NATURE OF REACTION OF ALLYL AND BENZYL HALIDES WITH
SOLUTIONS OF SODIUM PHENOXIDE AT 27°

Solvent	% O-Alkyla-tion[a]	% C-Alkyla-tion[a,b]
Dimethylformamide	100	0
Dioxane	100	0
Ethanol	100	0
Ethylene glycol dimethyl ether	100	0
Methanol	100	0
1-Propanol	100	0
Tetrahydrofuran	100	0
Water	55	45
Phenol[c]	25	75
2,2,3,3-Tetrafluoropropanol-1[d]	45	55
2,2,2-Trifluoroethanol[e]	50	50

[a] Analysis by gas chromatography. In each solvent yields were verified by isolation of products from typical experiments. Completely analogous results also have been obtained using potassium phenoxide, sodium p-cresoxide and potassium p-t-octylphenoxide. [b] In each case both the *ortho* and *para* isomers are found. [c] At 43°. [d] We thank the Organic Chemicals Department of the du Pont Co. for a generous gift of this alcohol. [e] We thank the Pennsalt Co. for a generous gift of this alcohol.

vents, in water, phenol and fluorinated alcohols, substances which are unusually effective at forming hydrogen bonds, the oxygen of the phenoxide ion is so intensely solvated that the availability of the oxygen for nucleophilic displacement is greatly decreased; as a consequence, displacements employing the otherwise unfavored *ortho* and *para* carbon atoms compete successfully.

The possibility that carbon alkylation in water, phenol and fluorinated alcohols derives from a carbonium ion process[2] is rejected for several reasons: (a) extrapolated initial rates for the reaction of allyl chloride with sodium phenoxide in water at 27.5°, over a twenty-six fold change in initial phenoxide ion concentration, give a second order rate constant $9 \pm 2 \times 10^{-2}$ l. mole^{-1} min.$^{-1}$ [3] (b) The allyl and benzyl halides are almost quantitatively accounted for by considering only the products of phenoxide alkylation. Carbonium ion formation would produce major quantities of solvolytic products, e.g., alcohols, and these are not found. (c) The reaction of allyl chloride with sodium hydroxide in water at 27.5°, unlike the corresponding reaction with sodium phenoxide, remains homogeneous and, when followed to 25% reaction, it yields a precise second order rate constant $3.47 \pm 0.18 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$ over a twenty-fold change in initial hydroxide concentration. The fact that this reaction of hydroxide ion, a poorer nucleophile than phenoxide ion, is unmistakably first order in hydroxide and first order in allyl chloride provides further support for the view that the reaction of allyl chloride with phenoxide is an SN2 process.

The full significance of these findings becomes apparent when it is recognized that the examples of carbon alkylation herein described are not unique in being second order processes; the purely

(3) The reactions of allyl chloride, and allyl bromide, with sodium phenoxide in water proceed at rates clearly dependent on the phenoxide ion concentration and this is not a salt effect. But, insolubility of the products results in extraction of some of the allylic halide from the aqueous phase and, hence, precise rate data cannot be obtained in the ordinary way.

oxygen alkylation reactions of sodium phenoxide with allyl bromide in methanol, and in ethanol, are also second order[4] and there can be little doubt that this is true of the other instances of purely oxygen alkylation recorded in Table I. Thus, the incorporation of different solvent molecules into an otherwise identically constituted activated complex produces a profound change in the course of a reaction. This is a result of far reaching implications and a broad study is in progress.

(4) K. Lauer and H. Shingu, *Ber.*, **69**, 2731 (1936).

(5) Predoctoral fellow 1957–1960 CF-7406-C2, National Cancer Institute, Public Health Service.

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CHEMISTRY OF ENOLATES. IV. SOLVENTS FOR ENHANCED CARBANION ACTIVITY[1]

Sir:

Alkylations and acylations of carbanions commonly are carried out in inert media such as aromatic hydrocarbons or diethyl ether.[2] In these solvents, the carbanions are associated with metallic cations as aggregates which do not conduct an electric current.

