pression in m.p. was observed upon admixture with an authentic sample of m.p. 212–213° (reported[28] m.p. 206°). The infrared spectra also proved to be identical.

Upon removal of the *n*-pentane from the above mother liquor, a sweet smelling oily residue remained which failed to crystallize.

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

An Investigation into the Importance of Heterogeneity as a Directive Influence in the Alkylation of Sodium 4-*t*-Butyl-2,6-dimethylphenoxide[1] with Benzyl Chloride

BY DAVID Y. CURTIN AND DOUGLAS H. DYBVIG[2]

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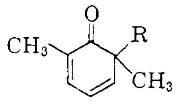
Sodium 4-*t*-butyl-2,6-dimethylphenoxide (I) has been found to undergo alkylation both on the oxygen atom and at an *ortho*-position to give 6-benzyl-4-*t*-butyl-2,6-dimethyl-2,4-cyclohexadienone (II) which, unlike similar dienones previously prepared, does not dimerize readily. The ratio of carbon to oxygen alkylation varies from a value of 1.4 in a heterogeneous experiment in toluene to about 0.17 in a homogeneous solution containing 16% of tetrahydrofuran. In the more polar media (containing 5.6 or 16% tetrahydrofuran) the alkylation follows second-order kinetics for the first 70% reaction. In the less polar media (0.84 and 1.3% tetrahydrofuran) which show light scattering the rate "constants" drift downward throughout the reaction. The effect of added tetrahydrofuran or inclusion of a quaternary ammonium salt is to accelerate the oxygen alkylation much more than the carbon alkylation. A heterogeneous reaction of tetramethylammonium 4-*t*-butyl-2,6-dimethylphenoxide with benzyl chloride in toluene containing 1.3% of tetrahydrofuran gives 70% of benzyl 4-*t*-butyl-2,6-dimethylphenyl ether (III) (oxygen alkylation) and approximately 0.5% of dienone II (carbon alkylation). A change in the amount of undissolved sodium salt (I) by a factor of about 10 fails to change appreciably the ratio of carbon to oxygen attack by benzyl chloride (in toluene). It is concluded that in these reactions, at least, heterogeneity *per se* has no significant effect on the ratio of carbon to oxygen alkylation.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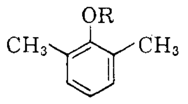
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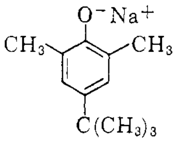
Previous studies[3,4] of the alkylation of salts of *o*-substituted phenols have shown that the reaction provides a direct method of synthesis of cyclohexadienones. For example, sodium 2,6-dimethylphenoxide was shown to react with allyl halides, benzyl halides and methyl iodide to give mixtures of dienone A and ether B. Certain properties of these dienones made reliable quantitative studies of their formation difficult, however. Thus, the dienones A derived from allylic halides undergo the Claisen rearrangement at temperatures only slightly above room temperature[5] and all of these dienones form dimers by a Diels–Alder reaction rather readily even at room temperature. For this reason, in the present work the reaction of benzyl chloride with the sodium salt (I) of 4-*t*-butyl-2,6-dimethylphenol was chosen for study since the derived dienone II might be expected to dimerize much less readily owing to steric strain introduced into the dimer by the presence of the *t*-butyl groups. The sodium salt I was prepared in analytical purity. An authentic sample of the dienone II was prepared by treatment of a suspension of the sodium salt I with benzyl chloride in toluene. Extensive chromatography was required to remove all traces of the $-OCH_2-$ absorption characteristic of III from the n.m.r. spectrum of II. As had been hoped, there was no evidence of dimerization of the dienone II even after several months at room temperature. Authentic ether III was prepared by the benzylation of the salt I in methanol. It had been supposed that the formation of dienone II plus ether III could be followed by titration of the liberated chloride ion, the dienone II determined quantitatively from the ultraviolet spectrum of the reaction mixture, and the ether III then determined by difference. It was found, however, that unless reaction mixtures were extracted with Claisen alkali, the ultraviolet spectroscopic determination of the dienone II gave values which were sometimes too high due to absorption in the dienone region by an oxidation product from the sodium salt I. This impurity was removable by the alkaline extraction, but it was generally more satisfactory to use infrared spectroscopy to determine dienone and ether directly.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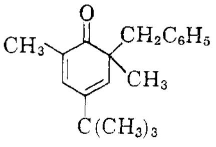
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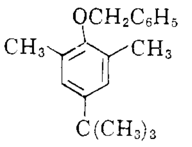
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The alkylation with benzyl chloride of the sodium salt I was examined in toluene (heterogeneous) and in toluene containing amounts of tetrahydrofuran varying from 0.75% to about 16%. Addition of 0.0024 mole of sodium salt I to 50 ml. of toluene gives a mixture which is clearly heterogeneous. When the toluene contains 0.84% of tetrahydrofuran, there is no visible precipitate, but the solution appears cloudy and on centrifugation some solid settles. Examination of the extent

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[1] We are indebted to the National Science Foundation for a Grant (G4467) which supported a part of this research. This work is taken from the Ph.D. thesis submitted by D. H. D. to the University of Illinois, 1960, which is available from Univ. Microfilms, Ann Arbor, Mich.

[2] National Science Foundation Fellow, 1959–1960.

[3] (a) D. Y. Curtin, R. J. Crawford and M. Wilhelm, *J. Am. Chem. Soc.*, **80**, 1391 (1958); (b) T. L. Brown, D. Y. Curtin and R. R. Fraser, *ibid.*, **80**, 4339 (1958); (c) D. Y. Curtin and R. R. Fraser, *ibid.*, **80**, 6016 (1958); (d) D. Y. Curtin and M. Wilhelm, *J. Org. Chem.*, **23**, 9 (1958); (e) D. Y. Curtin and R. R. Fraser, *J. Am. Chem. Soc.*, **81**, 662 (1959); (f) D. Y. Curtin, R. C. Tuites and D. H. Dybvig, *J. Org. Chem.*, **25**, 155 (1960).

[4] R. Barner and H. Schmid, *Helv. Chim. Acta*, **43**, 1393 (1960).

[5] D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957).

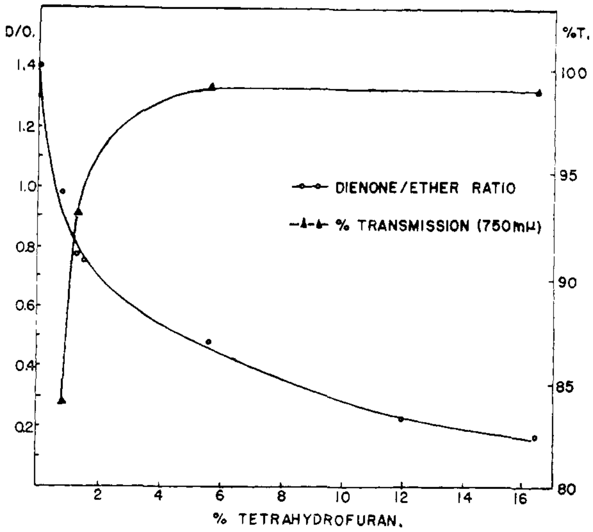

Fig. 1.—Variation with the % tetrahydrofuran of the dienone/ether ratio and of light scattering as measured by transmission of light of 750 mμ wave length in reaction mixtures at room temperature containing the sodium phenoxide I and benzyl chloride in toluene solution.

