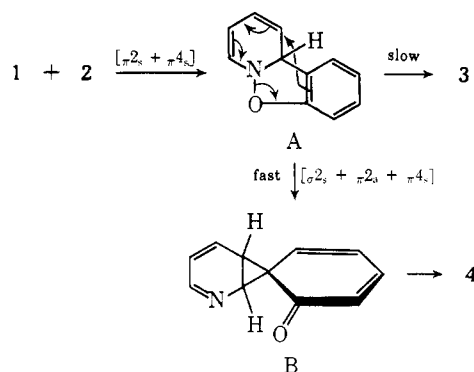
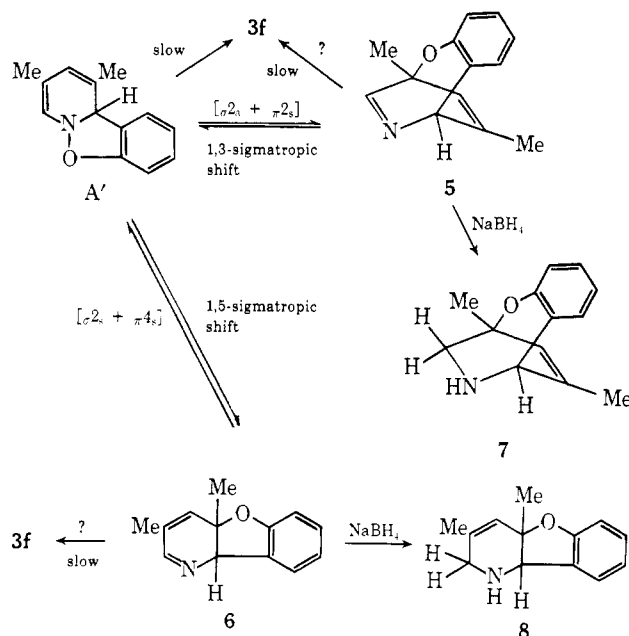


A probable mechanism for these rearrangements is as follows

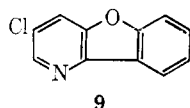


When the 3- and 5-positions are blocked, aromatization leading to **4** is not possible and the intermediate **A'** can undergo further sigmatropic shifts to give **5** and **6**.¹⁹



The alternative mode of ring opening of spirodienone (**B**) to give **3** is unlikely and, indeed, has been shown not to occur in the corresponding adduct formed from benzoylcyanocarbene and pyridine.²

To test the hypothesis of the above 1,5-sigmatropic shift (**A'** → **6**) the reaction of benzyne with 3,5-dichloropyridine 1-oxide at 0° was studied. As expected, 3-chloropyrido[3,2-*b*]benzofuran (**9**) (66.5%), mp 136–137°



dec, was obtained by the facile elimination of HCl from the dichloro derivative corresponding to **6**. This appears to be a convenient one-step route to this heterocyclic ring system.

8, nmr δ 6.58–7.40 (m, 4, aromatic), 5.52 (m, 1, H_4), 4.03 (s, 1, H_2), 2.95 (m, 2, H_6), 1.65 (d, 3, $J_{4,Me} = 0.75$ Hz, 5-Me), 1.70 (s, 1, D_2O exch, NH), and 1.36 (s, 3, 3-Me). Decoupling experiments confirmed the assignments.

(18) The rigid structure of **7** is supported by the presence of two distinct C_s methylene proton peaks. See, for example, F. Böhlmann, D. Schumann, and C. Arndt, *Tetrahedron Lett.*, 2705 (1965).

(19) Other modes of aromatization of **5** and **6** to **3f** are also conceivable.

We are currently extending the synthetic scope of this new β -hydroxyarylation reaction and investigating further aspects of the mechanisms of the rearrangements observed.

Acknowledgment. We wish to thank the National Institutes of Health (Grant No. CA 15628) for support of this work.

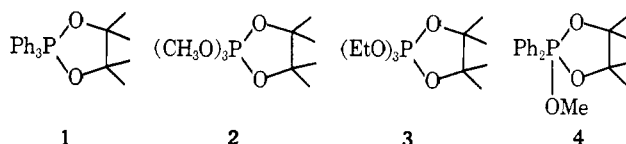
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Phosphorane Formation from the Reaction of Trivalent Phosphorus Compounds with Tetramethyl-1,2-dioxetane

Sir:

The reaction of tetramethyl-1,2-dioxetane (TMD) with triphenylphosphine has been shown¹ to form a stable phosphorane, **1**, in 94% yield. We now report the formation of phosphoranes **2**, **3**, and **4** from the



reaction of TMD with trimethyl phosphite, triethyl phosphite, and methyl diphenylphosphinite. The kinetics of phosphorane formation was also investigated.

