g. portion of the monohydrate was carefully weighed out on an analytical balance into a small beaker and added to 500 ml. of benzene in a 1 l. round bottom single-neck flask. A Dean-Stark water separator, filled with benzene, and a condenser were then attached. Boiling chips were added and the solution was brought to reflux. All the water of hydration was recovered in a matter of minutes but the solution was allowed to reflux for two hours to assure complete dehydration. In order to prevent traces of moisture in the condenser from being drawn back into the reaction flask during cooling, the water collector was removed from the flask immediately upon cessation of refluxing and replaced with a calcium chloride drying tube. If this was not done, significant amounts of the catalyst monohydrate later precipitated. When the solution had cooled completely, this drying tube was replaced by a standard taper glass stopper which was lubricated with "Cello" grease. The solution was stored in the dark since there was a tendency for it to develop a light purple color. Titration of the recovered catalyst from Experiment 12 showed that this solution was stable in the dark.

Since more catalyst was required in the benzhydrol experiments, 19.021 g. of the monohydrate was dissolved in 500 ml. of benzene according to the procedure of the preceding paragraph. Two identical batches of standard catalyst solution were made for all the experiments with benzhydrol.

Since the anhydrous catalyst was extremely hygroscopic and the monohydrate was very insoluble in benzene, it was impractical to make up these solutions on a strict molarity basis. It was assumed that the change in volume occasioned by solution of the catalyst was insignificant since the amount never constituted more than 4% by weight of the solvent.

The n-butyl alcohol of U.S.P. quality was supplied by Commercial Solvents. It was further purified by distillation through an asbestos wrapped 8 in. column packed with glass helices. The first and last 15% were discarded. The middle portion was stored in tightly stoppered bottles prior to use. The physical constants are recorded in Table X.

The triphenylcarbinol used in these experiments was prepared by methods described in "Organic Syntheses."[70] Since relatively large quantities of this material were required, the quantities were tripled with complete success. The purification procedure followed was that described by Draper.[55] The melting point of the carbinol was 161-162° (lit. m.p. 161-162°).

Benzhydrol was prepared by direct hydrogenation of Eastman white label benzophenone. Adkins describes this hydrogenation on 0.1 m. scale using a nickel catalyst and ethyl alcohol for the solvent.[71] The catalyst described by Adkins was not available at the time so Dr. Reeves suggested that copper chromite catalyst might be substituted in its place. In order to avoid the possibility of etherification of benzhydrol by ethanol, diethyl ether was used as the solvent. On the basis of preliminary experiments the scale of operation was increased to 4 m.

A 4 m. portion of benzophenone (737.0 g.) was dissolved in 866 ml. of anhydrous diethyl ether. This solution along with 6 g. of copper chromite was placed in a high pressure rocker-type bomb of 2500 ml. capacity. Hydrogen was introduced to give a pressure of 2400 pounds per sq. in. (at 16°). Since the pressure always dropped significantly in the initial rocking of the bomb (without heat), possibly because of solubility of the hydrogen in the solvent, the rocking was stopped at least once to boost the pressure back to 2400 pounds per sq. in. When the pressure remained constant, heat was applied and the temperature was raised rather rapidly to 110° and then raised more slowly to 130°. A plot of pressure versus time, as suggested by Dr. Reeves, was made as the heating was continued. These curves always had a preliminary upward slope up to about 125° followed by a rather broad plateau which terminated in a steep drop. The reaction was assumed to be complete at the end of this drop. The heat was turned off before 130° was reached in order to avoid seriously exceeding this temperature.

It is possible, at least in theory, to hydrogenate this product to diphenylmethane. The following empirical expression was quite useful in determining if this had occurred.

$$\frac{(\text{No. of lbs. press. drop})}{(0.5)\ (\text{m.})\ (\text{No. of H atoms reacted})} = \frac{1.205T^{\circ}}{(\text{Free vol. of bomb in l.})}$$

T° is the absolute temperature. The total pressure drop (cold basis) was 1400 as compared to the estimated value of 1200 pounds per sq. in.

The cooled solution was filtered to remove the catalyst. The diethyl ether was removed by evaporation and the crude benzhydrol was then recrystallized twice from 60-80° petroleum ether. A 70% yield of purified product (m.p. 65.8-66.3°) was obtained but this might have been improved by reworking the mother liquors. Melting points of 68° and 69° are reported for benzhydrol.[72, 73] These higher melting points could not be duplicated upon repeated recrystallization from different solvents. Neither could they be duplicated for benzhydrol made by the reduction of benzophenone with zinc and alkali.[72]

Standard Procedure.--The essential features of the standard procedure were outlined in the Discussion. Further pertinent details follow.

Before each experiment the reaction flask, water collector, and condenser were cleaned with hot chromic acid cleaning solution. This was followed by a thorough rinsing first with tap water and then with distilled water. The apparatus was dried in an oven at about 110°. Consistently good menesci were obtained only when this method of cleaning the condenser and water collector was followed.

All reactants were weighed out on a 100 g. capacity triple-beam balance accurate to ± 0.01 g. The accuracy of the balance was checked from time to time with calibrated weights.

All solutions of reactants in this section were made up to a total volume of 1888 ± 5 ml. at 25° by placing the volumetric containers in a water bath which was kept at this temperature. About 25 min. was assumed to be sufficient to establish thermal equilibrium between the solution and the bath.

Benzene was the only lubricant used on the standard taper joints directly above the collector tube. Trace amounts of ordinary lubricants seriously distorted the meniscus.

As mentioned in the Discussion, about 0.2 ml. of water was placed in the water collector when the solution was refluxed prior to adding the catalyst. When it was apparent that the reaction mixture contained no more water, the refluxing was stopped long enough to raise the condenser and adjust the water in the collector (with the steel shot raised) to exactly 0.20 ml. by means of an elongated medicine dropper. The condenser was then replaced and the solution again brought to reflux.

A special procedure was followed in transferring the catalyst solution since it was extremely hygroscopic. The stopper in the catalyst solution storage flask was quickly replaced by another that carried two glass tubes so arranged that dry air forced in through one tube caused the liquid catalyst to flow out the other into a buret that had been previously flushed with dry air. The filled buret was fitted with a calcium chloride drying tube and the meniscus adjusted to the proper calibration mark. The reaction flask had a small additional neck into which the buret tip was fitted by means of a cork. Zero time was taken as the time at which the catalyst was added. The 10 ml. buret used in these studies was calibrated by the use of a 2 ml. microburet made of pyrex glass loaned by Dr. Pickard. The 50 ml. buret was made of pyrex glass but was not calibrated.

Prior to taking each reading, a looped "Chromel" wire was used to shake down any adhering droplets of water in the condenser and collector tube. This shaking was started about 30 sec. prior to and continued right up to the time recorded for the reading. The steel shot was then slowly raised through the meniscus by an external magnet and the volume was read. A meniscus reader was used to avoid parallax. No error was introduced by taking the actual reading up to half a minute after the recorded time since these reactions were so slow that no water was ever observed to fall freely from the condenser tip during this time interval. The collectors had previously been calibrated using the 2 ml. microburet and were found to be accurate to 0.01 ml. Concurrent with each water reading a temperature reading was taken. Each reaction flask was fitted with a thermometer well which was partially filled with glass beads so that the thermometer bulb was just below the surface of the refluxing solution. This arrangement probably gave a better temperature and also eliminated stem correction. Glycerol was kept in the well to aid heat transfer. All the thermometers used in this work were calibrated at 83° against an Anschutz thermometer which had been calibrated by the National Bureau of Standards.

Readings were taken every 0.1 ml. where practicable for the first 80% of the reaction. A few readings were taken toward the end of the reaction. Boiling chips were added from time to time as the reaction progressed to prevent superheating which tended to occur. Barometric pressure was usually recorded about three times in the course of a reaction. It appeared that superheating was a more important factor in temperature variation within a given experiment than variation in barometric pressure.

Upon completion of reaction, the solution was cooled and transferred to a 3 l. separatory funnel. The solution was extracted with about 50 ml. of saturated sodium bicarbonate solution and then with small portions of distilled water until neutral. The solvent was removed by distillation from the steam bath using reduced pressure. The residue was transferred to a 100 ml. flask and the remainder of the solvent was removed using an electrically heated oil bath and the water pump. All unsymmetrical ethers in this section were isolated by oil pump vacuum distillations. In the benzhydrol etherifications, the by-product, dibenzhydryl ether was always recovered from the distillation residues by recrystallization.

The method of plotting the rate data is described in the Discussion. Tables VIII and IX, which were used to calculate the first order $\underline{k}$ values, were also useful for the transposition of the data for the new zero time which was arbitrarily taken to be the time at which 20% of the starting materials had been used up. The k values reported in Tables II and III were obtained by dividing the values in the right hand column of Tables VIII and IX by the corresponding time (min.) elapsed, this being based on the new zero time.