of transmission of visible light with a Cary spectrophotometer showed that such a solution transmitted 84% of the incident light. A similar solution with 1.3% tetrahydrofuran transmitted 93% of the incident light under the same conditions. Solutions with 5.6% or more tetrahydrofuran were clear with greater than 99% transmission, and should undoubtedly be classified as homogeneous. The variation with composition of the medium of the ratio of carbon alkylation to oxygen alkylation and also the variation of % transmission of visible light are shown in Fig. 1. It is seen that there is a smooth change from about 0.17 in the medium containing 16% tetrahydrofuran to 1.4 in pure toluene. It is clear moreover that solutions in which there is light scattering give higher proportions of alkylation on carbon.[6]

The best test of the effect of heterogeneity would appear to be to compare reactions in which the medium is held constant from one run to another and the amount of surface varied. Although this is not easy to achieve because of possible complications resulting from the equilibration of sodium halide and sodium phenoxide between the solid phase and solution, it seemed that it could be approximated by carrying a series of runs containing undissolved salt to approximately the same degree of completion. The results are shown in Table I. It is seen that the dienone/ether ratio is essentially independent of the % completion over the range studied and also that variation of the amount of solid phase by a factor of 10 makes no significant change in this ratio.[7]

TABLE I

REACTION OF 0.015 M BENZYL CHLORIDE WITH SUSPENSIONS OF SODIUM SALT I IN TOLUENE AT 110 ± 4°

Moles of I/benzyl chloride	% completion	Dienone/ether
1.3	18[a]	0.7
3.7	22[a]	.7
14	49[a]	.7
14	45[a]	.8
14	13[b]	.8

[a] In 23.3 hr. [b] In 10.5 hr.

These results are consistent with previous suggestions[3] that ion aggregation favors alkylation on carbon but fail to reveal any significant effect of the solid sodium phenoxide I on the carbon/oxygen ratio in the system studied. It seems to be likely but has not been established experimentally that the sodium salt I dissolves in toluene at 110° at a rate which is rapid relative to the rate of alkylation; that is, that the half-time of the rate of solution is appreciably less than 24 hr. It is of course still possible that there may be a kinetically important heterogeneous reaction. A striking example of a related reaction which can be made heterogeneous has been reported by Russell,[8] who studied the neutralization of α,α-dimethylbenzylpotassium in diethyl ether and found that when the neutralization with deuterium chloride was carried out in a series of reactions with successively higher salt/solvent ratios there was no change in the nature of the reaction in the region where the mixtures became heterogeneous. When a sufficient excess of the solid phase was added, however, the heterogeneous reaction became important.

In order to learn more about the effect of polar solvents on the carbon/oxygen ratio the rates of reaction of the sodium salt I with benzyl chloride in toluene containing 0.84, 1.3, 5.6 and 16.4% tetrahydrofuran were followed. The runs with 0.84 and 1.3% tetrahydrofuran showed a continuous decrease of the second-order "constants" when plotted as reactions first order in benzyl chloride and first order in salt I. The reactions in the two more polar media showed reasonably good second-order behavior to about 70% reaction, after which the rate fell rapidly. Since it could be shown that both the sodium salt and benzyl chloride were still present it seems possible that the rapid decrease in rate at this point may be associated with removal of the salt to the solid phase formed during the reaction or to a shift in an equilibrium involving a complex aggregate containing the sodium phenoxide and sodium bromide.[9] An apparently similar sudden fall-off in rate has been observed by Zaugg, Horrom and Borgwardt[10]

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(6) It should be noted that in all of the alkylations discussed in this paper, even if they were homogeneous initially, there was precipitation of a salt during the reaction.

(7) The ratios of 0.7–0.8 found here are appreciably smaller than the value of 1.4 plotted in Fig. 1. Since each of these values was reproducible we feel that the difference is real and must be attributed to the nearly 6-fold difference in the initial benzyl chloride concentrations in the two sets of experiments. It may be noted that the data suggest that there is some acceleration of both the carbon and oxygen alkylation by an increase in the amount of the solid sodium salt I. The possible variations of reaction temperature make it unclear whether this difference in rate is real, but if it is it suggests that there is a kinetically important heterogeneous reaction which becomes more important when more salt surface is present. If this is the case it must be concluded that the heterogeneous reaction gives a dienone/ether ratio which is not markedly different (under these conditions) from the ratio obtained in the homogeneous reaction.

(8) G. A. Russell, *J. Am. Chem. Soc.*, **81**, 2017 (1959).

(9) We are indebted to Dr. H. E. Zaugg for helpful discussion of this matter.

(10) H. E. Zaugg, B. W. Horrom and S. Borgwardt, *J. Am. Chem. Soc.*, **82**, 2895 (1960).

in a study of the alkylation of diethyl sodio-*n*-butylmalonate with *n*-butyl bromide in non-polar solvents.

The dienone/ether ratios were shown to be constant during a run and the rate constants were therefore partitioned to give the separate rates of formation of dienone II and ether III. The average values of duplicate runs are shown in Table II.

TABLE II

RATES OF REACTION OF SODIUM SALT I WITH BENZYL CHLORIDE IN TOLUENE AT 109.8 ± 0.1°

Tetra-hydrofuran, %	Obsd. rate, l./mole sec. × 10^4	Dienone/ ether ratio	k_d, l./mole sec. × 10^4	k_e, l./mole sec. × 10^4
5.6	2.4	0.48	0.8	1.6
16.4	4.6	0.17	0.7	3.9

Although the precision of the data is only fair, the result seems clear that a change of the amount of tetrahydrofuran from 5.6 to 16.4% has left the rate constant for the formation of dienone (carbon alkylation) essentially unchanged and more than doubled the constant for ether formation (oxygen alkylation).

It had been observed previously[3a] that the addition of tetrabutylammonium bromide to the reaction of sodium 2,6-dimethylphenoxide in diethyl ether both accelerated the reaction with allyl bromide and increased the amount of attack on oxygen. Zagorevsky[11] has observed that tetramethylammonium β-naphthoxide undergoes a higher fraction of oxygen alkylation than the potassium salt, and Zook and Gumby[12] have found that the alkylation of the potassium salt of butyrophenone is accelerated by the addition of tetrabutylammonium perchlorate or iodide but not by the addition of sodium iodide. Tetramethylammonium 4-*t*-butyl-2,6-dimethylphenoxide was prepared from the phenol and tetramethylammonium hydroxide followed by evaporation to dryness, but was not obtained in analytically pure form. A suspension of the slightly impure salt in toluene containing 1.3% tetrahydrofuran was allowed to react with benzyl chloride under reflux for 11 hours and found to give a 70% yield of the benzyl ether III and approximately 0.5% of dienone II. The carbon/oxygen ratio of 0.007 is in striking contrast to that of 0.77 obtained with the sodium salt.