Trimethyl phosphite (2.0 mg, 0.016 mmol) was added² to 1.8 mg TMD (0.016 mmol) in dry benzene at room temperature ($\sim 22^\circ$). Phosphorane **2** was formed rapidly in 69% yield.³ Pinacolone and trimethyl phosphate accounted for the remaining products (31%). Triethyl phosphite (3.0 mg, 0.018 mmol) was added to 1.8 mg of TMD (0.016 mmol) in dry benzene at 22° yielding phosphorane **3**⁴ in 70% yield as well as 30% pinacolone and triethyl phosphate. Methyl diphenylphosphinite (3.3 mg, 0.015 mmol) was added to TMD (1.6 mg, 0.014 mmol) in benzene to yield phosphorane **4** in 84% yield. Pinacolone and methyl diphenylphosphinate accounted for 16% of the reaction products. The 1H and ^{31}P nmr data for phosphoranes **1–4** are shown in Table I.

Unlike phosphorane **1**,¹ phosphoranes **2–4** were found to be thermally stable in benzene at 70° for 120 min. Phosphorane **2** (purified sample)⁵ was heated in benzene (sealed tube) at 90° for 12 hr with only slight decomposition. These observations were in accord with the prediction that replacement of an apical alkyl or aryl group by an alkoxy group should stabilize the phosphorane.⁶

Phosphoranes **1–4** were found to cleave with rearrangement to pinacolone and the corresponding phosphoryl compound when treated with concentrated sul-

(1) P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *J. Amer. Chem. Soc.*, **95**, 6486 (1973).

(2) Order of addition had no effect on product yields.

(3) Yields determined by nmr integrations.

(4) D. B. Denney and D. H. Jones, *J. Amer. Chem. Soc.*, **91**, 5821 (1969), report the synthesis of phosphorane **3** from the reaction of tetramethylethylene ethyl phosphite with diethyl peroxide.

(5) Pinacolone and most of the trimethyl phosphate were removed at high vacuum.

(6) (a) D. Gorenstein, *J. Amer. Chem. Soc.*, **92**, 644 (1970); (b) D. Gorenstein and F. H. Westheimer, *ibid.*, **92**, 634 (1970).

Table I. ^1H and ^{31}P Nmr Data for Phosphoranes 1–4

Phos- phorane	^{31}P chemical shift ^a	^1H nmr ^b (benzene)
1	+48.4 ¹	δ 1.00 singlet ¹
2	+54.3	δ 1.10 (12 H) singlet δ 3.68 (9 H) doublet $J_{\text{PH}} \sim 13$ Hz
3	^c	δ 1.15 (12 H) singlet δ 1.24 (9 H) triplet $J_{\text{HH}} \sim 7$ Hz each peak of which is a doublet $J_{\text{PH}} \sim 2$ Hz ^d δ 4.10 (6 H) apparent quintet $J_{\text{HH}} \sim J_{\text{PH}} \sim 7$ Hz ^d
4	+37.4	δ 1.03 (12 H) singlet δ 3.40 (3 H) doublet $J_{\text{PH}} \sim 12$ Hz

^a All ^{31}P nmr spectra are recorded on a Varian XL-100 nmr spectrometer at 40.5 MHz (^1H decoupled, ^2H lock, Fourier transform). Spectra were recorded of 0.1 M solutions of each phosphorane in benzene-deuteriobenzene (1:1) in 12-mm nmr tubes (solution volume 2.5–3 cm³). Triphenylphosphine oxide (δ –24.8) was used as external standard. The reported chemical shifts are relative to 85% phosphoric acid. ^b All ^1H nmr spectra were recorded on a Varian T-60 nmr spectrometer. ^c Denney and Jones (ref 4) reported δ + 60. ^d (i) Denney and Jones (ref 4) report similar coupling constants for the ethoxy groups for the phosphorane produced from the condensation of triethyl phosphite with β -naphthoquinone. (ii) B. C. Chang, W. E. Conrad, D. B. Denney, D. Z. Denney, R. Edelman, R. L. Powell, and D. W. White, *J. Amer. Chem. Soc.*, **93**, 4004 (1971), report similar coupling constants for the ethoxy groups of a similar triethoxyphosphorane. (iii) D. B. Denney and H. M. Relles, *ibid.*, **86**, 3898 (1964), report similar coupling constants for (EtO)₃P.

furic acid in benzene. Phosphoranes 2–4 were found to be very sensitive to moisture.⁷ Exposure to moist air resulted in slow hydrolysis of benzene solutions of the phosphoranes.