We wish to report greatly increased rates of alkylation of enolate anions in the dimethyl ethers of ethylene glycol and diethylene glycol (monoglyme and diglyme). In the latter solvent at 30°, ethylation of 0.13 M sodiobutyrophenone by 1.6 M ethyl bromide is 75% complete in 152 seconds. The time for a comparable ethylation in diethyl ether is 234 hours. Halides that alkylate at inconveniently slow rates in diethyl ether may now be employed; e.g., half-lives for the alkylations of 0.42 M potassiobutyrophenone in monoglyme by 2.0 M propyl and isobutyl chlorides are 6.25 and 50 hours, respectively.

The activity of the carbanion is increased by coordination of the solvent with the cation. Four- and six-coördinated solvates of several enolates have been isolated.[3] Coördination of the metal ion by the ketonic product of alkylation recently has been proposed to explain the autocatalysis of the alkylation reaction.[4] If solvates of the type shown are produced, conducting solutions would be expected. Solutions of sodio- and potassio-butyrophenone in monoglyme are indeed conductors of electricity. The molar conductivity of the sodium

I
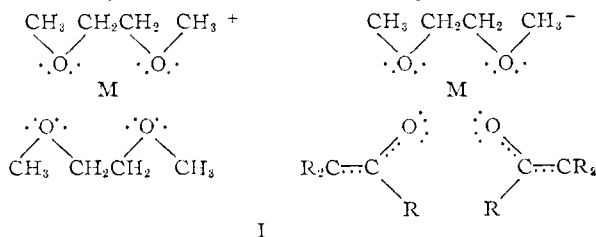
(1) This investigation was supported by a research grant (G-4475) from the National Science Foundation.

(2) C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. 8, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 59; J. Conia, *et al.*, *Bull. soc. chim. France*, 493 (1959); 1064 (1957); 1040, 1392 (1956).

(3) N. V. Sidgwick and F. M. Brewer, *J. Chem. Soc.*, 2379 (1925).

(4) H. D. Zook and W. L. Gumby, THIS JOURNAL, in press.

salt in 0.06 M solution at 24° is 0.08 ohm^{-1} cm.^{2} mole^{-1}, a value approximately equal to that for sodium triphenylmethide in diethyl ether. Solutions of sodium enolates in diethyl ether exhibit no conductivity.[5]

The formation of complex ions such as (I) rather than free carbanions is indicated by a cation effect on the rate of alkylation. Bimolecular rate constants for the propylation of 0.42 M solutions of potassio- and sodio-butyrophenone in monoglyme are 15.4 × 10^{-6} and 0.78 × 10^{-6} l. mole^{-1} sec.$^{-1}$, a rate ratio of 20 to 1. Similar ratios in diethyl ether are of the order of 100 to 1. Although the cation effect is considerably diminished in monoglyme, the rate controlling process involves more than a bimolecular substitution on the alkyl halide by a free carbanion. This argument is strengthened by the results of ebulliometric studies which show aggregation of the species present. Boiling point elevations for 0.5 molal solutions of sodio- and potassio-butyrophenone in monoglyme correspond to average aggregation numbers of 2.5–2.7, values only 16% below those measured in diethyl ether.[4]

Polyether solvents for carbanion reactions show promise in other respects. Increased solubility and change in composition of alkylation product have been found for sodiodiphenylacetophenone. Homogeneous solutions of this enolate in concentrations up to 0.1 M have been prepared in diglyme. This salt has limited solubility in monoglyme and is practically insoluble in diethyl ether. Ethylation occurs almost exclusively at the oxygen atom to give the enol ether, 1,2,2-triphenyl-1-ethoxyethene. In t-butyl alcohol, carbon alkylation to give α,α-diphenylbutyrophenone occurs to the extent of 25%. Specific solvation rather than heterogeneity[6] is responsible for this difference, for clear solutions are obtained initially in each case and remain homogeneous until sodium halide precipitates.

(5) D. G. Hill, J. Burkus, S. M. Luck and C. R. Hauser, THIS JOURNAL, **81**, 2787 (1959).