The large accelerating effect of the quaternary ammonium ion previously noted was observed here qualitatively by stirring the sodium salt I with an equimolar amount of tetrabutylammonium bromide dissolved in tetrahydrofuran, with enough toluene then added to make the solution 5.6% in tetrahydrofuran. Filtration gave a white solid, probably sodium bromide (48%). Addition of a 3.3-fold excess of benzyl chloride at room temperature resulted in the immediate formation of a precipitate and in 20 minutes 58% of the ether III (and a negligible amount of dienone II) had formed. It is apparent that the reaction of the quaternary salt would be too fast to follow using ordinary techniques at 110° where the sodium salt I goes at a convenient rate. For this reason, the rate of reaction of the sodium salt I in 5.6% tetrahydrofuran containing 5% of the stoichiometric amount of tetrabutylammonium bromide was followed as before. The data are shown in Table III. It is seen that the reaction no longer obeys, even approximately, a second-order rate law. The values of the integrated rate constants calculated at various fractions of reaction drop rapidly. By plotting *versus* time the concentrations of dienone and ether formed and taking slopes of the resulting line it can be seen that the instantaneous dienone/ether ratio is initially less than 0.05, but in the latter stages of the reactions the ratio is approximately 1. This approach to the value obtained with the sodium salt (0.6) suggests that the quaternary ammonium phenoxide aggregates, initially the principal reactive species, are being converted to the sodium phenoxide aggregates as the reaction proceeds, either by precipitation of tetrabutylammonium ion or by the operation of ion aggregate equilibria.[13] As was found with the effect of polar solvents, it is striking that the dienone-forming reaction is accelerated considerably less, if at all, by the presence of tetrabutylammonium ion than is the ether-forming reaction.

TABLE III

REACTION AT 109.8 ± 0.1° OF SODIUM SALT I WITH BENZYL CHLORIDE IN TOLUENE WITH 5% TETRAHYDROFURAN AND 5% (BASED ON I) OF TETRABUTYLAMMONIUM BROMIDE

% Completion	Integrated rate constant, l./mole sec. × 10^4	Dienone/ether ratio
22.9	53	0.06
30.8	20	.18
33.4	11	.23
46.7	4.9	.29
61.9	3.2	.40

Discussion.—The factors which may influence the position of alkylation of phenoxide ions and related ambident ions have been reviewed many times.[3a,3c,4,10,12,14–22] There is general agreement that the state of aggregation of the substrate can have an important bearing on the position of alkylation.[3a,10,12,14–16,18–20,22] Furthermore, as Barner and Schmid have pointed out, there seem to be at least two reactions leading to nuclear alkylation

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[11] V. A. Zagorevsky, *J. Gen. Chem.* (*U.S.S.R.*), **27**, 3055 (1957).

[12] H. D. Zook and W. L. Gumby, *J. Am. Chem. Soc.*, **82**, 1386 (1960).

[13] A more satisfying explanation, suggested by Dr. Nathan Kornblum to whom we are indebted, is that the quaternary salt is being destroyed during the reaction at 110°, either by a displacement or an elimination reaction brought about by one of the nucleophilic agents present.

[14] C. K. Ingold, *Ann. Repts. Chem. Soc.* (*London*), 142 (1926).

[15] A. Brändström, *Arkiv Kemi*, **6**, 155 (1953).

[16] A. N. Nesmeyanov and M. I. Kabachnik, *Zhur. Obshchei Khim.*, **25**, 41 (1955).

[17] N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

[18] N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

[19] H. E. Zaugg, D. A. Dunnigan, R. J. Michaels, L. R. Swett, T. S. Wang, A. H. Sommers and R. W. DeNet, *J. Org. Chem.*, **26**, 644 (1961), and previous work therein cited.

[20] I. Forsblad, *Arkiv Kemi*, **15**, 403 (1960).

[21] N. Kornblum, P. J. Berrigan, William J. LeNoble, *J. Am. Chem. Soc.*, **82**, 1258 (1960); N. Kornblum and R. Seltzer, *ibid.*, **83**, 3668 (1961).

[22] Hobbs, McMillen, Papadopoulos and C. A. VanderWerf, *ibid.*, **84**, 43 (1962).

of phenol salts.[4] One of these leads to selective *ortho* attack and occurs in non-polar media where salts are known to be present to a large extent as ion aggregates (or suspended solid). The other, recently discovered by Kornblum, Berrigan and LeNoble[21] and Barner and Schmid,[4] occurs in particularly good ionizing (and hydrogen bonding) media and leads to *ortho* alkylation accompanied by extensive amounts of *para* attack.[4] We are here concerned only with the first of these reactions. In spite of the large quantity of work on the reactions of ambident ions, there has been almost no case where the degree of aggregation of reactant has been kinetically determined and correlated with the nature of the products. A noteworthy exception to this statement is the study of the alkylation of β-keto esters by Brändstrom which has culminated in the determination by Forsblad[20] of the rate constants for alkylation on carbon and oxygen for both dissociated ions and ion pairs in the alkylation of salts of the ethyl ester of β-hydroxycoumarilic acid.

It is of interest then to consider the significance (or lack of it) of the observed second-order rate law demonstrated in the present study in the alkylation of the sodium salt I with benzyl chloride in toluene containing 5.6 and 16% tetrahydrofuran. It can be said with a good deal of confidence that the sodium salt of 4-*t*-butyl-2,6-dimethylphenol at a concentration of about 0.03 *M* (the initial concentration employed in the kinetic studies) is present as an equilibrium mixture of dissociated ions, ion pairs, triple ions and higher aggregates, the fraction of dissociated ions being extremely small. In support of this view it may be noted that Cleland[23] found dioctyldimethylammonium azide at a concentration of 0.06 *M* in benzene to be associated with an average aggregation number of 30. Also sodium diethyl *n*-butylmalonate has been found to have an average aggregation number of more than 40 at a concentration of 0.14 *M* in benzene solution[12], and the sodium salt of butyrophenone at concentrations of 0.13–0.63 *M* in diethyl ether has an average aggregation number of 3.[14] It is not unduly pessimistic to suppose that several reactions of the benzyl halide with ion aggregates of various sizes (including, possibly, the dissociated phenoxide ion) may be going on simultaneously. As has been pointed out by Swain and Kreevoy[24] in considering a similar situation, the observed second-order rate constant for the reaction of the sodium salt with benzyl chloride is $\Sigma f_n k_n$, where f_n is the mole fraction of sodium salt present in an aggregate of size n and k_n is the rate constant for that aggregate. The requirement that the reaction follow second-order kinetics is that $\Sigma f_n k_n$ be constant during a run. A particularly likely possibility is that each f_n is constant during a run. Another possible condition which is sufficient is that the ratio k_n/n be equal to the same constant, R, for all values of n. As Swain and Kreevoy have suggested in their discussion, the latter possibility seems less likely. In any event it is clear that the observed kinetic order during a single run throws no light on the most critical problem, that is, the nature of the reactive species responsible for C-alkylation and that responsible for O-alkylation. It will be apparent that observations that the experimental rate constant for oxygen alkylation is much more susceptible to increased amounts of tetrahydrofuran and to the presence of quaternary ammonium cations can be explained in at least two ways. One possibility is that the reaction of dissociated phenoxide anion is largely responsible for the O-alkylation and, since the mole fraction of dissociated ions in this medium must be a very small fraction whereas the mole fraction of aggregated sodium phenoxide is nearly 1, it is clear that the dissociated ion concentration should vary over much wider limits when the medium is changed. It seems equally plausible, however, that little or no reaction in the media studied is due to the dissociated ion and that the relative rates of oxygen and carbon alkylation of the ion aggregates have different susceptibilities to the addition of a polar solvent such as tetrahydrofuran. It has been pointed out[25] that "one factor which could in part, be responsible for carbon alkylation by ion pairs and/or other aggregates arises from the difference in geometry of the two transition states. The transition state resulting from attack at oxygen has the two atoms bearing most of the negative charge (oxygen and halogen) disposed in a linear fashion while the transition state resulting from carbon attack has a non-linear arrangement in which the metal ion can nestle between the two negatively charged atoms." This argument can of course be applied equally well to an aggregate of any size and Kornblum and Lurie[18] have employed it in discussing the reaction at a solid surface. This same geometrical difference can also explain a possible state of affairs whereby ion aggregates are solely responsible for both carbon and oxygen alkylation with the oxygen alkylation much more susceptible to the presence of a solvating solvent. It is also recognized that solvent sorting[26] can make a small amount of a relatively polar solvent such as tetrahydrofuran have an effect which is quite out of proportion to the mole fraction present.