The kinetics of phosphorane formation was investigated in benzene and in mixed acetonitrile–benzene at 23°. The rate of decay of the intensity of chemiluminescence of TMD in the presence of 9,10-dibromoanthracene was monitored before and after the addition of an excess of a phosphorus compound.⁹ The reaction of phosphorus compounds with TMD was found to be of the first order with respect to each reagent. The results have been summarized in Table II.

The negligible solvent effect in the reaction of trivalent phosphorus compounds with TMD, as well as with diethyl peroxide,¹² indicates that there is no polar character in the transition state and hence that the reaction must be either concerted or homolytic in character.¹³ Since by neither mechanism can 1 be formed with both

(7) D. B. Denney and S. T. D. Gough, *J. Amer. Chem. Soc.*, **87**, 138 (1965), report that similar phosphoranes were acid and moisture sensitive.

(8) Each phosphorus compound was added to TMD in dry acetonitrile-*d*₃. The products and relative yields were similar to those obtained in benzene.

(9) This is one of an increasing number of applications of Wilson and Schaap's kinetic method¹⁰ of converting the excitation energy of a carbonyl triplet into fluorescence by the use of 9,10-dibromoanthracene as an efficient heavy-atom energy acceptor.¹⁴ The luminescence intensity serves as an accurate measure of the instantaneous concentration of the TMD; the spontaneous decomposition responsible for the luminescence is negligibly slow compared to the reaction with the phosphorus compounds being measured. For another recent application of the Vasil'ev–Wilson energy transfer, see N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H.-C. Steinmetzer, and W. Adam, *J. Amer. Chem. Soc.*, **96**, 1627 (1974).

(10) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).

(11) V. A. Belyakov and R. F. Vasil'ev, *Photochem. Photobiol.*, **11**, 179 (1970).

(12) D. B. Denney, D. Z. Denney, C. D. Hall, and K. L. Marsi, *J. Amer. Chem. Soc.*, **94**, 245 (1972).

(13) Water brings about a change in mechanism, judged by observations on an optically active phosphine and its oxide: D. B. Denney and N. G. Adin, *Tetrahedron Lett.*, 2569 (1966).

Table II. Rate Constants for Reaction of Trivalent Phosphorus Compounds with TMD

Reagent	10^{-3} [TMD], ^a M	10^{-3} [X ₃ P], M	k_2 , ^c M ⁻¹ sec ⁻¹ Benzene	Acetonitrile– benzene ^b
Ph ₂ POMe	2.6 3.3	18 35	12 ± 2	10 ± 1
Ph ₃ P	6.6 6.1	70 65	1.0 ± 0.1	1.0 ± 0.1
(MeO) ₃ P	6.6 6.6	70 70–140	0.28 ± 0.03	0.16 ± 0.05
(EtO) ₃ P	2.6–6.6 6.6	35–280 70–140	0.30 ± 0.03	0.18 ± 0.05

^a All runs contained 7.8×10^{-4} M 9,10-dibromoanthracene, $T = 23 \pm 1^\circ$. ^b 550 μl of acetonitrile to 100 μl of benzene. ^c Disappearance of TMD was pseudo-first-order through at least three half lives.

oxy-substituents apical, an attractive reason is at hand for the tenfold jump in rate of formation from 1 to 4, namely the unfavorability of forcing a phenyl group into an apical position of the phosphorane. The fact that 2 and 3 form more slowly than 1 is consistent with an opposing depression of the general reactivity of the phosphorus atom as phenyl groups are replaced by alkoxy groups.¹⁴

Acknowledgments. This work was supported by grants from the National Science Foundation and the National Institutes of Health. C. L. Lerman thanks the National Institutes of Health for a training grant. We thank Dr. T. Wilson for the use of her chemiluminescence-monitoring system.

(14) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, N. Y., 1967.

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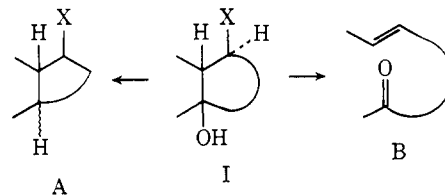
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Epoxynitrile Cyclization. A General Method of Ring Formation

Sir:

In an effort to find a method for the synthesis of cyclic structures of type I which are of interest, *inter alia*, as precursors of the related desoxy systems (*cf.* A *via* dehydration–reduction) or for use in the Wharton fragmentation¹ (I \rightarrow B), we have established that the base-



catalyzed isomerization of suitably constituted epoxynitriles (II \rightarrow III and/or IV) constitutes a new and quite general method of ring formation.

There are two important properties of the cyano group which make it the most generally useful of the several possibilities we have investigated. The high nucleophilicity consequent on the low acidity of the α -methy-

(1) P. S. Wharton and G. A. Hiegel, *J. Org. Chem.*, **30**, 3254 (1965).