Table VIII applies only to Experiment 1 in which the original starting concentrations of triphenylcarbinol and n-butyl alcohol were respectively 0.250 and 0.125 m./l. The following equation illustrates how a in the first order kinetic equation was obtained.

$$0.250 \text{ m./l.} - (0.20 \times 0.125 \text{ m./l.}) = 0.225 \text{ m./l.} = a$$

TABLE VIII

Orig. basis, % compl.	New basis, % compl.	(a-x)	$2.303 \log \frac{a}{a-x}$
20	0	0.225	————
30	12.5	0.2125	0.05716
40	25.0	0.200	0.1178
50	37.5	0.1875	0.1824
60	50.0	0.175	0.2514
70	62.5	0.1625	0.3255
80	75.0	0.150	0.4055
90	87.5	0.1375	————[a]
100	100.0	0.125	————[a]

a. The last 20% portion of the reaction was always discarded in the kinetic treatment.

Table IX applies to all other experiments in this section and the following section for which kinetic calculations were made. Since the starting concentration of the polyphenylcarbinol never exceeded that of n-butyl alcohol in these experiments, the following equation for determining a in the kinetic equation applies to all these experiments.

$$0.125 \text{ m./l.} - (0.20 \times 0.125 \text{ m./l.}) = 0.100 \text{ m./l.} = \underline{a}$$

TABLE IX

Orig. basis, % compl.	New basis, % compl.	(a-x)	$2.303 \text{ Log } \frac{a}{a-x}$
20	0	1.0000	————
30	12.5	0.0875	0.1335
40	25.0	0.0750	0.2877
50	37.5	0.0625	0.4701
60	50.0	0.0500	0.6933
70	62.5	0.0375	0.9810
80	75.0	0.0250	1.386
90	87.5	0.0125	————
100	100	0	————

The Kinetics of Triphenylmethyl n-Butyl Ether Formation

General.--The k values for these experiments are reported in Table II of the Discussion. In the material that follows, the reaction temperature (corrected) shown applies only to the 20% to 80% portion of the reaction. In tabulating the rate data, percentage completion and the corresponding time (min.) elapsed since the original zero time are recorded. No attempt was made to isolate the products in any of these experiments. The products were however isolated from many preliminary experiments which were done at a total volume of 500 ml. with half the quantities of reactants. Pertinent data from these experiments are also given. The triphenylmethyl n-butyl ether isolated from these preliminary experiments distilled at 172° at 0.2 mm. pressure (lit. 170° at 0.3 mm. pressure); $n_D^{24.8}$ 1.5843 (lit. n_D^{25} 1.58395). Data from duplicate experiments are also given.

The experiments are considered individually in the order in which they appear in Table II.

Experiment 1.---A reaction temperature of 80.3° to 80.9° was observed and a 99.8% yield of water was obtained.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
8.99	13	35.5	39	62.2	66
12.4	16	38.7	42	65.1	69
14.7	19	42.0	45	68.4	72
17.2	22	44.4	48	71.1	75
20.6	24	47.3	51	75.2	81
26.7	30	50.6	54	77.7	84
30.7	33	56.8	60	80.2	87
33.1	36	59.5	63	83.3	90

For a preliminary experiment at a total volume of 500 ml., the reaction temperature was 82.7° to 83.6° and the yields of water and product were respectively 97.4% and 83.0%. The first order k values at 30, 40, 50, 60, 70, and 80% completion were respectively 0.0162, 0.0169, 0.0175, 0.0188, 0.0203, and 0.0198 min.$^{-1}$.

Experiment 2.--The reaction temperature was 80.9° to 81.0° and the yield of water was 97.6%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
13.3	35	26.7	70	53.5	151
17.3	46	28.9	76	59.5	170
18.9	50	30.4	80	61.5	180
19.8	52	33.8	90	66.4	200
20.4	54	37.3	100	70.8	220
21.1	56	40.4	110	74.2	240
22.4	60	47.3	130	78.3	260
24.4	65	50.6	140	81.9	280

For a duplicate of this experiment, the reaction temperature was 80.9° to 81.2° and the yield of water was 96.8%. The first order k values taken at the usual percentages of completion were respectively 0.00486, 0.00525, 0.00535, 0.00561, 0.00595, and 0.00642 min.$^{-1}$.

For another duplicate of Experiment 2 except at four times the catalyst concentration, the reaction temperature was 80.4° to 81.0° and the yield of water was 93%. The first order k values were respectively (as above) 0.0227, 0.0232, 0.0239, 0.0240, 0.0230, and 0.0209 min.$^{-1}$.

For a preliminary experiment, at a total volume of 500 ml., the reaction temperature was 81.8° to 81.9° and the yields of water and product were respectively 97.8% and 95.0%. The first order k values listed as above were respectively 0.0181, 0.0192, 0.0197, 0.0204, 0.0208, and 0.0202 min^{-1}. Draper duplicated this preliminary experiment and his k values were slightly lower.[1]

Experiment 3.--The reaction temperature was 80.4° to 80.8° and the yield of water was about 95%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
15.3	51	31.6	110	54.2	220
17.6	60	34.0	120	55.7	230
19.1	65	37.5	135	59.9	255
20.4	70	40.9	150	60.5	263
22.1	75	42.8	160	65.7	288
23.8	80	47.2	180	69.1	331
26.6	90	50.8	200	75.5	392
28.8	100	52.2	210	79.9	443

For two preliminary experiments at a total volume of 500 ml., the reaction temperatures were 81.6° to 82.0° and 82.6° to 82.7° and the yields of water were 99.8% and 95.5%. The respective yields of product were 91.5% and 92.8%. The first order k values for the first of these (given as above) were 0.0142, 0.0149, 0.0154, 0.0155, 0.0150, and 0.0149 min^{-1}. For the second, the k values were 0.0141, 0.0139, 0.0140, 0.0139, 0.0136, and 0.0132 min^{-1}.

Experiment 4.--The reaction temperature was 81.1 to 81.3° and the yield of water was 100%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
10.0	35	30.3	110	58.0	260
14.8	50	32.8	120	61.3	281
17.5	60	37.9	150	66.0	320
18.9	65	43.0	170	68.7	341
20.0	70	46.8	190	70.4	360
21.6	75	48.8	200	71.7	371
25.3	90	52.5	220	78.2	450
27.8	100	55.2	240	84.4	548

For the preliminary experiment at a total volume of 500 ml., the reaction temperature was 82.0° to 82.2° and the yields of water and product were respectively 100.1% and 86.5%. The first order k values (as above) were 0.0136, 0.0139, 0.0139, 0.0134, 0.0128, and 0.0126 min^{-1}.

Experiment 5.--The reaction temperature was 80.4° to 80.5° and a 97.7% yield of water was obtained.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
18.2	75	36.0	160	59.5	320
19.5	80	39.9	180	61.8	345
20.4	85	41.5	190	66.8	400
24.0	100	46.1	220	73.4	475
26.2	110	47.5	230	77.7	540
28.5	120	49.1	240	79.0	560
31.1	135	52.0	260	80.0	580
34.1	150	57.2	300	81.4	600

Experiment 6.--The reaction temperature was 80.8° to 81.05° and the yield of water was 100%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
15.5	32	33.2	66	58.8	140
18.2	36	35.6	72	61.5	150
20.3	40	39.1	80	63.5	160
22.3	44	43.1	90	65.2	170
24.4	48	46.6	100	68.1	180
26.7	52	50.1	110	70.4	190
28.4	56	53.2	120	76.8	366
30.5	60	56.0	130	82.2	390

Experiment 7.--The reaction temperature was 80.4° to 80.8° and the yield of water was 98.5%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.8	124	40.0	328	62.2	630
20.0	140	42.2	351	66.7	717
22.4	160	46.7	403	68.9	766
26.6	196	48.9	433	71.1	820
28.9	217	51.1	457	75.5	938
31.1	239	55.8	523	77.8	1010
36.2	286	57.8	557	80.0	1080
37.7	302	60.9	607	86.7	1610

The Kinetics of Diphenylmethyl n-Butyl Ether Formation

General.--These experiments are considered in the same order that they appear in Table III which contains the first order k values. The reaction temperatures (corrected) shown apply only to the 20% to 70% portion of the reaction. The rate data for each experiment is tabulated as above. Following these rate data are listed the major data from duplicate experiments. The first order k values for these are given in the usual manner starting with the value at 30% completion. Using a 4 in. wrapped Vigreux column, the benzhydryl n-butyl ether was isolated by distillation at 120° to 122° at 0.2 mm. pressure (lit. 116° to 117° at 0.5 mm. pressure); n_D^{22} 1.5398 (lit. n_D^{25} 1.5408).[56] Dibenzhydryl ether was isolated from the distillation residues as described above; m.p. 108-109° (lit. 107.5-108°).[74]

