Free-Radical Chemistry of Organophosphorus Derivatives. Nonequivalence of Alkoxy Groups in $(RO)_4P\cdot$

Sir:

Both chemical[1] and spectroscopic (esr)[2] evidences have been presented to support the postulate that reactions of alkoxy free radicals with trialkyl phosphites involve discrete phosphoranyl radical intermediates, **1**.

$$R'O\cdot + P(OR)_3 \longrightarrow \underset{\mathbf{1}}{R'\dot{P}(OR)_3} \xrightarrow{\beta\ \text{scission}} R'\cdot + OP(OR)_3 \quad (1)$$

Esr hyperfine splittings for certain other phosphoranyl radicals, $F_4P\cdot$,[3] $Cl_4P\cdot$,[4] and $(CH_3)_3\dot{P}OC_4H_9\text{-}t$,[5] have been interpreted in terms of a geometry which approaches trigonal bipyramidal with the odd electron in an equatorial position. Unfortunately, for **1** the absence of hyperfine splittings precludes such an assessment of configuration. We report here results of a chemical study which show that the alkoxy groups of **1**, generated according to reaction 1, are not equivalent from a reactivity standpoint and hence, presumably, are also configurationally nonequivalent. Of at least equal interest is the postulate that the alkoxy radical of reaction 1 enters intermediate **1** in a stereospecific or at least stereoselective fashion.

Decomposition at 65° of dibenzyl hyponitrite[6] (**2**) dissolved in degassed benzene was found to proceed at a rate unaffected by the presence of added benzyl diethyl phosphite (**3**). When the phosphite was chemically labeled with a methyl group in the para position of the phenyl ring (phosphite **4**), the following typical products and percentage yields, based on phosphite consumed, were determined by glc (Scheme I). These products are clearly consistent with the operation of a free-radical process such as 1. The bibenzyls are to be expected from coupling and cross-coupling of benzyl and *p*-methylbenzyl radicals following transfer of oxygen to phosphorus. (The yields of bibenzyls are based on moles of **5** and **6** formed.) The predominant phosphate, **5**, is that which results from transfer of oxygen by the incoming benzyloxy group. Fifteen duplicate runs gave a **5**/**6** ratio of 1.17 ± 0.02.

Scheme I

$$\underset{\mathbf{2},\ 0.439\ \text{mmol}}{(C_6H_5CH_2ON)_2} + \underset{\mathbf{4},\ 0.459\ \text{mmol}}{p\text{-}CH_3C_6H_5CH_2OP(OC_2H_5)_2} \longrightarrow$$

$$\underset{\substack{\mathbf{5},\ 0.239\ \text{mmol}\\(52.1\%)}}{p\text{-}CH_3C_6H_5CH_2OP(O)(OC_2H_5)_2} + \underset{\substack{\mathbf{6},\ 0.200\ \text{mmol}\\(43.6\%)}}{C_6H_5CH_2OP(O)(OC_2H_5)_2} +$$

$$\underset{\substack{\mathbf{7},\ 0.057\ \text{mmol}\\(26\%)}}{C_6H_5CH_2CH_2C_6H_5} + \underset{\substack{\mathbf{8},\ 0.056\ \text{mmol}\\(25\%)}}{p\text{-}CH_3C_6H_5CH_2CH_2C_6H_5CH_3\text{-}p} +$$

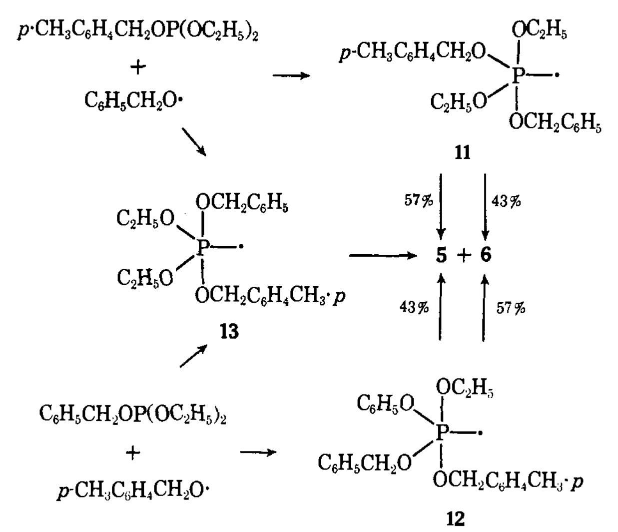
$$\underset{\substack{\mathbf{9},\ 0.108\ \text{mmol}\\(49\%)}}{p\text{-}CH_3C_6H_5CH_2CH_2C_6H_5}$$

Reaction of *p*-methylbenzyloxy radical with benzyl diethyl phosphite (**10**) at 65° (eq 2) gave the same products, again in high yields. (Yields of **5** and **6** from a typical experiment are given in parentheses.) However, the ratio of product phosphates was essentially the inverse of that encountered in Scheme I, *i.e.*, 6/5 = 1.22 ± 0.02 (15 duplicate determinations).[7]

$$p\text{-}CH_3C_6H_4CH_2O\cdot + \underset{\mathbf{10}}{C_6H_5CH_2OP(OEt)_2} \longrightarrow \mathbf{5}\ (41.5\%) + \mathbf{6}\ (49.3\%) \quad (2)$$

These results can be accounted for by Scheme II in terms of a phosphoranyl radical intermediate with the following reasonable assumptions: (a) the alkoxy radical attacks the face of the pyramidal phosphite to give a trigonal-bipyramidal intermediate with the entering benzyloxy group axial and the odd electron equatorial; (b) the ease of β scission essentially is unaffected by the presence of the *p*-methyl group.

