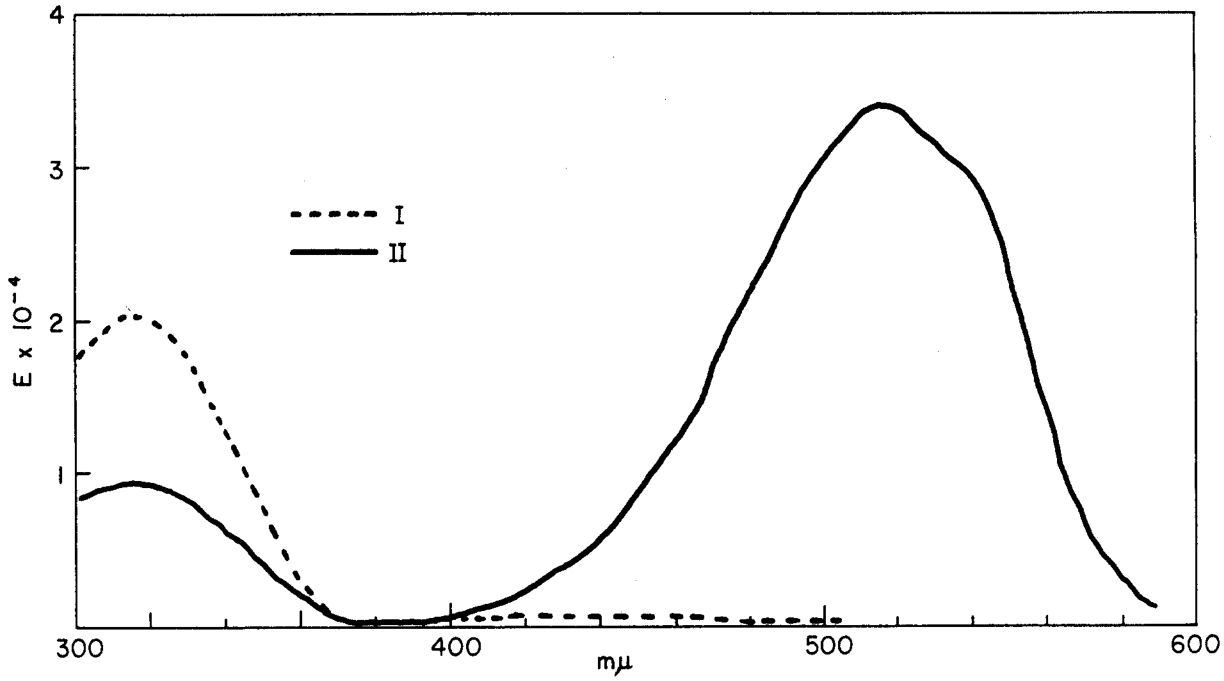

Fig. 1. Spectra of *p*-Phenylazo-*N*,*N*,*N*-trimethylammonium Methyl Sulfate and of the First Conjugate Acid of *p*-Dimethylaminoazobenzene.

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Reaction of Dialkyl Phosphites with Quinones[1]

Sir:

Dialkyl phosphites $(RO)_2P(O)H$ are known to add to unconjugated *olefins* in the presence of peroxides[2]. These have been regarded as radical chain processes propagated by the radical $(RO)_2\dot{P}(O)$. Benzaldehyde and *chloranil* combine photochemically with formation of the monobenzoate of tetrachlorohydroquinone[3]. For this reaction, Moore and Waters[3] postulated: (1) a photo-activation of the quinone to a diradical (or triplet state), $\cdot O\text{-}C_6Cl_4\text{-}O\text{-}O\cdot$, (2) a chain initiation step involving hydrogen abstraction from the aldehyde by the diradical and (3) a chain propagation sequence in which (a) the benzoyl radical added to unactivated quinone molecules giving aryloxy-radicals, $\cdot O\text{-}C_6Cl_4\text{-}O\text{-}COC_6H_5$ and (b) the latter reacted with benzaldehyde forming the product and regenerating benzoyl radicals.

