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 $15.4 \times 10^{-6}$ and $0.78 \times 10^{-6}$ 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 $\alpha,\alpha$-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.

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[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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RECEIVED DECEMBER 28, 1959

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## FREE RADICAL ISOMERIZATION OF ALKYLBENZENES

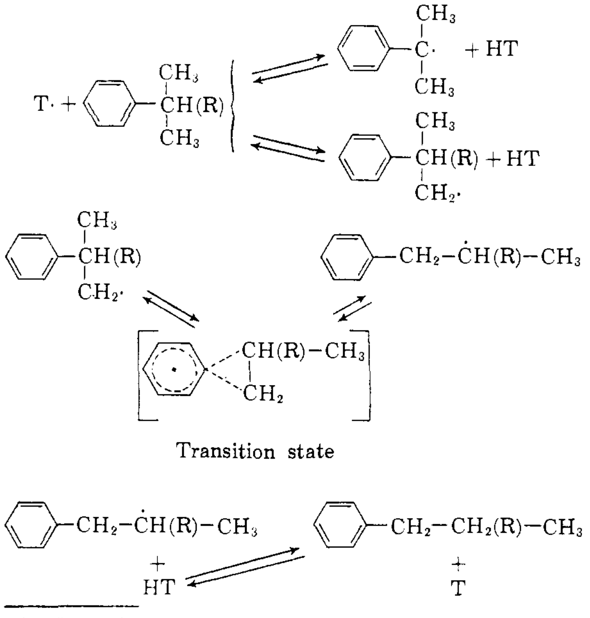
*Sir:*

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.*, by the use of an effective free radical chain transfer agent, HI, HBr, HCl, RSH, $H_2S$, *etc.*, in the presence of a free radical initiator. The chain transfer agents are either introduced directly ($C_6H_5SH$, $H_2S$, *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

$$\text{Radical source} \xrightarrow{\Delta} \text{In. (Initiator)}$$
$$\text{In.} + \text{HT} \longrightarrow \text{T.} + \text{InH}$$
$$\text{(Hydrogen Transfer AGENT)}$$



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[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.

[4] Conversion × Selectivity = Yield.

The proposed mechanism is substantiated by several lines of evidence: (1) substances[5] known to produce free radicals, either directly or as a result of chain transfer reactions, upon pyrolysis, and only such substances, catalyze this type of isomerization. By way of comparison, Lewis acids produce no such isomerizations (1,2-phenyl migrations),[10–12] but instead give rise to disproportionation reactions,[10] which yield benzene and polyalkylbenzenes, or to methyl migration processes.[11,12] No disproportionation or methyl migration occurs in the present isomerization reaction.

(2) Hydrogen bromide[13] and mercaptans[14] are noted chain transfer agents and even the relatively strong H–Cl bond in hydrogen chloride is susceptible to free radical attack.[15]

(3) The isomerization of *p*-cymene (1-methyl-4-isopropylbenzene) exclusively to 1-methyl-4-*n*-propylbenzene is consistent with known free radical rearrangements[16] in that the relative positions of the two ring substituents are unchanged during the isomerization.

[5] Iodine, alkyl iodides,[6] alkyl bromides,[6] disulfides,[7] sulfur,[8] mercaptans,[9] and, with less certainty, alkyl chlorides.[6]

[6] E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, 2nd ed., Reinhold Publishing Corp., New York, 1954, pp. 253–263.

[7] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 889 (1949).

[8] D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **78**, 3279 (1956).

[9] A. H. Sehon and B. deB. Darwent, *ibid.*, **76**, 4806 (1954).

[10] D. A. McCaulay and A. P. Lien, *ibid.*, **75**, 2411 (1953), and references cited therein.

[11] C. D. Nenitzescu, I. Mecsoiu, A. Glatz and M. Zalman, *Ber.*, **92**, 10 (1959).

[12] R. M. Roberts, Y. W. Han, C. H. Schmid and D. A. Davis, THIS JOURNAL, **81**, 640 (1959).