Experiment 8.--The reaction temperature was 80.8° to 80.9° and the yields of water and unsymmetrical ether (main product) were respectively 97.8% and 86.0%. About 4.0% of dibenzhydryl ether was isolated.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
15.5	41	40.0	101	62.1	161
17.8	47	44.4	112	66.7	177
20.0	52	48.8	123	68.8	187
24.4	62	51.1	129	71.0	195
28.8	74	53.3	135	73.2	204
33.3	84	55.5	141	75.5	215
35.6	90	57.7	147	77.7	230
37.8	96	60.0	151	82.2	262

Experiment 9.--The reaction temperature was 81.0° to 80.9° and the yields of water and main product were respectively 92.8% and 82.5%. The yield of dibenzhydryl ether was about 6%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
15.5	83	33.3	189	55.5	357
17.8	94	37.8	220	57.7	381
20.0	107	40.0	236	60.0	405
22.2	120	42.2	251	62.2	427
24.4	134	44.4	267	64.4	454
26.6	147	46.6	285	73.2	571
28.8	161	48.8	300	75.5	600
31.1	175	51.1	319	80.0	687

Experiment 10.--The reaction temperature was 81.2° to 81.3° and the yields of water and main product were respectively 93.2% and 87.0%. The yield of dibenzhydryl ether was about 4.0%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
13.6	117	37.8	359	60.3	698
20.0	173	40.2	387	62.5	747
22.2	194	42.4	417	67.1	845
24.5	215	48.6	506	69.1	901
26.7	237	51.6	544	71.7	967
29.1	260	53.5	576	76.3	1130
31.2	281	55.8	614	78.0	1190
33.3	307	58.0	652	80.3	1290

For a duplicate of this experiment, the reaction temperature was 80.8° to 81.1° and the yields of water and main product were respectively 93.7% and 88.7%. About 4% of dibenzhydryl ether was recovered. The first order k values were as follows; 0.00130, 0.00129, 0.00127, 0.00127, and 0.00124 min^{-1}.

Experiment 11.--The reaction temperature was 81.4° to 81.6° and the yields of water and main product were respectively 92.2% and 89.0%. The yield of crude dibenzhydryl ether was about 3%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.5	198	39.7	502	59.5	920
19.8	223	41.8	541	61.8	984
22.0	249	46.2	619	68.4	1200
26.3	304	48.4	664	70.6	1290
28.5	334	50.7	708	76.6	1550
30.7	365	53.0	757	78.7	1670
32.9	397	55.1	810	80.7	1800
35.1	429	57.3	862	81.9	1920

For a duplicate experiment the reaction temperature was 81.2° to 81.4° and the yield of water was 90.6%. The products were not isolated. The first order *k* values were as follows; 0.000993, 0.00100, 0.000990, 0.000949, and 0.000925 min^{-1}.

Experiment 12.--The reaction temperature was 81.5° to 81.7° and the yields of water and main product were respectively 93.2% and 88.6%. The yield of crude dibenzhydryl ether was about 4%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
20.0	266	40.2	632	71.3	1650
22.2	299	44.6	732	73.6	1780
24.5	333	53.6	961	76.2	2000
26.7	370	55.9	1030	78.0	2080
29.1	413	58.2	1100	80.2	2260
31.1	455	60.3	1180	82.9	2490
33.3	494	62.6	1270	87.8	3190

For a duplicate experiment the reaction temperature was 81.4° to 81.6° and the yields of water and main product were respectively 93% and 88.3%. About 5% of crude dibenzhydryl ether was recovered. The first order <u>k</u> values were as follows; 0.000840, 0.000804, 0.000779, 0.000768, and 0.000739 min^{-1}.

<u>Experiment</u> <u>13</u>.--The reaction temperature was 81.1° to 81.3° and the yields of water and main product were respectively 95.7% and 87.8%. The yield of crude dibenzhydryl ether was about 4%.

compl.	(min.)	compl.	(min.)	compl.	(min.)
15.9	53	42.4	155	67.1	298
20.0	68	44.6	166	69.0	315
22.2	75	46.8	177	71.7	334
24.5	83	49.1	186	73.7	354
29.1	99	51.4	197	75.9	379
33.6	118	58.0	235	78.1	405
35.8	126	60.3	251	80.2	429
40.2	145	65.0	282	82.4	461

<u>Experiment</u> <u>14</u>.-- The reaction temperature was 81.1° to 81.4° and the yields of water and main product were respectively 91.8% and 87.0%. The yield of crude dibenzhydryl ether was about 7.0%.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
15.5	298	32.9	718	58.4	1660
17.5	340	39.5	932	59.8	1730
19.8	387	41.8	1000	68.8	2260
22.0	435	46.2	1160	72.0	2490
24.1	490	48.4	1250	78.8	3200
30.7	660	50.7	1330	80.7	3400

THE ETHERIFICATION OF BENZYL ALCOHOLS

General Considerations

Starting Materials.--Commercially available starting materials were used whenever possible. The compounds not readily available were prepared by methods which are described below. Certain physical constants for all starting materials as well as for the solvents are listed in Table X.

TABLE X

PHYSICAL CONSTANTS OF STARTING MATERIALS

Compound	Physical Constants,[a] Observed		Literature	
C_6H_6	n_D^{25}	1.4980	n_D^{20}	1.5017
$C_{10}H_{18}$	n_D^{20}	1.4778	n_D^{18}	1.4808
$\left[CH_3(CH_2)_3\right]_2O$	n_D^{20}	1.3988	n_D^{20}	1.3992
$C_6H_5NO_2$	n_D^{25}	1.5498	n_D^{20}	1.5524
C_6H_{12}	n_D^{25}	1.4230	$n_D^{19.5}$	1.4266
$CH_3(CH_2)_2CH_2OH$	n_D^{20}	1.3970	n_D^{20}	1.3991
$CH_3CH_2CH(CH_3)OH$	n_D^{28}	1.3937	$n_D^{17.5}$	1.3968
$(CH_3)_3COH$	n_D^{28}	1.3831	n_D^{20}	1.3878
$CH_3(CH_2)_4CH_2OH$	n_D^{25}	1.4160	n_D^{20}	1.4133
$(HOCH_2CH_2)_2O$	n_D^{20}	1.4475	n_D^{20}	1.4475
p-$(CH_3)_2NC_6H_4CH_2OH$	n_D^{25}	1.5780	n_D^{14}	1.5727[b]
p-$CH_3OC_6H_4CH_2OH$	n_D^{25}	1.5438	$n_D^{24.4}$	1.5414
p-$CH_3C_6H_4CH_2OH$	m.p.	58.5-59.5°	m.p.	59.5°
$C_6H_5CH_2OH$	n_D^{25}	1.5382	n_D^{20}	1.5396
p-$ClC_6H_4CH_2OH$	m.p.	71.0-71.5°	m.p.	70.5-73.0°
p-$O_2NC_6H_4CH_2OH$	m.p.	93.0-93.5°	m.p.	92.0-93.0°

TABLE X - Continued

	Physical Constants,[a]	
Compound	Observed	Literature
$(p\text{-}CH_3OC_6H_4)_2O$	m.p. 39.0-40.0°	m.p. 39.0°[c]

a. These values are taken from standard handbooks unless otherwise noted.
b. Ref. 75.
c. Ref 76.

The purification of benzene and n-butyl alcohol was described in the preceding section.

Decalin (Pract.) was supplied by Paragon. It was further purified by distillation, the middle fraction distilling steadily at 190° to 192° at 758 mm. pressure being collected for use.

n-Butyl ether (Pract.) was supplied by Paragon. It was purified by distillation through an 8 in. wrapped column packed with glass helices, the portion distilling steadily at 140° at 750 mm. pressure being collected for use (lit. b.p. 142°).

H. J. Segrave made available the mixed solvent which consisted of a 1 to 3 ratio of nitrobenzene to cyclohexane. The nitrobenzene, which was of practical grade, was supplied by Matheson. It was purified by distillation through a 2 ft. heated column packed with glass helices at a 4 to 1 reflux ratio The material collected for use distilled at 209° to 210° at atmospheric pressure (lit. b.p. 210.9°). The cyclohexane, which was supplied by du Pont, was purified first by extraction with fuming sulfuric acid and then by distillation; the middle 70% portion distilling at 80° at atmospheric pressure was collected for use (lit. b.p. 80.0° to 81.0°).

The sec-butyl alcohol which was supplied by Shell was purified by distillation through a wrapped 8 in. column packed with glass helices. The fraction distilling at 98.5° to 99° at atmospheric pressure was collected for use (lit. b.p. 99.5°).

The tertiary butyl alcohol which was supplied by Shell was purified as in the preceding paragraph and the fraction distilling at 82.3° at atmospheric pressure was collected for use (lit. b.p. 82.9°).