Previous studies[3a] of the *homogeneous* alkylation of the sodium salt of 2,6-dimethylphenol in anhydrous diethyl ether had led to the conclusion that the ratios of dienone to O-alkylated product were of the order of 0.3–0.4. Subsequently Kornblum and Lurie[18] have suggested in a study of the alkylation with benzyl and allyl halides of sodium and potassium salts of phenol and *p*-*t*-octylphenol that "heterogeneity is a factor which must be reckoned with" and further that "heterogeneity confers an essentially irresistible preference for carbon alkylation. . ."[27]

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(23) R. L. Cleland, quoted in ref. 24.

(24) C. G. Swain and M. M. Kreevoy, *J. Am. Chem. Soc.*, **77**, 1122 (1955).

(25) D. Y. Curtin, Fifteenth National Organic Chemistry Symposium, Rochester, N. Y., 1957, Abstracts, p. 61; see also ref. 3a.

(26) See J. B. Hyne, *J. Am. Chem. Soc.*, **82**, 5129 (1960).

(27) It is understood that Kornblum and Lurie have used the words "heterogeneity" and "heterogeneous reaction" in a restricted sense to refer to reaction occurring at the surface of solid phenol salt and not to reaction occurring at the "surface" of large aggregates in solution. They have concluded that an important difference in behavior distinguishes highly ordered crystals from ion aggregates which may be disordered. The further possibility exists that there are crystal-like

The complexities of the two sets of systems make it impossible at the present time to explain the difference in the importance of "heterogeneity" in the work of Kornblum and Lurie on the one hand and in the present work on the other. It will be noted that there has been no detailed study thus far on the effect of varying either the amount or the nature of the salt surface on the rates or ratio of rates of carbon and oxygen alkylation of alkali metal phenoxides unsubstituted in the *o*-positions. However, there are both electronic and steric differences between the two systems as Kornblum and Lurie pointed out.[18] Furthermore, in the alkylation of their salts there is produced, each time a molecule of the salt reacts, a molecule of alkylphenol as well as the alkali metal halide, a complication not present in the reactions forming dienones. Kornblum, Berrigan and LeNoble[21] have pointed out that the course of the alkylation of phenol salts may be affected by the presence of hydroxylic species such as phenol (and presumably also alkylphenols).

Differences in point of view as to the relative importance of the factors determining the position at which ambident ions react are not surprising in view of the complexity of the situation. The major immediate problem, attack on which has hardly begun, is to discover more about the structures of ion clusters and the relationship between structure and rate of carbon and oxygen alkylation.

Acknowledgment.—We are very much indebted to Dr. S. G. Smith and Dr. P. A. S. Smith for much valuable advice and assistance with the preparation of this manuscript.

Experimental[28]

4-*t*-Butyl-2,6-dimethylphenol was prepared by a modification of the method of Carpenter and Easter[29] for the preparation of 4-*t*-butylphenol. A solution of 103 g. (0.97 mole) of 2,6-dimethylphenol (m.p. 49–50°) in 230 ml. of freshly distilled ethylene dichloride (b.p. 83-83.5°) was saturated with dry hydrogen chloride; 0.9 g. (0.0068 mole) of anhydrous aluminum chloride and, over a period of 1.5 hr., 243 g. (2.63 moles, 2.7-fold excess) of freshly distilled *t*-butyl chloride (b.p. 50–51°) were added to the stirred solution at 25°. After 2 hr. at 25° and 30 min. at 83° the reaction mixture was concentrated under reduced pressure to 250 ml. and then dissolved in 200 ml. of cyclohexane and filtered. Crystallization resulted in 139 g. of crude product, m.p. 70–80°. Recrystallization from cyclohexane and then sublimation (82° (0.4 mm.)) yielded 122 g. (71%) of white 4-*t*-butyl-2,6-dimethylphenol, m.p. 79–80° (lit.[30] 82.5°). The n.m.r. indicated the presence of two types of methyl hydrogen atoms present in a ratio of 3:2 at 8.82 and 7.87τ as well as a single ring-hydrogen absorption at 3.20 and a hydroxyl proton at 5.55τ. The ultraviolet spectrum in cyclohexane showed λ_{max} 282, ϵ 1,740.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.2. Found: C, 80.6; H, 10.1.

6-Benzyl-4-*t*-butyl-2,6-dimethyl-2,4-cyclohexadienone (II).—4-*t*-Butyl-2,6-dimethylphenol (9.80 g., 0.055 mole) in 100 ml. of toluene was converted to the sodium salt I with 1.15 g. (0.050 g.-atom) of sodium metal in a dry nitrogen atmosphere with stirring at reflux for 8 hr. To the resulting suspension was added 19.0 g. (0.15 mole) of freshly distilled benzyl chloride (b.p. 178.0–178.5°). After stirring under reflux for 13 hr. the pale yellow reaction mixture was extracted with Claisen alkali,[31] washed with water and dried over anhydrous magnesium sulfate. Acidification of the alkaline extracts gave 2.13 g. (30%) of the unreacted phenol (not further purified). Distillation of the neutral layer through a Holzman column gave, after a colorless low-boiling forerun of toluene and benzyl chloride, 9.27 g., b.p. 101–104° at 0.02–0.04 mm. Redistillation of a 3.48-g. sample gave 3.06 g., b.p. 95–96° at 0.05 mm. The carbon and hydrogen analysis of this material was correct for the product II, but the infrared spectrum contained beside the characteristic dienone absorption at 1637 and 1655 cm.$^{-1}$ weak absorption at 1118 and 1190 cm.$^{-1}$ characteristic of the ether III and the n.m.r. spectrum had absorption at 7.69τ indicating the presence of 5–10% of the ether III. Chromatography four times on neutral alumina (elution with cyclohexane) was required to obtain a sample of dienone which showed no trace of the ether III in the infrared spectrum or n.m.r. The yield of dienone II at an intermediate stage of purification where the ultraviolet indicated it to be 97% pure (on the basis of its absorption at 313 mμ) was 46%. The ultraviolet spectrum showed λ_{max} 313 mμ, ϵ 4470. The n.m.r. showed absorption due to the group $C_6H_5CH_2$ at 2.98 γ (aromatic hydrogens) and as a quartet at 6.75, 7.06, 7.30 and 7.65 γ (CH_2 group).[32] The two hydrogens attached to the dienone system appeared as a quintet centered at 3.40 and a doublet centered at 4.17τ. The methyl groups were at 8.24 and 8.71 and the *t*-butyl at 8.90τ. There was no absorption at 7.54τ, characteristic of the ether III. The carbonyl absorption appeared as a strong partially resolved doublet at 1637 and 1655 cm.$^{-1}$.