Scheme II



If the benzyloxy or *p*-methylbenzyloxy radical attacks the three least-hindered faces of the pyramidal phosphite[8] in a random manner, then two out of three times an unsymmetrical phosphoranyl radical such as **11** or **12** will arise in which the benzyloxy groups are nonequivalent. The third alternative, predicted statistically to be formed in one of three random attacks, is the structure **13** with both benzyloxy groups axial. The product distributions encountered in these reactions are then predicted by Scheme II if β cleavage of an axial benzyloxy (or *p*-methylbenzyloxy) group occurs 1.3 times as rapidly as that of an equatorial one.

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(1) W. G. Bentrude and R. A. Wielesek, *J. Amer. Chem. Soc.*, **91**, 2406 (1969).

(2) P. J. Krusic, W. Mahler, and J. K. Kochi, private communication; A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem.*, **83**, 800 (1971).

(3) W. Nelson, G. Jackel, and W. Gordy, *J. Chem. Phys.*, **52**, 4572 (1970); R. W. Fessenden and R. H. Schuler, *ibid.*, **45**, 1845 (1966); P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964); J. R. Morton, *Can. J. Phys.*, **41**, 706 (1963); J. Higuchi, *J. Chem. Phys.*, 50, 1001 (1969).

(4) G. F. Kokoszka and F. E. Brinckman, *J. Amer. Chem. Soc.*, **92**, 1199 (1970).

(5) J. K. Kochi and P. J. Krusic, *ibid.*, **91**, 3944 (1969).

(6) J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 2595 (1932); S. K. Ho and J. B. deSousa, *ibid.*, 1788 (1961).

(7) That the ratio of products 5 and 6 was actually inverted by approach of the potential intermediate from the opposite side was clearly seen from gas chromatograms of reaction mixtures. Yields and ratios were determined after careful sensitivity calibrations using appropriate internal standards and gas chromatographically pure samples of 5 and 6.

(8) Earlier work showed that alkoxy radicals attack trivalent phosphorus to give oxide in which the configuration at phosphorus is retained: W. G. Bentrude, P. E. Rusek, Jr., and J. H. Hargis, *Chem. Commun.*, 296 (1969). This is consistent with the type of attack proposed here. It may be preferable to think of the reaction to give 11, 12, or a symmetrical intermediate in terms of attack on the electron pair. This is immaterial to the argument.

Although the above analysis is certainly not unique, the trigonal-bipyramidal radical structure proposed is consistent with the results of esr studies[3–5] of other phosphoranyl radicals. Furthermore, the proposed stereospecific introduction of the entering alkoxy group into the axial position is in keeping with the rules[9] which appear to apply for the formation of pentacovalent phosphorus intermediates to which **1** and **11–13** probably are related in terms of bonding.

A previous study[1] of the reaction of ^{14}C-labeled *tert*-butoxy radical with tri-*tert*-butyl phosphite gave label distribution consistent with the irreversible formation of an intermediate $(RO)_4P\cdot$ which gives product containing essentially 75% of the available label. Unfortunately, the reactivity ratio (1.3/1.0)[10] which explains the product distributions encountered in the benzyl diethyl phosphite studies predicts a deviation from statistical label distribution for the tri-*tert*-butyl phosphite system which is so small as to be within the error limits of our radiochemical counting techniques.

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(9) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); K. Mislow, *ibid.*, 3, 266 (1970). To the extent that the entrance of the benzyloxy radical into **1** is only stereoselective rather than stereospecific, an increase in the axial/equatorial reactivity ratio would be required to explain the present data. This would also be true if some type of equilibration process, such as pseudorotation, were operative by which axial and equatorial substituents are interchanged. Nonetheless, the primary conclusions of this study, the nonequivalency of alkoxy substituents in **1** and the stereochemically nonrandom introduction of the benzyloxy radical in the formation of **1**, remain.

(10) This ratio is likely a function of the C–O bonds undergoing cleavage; thus it may be different for a *tert*-butoxy substituent. It should be made clear that β cleavage of a C–O bond in **1** is not the microscopic reverse of the proposed stereoselective or stereospecific P–O bond formation involved in formation of **1**. Violation of microscopic reversibility is not a consideration in the postulated cleavage of both axial and equatorial C–O bonds.