The n-hexyl alcohol supplied by Eastman was purified by D. G. Kubler by distillation using a 2 ft. heated column packed with glass helices at a 3 to 1 reflux ratio. The material boiling at 156° to 157° at atmospheric pressure was collected for use (lit. b.p. 157.2°). The refractive index was significantly higher than the literature value in spite of the careful purification.

Diethylene glycol which was supplied by Eastman was purified by distillation through a 7 in. Vigreux column. The fraction distilling at 242° at atmospheric pressure was collected (lit. b.p. 244.8°).

p-Dimethylaminobenzyl alcohol was made by direct hydrogenation of p-dimethylaminobenzaldehyde which was supplied by Matheson. The procedure followed was essentially that developed by T. L. Heying. A 0.231 m. portion (35 g.) of the aldehyde, dissolved in dry diethyl ether to give a total volume of 150 ml., together with 2 g. of copper chromite catalyst was placed in a 300 ml. bomb and hydrogen was introduced to give a total pressure of 2250 pounds per sq. in. Hydrogenation took place rapidly at 140° to 143°. Solvent removal and the subsequent distillations were carried out using reduced pressure under a nitrogen atmosphere. The first distillation using a 7 in. Vigreux column gave a 16 g. fraction distilling at 97° at 0.10 mm. pressure; n_D^{25} 1.5683. A redistillation of this fraction combined with analogous fractions from identical experiments gave a product that distilled at 108° to 115° at about 0.4 mm. pressure (lit. b.p. 123° at 1 mm. pressure).[75, 77] The refractive index was significantly higher than the literature value. Elementary analyses were carried out on the twice distilled product from a preliminary experiment; n_D^{14} 1.5808. The average of duplicate analyses is given. Calcd. for $C_9H_{13}ON$: C, 71.5; H, 8.67. Found: C, 71.7; H, 8.88. The yield of purified product was 19%. T. L. Heying reported a 65% yield of product (n_D^{17} 1.5786) on the basis of a single distillation but his refractive index value indicated that some p-N-dimethylaminotoluene was present. A considerable amount of this compound was isolated as well as a smaller amount of an unidentified crystalline solid; m.p. 88.5-89.5°. An analysis was made on this solid. Found: C, 80.26; N, 11.78; H, 8.80. The purified material was stored in a tightly stoppered bottle and placed in the refrigerator until used.

Anisyl alcohol supplied by Matheson was purified by distillation according to the procedure described by Adams;[78]

b.p. 114° at 0.2 mm. pressure.

The p-methylbenzyl alcohol, which would have involved a difficult preparation, was kindly provided by du Pont. This material was purified by recrystallization from 60-80° petroleum ether.

The benzyl alcohol (chlorine free) supplied by Eastman was purified by distillation through a 7 in. Vigreux column, the fraction distilling steadily at 93.5° at 12 mm. pressure being collected for use.

p-Chlorobenzyl alcohol was prepared from practical grade Eastman p-chlorobenzyl chloride by a method described in the literature.[79]

The p-nitrobenzyl alcohol was prepared from practical grade p-nitrobenzyl chloride supplied by Eastman by methods described in "Organic Syntheses".[80]

Dianisyl ether was obtained from several experiments identical to Experiment 30. Attempts to distil the ether were generally unsuccessful so recrystallization from 30-60° petroleum ether was the method of purification.

Standard Procedure.-- In general, the standard procedure was that described in the Discussion and in the preceding section. For experiments that required catalyst concentrations in excess of 0.004 m. per 1., the usual procedure was modified in the following manner; solid p-toluenesulfonic acid monohydrate was carefully weighed out and added to 500 ml. of benzene in a 2 l. reaction flask. Upon refluxing, the water of hydration was collected in the Dean-Stark water collector, and the catalyst went into solution. It was assumed that the volume change incident to solution of the catalyst was insignificant. The refluxing was then stopped long enough to adjust the water in the collector and to add the correct volume of hot solution of reactants which had been refluxed separately to remove trace amounts of water. Boiling chips were added and the current was again turned on. Refluxing commenced within 1 to 2 minutes, at which point, the time and temperature were taken. From this point on, the standard procedure was essentially the same as above.

A minor change in procedure was made in the method of final solvent removal and in the isolation of product where distillation was used (suggested by Ken Matsuda). It was found that the addition of about 0.1 g. of solid sodium bicarbonate to the residue after partial solvent removal and again just before the product began to distil materially reduced the amounts of residue. This procedure assured neutralization of any acid produced during the distillation.

The Etherification of Para Substituted Benzyl Alcohols with n-Butyl Alcohol

General.--The yields of product are reported in Table IV of the Discussion. Supplementary data for these etherifications are given in Table XI. These experiments are taken up individually in the order in which they appear in these tables. In the cases where the products were new compounds, the average of duplicate elementary analyses are given.* In all the experiments that follow, the physical constants from the literature for products which were known compounds are enclosed in parenthesis. Second order *k* values are given where these were calculated. The basis of the calculation is given in the Discussion. Pertinent data from duplicate experiments and closely related experiments will be given following the tabulation of the rate data for these experiments. The first order *k* values for these duplicate and related experiments will be given in the usual order starting with the 30% value and in all cases the units are 10^{-4} min^{-1}.

Experiment 15.—In order to minimize oxidation of the p-dimethylaminobenzyl alcohol, the apparatus was flushed with dry nitrogen prior to heating the reaction mixture. The p-dimethylaminobenzyl n-butyl ether was isolated by distillation through a 7 in. wrapped and heated Vigreux column. This ether distilled steadily without decomposition at 131° at 0.4 mm. pressure; n_D^{25} 1.5230. Calcd. for $C_{13}H_{21}ON$: C, 75.31; H, 10.21. Found C, 75.33; H, 10.22. The second order constants were as follows; 0.0168, 0.0150, 0.0145, 0.0138, and 0.0124 min.^{-1} mol^{-1}.

* Microanalyses by Mrs. Mary H. Aldridge and Mr. Byron Baer.

TABLE XI

SUPPLEMENTARY DATA FOR TABLE IV

Expt. No.	Yld. H_2O, %	Residue, g.	Temp.,[a] °C.	k, 10^{-4} min.$^{-1}$						
				30%	40%	50%	60%	70%	Av.	Av. dev.
15	78.0	1.53	81.3 ± 0.10	57.8	50.5	47.7	43.9	38.1	47.6	5.26
16	87.0	0.31	81.0 ± 0.05	39.3	40.4	38.5	37.6	36.2	38.4	1.20
17	72.0	1.52	81.9 ± 0.10	25.7	26.5	27.3	28.1	28.9	26.6	0.92
18	101.0	0.40	81.0 ± 0.05	5.19	5.27	5.52	5.73	5.96	5.51	0.31
19	101.0	2.20	81.9 ± 0.10	19.1	19.0	19.4	20.0	21.0	19.5	0.64
20	100.0	1.77	85.3 ± 0.00[b]	23.8	24.1	24.5	24.8	26.2	24.7	0.66

[a] The median temperature and the maximum variation (±) from this median.

[b] The solvent used was nitrobenzene and cyclohexane at a 1 to 3 ratio.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
13.3	26	35.5	83	62.2	217
18.6	38	40.8	103	66.6	255
22.2	45	44.4	115	71.1	313
24.0	49	48.8	134	75.4	380
26.7	54	53.2	155	80.0	503
31.1	66	57.7	180	83.9	627

For a duplicate experiment, the reaction temperature was 82.1° to 82.2° and the yields of water and product were respectively 92.4% and 71%. The first order k values (see above) were 41.7, 41.1, 39.5, 36.5, and 31.6.

Experiment 16.--The apparatus was flushed with dry nitrogen prior to heating the reaction mixture. The p-methoxybenzyl n-butyl ether was isolated by distillation through a 7 in. wrapped and heated Vigreux column. This ether distilled steadily without decomposition at 93° to 96° at about 0.1 mm. pressure; n_D^{26} 1.4950. The following analyses were obtained for this product from an earlier related experiment similar in all respects except that the catalyst concentration was four times that used in Expt. 16; n_D^{20} 1.4978. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.54; H, 9.53.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
13.3	36	35.5	108	67.1	293
17.8	46	40.0	125	69.8	337
20.0	53	48.8	168	74.3	378

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
22.2	60	53.2	198	76.9	420
26.6	75	57.8	222	77.9	445
31.6	93	62.2	252	84.6	637

For a duplicate experiment, the reaction temperature was 83.5° and the yields of water and product were respectively 95.8% and 82.8%. The first order k values were 44.5, 44.9, 45.2, 43.1, and 40.2.

For the related experiment, which was done at four times the catalyst concentration used in Expt. 16, the reaction temperature was 81.1° to 81.2° and the yields of water and product were respectively 99.8% and 92.4%. The first order k values were 334, 349, 362, 360, and 363. The second order k values were 0.0970, 0.103, 0.110, 0.112, and 0.116 $\text{min.}^{-1}\ \text{mol}^{-1}$.