When freshly prepared dienone was allowed to stand neat for 3.5 months the infrared spectrum was superimposable with the spectrum of the original sample.

Anal. Calcd. for $C_{19}H_{24}O$: C, 85.0; H, 9.0. Found: C, 84.7; H, 8.9.

Benzyl 4-*t*-Butyl-2,6-dimethylphenyl Ether (III).—4-*t*-Butyl-2,6-dimethylphenol (8.1 g., 0.046 mole) was converted to the sodium salt with 2.5 g. (0.046 mole) of sodium methoxide in 110 ml. of absolute methanol. The resulting solution was treated with 17.3 g. (0.137 mole) of benzyl chloride and heated under reflux for 19 hr. Extraction with Claisen alkali[31] gave 3.4 g. of recovered phenol and from the neutral fraction was obtained by distillation through a Holzman column 4.0 g. (35%) of the desired ether III. Further purification by chromatography (elution with hexane) on neutral activated alumina and distillation gave 0.49 g. of the ether, b.p. 125–126° at 0.3 mm. The infrared spectrum showed strong absorption at 1118 and 1190 cm.$^{-1}$ and no absorption in the carbonyl region characteristic of the dienone II. The n.m.r. showed aromatic absorption (benzyl group) at 3.00 and (the other aromatic ring) at 3.37τ. The benzyl methylene hydrogens absorbed at 5.52, the

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aggregates (or tight ion aggregates) and solvent-separated aggregates containing interspersed solvent, analogous to intimate ion pairs and solvent-separated ion pairs whose independent existence has been established by Winstein and his associates [see S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **79**, 169 (1958), and other papers of the series]. Ion aggregates of such varying structures could, of course, differ in their behavior.

Furthermore, Zook and Russo [H. D. Zook and T. J. Russo, *J. Am. Chem. Soc.*, **82**, 1258 (1960)] have provided evidence for specific solvation effects on the position of alkylation of ambident ions. Thus, ion aggregates in one solvent may give a different ratio of carbon/oxygen alkylation than in another solvent.

(28) All melting points are corrected. The n.m.r. spectra were measured by Mr. B. Shoulders and Mr. O. Norton with 20% solutions in carbon tetrachloride and with methylene chloride as an external standard. The instrument employed was a Varian Associates V-4300-C high resolution spectrophotometer equipped with a VK-3606 flux stabilizer and calibrated with a Hewlett–Packard 200-CD oscillator. Measurements were at 40 Mc. unless otherwise indicated. Ultraviolet spectra were measured with a Cary model 14M recording spectrophotometer and 1-cm. quartz cells by Mr. J. Chiu and Miss C. Juan. Some of the infrared spectra were obtained by Mr. P. McMahon, Mrs. J. Verkade, Mr. W. Dalton and Mr. D. Johnson. Infrared spectra were obtained with a Perkin–Elmer model 21 spectrophotometer with 0.1-mm. cells unless otherwise indicated. The principal spectra and other detailed data are available in the thesis of D. H. D.[1] Microanalyses were performed by Mr. J. Nemeth, Miss C. Higham, Miss J. Liu and Mrs. A. Bay.

(29) M. Carpenter and W. Easter, *J. Org. Chem.*, **19**, 95 (1954).

(30) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

(31) Claisen alkali was prepared by dissolving 350 g. of potassium hydroxide in 250 g. of water and diluting to 1 l. with absolute methanol.

(32) The n.m.r. spectrum has been presented and discussed in a review article by Martin [J. C. Martin, *J. Chem. Ed.*, **38**, 286 (1961)].

methyl groups at 7.94 and the *t*-butyl at 8.92τ. The ultraviolet showed λ_{max} 265 mμ of ε 680.

When and alkylation was carried out with sodium salt prepared in the same way from 1.8 g. (0.01 mole) of 4-*t*-butyl-2,6-dimethylphenol in 10 ml. of *n*-butyl alcohol with 3.8 g. (0.03 mole) of benzyl chloride for 13 hr. under reflux, dilution of a portion of the product with 1000 parts of cyclohexane and examination of the ultraviolet spectrum showed no absorption at 313 mμ. Extraction of the neutral fraction from Claisen alkali[30] and examination of the infrared spectrum indicated that there was no dienone (no carbonyl absorption at 1637, 1655 cm.$^{-1}$) and the intensity of the absorption at 1190 cm.$^{-1}$ indicated the presence of a 40% yield of ether III. The sample prepared in methanol and purified as described above was analyzed.

Anal. Calcd. for $C_{19}H_{24}O$: C, 85.0; H, 9.0. Found: C, 85.2; H, 8.9.

Sodium 4-*t*-Butyl-2,6-dimethylphenoxide (I).—The method employed was essentially that used by Kornblum and Lurie[18] to prepare salts of other phenols. To 18.9 g. (0.106 mole) of 4-*t*-butyl-2,6-dimethylphenol in 18 ml. of absolute methanol under nitrogen was added 4.16 g. (0.104 mole) of sodium hydroxide (97.0% assay) in 40 ml. of 80% aqueous methanol over a period of 15 min. Solvent was removed at 18 mm. pressure over a period of 3 hr. at 60° and the resulting white solid was further evacuated at 80° and 0.5 mm. pressure for 16 hr. The salt was then transferred to a dry-box flushed with nitrogen where it was pulverized and washed with two 45-ml. portions of dry pentane. Both the solid and filtrate remained colorless. The salt was then heated at 100° at 0.4 mm. for 20 hr., pulverized and finally heated at 90° (0.25 mm.) for 24 hr. to yield 19.8 g. (95%) of the sodium salt I as a white powder. The infrared spectrum obtained with a solution of approximately 0.1 g. of salt in 1.0 ml. of dry tetrahydrofuran (prepared under nitrogen) showed no absorption in the regions near 1700 and 3400 cm.$^{-1}$. When a weighed portion of the salt was mixed with a measured excess of standard 0.1002 *N* aqueous hydrochloric acid and the excess titrated with standard 0.0990 *N* sodium hydroxide solution (methyl red–brom cresol green indicator) the % sodium salt obtained in three determinations was 99.7, 101.5, 102.6%. (The hydrolysis was complicated by the insolubility of the phenol produced and the procedure was facilitated by the addition of 5 ml. of diethyl ether.)

The sodium salt I was stored under nitrogen in tightly stoppered brown glass bottles which in turn were stored under nitrogen over anhydrous calcium chloride in a desiccator. All subsequent transfers were made in a dry-box under a stream of dried nitrogen. Upon exposure to moisture in the air the salt became gummy and yellow with a characteristic phenol-like odor. In spite of all precautions the salt began to discolor after about 6 months storage. When about 0.1 g. of the salt so discolored was mixed with 25 ml. of toluene and filtered there was no large decrease in the amount of solid salt. Dilution of the yellow toluene extract to 100 ml. with cyclohexane gave a solution with an absorbance of 0.31 at 325 mμ in the ultraviolet. The substance responsible for the ultraviolet absorption was completely removed, however, by extraction with three 20-ml. portions of Claisen alkali[30] and two-extractions with water as shown by the complete absence of absorption in a subsequent spectrum. A sample of the original purified salt I described above was analyzed.

