a $DE\,7.8\%$ as large as in benzene, identical with the one mentioned earlier.

The situation as regards homoconjugative stabilization can be expected to be markedly different in the parent positive ion from ionization of I. Since ionization of an electron is from the α + 0.89 β MO, one could expect the positive ion to be stabilized by 0.11β more than the ground state, the ionization potential (I.P.) being lowered by 0.11β compared to a corresponding monoolefin. Another factor which should lower the I.P. of I has to do with the neglect of electron repulsion in the simplest HMO treatment. With the so-called ω -technique,⁷ some electron repulsion can be introduced within the framework of the LCAO method. Thus, by setting the Coulomb integral α equal to α $+ \omega q\beta$, where q is the charge on the carbon atom, and using ω equal to 1.4, Streitwieser^{7a} and Ettinger^{7b} have successfully correlated ionization potentials of many hydrocarbons. For a monoolefin q is 0.5 and the positive ion has one π -electron, so the ω -calculation lowers I.P. by $0.5(1.4)\beta$ or 0.7β . In the positive ion from I, with five π -electrons and q equal to one-sixth, the ω -calculation lowers I.P. by five-sixths (1.4) β or 1.17 β , 0.47 β more than in the case of the monoolefin. From the sum of the 0.47β and 0.11β terms and the existing correlations between I.P. values and MO calculations,⁷ we could expect the I.P. of I to be ca. 1e.v. lower than a corresponding monoolefin.

The electron impact I.P. of 1,4,7-cyclononatriene does indeed turn out to be unusually low. The figure obtained, 8.72 e.v., is less than that for benzene^{8a} (9.50), toluene⁹ (9.23), or *p*-xylene⁹ (8.88). It is also less than that for propylene^{8b,9} (9.94, 9.84) or 1,2-disubstituted olefins such as *cis*-2-butene^{8c} (9.34) or cyclopentene^{8c} (9.27). In fact, it is as low as, or lower than, the values for typical conjugated 1,3-dienes such as cyclopentadiene^{8d,9} (9.00, 8.9), isoprene¹⁰ (9.08), and 1,3-pentadiene^{8c} (8.68).

In considering the I.P. of I, we must recognize that ionization potentials of olefins appear to be subject to strain and alkyl-substituent effects. As regards strain, any effect due to slight strain⁴ in I is probably very small.¹¹ Since the olefinic groups in the cyclononatriene are 1,2-dialkyl substituted, cis-2-butene represents one of the best available reference compounds for comparison with I. This choice may well involve an overly generous allowance for alkyl substituent effects since the geometry of the crown conformation of I is not especially favorable to hyperconjugative stabilization of the positive ion due to C-H electron delocalization. Thus, the ca. 0.6 e.v. (14 kcal./mole) by which the I.P. of I is lower than that of 2-butene may well be a conservative measure of the decrease in ionization potential of the cyclononatriene.

The lowering of ionization potential due to proper juxtaposition of nonadjacent olefinic groups may well be a general phenomenon. For example, the ionization

(9) See ref. 7a for tabulated I.P. values and literature references.

(10) J. D. Morrison and A. J. C. Nicholson, J. Chem. Phys., 20, 1021 (1952).

(11) For example, I.P. is 9.05 for the highly strained bicycloheptene (I. P. Fisher and F. P. Lossing, unpublished work).

potential of bicyclo [2.2.1] heptadiene¹² is appreciably smaller than that of bicyclo [2.2.1] heptene.¹¹ This general phenomenon and semiempirical methods to calculate the effects are being explored further.

(12) S. Meyerson, J. D. McCollum, and P. N. Rylander, J. Am. Chem. Soc., 83, 1401 (1961).