Experiment 17.--Solid catalyst was used in this experiment. The p-methylbenzyl n-butyl ether was isolated by distillation through a 7 in. wrapped Vigreux column. The ether distilled at 55° at 0.15 mm. pressure; n_D^{25} 1.4866. Several fractions of almost identical refractive index were taken. The following analysis is that obtained for this product from an earlier related experiment similar in all respects except that the catalyst concentration was half that used in Expt. 17; n_D^{25} 1.4871. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.17. Found: C, 81.17; H, 10.21.

% comp.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
18.7	85	39.1	200	64.9	390
20.4	99	40.8	213	68.8	438
23.1	113	49.7	274	72.0	465
27.6	140	54.2	307	78.7	564
32.9	167	58.6	338	80.0	575
36.4	188	60.4	352	80.4	587

For the related experiment at half the catalyst concentration used in Expt. 17, the reaction temperature was 80.6° to 81.0° and the yields of water and product were respectively 94.5% and 44.6%. This last figure, seemingly low, is based on a redistillation while the higher yield shown for Expt. 17 is that for the once distilled product. The first order k values were 3.77, 3.84, 3.97, 4.09, and 4.06.

Experiment 18.--Benzyl n-butyl ether was isolated by distillation using a 7 in. wrapped Vigreux column. The yield of ether was based on the total weight of several fractions distilling from 46° to 50° at 0.15 mm. pressure; n_D^{25} 1.4857 to n_D^{25} 1.4888 (n_D^{25} 1.4892; n_D^{25} 1.4860).[1, 56] In spite of the rather wide range of refractive indices for these fractions, it is believed that the yield reported for this experiment is essentially correct. The separation of this ether and diphenylmethane is somewhat difficult. Part of the distillation data from Expt. 18 is given to show that good fractionation was achieved.

Fraction No.	Temp., C.°	Weight, g.	n_D^{25}
6	44	1.92	1.4860
7	46	4.52	1.4857
8	61	0.40	1.5133
9	61	0.80	1.5670

The refractive indices for the final fractions of the above distillation were somewhat erratic but on the basis of these values it is conservatively estimated that 2 g. of diphenylmethane was obtained which corresponds to about a 9.0% yield of this product.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
8.88	133	35.5	826	56.8	1490
13.3	240	38.7	902	58.2	1530
17.8	333	40.0	947	62.0	1660
22.2	441	49.7	1270	64.0	1790
26.3	569	52.0	1320	71.4	2120
30.4	682	53.3	1370	81.7	2710

For a duplicate experiment, the reaction temperature was 80.9° to 81.0° and the yields of water and product were respectively 100% and 64.5%. The 20% completion point in the reaction was accurately determined but the rate data for the 30% and 40% points were not obtained. The first order k values starting with the 50% completion point are 5.65, 6.05, and 6.33. These values are in good agreement with the corresponding k values obtained for Expt. 18.

A related experiment was carried out which was similar in all respects to Expt. 18 except that the solvent was a mixture of nitrobenzene and cyclohexane at a ratio of 1 to 3. It was believed that this modification would give a better yield of the ether since alkylation could not take place. The results were however inconclusive since the presumed product and nitrobenzene could not be separated by even a very careful fractionation.

Experiment 19.--Careful fractionation using a 7 in. wrapped and heated Vigreux column resulted in two products being isolated. p-Chlorobenzyl n-butyl ether distilled at 83° to 87° at 1 mm. pressure; n_D^{25} 1.5033 to n_D^{25} 1.5053. (The value from Expt. 20 is 1.5010.) This product was obtained in 10 fractions averaging 1 g. each. The ether analyzed about 0.7% high for carbon possibly due to traces of the alkylation product. A good analysis on this ether was however obtained from the product of Expt. 20 (see below) in which the possibility of alkylation was avoided. The p-chlorodiphenylmethane distilled at 113° to 122° at about 1.0 mm. pressure; n_D^{25} 1.5753 to n_D^{25} 1.5778. This is a known compound but no refractive index is reported in the literature. Since the product analyzed about 0.8% low for carbon further fractionation was attempted but no significantly better analyses were obtained. Somewhat later it was found that esterification of the catalyst took place at these high concentrations of catalyst to an appreciable degree. The presence of small amounts of this ester in the product would lead to lower carbon analyses values. This same product from a similar experiment gave a positive test for sulfur. In order to hydrolyze this ester, the product was dissolved in a mildly alkaline acetone-water solution and stirred at 75° for 16 hrs. After this treatment, the amount of sulfur indicated by the test was negligible. The purified product distilled at 127° to 129° at 3.5 mm. pressure; n_D^{25} 1.5813 to n_D^{25} 1.5818 (n_D^{25} 1.5830).[60] Analyses were carried out on the fraction having the higher refractive index. Calcd. for $C_{13}H_{11}Cl$: C, 77.03; H, 5.47. Found: C, 77.00; H, 5.60.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
13.3	85	36.4	244	57.8	449
17.8	110	40.0	277	75.6	660
22.2	141	44.4	315	84.4	859
26.7	178	48.8	363	97.8	1380

For a duplicate experiment the reaction temperature was 80.7° to 80.9° and the yield of water was 101%. The yields of ether and alkylation product were respectively 41.4% and 30.4%. The first order k values were 18.3, 18.5, 19.3, 20.1, and 21.4. The second order k values were 0.00533, 0.00548, 0.00587, 0.00629, and 0.00685 $\text{min.}^{-1}\ \text{mol}^{-1}$.

Experiment 20.--This experiment was carried out using the mixed solvent referred to above. Very careful fractionation was necessary in order to separate the main product.

from traces of nitrobenzene. The distillation was made through a 7 in. wrapped Vigreux column. The p-chlorobenzyl n-butyl ether distilled steadily at 121° to 123° at 9.5 mm. pressure which was controlled by the use of a Newman regulator;[81] n_D^{25} 1.5010 to n_D^{25} 1.5029. Analyses were carried out on a fraction having the lower of the above refractive index values. Calcd. for $C_{11}H_{15}OCl$: C, 66.50; H, 7.61; Cl, 17.86. Found: C, 66.75; H, 7.74; Cl, 17.84. In the final stages of the above distillation (at higher temperatures), a white solid crystallized in the condenser. This material was recovered and recrystallized from 60-80° petroleum ether; m.p. 54-55°. This was bis-(4-chlorobenzyl) ether which is described in the literature; m.p. 54-55°.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
13.3	41	35.6	163	57.8	330
17.8	61	40.0	192	62.2	370
22.2	86	44.4	220	66.6	410
26.7	111	48.8	255	74.2	487
31.1	134	53.3	290	80.8	575

The second order <u>k</u> values are as follows; 0.00393, 0.00420, 0.00460, 0.00510, and 0.00546 $min.^{-1}$ mol^{-1}.

The Etherification of Anisyl Alcohol
With Para Substituted Benzyl Alcohols

General.--The yields of product are reported in Table V of the Discussion. Supplementary data for these etherifications are given in Table XII.

Experiment 21.--After solvent removal the residue which contained p-methoxybenzyl p-methylbenzyl ether as well as unreacted p-methylbenzyl alcohol was dissolved in approximately 50 times its volume of 60-80° petroleum ether at about 70°. Precipitation of the unreacted carbinol (which was in excess) occurred when this solution was placed in the refrigerator. The liquid phase which contained very little of the carbinol was then drained off. This entire procedure was repeated several times since the above ether was also quite insoluble in this solvent. The petroleum ether was removed with mild heating under reduced pressure. The crude product together with about 0.1 g. of solid sodium bicarbonate was placed in a Hickman still which was fitted with a magnetic stirrer and an interchangeable receiver. Distillation commenced at 75° at 0.3 mm. pressure. This distillate (2 g.) which solidified in the receiver was p-methylbenzyl alcohol; m.p. 58-59° (lit. 58.5-59.5°). The unsymmetrical ether distilled steadily without decomposition at 152° to 158° at 0.4 mm. pressure; n_D^{25} 1.5572. A previous attempt to isolate this product by the usual distillation procedure led to decomposition of the ether.

TABLE XII

SUPPLEMENTARY DATA FOR TABLE V

Expt. No.	Yld. H_2O, %	Residue, g.	Temp.,[a] C°.	k, 10^{-4} min.$^{-1}$ 30%	40%	50%	60%	70%	Av.	Av. dev.
21	88.4	0.5	81.0 ± 0.00	49.4	44.3	41.2	38.3	35.8	41.8	5.04
22	96.8	2.5	82.5 ± 0.05	80.8	75.7	74.0	70.7	69.3	74.1	3.32
23	97.5	0.9	81.2 ± 0.05	167	164	163	159	153	161	4.20
24	98.3	0.9	81.0 ± 0.00	445	479	481	494	478	475	13.6
25	93.8	4.5	81.0 ± 0.05	111	115	104	94.9	86.1	103	9.20
26	96.8	4.0	81.0 ± 0.05	66.7	62.5	59.2	57.7	54.8	60.2	3.54

a. The median temperature and the maximum deviation (±) from this median.

Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.49. Found: C, 79.7; H, 7.61.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.8	42	40.0	113	62.2	244
22.2	53	44.4	135	66.6	283
26.7	65	48.8	157	71.1	337
33.3	87	53.3	181	75.5	410
35.6	98	57.8	211	80.0	547

For a duplicate of this experiment the reaction temperature was 85.5° and the yield of water was 92.0%. As stated above the product decomposed during the distillation. The first order k values were 54.4, 50.9, 47.7, 45.6, and 41.6.

Experiment 22.--Careful fractionation using a 7 in. wrapped and heated Vigreux column resulted in a good separation of the excess benzyl alcohol from the unsymmetrical ether. As in most of these isolations, the fractionation was followed by frequent refractometer readings. The p-methoxybenzyl benzyl ether distilled steadily without decomposition at 98.5° to 108° at about 0.1 mm. pressure, n_D^{25} 1.5616 to n_D^{25} 1.5622. This product was taken in nine fractions of about 3 g. each. A sample from the above combined fractions was analyzed. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 79.22; H, 7.19.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.8	32	40.0	76	62.2	143
22.2	40	44.5	85	66.7	163
26.7	48	48.9	99	71.1	183

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
31.1	55	53.8	112	75.6	210
35.8	66	57.8	127	80.0	246

Experiment 23.--The preliminary separation of the excess unreacted carbinol was carried out in much the same manner as described for Expt. 21. The final isolation of the product was however carried out in the same manner as for the preceding experiment. A forerun, which was mainly p-chlorobenzyl alcohol, solidified in the condenser. This material was removed from the condenser prior to distillation of the product. The p-methoxybenzyl p-chlorobenzyl ether distilled steadily and without decomposition at 122° to 126° at 0.9 mm. pressure; n_D^{25} 1.5681 to n_D^{25} 1.5690. One of several fractions with a refractive index n_D^{25} 1.5689, was analyzed. Calcd. for $C_{15}H_{15}O_2Cl$; C, 68.57; H, 5.75; Cl, 13.50. Found: C, 68.40; H, 6.07; Cl, 13.50.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.8	16	40.0	35	62.2	65
21.3	18	44.4	40	66.6	73
26.6	23	48.8	45	71.1	85
31.1	27	53.3	50	75.5	98
35.5	31	57.7	58	80.0	115

Experiment 24.--The preliminary separation of the carbinol (which was in excess) was carried out in the same manner as in Expt. 21. The isolation of the unsymmetrical

ether was carried out in the same manner as in Expt. 22. A very small forerun of p-nitrobenzyl alcohol, which solidified in the condenser, was obtained. The p-methoxybenzyl p-nitrobenzyl ether distilled steadily and without decomposition at 179° to 185° at 0.2 mm. pressure; n_D^{25} 1.5824 to n_D^{25} 1.5833. One of several fractions with a refractive index, n_D^{25} 1.5830, was analyzed. Calcd. for $C_{15}H_{15}O_4N$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66.39; H, 6.01; N, 5.35.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.8	7	47.1	16	66.7	25
22.2	8	49.8	17	69.3	27
27.6	10	52.8	18	70.2	29
32.0	11	58.5	21	70.9	30
39.6	13	61.3	22	75.5	36
42.6	14	65.3	24	80.0	44

Experiment 25.---The anisyl alcohol, which was in excess in this experiment, was removed from the residue after solvent removal at 125° at 0.2 mm. pressure. Since it had been shown previously that p-methoxybenzyl p-methylbenzyl ether decomposed readily when distilled at higher temperatures, a Hickman still at very low pressure was used to isolate this product. The product distilled smoothly without decomposition at 135° to 136° (bath temp.) at 0.0005 to 0.0012 mm. pressure; n_D^{25} 1.5838 to n_D^{25} 1.5842. A sample from the middle fraction, n_D^{25} 1.5842, was analyzed. Calcd. for $C_{17}H_{21}O_2N$: C, 75.24; H, 7.79; N, 5.16. Found: C, 75.35; H, 8.03; N, 5.53.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
18.9	54	31.1	69	57.7	120
19.3	55	35.6	74	62.2	135
20.9	56	40.0	80	66.6	151
21.6	57	44.4	88	71.1	173
24.0	60	48.9	98	75.5	205
26.6	63	52.3	108	80.0	249

Experiment 26.--The product, dianisyl ether, was isolated by recrystallization from 30-60° petroleum ether; m.p. 39.5-40° (m.p. 39°). It was found in earlier similar experiments that final solvent removal carried out at temperatures above 85° resulted in complete polymerization of this product. Dianisyl ether is however reported to distil at 197° to 214° at 6 mm. pressure.[76] A small amount of this ether was obtained by distillation in Expt. 29 (see below).

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
18.2	39	40.0	87	62.1	173
23.1	46	44.4	105	66.6	201
26.6	53	49.4	119	71.1	228
31.1	65	53.3	132	75.5	270
35.5	76	57.7	150	80.0	322

For a related experiment, similar in every respect except that the catalyst concentration was doubled, the reaction temperature was 80.4° and the yields of water and product were respectively 101% and 77.3%. The first order k values were 205, 199, 196, 187, and 188.

The Etherification of Anisyl Alcohol with Primary, Secondary and Tertiary Butyl Alcohol

General.--The yields of product are given in Table VI of the Discussion. Supplementary data for these etherifications are given in Table XIII.

Experiment 28.--The anisyl sec-butyl ether, isolated by distillation through a 7 in. wrapped Vigreux column, distilled steadily at 67° to 69° at 0.1 mm. pressure; n_D^{25} 1.4932 to n_D^{25} 1.4935. One of the many fractions with the refractive index, n_D^{25} 1.4933 was analyzed. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.05; H, 9.46.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.8	69	50.3	266	71.3	559
22.6	91	55.1	315	76.4	726
31.1	136	60.0	365	78.6	811
36.0	162	62.2	394	78.9	826
40.9	192	68.4	491	80.0	868
47.1	232	70.4	519	83.1	1220

Experiment 29.--The anisyl t-butyl ether, isolated by distillation through a 7 in. wrapped Vigreux column, distilled steadily and without decomposition at 61° to 65° at about 0.12 mm. pressure; n_D^{25} 1.4943 to n_D^{25} 1.4947. One of two fractions with the refractive index, n_D^{25} 1.4943, was analyzed. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found:

TABLE XIII

SUPPLEMENTARY DATA FOR TABLE VI

Expt. No.	Yld. H_2O, %	Residue, g.	Temp.,[b] C°.	k, 10^{-4} min.$^{-1}$						
				30%	40%	50%	60%	70%	Av.	Av. dev.
27[a]	96.7	0.3	81.0 ± 0.05	39.3	40.4	38.5	37.6	36.2	38.4	1.20
28	94.6	0.7	79.4 ± 0.00	26.2	26.1	25.8	24.1	21.7	24.8	1.50
29	97.3	1.5	79.0 ± 0.00	19.1	17.9	17.0	16.2	15.2	17.1	1.14

a. This is the same as Expt. 16.

b. The median temperature and the maximum variation (±) from this median.

C, 74.35; H, 9.30. Upon raising the temperature, after the main product had ceased to distil, a second product was obtained which distilled at 130° to 141° at 0.1 mm. pressure. This product, which was dianisyl ether, was recrystallized from 30-60° petroleum ether; m.p. 37-38° (m.p. 39°).

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.8	99	44.6	319	61.5	556
22.2	125	48.4	361	62.4	579
27.1	159	50.6	394	69.4	727
31.1	191	53.7	436	70.7	774
35.5	229	57.3	491	72.0	811
39.5	265	58.9	515	81.1	1210

The Effect of Varying the Ratio of the n-Butyl Alcohol to the Benzyl Alcohol

General.--The yields of products are reported in Table VII of the Discussion. Supplementary data for these experiments are given in Table XIV.