Anal. Calcd. for $C_{12}H_{17}NaO$: C, 72.0; H, 8.6; Na, 11.48. Found: C, 72.2; H, 8.8; Na, 11.43.

Analysis of Alkylation Reaction Mixtures.—For the infrared analyses standard solutions of dienone II and ether III were prepared in toluene and employed to make working curves showing the change of absorbance at 1637 cm.$^{-1}$ (dienone) and 1118 cm.$^{-1}$ (ether) with concentration. The two products were shown not to interfere with each others absorption. These working curves were used to calculate the concentration of dienone and ether in the reaction mixture. A synthetic mixture of dienone and ether known to have a ratio of the components of 0.45 was found by infrared analysis as described to have a ratio of 0.44. To another sample of this standard solution in toluene was added tetrahydrofuran, sodium aryloxide I, and benzyl chloride in concentrations in which they are present in a typical reaction mixture. The neutral fraction was then extracted and analysis by the infrared method above gave a ratio of 0.44.

Ultraviolet analyses of standard solutions of the dienone II in cyclohexane were very reliable. Beer's law was obeyed over a concentration range of 9.8×10^{-6} to 1.94×10^{-4} *M*. Analysis (using the intensity of absorption at 313 mμ) of a standard mixture of dienone II and ether III present in nearly equal amounts gave an absorbance which was 99.7% of the calculated value. It was found, however, that the sodium salt I when not freshly prepared developed impurities absorbing in the same region as the dienone (313 mμ). These impurities could easily be extracted with alkali, but the extraction selectively removed tetrahydrofuran and affected the results so that the ultraviolet analysis, although given in many cases, was not depended on for analysis of mixtures. Detailed data referred to in this discussion are available in the thesis of D.H.D.[1]

In order to make sure that the dienone II was stable to extraction with Claisen alkali a portion of slightly impure dienone (containing 3% ether) was diluted to 400 ml. with cyclohexane and examined by ultraviolet analysis which showed the absorbance at 313 mμ to be 0.379. After extraction by three 30-ml. portions of Claisen alkali, and two 30-ml. portions of demineralized water, the solution was dried ($MgSO_4$) and concentrated. The concentrate was diluted to 400 ml. with cyclohexane and examined once again at 313 mμ where an absorbance of 0.380 was obtained.

Purification of Solvents.—All toluene was freshly distilled from sodium prior to use. Tetrahydrofuran was refluxed over sodium wire and sodium hydroxide for 2 weeks, distilled and stored over sodium in a nitrogen atmosphere prior to use. Eastman Kodak Co. reagent grade cyclohexane was used for the ultraviolet analyses without further purification.

Heterogeneous Alkylation of Sodium 4-*t*-Butyl-2,6-dimethylphenoxide (I) with Benzyl Chloride in Toluene. (a) With Excess Benzyl Chloride.—To a suspension of 0.220 g. (1.10×10^{-3} mole) of the sodium salt I in 31 ml. of toluene under nitrogen was added 0.32 g. (2.5×10^{-3} mole, 2.3-fold excess) of benzyl chloride. The heterogeneous reaction mixture was stirred under reflux for 22 hr. After the mixture had settled a 1.0-ml. aliquot was removed from the supernatant liquid (which amounted to 32 ml.) and diluted 50-fold with cyclohexane. An absorbance of 0.909 at 313 mμ in the ultraviolet indicated a 29.6% yield of dienone.

After extraction with Claisen alkali,[30] another 1.0-ml. aliquot was withdrawn from the 55-ml. neutral fraction and diluted to 25 ml. with cyclohexane. The absorbance of this solution at 313 mμ in the ultraviolet was 0.927. Allowing for the previous aliquot, this represented a 26.7% yield of dienone.

The neutral layer, which was concentrated to weigh 6.37 g., was examined in the infrared and found to contain 25.9% and 18.8% yields of dienone and ether, respectively. The dienone ether ratio was thus 1.4 on the basis of the infrared measurements.

A second reaction of 0.421 g. (2.10×10^{-3} mole) of the salt I in 43 ml. of toluene with 0.83 g. (6.5×10^{-3} mole, 3.1-fold excess) of benzyl chloride for 22 hr. was carried out as before. It is noteworthy that the reaction was originally heterogeneous but at the end of the reaction appeared only slightly cloudy. The % reaction estimated by a Mohr titration of chloride ion liberated was 83%; estimated by the weight (0.445 g.) of distilled neutral fraction (b.p. 90° at 0.4 mm.) it was 81%. An ultraviolet spectrum of the total reaction mixture (absorbance at 313 mμ) led to a calculated yield of dienone II of 48% and estimating the ether III as the difference between this and the total amount of reaction from titration gave a dienone/ether ratio of 1.4. A determination of the amounts of dienone and ether from the infrared spectrum gave a value of 1.6.

A third reaction with a 10-fold excess of benzyl chloride gave dienone II in a yield of 60.7% as determined by an ultraviolet spectrum of the original reaction mixture, 58.1% by an ultraviolet spectrum of the neutral fraction after extraction with Claisen alkali and 54.3% by infrared analysis of the neutral fraction. The amount of ether III determined by infrared was 45.2% which leads to a dienone/ether ratio of 1.2.

(b) **With Excess Sodium Salt III. The Effect of Varying the Amount of Undissolved Salt III.**—These reactions were carried out and analyzed as were those above. The quantities of starting materials and conditions are reported together with the results in Table IIIA. Ultraviolet spectra were obtained of the neutral fraction (after Claisen alkali

TABLE IIIA

RESULTS OF VARIATION OF SOLID PHASE[a]

Na salt, moles/l. × 10^{+2}	C_6H_5-CH_2Cl, moles/l. × 10^{+2}	Dienone, % (u.v.)	Dienone, % (i.r.)	Ether, % (i.r.)	Compl., % (i.r.)	Dienone ether (i.r.)
1.93	1.46[c]	8.5	7.2	10.6	17.8	0.68
5.42	1.46[c]	10.4	8.6	13.2	21.8	.65
21.0	1.46[c]	25.0	20.5	28.2	48.7	.73
20.2	1.48[d]	22.9	19.4	25.9	45.3	.75
20.1[b]	1.48[e]	6.7	5.6	7.2	12.8	.78

[a] These reactions were carried out at 110 ± 4° for 23.3 hr., except as noted. [b] Reaction time was 10.5 hr. [c] Volume of reaction mixture was 50 ml. [d] Volume of reaction mixture was 35 ml. [e] Volume of reaction mixture was 19.5 ml.

extraction) by diluting 1.0-ml. aliquots 1000-fold with cyclohexane. The infrared determinations were made with the neutral fraction as before.