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Racemization and Oxygen Exchange of Trisubstituted Phosphine Oxides¹

Sir:

The recent study of the racemization and oxygen exchange of aralkyl sulfoxides by hydrogen chloride under a variety of conditions has prompted a similar study with trisubstituted phosphine oxides.²

Phenylmethylpropylphosphine oxide, $[\alpha]^{26}_{D} + 18.5^{\circ}$, in dry dioxane saturated with hydrogen chloride was allowed to stand at room temperature for 9 days, at which time the specific rotation was $+0.3^{\circ}$. Periodic measurement of the rotation during the 9-day period gave the following results: after 20 hr., $+15.8^{\circ}$; 64 hr., $+10.8^{\circ}$; and 7 days $+3.4^{\circ}$. The phosphine oxide was recovered in 80% yield and shown to be racemic. In another experiment the phosphine oxide, 0.00148mole, was dissolved in a hydrogen chloride saturated solution of 1 ml. of water, containing ca. 1.45 atom $\frac{6}{20}$ excess ¹⁸O, and 4 ml. of dioxane. The solution rapidly became yellow and measurement of the rotation was extremely difficult. After 55 days at room temperature, the phosphine oxide was recovered and shown to be racemic. Oxygen-18 analysis showed it contained 0.87 atom % excess of 18O.3 In a similar experiment triphenylphosphine oxide containing 0.85 atom % excess ¹⁸O was treated for 80 days with hydrogen chloride dissolved in water-dioxane (1:4). The oxide was recovered and shown to contain 0.55 atom % excess ¹⁸O.

The results of these experiments clearly demonstrate that phosphine oxides are subject to racemization under the conditions specified. The process is certainly much slower than that found for the aralkyl sulfoxides. The diminution in rate in the presence of water is in accord with the sulfoxide experiments. Unfortunately, it was not possible to correlate oxygen exchange with rate of racemization; however, it is interesting to note that water is not required for racemization. Mislow, et al.,² have suggested that sulfoxide racemization occurs by formation of R₁R₂SCl₂⁴; however, it is not necessary to form R1R2R3PCl2 to have racemization of the phosphine oxide. Undoubtedly the first step involves protonation of the oxide oxygen. This should be a rapid and reversible reaction, and also one highly dependent on the basicity of the medium. Addition of chloride ion yields II, the pentacovalent compound. Racemization can

 ^{(7) (}a) A. Streitwieser, Jr., J. Am. Chem. Soc., 82, 4123 (1960); (b) R. Ettinger, Tetrahedron. 20, 1579 (1964).

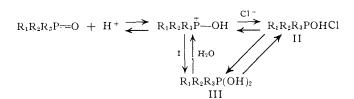
^{(8) (}a) I. P. Fisher, T. F. Palmer, and F. P. Lossing, J. Am. Chem. Soc.,
86, 2741 (1964); (b) J. Collin and F. P. Lossing, *ibid.*, 79, 5848 (1957); (c)
J. Collin and F. P. Lossing, *ibid.*, 81, 2064 (1959); (d) A. G. Harrison, L. R.
Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, 82, 5593 (1960).

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

⁽²⁾ K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, J. Am. Chem. Soc., 86, 1452 (1964).

⁽³⁾ Result of one analysis only. Because of the extreme hygroscopicity of this material the value may be low.

⁽⁴⁾ This could be an intermediate or transition state.



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 $R_1R_2R_3$ -PCl₂ 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 water⁸ 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.

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(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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Formation and Reactions of Alkoxyphosphonium Alkoxides¹

Sir:

Alkoxyphosphonium salts (I) are formed as inter-

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 peroxide⁴ 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

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 ¹⁸O-labeled ethanol. In both cases the appropriate phosphine oxide was formed in high yield (86-90%). The triphenylphosphine oxide contained 78% of the ¹⁸O expected if complete equivalence of all the ethoxy groups had been obtained in the system. Fifty-four per cent of the theoretical amount of ¹⁸O 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

$$R_{3}P + (CH_{3}CH_{2}O)_{2} \xrightarrow{R'-OH} R_{3}P - OC_{2}H_{5} + (R'O^{-} + C_{2}H_{5}O^{-})$$

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.⁸

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

$$(C_4H_9)_3P + (C_2H_5O)_2 \longrightarrow (C_4H_9)_3P(OC_2H_5)_2$$

$$\downarrow C_2H_9OH \qquad \swarrow \qquad II \qquad \downarrow C_2H_5OH \qquad (C_4H_9)_4P=O+C_2H_5OH \qquad III \qquad + CH_2=CH_2OH \qquad + CH_2OH \qquad + CH_2=CH_2OH \qquad + CH_2OH \qquad + CH_2O$$

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 SN2 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 methylethylphenylbnozylphosphonium 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).