

Table I. Absorption Maxima of Contact and Solvent-Separated Fluorenyl Ion Pairs in Various Solvents

Counterion	Solvent	ϵ	λ_{\max}		Fraction of F ⁻ M ⁺ at 25°
			F ⁻ , M ⁺	F ⁻ M ⁺	
Li	Toluene	2.38	348	...	0.0
Li	Dioxane	2.20	346	...	0.0
Na			353	...	0.0
Li	Me-THF	4.6	347	373	0.25
Na			355	373	0.0
Li	THF	7.40	350	373	.80
Na			356	373	0.05
Cs			364	...	0.0
NBu ₄			368	...	0.0
Na	THF at -80°	12.2	...	373	1.00
Li	DME ^a	7.10	...	373	1.00
Na			359	373	.95
Cs			364	...	0.0
Li	Pyridine	12.3	...	373	1.00
Na			...	373	1.00

^a 1,2-Dimethoxyethane.

results listed in Table I. It is apparent from the last column in the table that at any temperature the Li salt always yields the highest fraction of solvent-separated ion pairs, whereas the poorly solvated Cs⁺ or NBu₄⁺ salt shows no evidence of solvent-separated pairs in THF even at -80°. Note also that the positions of the absorption bands are very little, if at all, affected by the polarity of the medium. Studies of spectra of F⁻, Li⁺ in mixtures of dioxane and THF indicate that the formation of F⁻||Li⁺ probably involves two molecules of THF.

Investigation of dianions of tetraphenylethylene, the dimeric dianions of 1,1-diphenylethylene, etc., again indicates existence of solvent-separated ion pairs in equilibrium with the contact ion pairs. Apparently, recent data⁷ relating to shifts in absorption spectra of carbanions with changing solvent polarity should be interpreted in terms of formation of two distinct ion pairs rather than in terms of a shift induced by the polarity of the medium.

Shifts in absorption bands to higher wave length at low temperature have also been observed for aromatic radical ions.⁸ The change was attributed to formation of free ions. However, reinvestigation of some of these spectra (e.g., sodium and lithium naphthalenide) in the presence of sodium tetraphenylboron again indicates that an equilibrium between contact and solvent-separated ion pairs is the most probable cause of the observed phenomena.

It may be anticipated that the reactivity of solvent-separated ion pairs approaches that of the free carbanions and this may account, at least partly, for the higher reaction rates observed in the more polar solvents. This problem is currently under investigation. The study of solvent-separated carbanion pairs will undoubtedly shed more light on the role of solvent in such reactions as electrophilic substitutions on saturated carbon, etc.

A more detailed description of these investigations will be published later.

(7) R. Waack and M. A. Doran, *J. Phys. Chem.*, **67**, 148 (1963); A. Streitwieser, Jr., and J. I. Brauman, *J. Am. Chem. Soc.*, **85**, 2633 (1963).

(8) G. J. Hoijtink and P. J. Zandstra, *Mol. Phys.*, **1**, 151 (1958); J. Dieleman, Thesis, Free University, Amsterdam, 1963.

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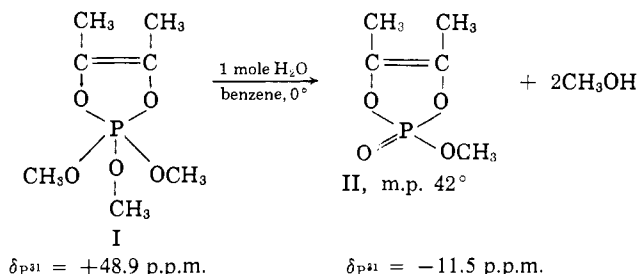
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Enediol Cyclic Phosphates¹

Sir:

Five-membered cyclic phosphates derived from 1,2-glycols and from *o*-dihydroxyarenes have received much attention²; however, enediol cyclic phosphates are virtually unknown.³ We report here a novel approach to this highly reactive type of phosphate.