During our studies on the mechanism of action of oxidizing agents on organophosphorus compounds,[4] we have related the two sets of observations described above. It was found that dialkyl phosphites and chloranil reacted smoothly with formation of the mono-dialkoxyphosphinyl derivatives of tetrachlorohydroquinone, I and II. The results obtained under several conditions are summarized in Table I.

TABLE I
Reaction of Dialkyl Phosphites, $(RO)_2P(O)H$ with Chloranil[a]

Temp., ° C.	Conditions	Time	Yield,[b] %	
			R=CH_3	R=C_2H_5
25	Dark	4.5 hr.	26(I)	24(II)
25	360–370 mμ[c]	4.5 hr.	64(I)[d]	66(II)[d]
25	Dark	3 days	100(I)	97(II)
100	Dark	1 hr.	95(I)	91(II)

[a] All reactions were carried out in an excess of freshly distilled dialkyl phosphites, in a nitrogen atmosphere. [b] Of dialkoxyphosphinyl derivatives of tetrachlorohydroquinone (I and II), based on chloranil. The material balance was unreacted chloranil. [c] Irradiation in quartz flask with a Hanovia 100-w Utility Model ultraviolet lamp and filter. [d] Quantitative yield in about 15–20 hr.

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(1) This work was carried out under Public Health Service Grant CY-3250.

(2) (a) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **79**, 1961 (1957); (b) W. E. Hanford and R. M. Joyce, U.S. Patent 2,478,390; (c) J. A. Bittles, Jr. and R. M. Joyce, U.S. Patent 2,559,754; (d) E. C. Ladd and M. P. Harvey, U.S. Patent 2,664,438; (e) N.V. de Bataafsche Petroleum Maatschappij, Brit. Patent 660,918; (f) A. R. Stiles and F. F. Rust, U.S. Patent, 2,724,718.

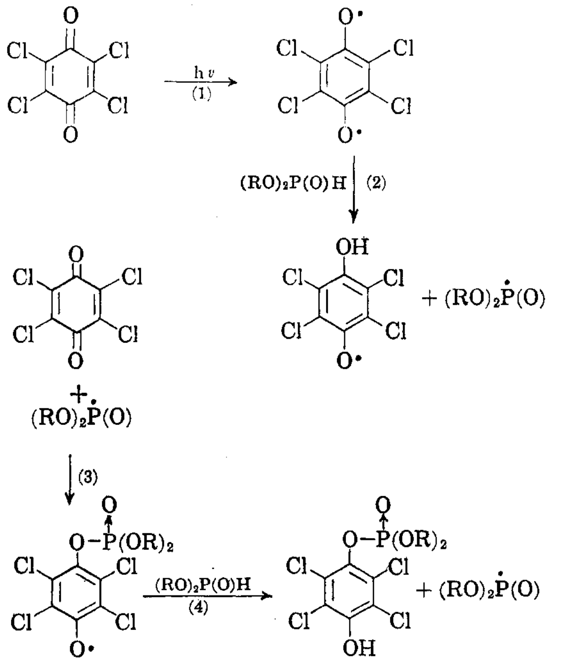
(3) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953).

(4) (a) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956); (b) F. Ramirez and S. Dershowitz *J. Org. Chem.* (in press).

The reactions were significantly accelerated by light of the wave-length range 360–370 mμ. In this wave-length range, the dialkyl phosphites are transparent while chloranil exhibits an absorption band. Hence, if the reactions are regarded as radical chain processes,[2,3] it seems likely that the photochemical effect is due to the excitation of the chloranil to its diradical, as shown in the following sequence. The photodissociation $(RO)_2P(O)H \rightarrow (RO)_2\dot{P}(O) + H\cdot$ cannot provide the required radicals at 360–370 mμ.

Logical extensions of this simple and practical method for the preparation of hydroxyarylalkyl phosphates, and the significance of the "dark" reactions, are under investigation.