(6) For the effect of heterogeneity on the alkylation of phenoxide ions, see N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

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FREE RADICAL ISOMERIZATION OF ALKYLBENZENES

Sir:

Heretofore, radicals capable of undergoing rearrangement, such as the neophyl radical, have been obtained in high yields only by the decomposition of aldehydes[1] or other stoichiometric reactions.[2] Also, these radicals have been prepared in low yields by a free radical initiated pyrolysis of alkylbenzenes.[3] We have been able to produce these free radicals, in high yields, from the parent hydrocarbon, e.g., cumene, *tert*-butylbenzene, etc.,

(1) L. H. Slaugh, THIS JOURNAL, **81**, 2262 (1959), and references cited therein.

(2) M. S. Kharasch and W. H. Urry. *ibid.*. **66**, 1438 (1944).

(3) H. Pines and C. N. Pillai, *ibid.*. **81**, 3629 (1959); V. N. Ipatieff, B. Kvetinskas, E. E. Meisinger and H. Pines, *ibid.*, **75**, 3323 (1953), also have prepared these radicals by the high pressure pyrolyses (816 atm., 479–528°) of alkylbenzenes over copper turnings.

by the use of an effective free radical chain transfer agent, HI, HBr, HCl, RSH, H$_2$S, etc., in the presence of a free radical initiator. The chain transfer agents are either introduced directly (C$_6$H$_5$SH, H$_2$S, etc.), or formed as a result of pyrolysis of a halogen or sulfur containing promoter. The initiators may be halogen, thiyl or hydrocarbon radicals resulting from the pyrolysis of the promoter or the alkylbenzene, respectively. One important requirement for the reaction is that the radical produced from the chain transfer agent must be sufficiently reactive to abstract hydrogens from the beta position of the alkylbenzene.

The net result of the above reactions has been the isomerization of isopropylbenzenes to n-propylbenzenes, *tert*-butylbenzene to isobutylbenzene, and *sec*-butylbenzene to n-butylbenzene, as well as the reverse reactions. The method consists of heating (400–525°, 10–60 min.) an alkylbenzene, in an autoclave or flow reactor (300–1500 p.s.i.g.), with as little as 1.0 mole % of any of these promoters: organic chlorides, organic bromides, organic iodides, iodine, mercaptans, disulfides, hydrogen sulfide or elemental sulfur. Organic bromides appear to be the best promoters. As an example of the reaction, 2.0 mole % of benzyl bromide promotes a 53% conversion of cumene, with an 81% selectivity,[4] to n-propylbenzene. Equally good results were obtained for the isomerization of *tert*-butylbenzene to isobutylbenzene. The isomerization of *sec*-butylbenzene to n-butylbenzene, however, gave lower yields. The side products in each case were lower molecular weight hydrocarbons. In the absence of a promoter, less than 1.0% isomerization of cumene occurred, under our experimental conditions.

A mechanism is proposed for this free radical isomerization of alkylbenzenes

Transition state
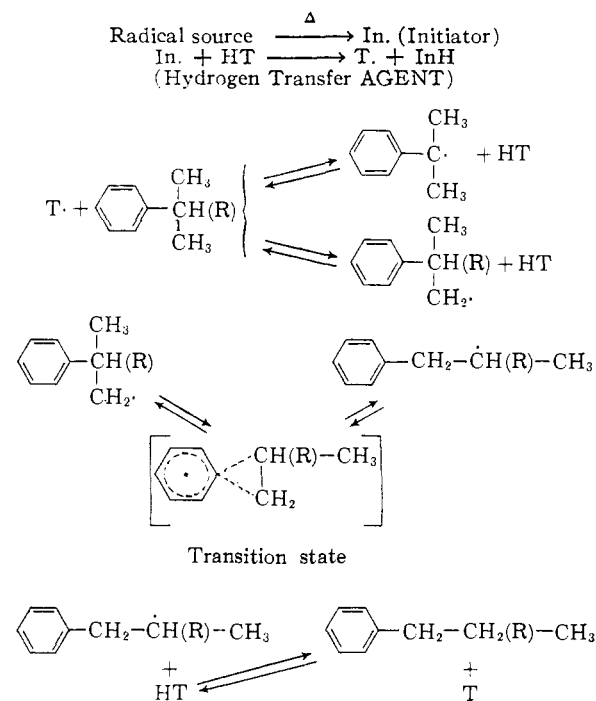
(4) Conversion × Selectivity = Yield.