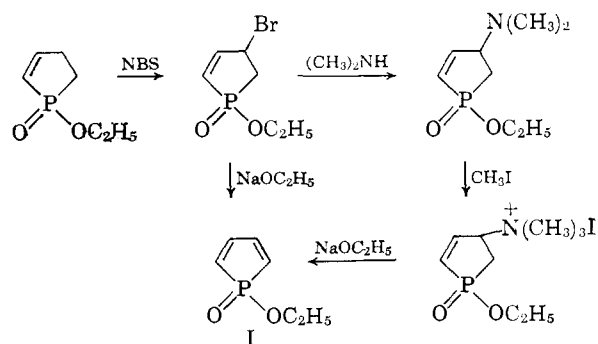


1-Ethoxyphosphole 1-Oxide<sup>1</sup>

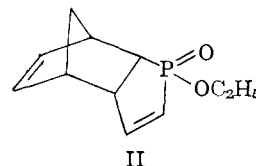
Sir:

We wish to report the synthesis of the very reactive heterocyclic phosphinic acid ester, 1-ethoxyphosphole 1-oxide (I).<sup>2,3</sup> 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<sup>4</sup> 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  $m\mu$ . 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;  $\lambda_{max}$  293  $m\mu$  ( $\epsilon$  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  $m\mu$ . 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  $m\mu$ , and the optical den-

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)  $\mu$ . The complicated n.m.r. spectrum of II is consistent with the structure assigned, although the stereochemistry is uncertain.



1-Ethoxyphosphole 1-oxide is similar in its absorption spectrum to thiophene dioxide,<sup>5</sup> ( $\lambda_{max}$  289  $m\mu$  ( $\epsilon$  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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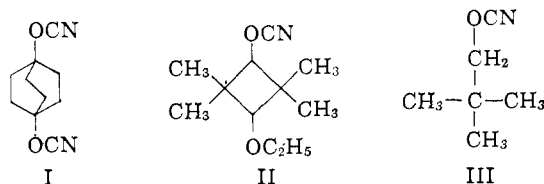
## Aliphatic Cyanates

Sir:

We wish to report the first synthesis of aliphatic cyanates.<sup>1,1a</sup>

Reasonably stable cyanates,  $R-O-C\equiv N$ , 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° (1.85 mm.)).<sup>2</sup>



(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.

(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. Sins, *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).