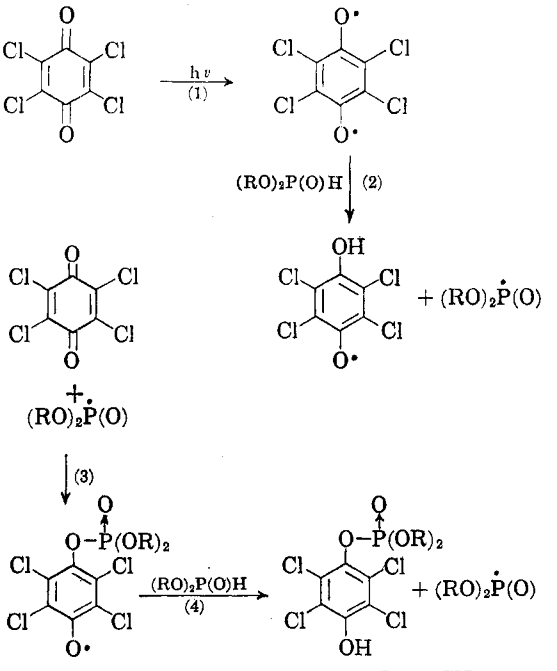
The reactions were significantly accelerated by light of the wave-length range 360–370 mμ. In this wave-length range, the dialkyl phosphites are transparent while chloranil exhibits an absorption band. Hence, if the reactions are regarded as radical chain processes,[2,3] it seems likely that the photochemical 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→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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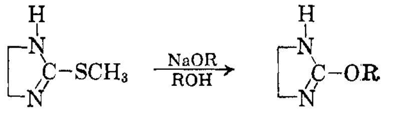
2-Alkoxyimidazolines

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compound I and many related structures react with amines to give products in which the methylmercapto group has been replaced by an amino group,[1–3] no example could be found in the literature of the conversion of an alkylisothiourea such as I to an alkylisourea although this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.



I

IIa–d

a. R=CH_3
b. R=C_2H_5
c. R=i-C_3H_7
d. R=n-C_4H_9

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).

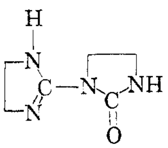
(3) A. F. McKay and D. L. Garmaise, *Can. J. Chem.*, 35, 8 (1957.)

Anal. Calcd. for $C_{12}H_{15}N_6O_8$: C, 40.34; H, 4.23; N, 19.60. Found: C, 40.62; H, 4.23; N, 19.36.

A major portion (66%) of unchanged I was recovered in this case. The n-butoxy derivative IId was obtained in 47% yield; m.p. 55–58°; $\lambda_{\max}^{\text{Nujol}}$ 3.15, 6.14, 6.58, 6.71 μ; acid fumarate m.p. 126–128°.

Anal. Calcd. for $C_{11}H_{18}N_2O_5$: N, 10.85. Found: N (Kjeldahl), 10.82.

From the preparations of IIb and IId, another product was isolated in low (10–15%) yield. A consideration of the analysis (Calcd. for $C_6H_{10}N_4O$: C, 46.74; H, 6.54; N, 36.34. Found: C, 46.77; H, 6.51; N, 36.31), infrared spectrum ($\lambda_{\max}^{\text{Nujol}}$ 3.00, 3.18, 5.82, 6.22, 6.64, 6.70 μ) and other properties of this relatively high melting (210°) monoacidic base (pK_a 6.0; neut. equiv. 160) has led to assignment of the 1-(2-imidazolin-2-yl)-2-imidazolidinone structure (III) to this compound.



III

Further studies on imidazolines II and III and related compounds are in progress.