Experiment 30.--Diphenylmethane, which was the only product, was isolated by distillation through a 7 in. Vigreux column. It distilled steadily at 66° to 68° at 0.3 mm. pressure; n_D^{25} 1.5742 to n_D^{25} 1.5750 (n_D^{25} 1.5745).[60] On the basis of the refractive index obtained for the first fraction (0.35 g.) from the above distillation, it may be concluded that not more than trace amounts of benzyl n-butyl

TABLE XIV

SUPPLEMENTARY DATA FOR TABLE VII

Expt. No.	Yld. H_2O, %	Residue, g.	Temp.,[b] °C.	k, 10^{-4} min.$^{-1}$						
				30%	40%	50%	60%	70%	Av.	Av. dev.
30	100	1.6	79.4 ± 0.05	267	245	265	322	300	280	25.0
31	99.0	1.0	81.0 ± 0.05	34.7	35.7	35.3	35.9	35.5	35.4	0.340
32	99.0	0.4	81.4 ± 0.00	——[c]	——	——	——	——	——	——
33	100	0.8	80.4 ± 0.05	27.3	30.9	31.8	33.4	36.2	33.2	2.56
34[a]	101	0.4	81.0 ± 0.05	5.07	5.27	5.52	5.73	5.96	5.51	0.310
35	95.0	1.8	81.1 ± 0.20	80.9	80.0	75.8	72.2	65.2	74.8	4.90
36[d]	96.7	0.3	81.0 ± 0.05	39.3	40.4	38.5	37.6	36.2	38.4	1.20

a. Same as Expt. 18, Table XI.

b. The median temperature and the maximum variation (±) from the median.

c. No rate data were taken.

d. Same as Expt. 16, Table XI.

ether were formed in the reaction.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
16.9	13	31.5	20	59.5	37
19.1	14	34.7	22	62.2	40
21.3	15	39.5	26	68.0	45
24.0	16	48.9	31	75.5	50
27.6	18	56.8	35	80.0	57

Experiment 31.--Separation of the benzyl n-butyl ether and diphenylmethane was made by distillation using a 7 in. wrapped and heated Vigreux column. The ether distilled steadily at 78° to 81° at about 3.5 mm. pressure; n_D^{25} 1.4871 to n_D^{25} 1.4910 (n_D^{25} 1.4892; n_D^{25} 1.4860).[1, 56] The diphenylmethane distilled at 100° to 102° at 3.0 mm. pressure; n_D^{25} 1.5714 to n_D^{25} 1.5718 (n_D^{25} 1.5745).[60] It was stated in connection with Expt. 18 that this was a difficult separation. Part of the original distillation data (in the transition region) from Expt. 31 is given in the following table to show that good fractionation was achieved.

Fraction No.	Temp., C.°	Weight, g.	n_D^{25}
10	70	0.15	1.4883
11	72	0.21	1.4900
12	100	0.33	1.5203
13	103	0.87	1.5690

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
19.1	56	40.0	140	62.2	265
22.2	67	44.4	163	67.5	300
27.1	87	48.8	186	72.0	329
31.1	103	53.3	213	76.0	361
35.5	121	59.5	250	80.0	403

Experiment 32.---The only product, benzyl n-butyl ether was isolated by distillation through a 7 in. wrapped and heated Vigreux column using a Newman pressure regulator.[81] It distilled steadily at 92° to 96° at 10 mm. pressure; n_D^{25} 1.4853 to n_D^{25} 1.4898 (n_D^{25} 1.4892; n_D^{25} 1.4860).[1, 56]

Experiment 33.---The separation of benzyl n-butyl ether and diphenylmethane was carried out according to the procedure described in Expt. 31 except that the Vigreux column was not heated. The ether distilled steadily at 52° to 53° at about 0.3 mm. pressure; n_D^{25} 1.4963 to n_D^{25} 1.5070 (n_D^{25} 1.4892; n_D^{25} 1.4860).[1, 56] These high refractive indices indicate that probably as much as 5% of diphenylmethane was present. In spite of this however, the yield of ether reported in Table VII is essentially correct. The diphenylmethane distilled at 64° to 69° at about 0.4 mm. pressure; n_D^{25} 1.5746 to n_D^{25} 1.5750 (n_D^{25} 1.5745).[60]

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
17.8	44	35.6	127	62.6	281
20.0	51	40.0	144	66.6	298

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
22.2	60	44.4	166	71.1	322
26.7	80	48.8	192	84.4	441
31.1	108	53.3	220	87.1	462

An experiment similar in every respect to Expt. 33 except that the total volume of solution was 500 ml. was performed by Dr. Draper. The yields of ether and alkylated product were respectively 40% and 33%.[1]

Experiment 35.--The apparatus was flushed with dry nitrogen prior to heating the reaction mixture. The anisyl n-butyl ether was isolated by distillation as described in Expt. 16. It distilled steadily at 62° to 64° at 0.1 mm. pressure; n_D^{25} 1.4953 to n_D^{25} 1.4961 (from Expt. 16, n_D^{25} 1.4950). Upon raising the temperature, after all the above product had been collected, a second product was obtained distilling at 130° at 0.1 mm. pressure which later solidified. This material was purified by recrystallization from 30-60° petroleum ether; m.p. 50-51.5°. Several analyses of this compound obtained from other similar experiments failed to establish its identity. Found: C, 78.83; H, 6.98; CH_3O, 25.56.

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
18.7	28	40.0	65	64.4	141
23.7	35	44.4	77	67.1	159
26.6	41	48.8	90	72.0	197

% compl.	Time (min.)	% compl.	Time (min.)	% compl.	Time (min.)
31.1	48	53.3	103	75.5	267
35.5	57	57.7	118	80.0	360

For a duplicate experiment, the reaction temperature was 81.7° to 81.8° and the yields of water and main product were respectively 93.7% and 46.3%. None of the above unidentified by-product was isolated but 6.82 g. of residue was obtained. The first order k values were 89.0, 91.4, 84.8, 79.3, and 69.2.

For a related experiment, similar in every respect except that the catalyst concentration was doubled, the reaction temperature was 80.0° and the yields of water and main product were respectively 95.6% and 71.4%. A 2.2 g. portion of the unidentified by-product was obtained; m.p. 50-51.5°. The first order k values were 296, 302, 294, 280, and 241. The total reflux time for this experiment was 398 min. A duplicate of this experiment which was refluxed for a total of 325 min. gave an identical yield of ether. Two other duplicates however, which were permitted to reflux 1500 min. or longer, gave yields of ether that were less than half of those above.

The Effect of Varying the Catalyst Concentration

General.--The bulk of the data pertinent to this phase of the investigation are found in many of the previous experiments listed in Tables XI, XIII, and XIV. Additional data are obtained from experiments related to those in the tables.

The Effect of Varying the Catalyst Concentration on the Reaction of Benzyl Alcohol with n-Butyl Alcohol.--Pertinent data on the effect of doubling the catalyst concentration at a 1 to 1 ratio of these alcohols are found in Expts. 30 and 33 (Table XIV). The analogous data at a 1 to 3 ratio are found in Expts. 31 and 34 (Table XIV).

The Effect of Varying the Catalyst Concentration on the Etherification of Anisyl Alcohol with n-Butyl Alcohol.--A comparison of the data from Expt. 16 with that from its related experiment illustrates the effect of quadrupling the catalyst concentration when n-butyl alcohol is in 200% excess. A similar comparison of the data from Expt. 35 with that from its related experiment shows the effect of doubling the catalyst concentration when these alcohols are present in equivalent amounts.

The Effect of Varying the Catalyst Concentration on the Self-Etherification of Anisyl Alcohol.--A comparison of the data from Expt. 26 with that from its related experiment shows the effect of doubling the catalyst concentration on this reaction.

The Effect of Varying the Catalyst Concentration on the Etherification of p-Methylbenzyl Alcohol with n-Butyl Alcohol.--A comparison of the data for Expt. 17 with that for its related experiment illustrates the effect of halving the catalyst concentration.

Related Etherifications

Self-Etherifications of Benzyl Alcohol.--A 0.250 m. portion of benzyl alcohol dissolved in decalin to give a total volume of 500 ml. was refluxed for a total of 29 hrs. at a catalyst concentration of 0.004 m. per l. and a 95% yield of water was obtained. The yield of product distilling at 125° to 129° at 1.0 mm. pressure was 33.7%; n_D^{25} 1.5596 to n_D^{25} 1.5612 (n_D^{25} 1.5597).[55]

An attempt to perform this self-etherification using dibutyl ether as the solvent resulted in cleavage of the latter.

Almost total destruction of the catalyst was shown to take place within a very short time at the above reflux temperatures. An attempt was made therefore, to perform this self-etherification in decalin as above but without catalyst. A total reflux time of 250 hrs. resulted in a 79% yield of water and a 22% yield of fairly satisfactory product.

In the final attempt to achieve this self-etherification, 100 ml. (3.84 m.) of benzyl alcohol was refluxed without catalyst for a total of 60 hrs. The rate or amount of etherification could not be followed since the water and the alcohol had essentially the same density but a 45% yield of the ether was obtained; n_D^{25} 1.5622 (n_D^{25} 1.5597).[55]

Attempted Etherification of Benzyl Alcohol with n-Hexyl Alcohol.--A 0.125 m. portion of benzyl alcohol was added to n-hexyl alcohol to give a total volume of 250 ml. The catalyst concentration was successively doubled until a final concentration of 0.004 m. per l. was reached. A 120% yield of water, calculated for benzyl n-hexyl ether, was obtained in 28 hrs. of reflux. The attempt to isolate the products by fractionation was unsuccessful.

