



VI or VII,¹⁵ or both (here M is RhCl[(C₆H₅)₃P]_n), that these give VIII,¹⁶ and that VIII is converted into II.¹⁷ This mechanism also accounts for the formation of III^{18,19} if VII extrudes [(C₆H₅)₃P]_nRhCl;^{4,20} the alternative, that III is formed from I independently of II and IV by a metal-catalyzed concerted electrocyclic reaction,^{2,3} is not required by any of the data.

Acknowledgment. We are grateful to the National Science Foundation (NSF-GP7809) for its support.

(15) Metal insertion into cyclopropanes: (a) N. A. Bailey, R. D. Gillard, M. Keeton, R. Mason, and D. R. Russell, *Chem. Commun.*, 396 (1966); (b) D. M. Adams, J. Chatt, R. G. Guy, and N. Sheppard, *J. Chem. Soc.*, 738 (1961); (c) D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *ibid.*, A, 845 (1968).

(16) Transition metal hydrides: (a) A. P. Ginsburg, *Transition Metal Chem.*, 1, 112 (1965); (b) M. L. H. Green and K. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 115 (1965).

(17) Insertion into metal-hydrogen bonds: (a) G. W. Parshall, *J. Am. Chem. Soc.*, 90, 1669 (1968); (b) W. H. Knoth, *ibid.*, 90, 7172 (1968); (c) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965); (d) G. Hata, H. Kondo, and A. Miyake, *J. Am. Chem. Soc.*, 90, 2278 (1968).

(18) It also can reasonably account for the observation that the kinetic deuterium isotope effects for the formation of II and III are in the ratio 2.4:1.

(19) The nmr spectrum (two multiplets at τ 8.33 and 8.75 in the intensity ratio 4.07:4.00) of the III formed from Ib is also consistent with the mechanism.

(20) (a) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, A, 1054 (1968); (b) D. R. Eaton and S. R. Stuart, *J. Am. Chem. Soc.*, 90, 4170 (1968).

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Free-Radical Chemistry and Photochemistry of Organophosphorus Intermediates. VII. Intermediacy and Configuration of Phosphoranyl Radicals in the Reaction of Labeled *t*-Butoxy Radical with Tri-*t*-butyl Phosphite

Sir:

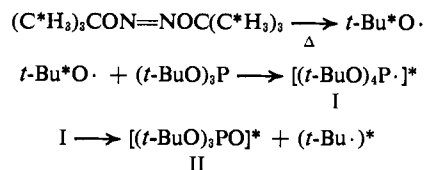
The oxidation of trivalent phosphorus compounds, such as phosphines and phosphites, by alkoxy radicals has been shown to produce the product of oxygen transfer from the alkoxy radical to phosphorus.¹ Several



questions may be asked regarding the oxygen-transfer process. (1) Does the species A exist as a discrete intermediate, or is it simply the transition state for oxygen transfer? (2) If A is a discrete intermediate, is its formation reversible? (3) Again, if A is a discrete intermediate, what is its structure and lifetime? Although phosphoranyl radicals, such as A, are commonly proposed as possible intermediates in reactions

(1) (a) C. Walling and M. S. Pearson, *J. Amer. Chem. Soc.*, 86, 2262 (1964), and references to earlier work contained therein; (b) S. A. Buckler, *ibid.*, 84, 3093 (1962); (c) J. B. Plumb, R. Obrycki, and C. E. Griffin, *J. Org. Chem.*, 31, 2455 (1966); (d) W. G. Bentrude, *Tetrahedron Lett.*, 3543 (1965); (e) J. I. G. Cadogan, *Advan. Free-Radical Chem.*, 3, 220 (1967).

of radicals with trivalent phosphorus, little or no information relating to these questions is available from past work.^{1e} To help answer these questions, we have allowed di-*t*-butyl-2-¹⁴C hyponitrite² to decompose completely at 65° in the presence of tri-*t*-butyl phosphite⁴ (>95% pure) in deoxygenated benzene. The phosphate was produced almost quantitatively and was purified by multiple recrystallizations from hexane.



As shown in Table I (expt 1–3), approximately 75% of the product phosphate is ¹⁴C labeled. Controls (expt 4 and 5) showed that the label is not significantly incorporated into the unreacted phosphite or into the product phosphate after its formation.

