## 1-Ethoxyphosphole 1-Oxide[1]

Sir:

We wish to report the synthesis of the very reactive heterocyclic phosphinic acid ester, 1-ethoxyphosphole 1-oxide (I).[2,3] The ester dimerizes too readily to allow its isolation, but it has been identified by its ultraviolet spectrum and by trapping it as a Diels–Alder adduct with cyclopentadiene. The synthesis from 1-ethoxy-2-phospholene 1-oxide[4] is given below.
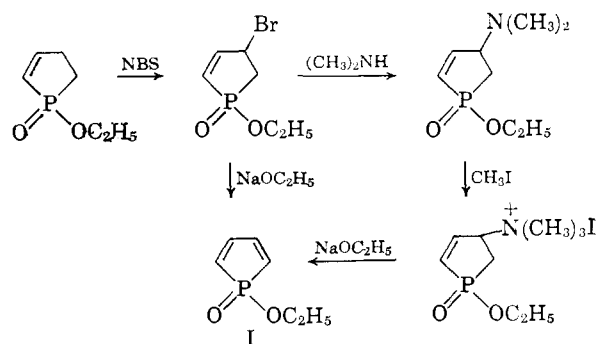
Both the bromide and the dimethylamino compounds are oils, and although the structures are reasonable on the basis of spectral evidence neither has been obtained pure. The quaternary ammonium iodide, crystallized from ethanol–acetone, melts sharply at 141–141.5°. *Anal.* Calcd. for $C_9H_{19}INO_2P$: C, 32.65; H, 5.78; I, 38.33; N, 4.23; P, 9.36. Found: C, 32.73; H, 5.87; I, 38.40; N, 4.27; P, 9.35. The iodide was converted in solution to the corresponding chloride by shaking in water with silver chloride; the resulting salt has an extinction coefficient of less than 2 above 240 mμ. When the quaternary ammonium salt in 0.0018–0.00046 M solution in ethanol is treated with sodium ethoxide (0.01 to 0.0017 M), it reacts at 25° to produce a compound to which the structure I has been assigned; λ_{max} 293 mμ (ϵ 1050); the rate constant for the elimination is roughly 10^2 l./mole sec. Compound I (identified by ultraviolet absorption and rate of dimerization) may also be prepared from the bromide, although here the approximate rate constant for its formation is only 3 l./mole sec. In ethanol, I undergoes a second-order reaction, with a rate constant at 25° of 0.55 l./mole sec., and concomitant disappearance of the absorption at 293 mμ. The rate of the dimerization is about the same in the presence of added potassium iodide, trimethylamine, acetic acid, or excess sodium ethoxide, although the reaction product decomposes in the presence of this last reagent. The phosphinate ester, I, is presumably saponified by aqueous alcoholic sodium hydroxide. The ultraviolet maximum of the product is shifted to 288 mμ. and the optical den-

(1) This research was supported by the National Science Foundation under Grant No. GP-2098.

(2) A number of substituted 1-phenylphospholes have previously been reported, but are relatively unreactive: F. C. Leavitt, T. A. Manuel, and F. Johnson, *J. Am. Chem. Soc.*, **81**, 3163 (1959); E. H. Braye and W. Hübel, *Chem. Ind.* (London), 1250 (1959); A. W. Johnson and J. C. Tebby, *J. Chem. Soc.*, 2126 (1961); J. B. Hendrickson, R. E. Spenger, and J. J. Sims, *Tetrahedron Letters*, 477 (1961); I. G. M. Campbell, R. C. Cookson, and M. B. Hocking, *Chem. Ind.* (London), 359 (1962); G. S. Reddy and C. D. Weis, *J. Org. Chem.*, **28**, 1822 (1963).

(3) Preliminary reports describe three 1-phenylphosphole 1-oxides; see R. E. Donadio, *Dissertation Abstr.*, **20**, 495 (1959); E. Howard and R. E. Donadio, Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1959, p. 100P.

(4) U. Hasserodt, K. Hunger, and F. Korte, *Tetrahedron*, **19**, 1563 (1963).

sity decreases more slowly; apparently the anion dimerizes less readily than the ester. With a 50-fold or 100-fold excess of cyclopentadiene in ethanol at 25°, I reacts with a second-order rate constant of approximately 0.05 l./mole sec. to produce the Diels–Alder adduct, II. This compound has been purified by column chromatography over Woelm grade 1 alumina with elution by chloroform, followed by molecular distillation. *Anal.* Calcd. for $C_{11}H_{15}O_2P$: C, 62.84; H, 7.19; P, 14.74. Found: C, 62.50; H, 7.45; P, 14.48. Principal infrared absorptions occur at 3.22 (shoulder), 3.32, 6.32, 7.50, 8.22 (broad), 9.65 (broad), 10.52 (broad), 11.72, 11.99, and 13.21 (broad) μ. The complicated n.m.r. spectrum of II is consistent with the structure assigned, although the stereochemistry is uncertain.