Etherifications with Diethylene Glycol.--A 26.5 g. portion (0.250 m.) of diethylene glycol dissolved in benzene to give a total volume of 500 ml. was refluxed for a total of 155 hrs. The catalyst concentration was successively doubled until a final concentration of 0.512 m. per l. was reached but no reaction occured.

Diethylene glycol was however completely etherified by benzhydrol. A 23.0 g. portion (0.125 m.) of benzhydrol and a 6.63 g. portion (0.0625 m.) of diethylene glycol were dissolved in benzene to give a total volume of 500 ml. Upon refluxing, a 70% yield of water was obtained in 355 minutes at a catalyst concentration of 0.004 m. per l. Isolation was made by the use of a Hickman still. The product came over at 147° to 159° at 0.0012 mm. pressure; n_D^{20} 1.5809 to

n_D^{20} 1.5838. Analyses were carried out on the fraction having the lower of the above refractive indices. Calcd. for $C_{30}H_{30}O_3$: C, 82.14; H, 6.90. Found: C, 81.88; H, 6.99.

Self-Etherification of n-Hexyl Alcohol.--The experimental procedure is described in detail in the Discussion. Other details are given in Table XV.

In order to remove completely the hexene-1, as well as the residual water remaining from the catalyst extraction, each fraction was heated to 145° at 760 mm. pressure. The water and impure hexene-1 recovered were separated and the latter weighed. The unreacted n-hexyl alcohol was next recovered by distillation at 135° at 60 mm. pressure, the process being followed by frequent refractive index determinations on the distillate. The product, isolated by distillation through a 7 in. wrapped and heated Vigreux column, distilled at 80° to 83° at 5 mm. pressure; n_D^{25} 1.4184 to n_D^{25} 1.4190 (1.4202).[67]

After the ether had all been collected, a second product assumed to be the sulfonate ester of n-hexyl alcohol was obtained upon further distillation. This product came over rapidly at 151° at 0.4 mm. pressure. Since the amounts of this product were small, all of these high boiling fractions from the whole experiment were combined and redistilled at 136° to 138° at 0.2 mm. pressure; n_D^{26} 1.4954 to n_D^{26} 1.4959. Analyses were carried out on one of the fractions having the higher of the above refractive indices. Calcd. for $C_{13}H_{20}O_3S$: C, 60.90; H, 7.86. Found: C, 62.27; H, 8.05.

TABLE XV

THE SELF-ETHERIFICATION OF n-HEXYL ALCOHOL

Fraction No.[a]	Water collected, ml.	Temp. range, °C.	Total time, min.[c]	Hexene-1 recovered, g.	n-Hexanol recovered, g.[d]	Sulfonate ester, g.	Residue, g.	Dihexyl ether, %
1	13.5[b]	155-161	218	2.57	74.5	0	1.6	86
2	6.74	161-167	415	2.78	55.2	1.5	1.1	85
3	4.5	167-178	708	1.60	28.7	4.8	0.9	94
4	2.26	178-205	1490	0	4.70	7.0	1.2	75

[a] Each fraction was 108.0 g. except No. 4 which was 85.9 g.

[b] This included 4.5 ml. that came from catalyst dehydration.

[c] This is the total reflux time.

[d] The low boiling product was assumed to be hexene-1.

The analyst reported that the sample decomposed during the analyses so the above results may not be too meaningful.

The Transetherification of Dianisyl Ether with n-Butyl Alcohol -- A 16.14 g. portion (0.0625 m.) of dianisyl ether together with 27.78 g. (0.375 m) of n-butyl alcohol was dissolved in benzene to give a total volume of 864 ml. at 25°. The reaction mixture was brought to reflux and 80 ml. of the standard catalyst solution used for the experiments of Table III was then added. A 97% yield of water calculated for transetherification was obtained in 2800 minutes at a catalyst concentration of 0.004 m. per l. The anisyl n-butyl ether, isolated as described in Expt. 16, distilled steadily at 58° to 63° at about 0.1 mm. pressure; n_D^{25} 1.4953 to n_D^{25} 1.4959 (value from Expt. 16, n_D^{25} 1.4950). The yield of product was 93.6%.

For a duplicate of this experiment, the yields of water and product were respectively 92.3% and 91.0%.

The Esterification of the Catalyst by n-Butyl Alcohol.-- This was originally an attempt to determine if any significant self-etherification of n-butyl alcohol took place at the very high catalyst concentrations used in the unsuccessful attempts to etherify p-nitrobenzyl alcohol with n-butyl alcohol. A 48.69 g. portion (0.256 m.) of the catalyst monohydrate was added to 375 ml. of benzene and dried azeotropically. The n-butyl alcohol (0.375 m.) mixed with sufficient benzene to give a total volume of 97 ml. was then added to the benzene solution of the catalyst. The water collector was replaced and the solution brought to reflux. A 50% yield of water calculated for esterification was obtained in 292 hrs. of continuous reflux. The product, isolated by distillation through a 7 in. wrapped and heated Vigreux column, was collected at 132° to 138° at 0.3 mm. pressure; n_D^{25} 1.5018 to n_D^{25} 1.5020 (n_D^{20} 1.5050).[82] There was no trace of dibutyl ether but the yield of n-butyl-p-toluenesulfonate was 23%.

A related experiment, which was similar in every respect except that only half as much n-butyl alcohol was used, gave a 47% yield of water calculated for esterification in 240 hours of continuous reflux. No attempt was made to isolate the products.

SUMMARY

A previous investigator in this laboratory found that reactions of the following type proceeded readily in over 90% yield when a benzene solution of the reactants and catalyst was refluxed in an apparatus equipped with a Dean-Stark water collector.[1]

$$(C_6H_5)_3COH + CH_3(CH_2)_3OH \xrightarrow{p\text{-}CH_3C_6H_4SO_3H} (C_6H_5)_3CO(CH_2)_3CH_3 + H_2O$$

It was also established by noting the rate at which the by-product water collected that the rate was proportional to the concentration of one of the alcohols.

In the present investigation, the kinetics of the reaction were studied in more detail with emphasis on increasing the accuracy of the method and on determining the effect of varying the ratio of reactants. By means of an improved procedure, it was found that the rate constant calculated on the basis of triphenylcarbinol over the 20% to 80% portion of the reaction was $34.4 \pm 0.20 \times 10^{-4}$ min^{-1} when 0.250 m of triphenylcarbinol, 0.750 m. of n-butyl alcohol and 0.000125 m. of catalyst in a total volume of 2 l. of benzene solution were reacted. The rate was approximately proportional to the first power of the catalyst concentration.

When benzhydrol replaced triphenylcarbinol in the above reaction it was necessary to increase the catalyst concentration thirty-two fold. The corresponding rate constant was $13.5 \pm 0.16 \times 10^{-4}$ min.$^{-1}$ and the rate fell over

40% when the concentration of n-butyl alcohol was doubled. Doubling the catalyst concentration almost tripled the reaction rate.

It was found that the following type of reaction proceeded in good yield in most cases when a three-fold excess of n-butyl alcohol was used.

$$p\text{-}RC_6H_4CH_2OH + CH_3(CH_2)_3OH \xrightarrow{p\text{-}CH_3C_6H_4SO_3H} p\text{-}RC_6H_4CH_2O(CH_2)_3CH_3 + H_2O$$

As the electron attracting ability of R- was increased in the following sequence $(CH_3)_2N$-, CH_3O-, CH_3-, H-, Cl-, the catalyst concentration required increased greatly, the total increase being 2048 fold.

When R- was H- and an eight-fold excess of n-butyl alcohol was used, an 80% yield of the ether was obtained but when no excess of butyl alcohol was present the benzene solvent was alkylated to give a 74% yield of diphenylmethane.

When the butyl alcohol in the preceding equation was replaced by p-methoxybenzyl alcohol, the analogous products were obtained in 73% to 93% yields. As R- was changed, at constant catalyst concentration, from CH_3-, to H-, to Cl-, to O_2N-, the rate increased thirteen-fold overall. These changes in rate are ascribed to the varying ability of the benzyl alcohols to form hydrogen bonds with and thereby "deactivate" the catalyst.

n-Butyl alcohol etherified p-methoxybenzyl alcohol faster than sec-butyl alcohol which in turn reacted faster than t-butyl alcohol.

It was interesting to find that a 90% yield of ether could be obtained merely by refluxing n-hexyl alcohol in the presence of p-toluenesulfonic acid and removing the by-product water as it formed.

The results were correlated insofar as possible with the carbonium ion mechanism of etherification. In general, the results can be correlated very satisfactorily on the basis of this mechanism.

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