Table I. Carbon-14 Product Labeling from the Decomposition of Labeled Di-*t*-butyl Hyponitrite in the Presence of Tri-*t*-butyl Phosphite^a

Expt	[Phosphite] ^b	[Hyponitrite] ^b	<i>f</i> , ^c phosphate act.
1	0.35	0.37	0.76
2	0.45	0.45	0.73
3	0.40	0.05	0.75
4	0.18 ^d	0.098	0.017 ^d
5	0.40	0.05	0.003 ^e

^a In deoxygenated benzene at 65°. ^b Moles/liter. ^c Fraction of labeled product. The (¹⁴CH₃)₃COH used to produce the hyponitrite was employed as the standard of activity: $f = [\text{disintegrations}/(\text{min mmol of phosphate})]/[\text{disintegrations}/(\text{min mmol of labeled } t\text{-butyl alcohol})]$. ^d Decomposition of labeled hyponitrite in the presence of unlabeled phosphite. ^e Unreacted phosphite recovered as the thiophosphate.

These results suggest and are consistent with the essentially irreversible formation of a phosphoranyl radical *intermediate*, I, in a manner which allows a statistical scrambling of label. This could result either because the alkoxy groups are configurationally equivalent (as in III or a square-pyramidal intermediate) or because the intermediate, though unsymmetrical, *e.g.*, IV, has a lifetime sufficient to allow equilibration of configurationally nonequivalent groups by some process such as pseudorotation.^{5,6} Alternatively, the groups in an asymmetric intermediate like IV might be reactionally equivalent.

(2) The labeled hyponitrite was prepared from labeled *t*-butyl chloride using the method of Kiefer and Traylor.³ Labeled *t*-butyl-2-¹⁴C chloride was prepared from (¹⁴CH₃)₃COH (New England Nuclear).

(3) H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 6163 (1966).

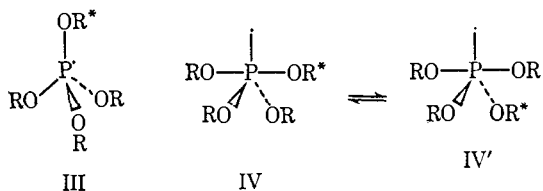
(4) V. Mark and J. R. Van Wazer, *J. Org. Chem.*, 29, 1006 (1964).

(5) ESR studies have suggested that $\cdot\text{PCl}_4$ exists in a bipyramidal configuration at low temperature⁷ and that the configuration of $\cdot\text{PF}_4$ ⁸ approaches a bipyramidal configuration at low temperature while at room temperature rapid inversion (pseudorotationlike) allows equilibration of the fluorines to occur. ESR studies also suggest⁷ that substitution of halogen for alkyl groups changes the configuration of substituents about phosphorus.

(6) We have been unable to write any kind of reasonable random attack mechanism whereby the labeling results might be accommodated by a simple displacement or a rigid asymmetric intermediate.

(7) G. F. Kokoszka and F. E. Brinckman, *Chem. Commun.*, 349 (1968).

(8) P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 4363 (1964).



Previous studies in this laboratory⁹ have shown that oxygen transfer from alkoxy radicals to cyclic six-membered ring phosphites and optically active phosphines occurs with retention of configuration at phosphorus. Pseudorotation of phosphoranyl radical intermediates might be expected to lead to some inverted product in these oxidations. The specificity observed could result from reactions involving phosphoranyl intermediates which are either short lived or configurationally stable. The configuration, configurational stability, and lifetime of phosphoranyl radicals probably depend on the nature of the substituents on phosphorus and the configurational requirements imposed by the substituents (*e.g.*, whether the substituents are part of a ring structure). These effects are currently under investigation in our laboratory.

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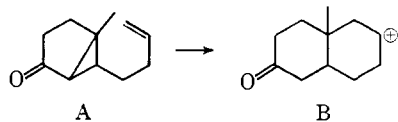
(9) W. G. Bentrude, J. H. Hargis, and P. E. Rusek, Jr., *Chem. Commun.*, 296 (1969).

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Olefin Participation in the Acid-Catalyzed Opening of Acylcyclopropanes. III. Formation of the Bicyclo[2.2.1]heptane System

Sir:

We have previously shown^{1,2} that acylcyclopropanes can undergo acid-catalyzed transformation with participation of a suitably disposed olefinic center and formation of a new ring (*cf.* A \rightarrow B). The cyclohexyl cation



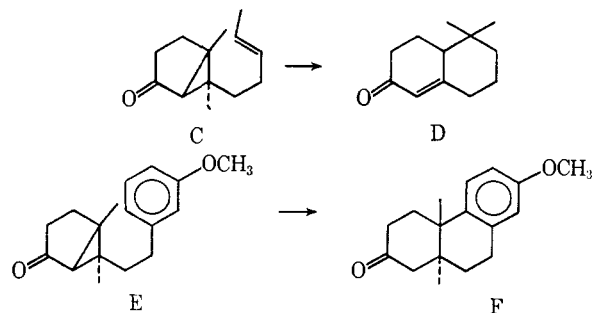
generated in the process has been shown to be capable of rearrangement (C \rightarrow D)¹ or, in a particularly favorable case, of simple proton loss (E \rightarrow F).² We now report on a case in which the cation is efficiently trapped by the *enol* generated *via* the acylcyclopropane opening.