Dimethyl-(4-hydroxy-2,3,5,6-tetrachlorophenyl) phosphate (I), m.p. 236–238° (from methanol) was soluble in aqueous sodium hydroxide solution and had a strong band at 7.98 μ (bonded phosphate $P \rightarrow O$)[4b]; calcd. for $C_8H_7O_5PCl_4$: C, 27.0; H, 2.0; found: C, 27.2; H, 2.2. Diethyl-(4-hydroxy-2,3,5,6-tetrachlorophenyl) phosphate (I), m.p. 180–181° (from cyclohexane) had a band at 7.92 μ; calcd. for $C_{10}H_{11}O_5PCl_4$: C, 31.3; H, 2.9; found: C, 31.5; H, 3.1. The phenolic phosphates I and II could also be made, but in low yields, by the rather complex reaction of tetrachlorohydroquinone and one equivalent of the dialkyl phosphorochloridate, in the presence of one equivalent of sodium alkoxide.



I, R=CH_3
II, R=C_2H_5

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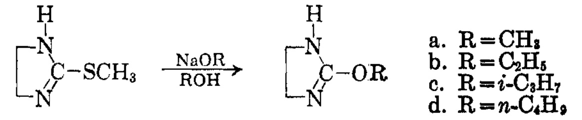
2-Alkoxyimidazolines

Sir:

We wish to report the conversion of 2-methylmercapto-2-imidazoline, "S-methylethylenethiourea," I, to 2-alkoxy-2-imidazolines II by treatment with sodium alkoxides in the corresponding alkanol. Although compound I and many related



I IIa–d

structures react with amines to give products in which the methylmercapto group has been replaced by an amino group,[1–3] no example could be found in the literature of the conversion of an alkylisothiourea such as I to an alkylisourea although this displacement reaction is of a type that might be anticipated.

Equimolar quantities of I and sodium methoxide after 18 hr. heating under reflux in methanol provided, along with 20% of ethyleneurea, 20–25% of 2-methoxy-2-imidazoline (IIa) as somewhat volatile, water-soluble, colorless crystals, m.p. 70–72°; λ_{max}^{Nujol} 3.15, 6.11, 6.59 μ; no selective absorption from 210–350 mμ in methanol and acid solution; pK_a 5.8, neut. equiv. 101; acid fumarate m.p. 136–139°.

Anal. Calcd, for $C_8H_{12}N_2O_5$: C, 44.44; H, 5.60; N, 12.96. Found: C, 44.70; H, 5.52; N, 13.27.

Picrate m.p. 168–170°.

Anal. Calcd. for $C_{10}H_{11}N_5O_8$: C, 36.48; H, 3.37; N, 21.27. Found: C, 36.53; H, 3.23; N, 20.86.

The free base IIa tended to become oily on standing; when it was pressed in potassium bromide disks for infrared study, extensive alterations in structure occurred as judged by the appearance of new bands at 5.8 and 5.9 μ. However, 2-methoxyimidazoline was recovered essentially unchanged after standing overnight both in normal sodium hydroxide and normal hydrochloric acid solution.

In a similar fashion I and sodium ethoxide led to 2-ethoxy-2-imidazoline (IIb, 13%), m.p. 48–50°; λ_{max}^{Nujol} 3.23, 6.14, 6.59, 6.73 μ; acid fumarate m.p. 123–125°.

Anal. Calcd. for $C_9H_{14}N_2O_5$: N, 12.17. Found: N (Kjeldahl), 12.16.

Prolonged heating of I with sodium isopropoxide gave IIc (11%), m.p. 65–67°, λ_{max}^{Nujol} 3.16, 6.16, 6.63, 6.74 μ; picrate m.p. 127–128°.

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[1] S. R. Aspinall and E. J. Bianco, *J. Am. Chem. Soc.*, 73, 602 (1951).

[2] C. K. Cain, U. S. Patent 2,742,481 (1956).

[3] A. F. McKay and D. L. Garmaise, *Can. J. Chem.*, 35, 8 (1957.)