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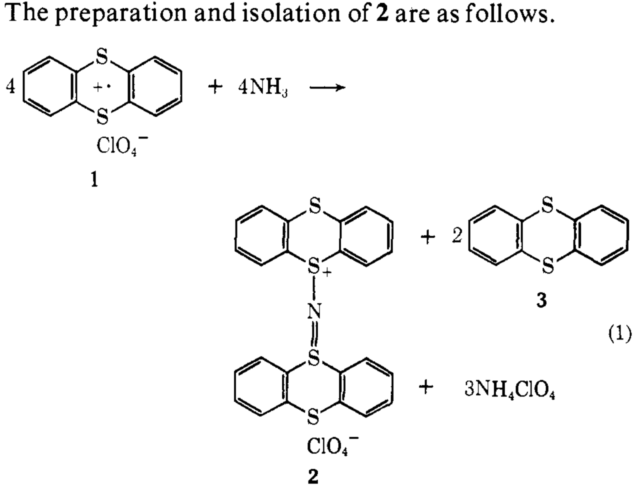
Ion Radicals. XXIV. Reaction of Thianthrene Perchlorate with Ammonia[1–3]

Sir:

Reactions of cation radicals with amines have been confined in past years to the use of pyridines, which engage in pyridination[4,5] or proton-transfer reactions.[6] Hardly anything at all is known about the reaction of aliphatic amines with cation radicals. *n*-Butylamine is reported to discharge the color of the anthracene cation radical from a silica–alumina surface, *via* displacement of the hydrocarbon from the catalyst surface, rather than by nucleophilic reaction with the ion radical.[7]

We have now found that when dry ammonia gas is bubbled into a solution of thianthrene perchlorate (**1**)[8] in either nitromethane or acetonitrile, 5,5-dihydro-5-(5-thianthreniumylimino)thianthrene perchlorate (**2**)[9] is formed.

The stoichiometry of the reaction is given in eq 1. The preparation and isolation of **2** are as follows.



Ammonia gas was bubbled into a solution of 201 mg (0.636 mmol) of **1** in 20 ml of nitromethane. The color of **1** disappeared rapidly. Excess of ammonia was removed with a stream of dry nitrogen. Ammonium perchlorate was filtered off and identified by infrared (Nujol mull).[10] (Ammonium perchlorate was too soluble to precipitate when reaction was carried out in acetonitrile.) Tlc of the solution showed two spots only: thianthrene (**3**), R_f (benzene) = 0.59, and **2**, R_f (all solvents used) = 0. The nitromethane solution was extracted with cyclohexane until tlc no longer showed the presence of **3**. Ultraviolet assay of the cyclohexane solution gave 67.2 mg (0.311 mmol, 98%) of **3**. A similar experiment using 164 mg (0.518 mmol) of **1** gave 54 mg (0.250 mmol, 96%) of **3**. The nitromethane solution was evaporated leaving a white solid, which was washed with water and cyclohexane and dried, giving 42 mg (0.078 mmol, 49%) of **2**. Crystallization from methanol gave mp 240–241° dec. Compound **2** decomposes on heating giving, in part, ammonia and thianthrene. Therefore, the melting point was obtained by plunging a filled capillary into a preheated bath.

Anal. Calcd for $C_{24}H_{16}S_4NClO_4$: C, 52.8: H, 2.93; S, 23.5; N, 2.56; Cl, 6.49. Found:[11] C, 52.6; H, 3.00; S, 23.2; N, 2.99; Cl, 6.94.

The nmr spectrum in DMSO had δ_H 7.6 (m, 12 H) and 8.0 (m, 4 H) consistent with the 1,1′,2,2′,3,3′,7,7′,8,8′,9,9′ protons and the 4,4′,6,6′ protons of **2**. The ultraviolet spectrum in acetonitrile had maxima at 335, 291, and 227 nm, $\epsilon = 5 \times 10^2$, 1.1×10^3, and 4.3×10^3, respectively.

The structure of **2** was deduced from hydrolysis experiments which are summarized in Scheme I.

A mixture of 133 mg (0.243 mmol) of **2** in 40 ml of methanol and 15 ml of 15% aqueous sodium hydroxide was boiled for 5 hr. Tlc showed only two products, **4**, R_f (ether) = 0.10, and **5**, R_f (ether) = 0.59. Both prod-

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(1) Part XXIII: C. V. Ristagno and H. J. Shine, *J. Org. Chem.*, **36**, 4050 (1971).

(2) Supported by the National Science Foundation, Grant No. GP-25989X.

(3) In earlier papers we have used incorrectly the name thianthrenium to designate the cation radical in cation–radical salts.

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(7) R. M. Roberts, C. Barter, and H. Stone, *J. Phys. Chem.* **63**, 2077 (1959).

(8) Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969).

(9) We wish to thank Dr. K. L. Loening, Nomenclature Division, Chemical Abstracts Service, for naming this compound.

(10) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(11) Schwarzkopf Laboratories, Woodside, N. Y.