Reaction of Tetramethylammonium 4-*t*-Butyl-2,6-dimethylphenoxide with Benzyl Chloride in Toluene Containing Tetrahydrofuran.—The tetramethylammonium salt was prepared from 1.800 g. (0.0101 mole) of 4-*t*-butyl-2,6-dimethylphenol and 9.185 g. of 10% aqueous tetramethylammonium hydroxide (0.0101 mole) in 25 ml. of absolute methanol under nitrogen. After evaporation of the solvent the solid was heated at 100° (0.4 mm.) for 3 hr. and ground under nitrogen at 100° (0.5 mm.) for 20 hr. to give 2.40 g. (94.4% yield) of salt which was analyzed.

Anal. Calcd. for $C_{16}H_{29}NO$: C, 76.4; H, 11.6; N, 5.6. Found: C, 75.5; H, 11.8; N, 5.7.

A second preparation gave similar results. To 0.3213 g. (1.28 × 10^{-3} mole) of the tetramethylammonium salt under nitrogen was added 0.46 ml. of tetrahydrofuran (1.3% of final volume), followed by 35 ml. of toluene in 5-ml. portions with stirring. To this heterogeneous mixture was added 0.37 g. (2.9 × 10^{-3} mole) of benzyl chloride and the mixture heated under reflux for 11 hr. After separation of acidic material by Claisen alkali extraction, a 1.0-ml. aliquot was withdrawn from the 36-ml. neutral solution and diluted to 100 ml. with cyclohexane. This solution had an absorbance of 0.012 at 313 mμ in the ultraviolet spectrum corresponding to a yield of less than 0.8% of dienone. Infrared analysis of the concentrated neutral layer (8.74 g.) indicated the yields of dienone and ether to be 0.5% and 70%, respectively.

In another experiment 0.9259 g. (4.63 × 10^{-3} mole) of the sodium salt I and 1.4929 g. (4.63 × 10^{-3} mole) of tetrabutylammonium bromide were dissolved in 7.85 ml. of tetrahydrofuran (5.6% of final volume) under nitrogen and 131 ml. of toluene added. After stirring for 12 hr. at room temperature the mixture was filtered under nitrogen to give 0.227 g. (2.21 × 10^{-3} mole) of sodium bromide (indicated by its insolubility in acetone and failure to fuse below 500° and the fact that it dissolved in water to give a neutral solution). To the clear filtrate (136 ml.) was added 1.76 g. (1.51 × 10^{-2} mole) of benzyl chloride. A white precipitate formed immediately. After 20 min. at 27°, a 15.0-ml. aliquot was removed, extracted with Claisen alkali, washed, dried and concentrated to 5.315 g. Infrared analysis showed the yield of ether III to be 57.7% and the dienone to amount to less than 0.04%. After 720 min. more at 109.8° the yield of ether was 67.2% and dienone still less than 0.04%.

Rate Studies of the Alkylation of Sodium 4-*t*-Butyl-2,6-dimethylphenoxide in Toluene–Tetrahydrofuran Mixtures.—In each run to be described the following procedure was employed. To the sodium salt, weighed into a dry flask (under nitrogen) equipped with a magnetic stirring bar, was added the desired amount of tetrahydrofuran, followed by stepwise addition of the toluene with stirring to effect solution. Benzyl chloride was added with stirring. Aliquots were withdrawn by means of a capillary syringe and transferred (in a dry-box) to dry combustion tubes which were sealed under nitrogen and placed in a constant temperature bath. Upon removal from the bath they were placed in ice-water and finally Dry Ice–acetone to quench the reaction. The methods used to analyze the reaction mixtures are indicated below. Table IV summarizes the concentrations of reactants and solvents employed. Representative rate data are presented in Table V. Table VI summarizes the results.

TABLE IV

COMPOSITION OF REACTION MIXTURES USED FOR RATE STUDIES IN TETRAHYDROFURAN–TOLUENE MIXTURES

Reaction	$C_6H_5CH_3$, ml.	THF, ml.	Na salt, moles/l. × 10^{+2}	$C_6H_5CH_2Cl$, moles/l. × 10^{+2}	% THF (by vol.)
I[a,c]	38.0	0.50	3.56	8.5	1.3
II[a,c]	20.0	1.2	3.54	8.2	5.6
III[b,d]	159.0	9.5	3.55	8.2	5.6
IV[a,c]	34.4	6.8	3.50	4.6	16.4
V[b,d]	67.0	13.2	3.48	8.1	16.3

[a] Workup by procedure A. [b] Workup by procedure B. [c] A 3.0-ml. aliquot was used to fill each tube. [d] A 15.0-ml. aliquot was used to fill each tube.

TABLE V

RATES OF ALKYLATION OF SODIUM 4-*t*-BUTYL-2,6-DIMETHYLPHENOXIDE (I) WITH BENZYL CHLORIDE IN TOLUENE–TETRAHYDROFURAN AT 109.8 ± 0.1°

Tetrahydrofuran, %	Time, sec. × 10^{-4}	0.0100 *N* $AgNO_3$, ml.	% compl.	*k*,[a] l./mole sec. × 10^{+4}	Dienone ether (i.r.)
C_0^{RCl} 0.085 *M*, C_0^{ArONa} 0.0356 *M*					
1.3[b]	0.18[c]	0.74	6.9	4.6	0.70
	1.01[d]	2.99	28.0	4.2	.87
	2.29[d]	4.96	46.5	3.6	.88
	2.29[d]	5.17	48.5	3.8	.83
	3.71[c]	6.42	60.0	3.4	.81
	9.05[c]	8.32	78.0	2.5	.67
	9.05[e]	8.30	77.8	2.5	.63
C_0^{RCl} 0.082 *M*, C_0^{ArONa} 0.0354 *M*					
5.6[f]	0.18[c]	0.50	4.7	3.5	0.45
	1.01[d]	1.96	18.5	2.4	.40
	2.92[d]	3.61	34.0	2.4	.51
	3.71[e]	4.78	45.0	2.2	
	9.05[e]	7.87	74.1	2.3	0.47
C_0^{RCl} 0.046 *M*, $C_0^{ArNO_2}$ 0.0350 M					
16.4[f]	0.18[c]	0.38	3.6	3.1	0.17
	1.08[e]	1.84	17.5	4.4	.16
	2.52[e]	3.46	33.0	4.0	.13
	4.32[e]	5.04	48.0	4.2	.14
	7.47[e]	6.72	64.0	4.4	.11
	10.8[e]	7.50	71.4	4.0	.15

[a] Calculated from the expression [33]

$$k = \frac{1}{t([C_6H_5CH_2Cl]_0 - [NaOAr]_0)} \ln \frac{[NaOAr]_0([C_6H_5CH_2Cl]_0 - [Cl^-])}{[C_6H_5CH_2Cl]_0([NaOAr]_0 - [Cl^-])}$$

This solution contained a very fine suspension which settled partially on standing for several hours. [c] This solution appeared clear to the eye when removed from the constant temperature bath. No attempt was made to observe a Tyndall effect. [d] This reaction mixture appeared partially cloudy when removed from the bath. [e] This tube contained a visible precipitate when removed from the bath. [f] This solution appeared clear when viewed by reflected light.