A stirred solution of the biacetyl-trimethyl phosphite 1:1 adduct,⁴ I (19.97 g.) in benzene (20 ml.) was cooled in an ice-salt bath and treated with 1 mole equiv. of water (1.71 g.). The solution temperature went up from -4° to +18° within 2 min.; the solvent was immediately removed, under vacuum at 25°. The H¹ and P³¹ n.m.r. of the liquid residue showed the presence of the cyclic phosphate II and of dimethylphosphoacetoin^{2e,5} (V) in a 1:2.4 proportion; only traces of trimethyl phosphate (VII) were present. Distillation in a 24-in. spinning-band column gave acetoinediol cyclophosphate⁶ (II), b.p. 48-49° (0.06 mm.), *n*^{25D} 1.4310, in 30% yield. On standing at 20°, the liquid II crystallized to colorless needles, m.p. 42-43°, not changed by recrystallization from benzene-hexane; the properties of the crystals and of the liquid were identical. *Anal.* Calcd. for C₅H₉O₄P: C, 36.6; H, 5.5; P, 18.9. Found: C, 36.1; H, 5.6; P, 18.4.

(1) Investigation supported by Public Health Service Research Grant No. CA-04769-06 from the National Cancer Institute, and the National Science Foundation (G-19509).

(2) (a) The literature to 1961 was reviewed by H. G. Khorana, "Some Recent Developments in the Chemistry of Phosphate Esters of Biological Interest," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 3; (b) A. Todd, *Proc. Chem. Soc.*, 199 (1962); (c) G. M. Blackburn, J. S. Cohen, and A. Todd, *Tetrahedron Letters*, No. 39, 2873 (1964); (d) F. Covitz and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 1773 (1963); (e) F. Ramirez, A. V. Patwardhan, N. B. Desai, and S. R. Heller, *ibid.*, in press; (f) K. D. Berlin and M. Nagabhushanam, *Tetrahedron*, **20**, 2709 (1964); (g) J. Calderon and G. Moreno, *Anal. Real Soc. Espan. Fis. y Quim.*, **56B**, 603 (1960); (h) G. H. Birum, U. S. Patent 3,042,699 (1963); (i) W. Lanham, U. S. Patent 2,974,158 (1961); (j) T. Ukita, U. S. Patent 3,006,911 (1961).

(3) *Index Chemicus*, No. 5, 15, 46132 (1964), lists the title of a preliminary communication by V. A. Kukhtin and I. P. Gozman, *Dokl. Akad. Nauk USSR*, **158**, 157 (1964), claiming the preparation of an enediol cyclic phosphate by a procedure different from ours.

(4) The literature was reviewed by F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964).

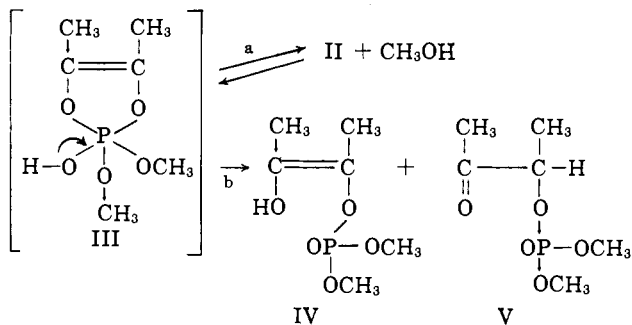
(5) $\delta_{P^{31}}$ in p.p.m.: dimethylphosphoacetoin, keto-V, +0.25; enol-V, +2.5; trimethyl phosphate, VII, -2.5.

(6) 4,5-Dimethyl-2-methoxy-2-oxo-1,3,2-dioxaphospholene.

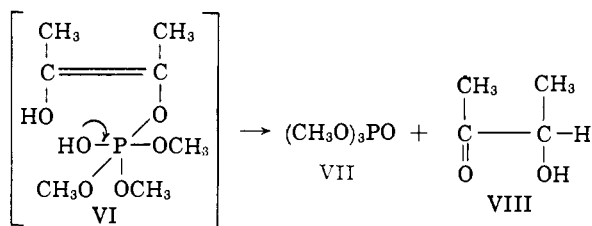
Spectral values are: H^1 n.m.r. (τ in p.p.m.): a 3 H^1 doublet, $J_{HP} = 11.5$ c.p.s., at 6.24 (CH_3O), and a 6 H^1 singlet at 8.10 (CH_3 on olefin); P^{31} n.m.r.^{2e} (neat, at 40.5 Mc.p.s., in p.p.m. vs. 85% H_3PO_4): a 1:3:3:1 quartet, $J_{PH} = 12$ c.p.s., at -11.5 ± 0.1 (Figure 1). Strong bands in the infrared spectrum (in CCl_4) were caused by the $P=O$ stretching vibrations (7.60 and 7.69 μ), by the $POCH_3$ stretchings (9.48 and 8.40 μ), and by the vinyl $C-O$ stretching (8.30 μ). Also, strong bands were found at 8.85, 10.10, and 11.20 μ .