[13] K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958); G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.*, **12**, 469 (1944).

[14] C. Walling, THIS JOURNAL, **70**, 2561 (1948); R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948).

[15] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 2767 (1948).

[16] W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

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RECEIVED JANUARY 11, 1960

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## A NOVEL SYNTHESIS OF 1,1-DIHALOOLEFINS

*Sir:*

The nucleophilic character of tertiary phosphines[1] and the recent observation that carbenes are electrophilic[2] suggested to us that the interaction of these two reagents should produce phosphinemethylenes. We wish now to report the formation of the ylid triphenylphosphine dichloromethylene I and its use in the synthesis of 1,1-dichloroolefins.

$$(C_6H_5)_3P + :CCl_2 \longrightarrow \underset{\text{I}}{(C_6H_5)_3P{=}CCl_2}$$

$$\text{I} + (C_6H_5)_2C{=}O \longrightarrow \underset{\text{II}}{(C_6H_5)_2C{=}CCl_2} + (C_6H_5)_3PO$$

Treatment of a suspension of potassium *t*-butoxide and triphenylphosphine in pentane with chloroform at 0–5° produced I as a golden yellow solid. Preliminary attempts to isolate I in the pure state led to isolation of large amounts of triphenylphosphine oxide and as yet other unidentifiable products. The parent compound, triphenyl-phosphinemethylene, also has been shown by Wittig and Geissler[3] to be unstable.

Reaction of the yellow solid with benzophenone in pentane–ether mixture gave rise to 1,1-diphenyl-2,2-dichloroethylene (II), triphenylphosphine oxide, and unreacted benzophenone. A quantitative yield of potassium chloride also was isolated. II was isolated in 46% yield based on benzophenone consumed: m.p. 79–80°. A mixture melting point with an authentic[4] sample was not depressed and the infrared spectra of the two were superimposable. Triphenylphosphine oxide (m.p. 152–153°) was isolated in 92% yield and shown to be identical with an authentic[1] sample. The unreacted benzophenone was recovered as its 2,4-dinitrophenylhydrazone (48% recovery; m.p.[5] 238–239°).

The high yield of triphenylphosphine oxide as compared to the dichloroethylene may indicate competitive reaction of the phosphine dichloromethylene with *t*-butyl alcohol which was formed during carbene preparation. The reaction of carbenes[6] with tertiary phosphines to yield compounds of type I is being investigated. The reaction of phosphinedihalomethylenes with carbonyl compounds would lead to unusual 1,1-dihaloolefins which normally would be difficult to prepare.

[1] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 23, 98; J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience Publishers, New York, N. Y., 1958.

[2] P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 5430 (1956); W. E. Doering and A. F. Hoffmann, *ibid.*, **80**, 5274 (1958).

[3] G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953).

[4] We are indebted to Dr. L. A. Miller of our Dayton Laboratories for the authentic sample. See also E. E. Harris and G. B. Frankfoster, THIS JOURNAL, **48**, 3144 (1926), and "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 270.

[5] N. R. Campbell, *Analyst*, **61**, 392 (1936).

[6] J. Hine and K. Tanabe, THIS JOURNAL, **79**, 2654 (1957); J. Hine and J. J. Porter, *ibid.*, **79**, 5493 (1957); J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957); W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957).

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RECEIVED JANUARY 2, 1960

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## ION EXCHANGE MEMBRANES FOR USE IN HIGH RADIATION FIELDS[1]

*Sir:*

The radiation instability of organic membranes has limited their use for processing high radioactive solutions. The necessary frequent replacement of these membranes by remote handling techniques would be difficult and expensive not only because of the cost of the membrane itself but also because of the damage to the electrodes, particularly where platinum is used. At Brookhaven National Laboratory one approach to the solution of this problem has been the development of an inexpensive membrane that can be replaced easily.

Work done at this Laboratory has indicated that a matrix between the particles to minimize diffusion is not necessary for an efficient ion exchange membrane. Membranes were therefore

[1] Work performed under the auspices of the U. S. Atomic Energy Comm.