$$R_1R_2R_3P=O + H^+ \rightleftarrows R_1R_2R_3\overset{+}{P}-OH \overset{Cl^-}{\rightleftarrows} R_1R_2R_3POHCl$$
$$II$$
$$I \;\; \Big\updownarrow H_2O$$
$$R_1R_2R_3P(OH)_2$$
$$III$$

occur at this stage by internal motion, *i.e.*, flipping of the groups' positions in either a trigonal-bipyramidal structure or similar motion in a square pyramid. Such motion has been observed in other pentacovalent phosphorous compounds and there seems little reason for not expecting it here.[5] It is possible, of course, that $R_1R_2R_3$-PCl_2 is formed in a subsequent step and such a reaction would most certainly lead to racemization. Oxygen exchange can occur *via* the dihydroxy compound (III).[6] Similar exchanges have been recently discovered in reactions of alkoxyphosphonium salts.[7] It is interesting to note that triphenylphosphine oxide does not exchange oxygen on boiling with water[8] or in concentrated sulfuric acid.[9]

(5) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(6) In all of these reactions the results can in general be explained by a pentacovalent intermediate or a transition state with five groups coordinated to phosphorus.

(7) D. B. Denney, H. M. Relles, and A. K. Tsolis, *J. Am. Chem. Soc.*, **86**, 4487 (1964).

(8) M. Halmann and S. Pinchas, *J. Chem. Soc.*, 3264 (1958).

(9) S. Oae, T. Kitao, and Y. Kitaoka, *Chem. Ind.* (London), 291 (1961).

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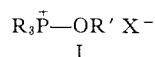PRINCETON UNIVERSITY
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RECEIVED AUGUST 24, 1964

Formation and Reactions of Alkoxyphosphonium Alkoxides[1]

Sir:

Alkoxyphosphonium salts (I) are formed as inter-

$$R_3\overset{+}{P}-OR' \; X^-$$
$$I$$

mediates in a wide variety of reactions in organophosphorus chemistry.[2] Little is known about their stability and properties other than that they, in general, decompose rapidly by typical displacement and/or eliminative processes.[3] Because of their importance to our understanding of mechanisms in organophosphorus chemistry a study of the formation and properties of these materials has been initiated. The results of these experiments illustrate that simple decomposition of these intermediates is not the only reaction which takes place in these systems.

Triphenylphosphine and phenyldipropylphosphine were allowed to react with diethyl peroxide[4] in an excess

(1) Research supported by the National Science Foundation under NSF GP-202.

(2) J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962).

(3) D. B. Denney and R. R. DiLeone, *J. Am. Chem. Soc.*, **84**, 4737 (1962), have reported on the preparation of

$$(C_6H_5)_3P-O-\!\!\!\diamondsuit\!\!\!\; \;\; Cl^-$$
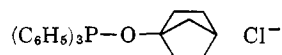
which is stable toward decomposition because of the bridgehead nature of the oxygen-bearing carbon.

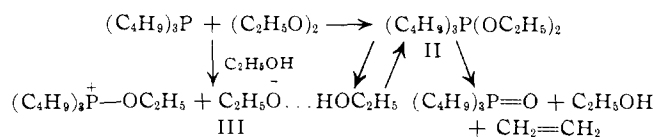(4) L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

of ^{18}O-labeled ethanol. In both cases the appropriate phosphine oxide was formed in high yield (86-90%). The triphenylphosphine oxide contained 78% of the ^{18}O expected if complete equivalence of all the ethoxy groups had been obtained in the system. Fifty-four per cent of the theoretical amount of ^{18}O was found in the phenyldipropylphosphine oxide. In a complementary experiment tributylphosphine was allowed to react with diethyl peroxide in 1-propanol. Besides tributylphosphine oxide there was formed ethanol, ethyl propyl ether, and dipropyl ether.[5]

The results of these experiments are explainable in terms of the formation of alkoxyphosphonium alkoxides

$$R_3P + (CH_3CH_2O)_2 \overset{R'-OH}{\longrightarrow} R_3\overset{+}{P}-OC_2H_5 + (R'O^- + C_2H_5O^-)$$
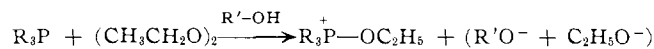
which undergo varying amounts of exchange in competition with the irreversible decomposition to phosphine oxides, ethers, alcohols, and possibly olefins. Whether exchange proceeds through a pentacovalent intermediate, R_3POROR', cannot be deduced from this evidence. It is important to note that the amount of exchange is a function of relatively minor structural changes.[6]