The *endo*-bicyclo[3.1.0]hexanone I was synthesized from the dienic acetal II³ by the usual sequence *via* the aldehyde III, R = H [λ (film) 3.65, 5.78 μ ; δ (CDCl₃) 9.69 (s, 1, H)], acid III, R = OH (silver oxide oxidation)

(1) G. Stork and M. Marx, *J. Am. Chem. Soc.*, **91**, 2371 (1969).

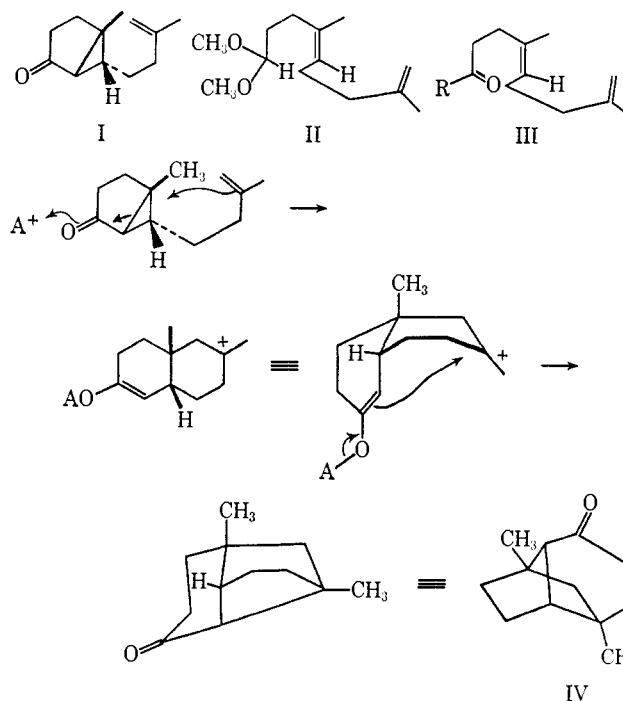
(2) G. Stork and M. Gregson, *ibid.*, **91**, 2373 (1969).

(3) G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Letters*, in press.



[λ (film) 5.84 μ ; δ (CDCl₃) 11.20 (s, 1 H)], acid chloride III, R = Cl (sodium salt and oxalyl chloride) [bp 78–84° (~0.3 mm); (film) 5.53 μ], and diazo ketone III, R = CHN₂ [λ (film) 3.28, 4.74, 6.08 μ]. The latter then (5-hr reflux with copper bronze in cyclohexane) gave the desired I.⁴ This was homogeneous by glpc (DEGS, 180°) and had λ (film) 3.28, 5.80, 6.08, 11.3 μ ; δ (CDCl₃) 1.35 (s, 1 H) and 4.76 (s, broad, 2 H). A pure sample of 300 mg of I, obtained by preparative glpc (FFAP, 210°), was cyclized by keeping its solution in 8 ml of benzene and 2 ml of stannic chloride for 12 hr at room temperature. The major product (70% yield) was isolated by preparative glpc (DEGS, 150°). The new ketone IV, 2,4-dinitrophenylhydrazone mp 160–161° (*Anal.* Found: C, 60.07; H, 6.27), had properties in agreement with the assigned structure: λ (film) 5.85 μ ; δ 1.05 (s, 3 H), 1.13 (s, 3 H), no olefinic protons; molecular ion at *m/e* 178.

It is clear that the *concerted*⁵ participation of the terminal olefin of I leads to a geometry in which the enol is in a position to trap the resulting carbonium ion, as shown below. The possibility that ketonization might have intervened, and that a different system could have resulted *via* the other enol, was ruled out by show-



(4) The same sequence starting with the other geometric isomer of II gave a different cyclopropyl ketone, with an *exo* substituent, as expected (*cf.* ref 2).

(5) The concerted nature of the cyclization follows from unpublished experiments by Gregson which show that the *exo* isomer of I gives no IV under these cyclization conditions.