II
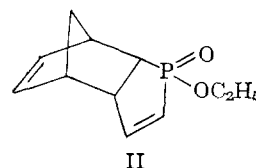
1-Ethoxyphosphole 1-oxide is similar in its absorption spectrum to thiophene dioxide,[5] (λ_{max} 289 mμ (ϵ 1230)), but is even more reactive than the latter. Research is continuing with the objective (among others) of preparing phosphinate esters with phosphorus at a bridge position of bicyclic systems.

(5) W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932 (1954).

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Aliphatic Cyanates

Sir:

We wish to report the first synthesis of aliphatic cyanates.[1,1a]

Reasonably stable cyanates, R—O—C≡N, can be prepared if (1) the aliphatic group, R, is sufficiently bulky to prevent facile trimerization, and (2) the carbonium ion, R$^+$, is of sufficiently high energy to minimize solvolysis (and rearrangement) of the cyanate under the conditions of synthesis.

Thus 1,4-dihydroxybicyclo[2.2.2]octane, 3-ethoxy-2,2,4,4-tetramethylcyclobutan-1-ol, or neopentyl alcohol, when treated successively with sodium hydride (or butyllithium) and cyanogen chloride, yielded the corresponding cyanates I (41%, m.p. 155–156°), II (30%, b.p. 63° (0.1 mm.)), and III (4.4%, b.p. 123° (185 mm.)).[2]

I   II   III
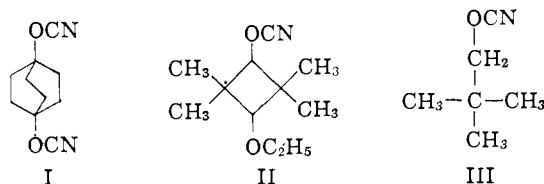
(1) The syntheses of several aromatic cyanates have recently been reported: (a) R. Stroh and H. Gerber, *Angew. Chem.*, **72**, 1000 (1960); (b) M. Hedayatullah and L. Denivelle, *Compt. rend.*, **256**, 4029 (1963); (c) D. Martin, *Angew. Chem., Intern. Ed. Engl.*, **3**, 311 (1964).

(1a) NOTE ADDED IN PROOF.—K. A. Jensen and A. Holm, *Acta Chem. Scand.*, **18**, 826 (1964), report the preparation of ethyl cyanate.

(2) Satisfactory elemental analyses and n.m.r. spectra for all new compounds were obtained.

These compounds exhibited intense C–O–C absorptions at *ca.* 1120 cm.$^{-1}$ and strong C≡N absorptions (doublets, probably because of Fermi resonance splittings) at 2220–2280 cm.$^{-1}$ of about one-fourth the intensity of that of the corresponding isocyanate.

cis-3-Ethoxy-2,2,4,4-tetramethylcyclobutan-1-ol (m.p. 56–57°) was prepared by successive reaction of *cis*-tetramethylcyclobutanediol with 1 mole of sodium hydride and excess ethyl bromide. 1,4-Dihydroxybicyclo[2.2.2]octane (m.p. 281–282°) was prepared by hydrolysis of 1,4-dichlorobicyclo[2.2.2]octane[3] at 215° in the presence of cuprous ion.

The dicyanate (I) rearranged to the diisocyanate (IV, m.p. 111.5–112) when treated with boron trifluoride etherate or when eluted with benzene through a column of acid-washed alumina. The product was identical (mixture melting point, infrared spectrum) with a sample prepared[4] by the Curtius reaction of bicyclo[2.2.2]octane-1,4-dicarboxylic acid.[5] This rearrangement is strongly reminiscent of the corresponding rearrangement of thiocyanates to isothiocyanates which has been shown to proceed by an ionization–recombination process.[6]

Compound I reacted with methanol to yield 1,4-dihydroxybicyclo[2.2.2]octane, dimethyl iminocarbonate, and trimethyl cyanurate. These interconversions verify the structural assignments.
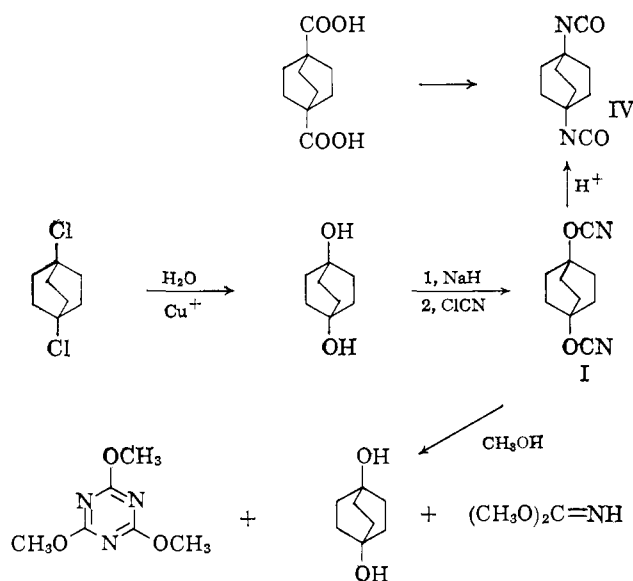
Preliminary results suggest that cyanates may have synthetic utility for the conversion of hydroxyl substituents to nitrogen functions using the sequence ROH → ROCN → RNCO. Details and further examples will appear in a subsequent paper.