The reaction of tributylphosphine with diethyl peroxide in the absence of solvent was followed by continuous investigation in the n.m.r. It was easily seen that the initial products of the reaction were tributylphosphine oxide, ethanol, and presumably ethylene.[7] After about 40 min. (*ca.* 1 half-life) diethyl ether was being formed to the practical exclusion of ethanol. The final products, identified by n.m.r. and g.l.p.c., were tributylphosphine oxide, ethanol, and diethyl ether. The relative yields of the latter two components were 69 and 31%, respectively. The change in rate of product formation with time of reaction is particularly unusual and indicates a general change in reaction course. This is most probably due to the formation of ethanol. Two explanations can be offered for its effect. In the absence of alcohol the reaction may yield the pentacovalent compound II in the initial step.[8] This could decompose

$$(C_4H_9)_3P + (C_2H_5O)_2 \longrightarrow (C_4H_9)_3P(OC_2H_5)_2$$
$$\Big\downarrow C_2H_5OH \qquad\qquad II$$
$$(C_4H_9)_3\overset{+}{P}-OC_2H_5 + C_2H_5O^- \;\; HOC_2H_5 \;\; (C_4H_9)_3P=O + C_2H_5OH$$
$$III \qquad\qquad\qquad\qquad + CH_2=CH_2$$

directly to phosphine oxide, ethanol, and ethylene or ionize to tributylethoxyphosphonium ethoxide. Subsequent decomposition would then have to yield the products but as alcohol was formed an increase in S_N2 product, diethyl ether, would be required. On the other hand, as alcohol is formed displacement by the phosphine may yield ions III directly. The function of the alcohol would be to hydrogen bond with the forming ethoxide ion. Indeed, it was noted that the reaction in 1-propanol was at least as fast as the neat reaction despite the large change in concentration.

(5) Small amounts of diethyl ether might have been formed and escaped detection.

(6) The extensive exchange observed in these systems supports the mechanism suggested by C. B. Parisek, C. S. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **82**, 5503 (1960), for the conversion of optically active methylethylphenylbenzylphosphonium butoxide to highly racemized methylethylphenylphosphine oxide. See also M. Grayson and P. T. Keough, *ibid.*, **82**, 3919 (1960), in this regard.

(7) No evidence for the formation of tributyldiethoxyphosphorus was obtained by this technique.

(8) D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Am. Chem. Soc.*, **83**, 1726 (1961); D. B. Denney and H. Relles. *ibid.*, **86**, 3897 (1964).

Although it is not possible at this time to provide a complete mechanistic picture for the reactions described, it is clear that they are subject in a major way to minor changes in structure and reaction conditions. These results show that attempts to generalize from isolated experiments such as a stereochemical investigation will in most cases be meaningless, for the stereochemistry of the reaction may change as the reaction progresses. For example, the reaction of diethyl peroxide with optically active phosphine may yield early in the reaction entirely different optical results from those near the end.[9]

(9) R. F. Hudson and M. Green, Angew. Chem. Intern. Ed. Engl., **2**, 11 (1963), have indicated some other problems which are encountered in stereochemical studies with compounds of this type.

(10) National Science Cooperative Graduate Fellow, 1962–1963; Public Health Service Fellow, 1963–1964.

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Proton Transfers in Dipolar Aprotic Solvents.
I.   Transfers to Fluorenyl and Trityl Anions in Dimethyl Sulfoxide Solution

Sir:

Recently, both Cram[1] and Schriesheim[2] have presented evidence that proton transfers from *t*-butyl alcohol and other hydroxy compounds to strong hydrocarbon bases in dimethyl sulfoxide (DMSO) solution are diffusion controlled. In this preliminary paper, we report results of competitive proton abstractions from several types of acids by the triphenylmethyl (trityl) and fluorenyl anions in DMSO solution which indicate that diffusion control may be a general characteristic of proton-transfer reactions in such solvents, independent of the nature of the acid and base involved. We suggest a hypothesis which is consistent with the present data and has broad implications as to the general nature of proton-transfer reactions.

Fluorenyl anion in DMSO was produced by adding 1 mmole of fluorene to 2 mmoles of potassium *t*-butoxide in 20 ml. of dry (<60 p.p.m.) degassed DMSO. Trityl anion was produced by adding 1 mmole of triphenylmethane to a solution of 2 mmoles of methylsulfinyl carbanion[3] in 25 ml. of DMSO.