TABLE VI

RATES OF REACTION OF SODIUM SALT I WITH BENZYL CHLORIDE IN TOLUENE AT 109.8 ± 0.1°

Tetrahydrofuran, %	Obsd. rate, l./mole sec. × 10^4	Dienone/ether ratio	*k*d, l./mole sec. × 10^4	*k*e, l./mole sec. × 10^4
5.6	2.3 ± 0.1	0.46	0.73 ± 0.03	1.6 ± 0.07
5.6	2.4 ± .3	.50	.80 ± .1	1.6 ± .2
16.4	4.2 ± .2	.14	.52 ± .02	3.7 ± .2
16.3	4.9 ± .2	.20	.82 ± .02	4.1 ± .2

Procedure A.—Upon removal from the constant temperature bath, the tubes were extracted with three 8-ml. portions of demineralized water. The combined aqueous extracts were acidified with dilute nitric acid, neutralized with 5% sodium bicarbonate solution, and titrated with 0.010 *N* silver nitrate solution, using the Mohr method. A 1.0-ml. aliquot was withdrawn from the dried ($MgSO_4$) organic layer and diluted with cyclohexane for ultraviolet analysis. The remaining organic portion was extracted with three 5-ml. portions of Claisen alkali and two 5-ml. portions of water, concentrated, and examined in the infrared to determine the dienone ether ratio.

Procedure B.—Upon removal from the constant temperature bath, each tube was extracted with three 10-ml. portions of demineralized water. The combined aqueous extracts were neutralized in the manner previously described and titrated with 0.10 *N* silver nitrate solution. The organic layer was extracted with three 10-ml. portions of Claisen alkali and washed with two 10-ml. portions of water. From the dried neutral layer ($MgSO_4$) was withdrawn 1.0 ml. which was diluted with cyclohexane for ultraviolet analysis. An additional 10 ml. was concentrated and used for quantitative infrared analysis.

It was demonstrated that reactions after slowing down at a late stage still contained 4-*t*-butyl-2,6-dimethylphenol, presumably as the sodium salt. The phenol could be determined quantitatively in a synthetic mixture with toluene and benzyl chloride by extraction with Claisen alkali and examination of the ultraviolet absorption at 282 mμ (λ_{max} for the phenol). Using this method with a mixture 8.35 *M* gave a value of 8.56×10^{-4} *M*. Using this method a reaction which had been found by chloride titration to have proceeded 80.7% to completion was shown by extraction and ultraviolet analysis to contain 19% of unreacted phenol, and a reaction which had gone 75.9% to completion contained 18% of starting phenol.

Rate of Alkylation of Sodium 4-*t*-Butyl-2,6-dimethylphenoxide (I) in the Presence of Tetrabutylammonium Bromide.—To 0.7265 g. (3.63×10^{-4} mole) of the sodium salt I and 0.0584 g. (1.81×10^{-4} mole, 5.0% of the stoichiometric amount) of the ammonium salt was added 5.74 ml. of tetrahydrofuran (5.7% of final volume) and 95.5 ml. of toluene (under nitrogen, with stirring), followed by 1.06 g. (8.38×10^{-4} mole, 2.3-fold excess) of benzyl chloride. Five combustion tubes were filled in a dry-box under nitrogen with 15.0-ml. aliquots of this solution (the addition of toluene to the solution of the two salts in tetrahydrofuran caused some cloudiness) and immediately placed in a constant temperature bath at 109.8 ± 0.1°.

Upon removal from the bath, halide ion was removed by extraction, Claisen's alkali was used to remove acidic products, and the neutral fraction was concentrated prior to infrared analysis to determine the dienone:ether ratio. The results are summarized in Table VII.

TABLE VII

RATE OF ALKYLATION OF SODIUM 4-*t*-BUTYL-2,6-DIMETHYLPHENOXIDE IN 5.6% TETRAHYDROFURAN IN TOLUENE IN PRESENCE OF TETRABUTYLAMMONIUM BROMIDE AT 109.8 ± 0.1°

Time, sec. $\times 10^{-4}$	0.100 *N* $AgNO_3$, ml.	% compl.	*k*,[a] l./mole sec. $\times 10^{+4}$	Dienone ether (i.r.)
0.061	1.49	22.9	53	0.06
.24	1.91	30.8	20	.18
.46	2.05	33.4	11	.23
1.73	2.76	46.7	4.9	.29
4.26	3.57	61.9	3.2	.40

[a] Assuming chloride ion to be formed in a second-order reaction.

Light Scattering by the Reaction Mixtures for the Alkylations in Toluene and Tetrahydrofuran.—The absorbance of each of the reaction mixtures, with varying amounts of tetrahydrofuran in toluene, was measured (at room temperature, prior to reaction) in the visible spectrum from 800 to 600 mμ using toluene or a blank reaction mixture (all of the components except the sodium salt) in the reference cell (the same reading was obtained each way). The reaction mixtures with 5.6 and 16.4% tetrahydrofuran showed absorbances at 750 mμ of only 0.003. That with 1.3% had an absorbance of 0.032 and that with 0.84% tetrahydrofuran 0.076.

[CONTRIBUTION NO. 133 FROM THE GRADUATE DEPARTMENT OF BIOCHEMISTRY, BRANDEIS UNIVERSITY, WALTHAM 54, MASS.]

The Solvolysis of 1-Acetylimidazole in Concentrated Acid and Salt Solutions

BY STEPHEN MARBURG AND WILLIAM P. JENCKS

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The rates of solvolysis of 1-acetylimidazole in acid solutions, in which it is completely converted to its conjugate acid, and of 1-acetyl-3-methylimidazolium cation are decreased by added concentrated salts and acids, with the exception of F^- and $SO_4^=$. In the case of $NaClO_4$ the logarithm of the rate is proportional to the salt concentration over a 500-fold range of rate variation. Widely different effects are found with different salts and acids, and the results cannot be correlated with simple functions of a_{H_2O} or $C_H{}^+$ and h_0. The order of rate-decreasing effectiveness is $ClO_4^- > OTs^- > Br^- > Cl^- \sim NO_3^- > SO_4^= > F^-$ and $La^{+++} \sim Mg^{++} \sim Ca^{++} > Li^+ \sim Na^+ \sim K^+ > Cs^+ \sim NH_4^+ \sim (CH_3)_4N^+ \sim$ imidazolium$^+ \sim H^+$. It is concluded that, although the observed rate decreases undoubtedly reflect the decreased availability of water in concentrated electrolyte solutions, large influences of other factors on the substrate and transition state must be considered in any quantitative treatment of such reactions.

The remarkably high protonating ability of moderately concentrated aqueous solutions of strong acids may be in large part accounted for in terms of equilibrium (1) by the decrease in the availability of water in such solutions, without invoking

$$H(H_2O)_4^+ + B \rightleftarrows BH^+ + 4H_2O \qquad (1)$$

major activity coefficient effects.[1] The high protonating ability of acids in certain concentrated salt solutions may be explained in part in a similar manner, since electrolyte hydration will also decrease water availability, and in part by salting out of the free base by concentrated salt.[2,3] If protonation of a substrate, S, shows activity coefficient behavior similar to that of an indicator, B, a reaction of SH^+ that does not involve addition or loss of water in the transition state will generally follow the acidity function, h_0. A reaction that does require water will generally increase in rate less rapidly than h_0 because of the decreased availability of water in concentrated acid solutions.[4] If only one molecule of water is required and if activity coefficient effects are small, such a reaction might be expected to follow $h_0 a_{H_2O}$. Surprisingly, a num-

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(3) F. A. Long and D. McIntyre, *ibid.*, **76**, 3243 (1954).