The course of the hydrolysis of the oxyphosphorane I was quite sensitive to temperature and to the nature of the solvent. Thus, when the temperature was allowed to rise to the boiling point of the benzene solution, the amount of II was very small and the amount of trimethyl phosphate (VII) increased considerably. The hydrolysis was conveniently followed by H^1 and P^{31} n.m.r. spectroscopy; details will be given in the forthcoming paper.

The hydrolysis of the *unsaturated* oxyphosphorane I is a nucleophilic substitution⁷ at quintuply connected phosphorus, *proceeding with considerable preservation of the ring*. It is suggested that an unstable oxyphosphorane III results from this substitution. Evidence has been given⁸ for the operation of this mechanism in the hydrolysis of cyclic *saturated* oxyphosphoranes. III can collapse: (a) to the cyclic phosphate II and methanol; (b) to dimethylphosphoacetoin,⁵ enol-IV, and keto-V. Some of the open phosphate V isolated in the hydrolysis came from the reaction of methanol with the cyclic phosphate II (*vide infra*); however, some V was formed directly, *i.e.*, from III.



Probably, the trimethyl phosphate (VII) obtained in the hydrolysis of I did not result from a secondary reaction of methanol with open phosphate V.⁹ Compound VII could come from the unstable open oxy-



(7) SN_2 , SN_1 , or *via* an intermediate with hexacoordinated phosphorus; no information is available on this point, which is under study in this laboratory.

(8) (a) F. Ramirez, O. P. Madan, N. B. Desai, S. Meyerson, and E. M. Banas, *J. Am. Chem. Soc.*, **85**, 2681 (1963); (b) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963).

(9) Dimethylphosphoacetoin (V) and trimethyl phosphate are not affected by water in benzene solution under comparable conditions. The hydroxide ion catalyzed hydrolysis of V to acetoin and dimethylhydrogen phosphate in water is at least 2×10^6 times faster than that of trimethyl phosphate: F. Ramirez, B. Hansen, and N. B. Desai, *ibid.*, **84**, 4588 (1962).

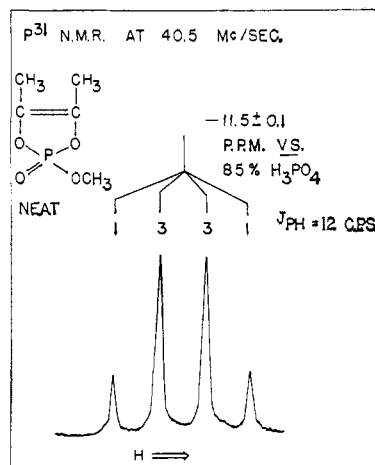
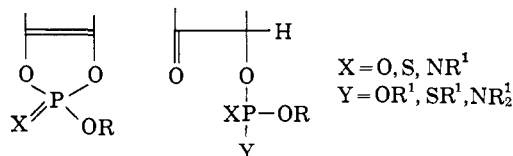


Figure 1.

phosphorane VI resulting from an initial attack of water on I, with ring opening. Since acetoin (VIII) is more acidic than methanol, the collapse of VI should proceed to give VII + VIII.

The cyclic phosphate II reacted with 1 mole equiv. of methanol at 20°. H^1 n.m.r. disclosed the initial formation of the enol-IV and keto-V forms of dimethylphosphoacetoin.^{2e,5} Finally, only the keto form remained. The methanolysis could involve the same intermediate III suggested for the hydrolysis of I, *i.e.*, the collapse of III to cyclic phosphate II is probably reversible. The addition of water to the phosphoryl group of five-membered cyclic phosphotriesters has been suggested⁸ to explain the rapid hydrolysis of the latter to cyclic phosphodiester.

The demonstration that both saturated^{2e,8} and unsaturated cyclic oxyphosphoranes can be transformed stepwise into cyclic and open phosphates holds promise as a method of synthesis of a variety of phosphate derivatives, for example



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The Abnormal Hydrolysis of Cyclic Diphosphonium Salts

Sir:

We wish to report the synthesis and basic hydrolysis of 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane dibromide (Ia, $X = Br$) to ethylenebis(diphenylphosphine) monoxide (II).