The acids were added to these solutions by hypodermic syringe while maintaining rapid stirring by means of a magnetic stirrer. The resulting solutions were poured into 50 ml. of water, extracted with three 20-ml. portions of ether, washed with water, dried with sodium sulfate, and evaporated on a steam bath. The crude products were recrystallized twice from ethanol and analyzed for deuterium by infrared spectrophotometry. The results are reported in Table I.

The data obtained from the addition of D_2O to trityl and fluorenyl anions indicate a rapid exchange of hydrogens of the solvent with deuterium. In fact, 5 min. after mixing, complete equilibration of hydrogen and deuterium throughout the system is

(1) D. J. Cram, et al., J. Am. Chem. Soc., **84**, 4358 (1962), and earlier references cited there.

(2) A. Schriesheim, et al., ibid., **85**, 3002 (1963), and earlier references cited there.

(3) E. J. Corey and M. Chaykofsky, ibid., **84**, 866 (1962).

TABLE I

COMPETITIVE PROTON TRANSFERS IN DIMETHYL SULFOXIDE SOLUTION

Reacted with	% Fluorene	% 9-d_1	% 9,9-d_2
A. Fluorenyl anion			
3.0 ml. of H_2O, worked up in D_2O	100	0	0
3.0 ml. of D_2O, worked up after 1 min.	2	55	43
3.0 ml. of D_2O, worked up after 5 min.	59	41	0
9.2 mmoles of nitromethane-d_3, worked up after 1 min.	32	58	10
9.2 mmoles of nitromethane-d_3, worked up after 5 min.	13	82	12
9.2 mmoles of nitromethane-d_3 plus[a] 4.0 mmoles of *p*-toluenesulfonic acid monohydrate, worked up after 1 min.	64	36	0

	% $(C_6H_5)_3$-CD	% $(C_6H_5)_3$-CH
B. Trityl anion		
5.0 ml. of D_2O, worked up after 3 min.	49	46
9.2 mmoles of nitromethane-d_3, worked up after 2 min.	85	15
9.2 mmoles of nitromethane-d_3 plus 5.8 mmoles[a] of phenol, worked up after 2 min.	55	44
9.2 mmoles of nitromethane-d_3 plus 5.8 mmoles[a] of phenol, worked up after 10 min.	55	44
9.2 mmoles of nitromethane-d_3 plus 4.0 mmoles[a] of *p*-toluenesulfonic acid monohydrate, worked up after 1 min.	43	57

[a] The acids were mixed in a hypodermic syringe and immediately injected into the solution of the base.

obtained. Thus, the questioned[4,5] value of the equilibrium constant for the reaction of dimethyl sulfoxide with trityl anion obtained by quenching the equilibrium mixture[3] is a result of rapid deuterium exchange with solvent.

The small amount of fluorene-9,9-d_2 and the relatively slow changes in deuterium content with time in the experiments with fluorenyl anion and nitromethane-d_3 show that the proton transfer is only slowly reversible in this system. The difference in exchange rate with nitromethane and water must be due to the tremendously enhanced basicity of hydroxide[1] relative to nitromethane anion in DMSO solution. The complete absence of fluorene-9,9-d_2 in the reaction involving *p*-toluenesulfonic acid, and the absence of changes in deuterium content with time in the reactions of the acids with trityl anion, indicate that the proton transfers are irreversible in these systems.

In each of the experiments utilizing a mixture of acids, the product contains an amount of deuterium corresponding to *equal rates of proton transfer from nitromethane, phenol, p-toluenesulfonic acid, and water.*[6] This is in striking contrast to the observation in aqueous solution[7] that nitromethane reacts with hydroxide ion at a rate 10^6 slower than does phenol.

A single simple hypothesis is capable, however, of rationalizing the present data along with a body of previously unexplained observations. If one reasonably assumes that *the ionization of a carbon acid in hydroxylic solvents must involve a large amount of solvent*

(4) E. C. Steiner and J. M. Gilber, ibid., **85**, 3054 (1963).

(5) A. Ledwith and N. MacFarlane, Proc. Chem. Soc., **108** (1964).

(6) Under the present conditions of large excess of acid, true competition should be obtained even though the reactions are probably fast in comparison to the time required for mixing.

(7) M. Eigen, Angew. Chem. Intern. Ed. Engl., **3**, 1 (1964).