(3) (a) R. Lukes and J. Langthaler, *Collection Czech. Chem. Commun.*, **24**, 2109 (1959); (b) J. C. Kauer and R. E. Benson, in preparation.

(4) J. C. Kauer, R. E. Benson, and G. W. Parshall, *J. Org. Chem.*, **30**, in press.

(5) J. D. Roberts, W. T. Moreland, and W. Frazer, *J. Am. Chem. Soc.*, **75**, 637 (1953).

(6) P. A. S. Smith and D. W. Emerson, *ibid.*, **82**, 3076 (1960); A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *ibid.*, **83**, 2729 (1961).

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1,5-Cyclooctadiene Complexes of Gold(I) and Gold(III)

Sir:

Recent reviews[1,2] note the fact that olefin complexes of gold have not been isolated, although an auric–styrene complex has been postulated as an unstable intermediate in the reduction of some gold complexes by styrene.[3] Both Au(III) and Au(I) olefin complexes might well be expected to exist, being isoelectronic with Pt(II) and Ag(I), respectively, which form well-defined olefin complexes.

The isolation of two gold complexes with 1,5-cyclooctadiene is now reported. Mixtures of chloroauric acid and olefins in ether were found to be decolorized by ultraviolet light prior to their reduction to gold metal. In the case of 1,5-cyclooctadiene, white crystals (I) were formed which were washed with ether and dried *in vacuo.* Compound I is insoluble in common organic solvents such as chloroform, acetone, and alcohols and slowly decomposes, particularly in the presence of light. *Anal.* Calcd. for $Au_2Cl_2C_8H_{12}$: Au, 68.7; C, 16.8; H, 2.1; Cl, 12.4. Found: Au, 67.3; C, 17.4; H, 2.4; Cl, 12.6. An infrared spectrum of I in KBr showed the following absorptions: 3000 (w), 2975 (w), 2950 (w), 2930 (m), 2880 (m), 2820 (m), 1490 (m), 1430 (m), 1340 (m), 1240 (m), 1130 (s), 1073 (s), 1000 (m), 990 (m), 885 (s), 865 (m), 800 (s), 725 (s), 650 (m), 610 (s), 575 (s), and 450 (s) cm.$^{-1}$. The same complex was formed from solutions containing isopropyl alcohol. Aurous chloride also forms I by warming with 1,5-cyclooctadiene and ethanol. At room temperature, however, and in the absence of ethanol and light, a small amount of another light-sensitive white solid was found (II), having a completely different infrared spectrum: 3000 (w), 2980 (m), 2940 (m), 2890 (w), 2880 (w), 1530 (m), 1520 (s), 1455 (s), 1410 (s), 1385 (m), 1245 (s), 1195 (m), 1045 (s), 1015 (s), 1000 (m), 930 (m), 895 (m), 815 (m), 775 (s), 590 (s), 530 (m), and 440 (m) cm.$^{-1}$.

Chloroauric acid, when warmed with 1,5-cyclooctadiene in solutions of ethers or glycol ethers, gave white solids identified as mixtures of I and II from their infrared spectra. *Anal.* (for one such mixture). Calcd. for $AuCl_3C_8H_{12}$: Au, 48.0; C, 23.4; H, 2.9; Cl, 25.9. Found: Au, 53.3; C, 22.3; H, 3.0; Cl, 21.7. A mixture of 22.4% $(AuCl)_2C_8H_{12}$ and 77.6% $AuCl_3C_8H_{12}$ would require: Au, 51.7; C, 22.0; H, 2.7; Cl, 22.9. II therefore appears to be $AuCl_3 \cdot C_8H_{12}$. Its formation from aurous chloride is not too surprising in view of the ready disproportionation of aurous to auric and gold metal. Presumably in the presence of ethanol, a reduction of II to I also occurs. II was found to have a slight solubility in carbon tetrachloride and a higher solubility in chloroform, though insufficient for identification by n.m.r. Both I and II gave 1,5-cyclooctadiene as the only volatile material on warming to 50° with triphenylphosphine in carbon tetrachloride. Heating I and II alone also gave 1,5-cyclooctadiene, the decomposition proceeding rapidly at 170 and 140°, respectively.

Two possibilities must be considered for the structure of each of these complexes: (1) a simple olefin

(1) M. A. Bennet, *Chem. Rev.*, **62**, 611 (1962).

(2) J. Chatt and R. G. Guy, *Advan. Inorg. Radiochem.*, **4**, 77 (1962).

(3) F. H. Brain, C. S. Gibson, J. A. J. Jarvis, R. F. Phillips, H. M. Powell, and A. Tyabji, *J. Chem. Soc.*, 3686 (1952).