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Concerning the Structure of C_{27}-Phthienoic Acid

Sir:

The physiologically active C_{27}-phthienoic acid, isolated[1] from tubercle bacillus, has previously been reported[2] to have the partial structure, 2-methyl-4,x-dialkyl-2-alkenoic acid. Investigators at Oxford[3] have degraded by oxidation the mixture of acids with more than twenty carbons from tubercle bacillus, and on this basis assigned the structure, 2,4,6-trimethyl-2-tetracosenoic acid, to a component of this mixture termed "mycolipenic acid," although there had not been presented evidence of isolation of any pure component from the mixture. More recently, there has been reported[4] synthesis of optically active 2,4,6-trimethyl-2-tetracosenoic acid and comparison with an acid isolated from tubercle bacillus, but limited data were included. Although we have shown[5] that the mixture of higher acids from tubercle bacillus contains thirteen or more components, of which at least nine are unsaturated, it has nevertheless been stated by Bailey, Polgar, and Robinson[6] that "there can be very little doubt but that C_{27}-phthienoic and mycolipenic acid are identical." We are aware of no experimental evidence in support of this idea and much to the contrary[5]; however, it has been accepted to the point that there has appeared a paper[7] entitled "Synthesis of Racemic Methyl Phthienoate." Since we now have evidence, which appears firm, that C_{27}-phthienoic acid is *not* 2,4,6-trimethyl-2-tetracosenoic acid, this preliminary report is submitted in the hope of preventing additional confusion in the literature.

Ozonolysis at −14° in chloroform solution, followed by oxidation with silver oxide, of 2,4-dimethyl-2-docosenoic acid gave 2-methyleicosanoic acid in 60% yield and a 40% yield of neutral material which was shown to be about 3 parts 2-eicosanone and 1 part 2-eicosanol. Similar ozonolysis, in two lots, of a total of 743 mg. of pure C_{27}-phthienoic acid yielded 282 mg. of a crystalline C_{24} acid[8], m.p. 39–43°, $[\alpha]_D^{21}$ +4.96°, eq. wt. 364. In gas phase chromatography on silicone grease at 245° of the methyl ester of this acid, retention time was 6 min. 15 sec. Retention time of 6 min. 18 sec. for methyl 2,4-dimethyldocosanoate confirms the C_{27} formula for C_{27}-phthienoic acid. Chromatography on alumina of the neutral material from ozonolysis (total 302 mg.) yielded three crystalline ketone fractions and one alcohol fraction (infrared characterization), eluted in that order and weighing respectively 63, 28, 21 and 59 mg. Gas phase chromatography of the ketone fractions (numbered in order of elution from alumina), and of certain synthetic ketones, yielded retention times recorded in Table I.

Retention times in Table I, coupled with analyses for C, H, and O, show that "ketone-1" is a dioxygen

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[1] J. Cason and G. Sumrell, *J. Biol. Chem.*, **192**, 405 (1951).

[2] (a) J. Cason, N. K. Freeman, and G. Sumrell, *J. Biol. Chem.*, **192**, 415 (1951); (b) J. Cason and C. F. Allen, *J. Biol. Chem.*, **205**, 449 (1953).

[3] N. Polgar, *J. Chem. Soc.*, 1008 (1954).

[4] D. J. Millin and N. Polgar, *Proc. Chem. Soc.*, 122 (1957).

[5] J. Cason and G. J. Fonken, *J. Biol. Chem.*, **220**, 391 (1956); C. F. Allen and J. Cason, *J. Biol. Chem.*, **220**, 407 (1956).

[6] A. S. Bailey, N. Polgar, and R. Robinson, *J. Chem. Soc.*, 3031 (1953).

[7] C. Collin-Asselineau, J. Asselineau, S. Ställberg-Stenhagen, and E. Stenhagen, *Acta Chem. Scand.* **10**, 478 (1956).

[8] Polgar[3] reported data only for the crude acid from permanganate oxidation, m.p. 34–35°, $[\alpha]_D^{16}$ +7.1°; for synthetic (+)-2,4-dimethyldocosanoic acid, after purification *via* the quinine salt, $[\alpha]_D^{22}$ +7.4°, no m.p. reported [G. I. Fray and N. Polgar, *J. Chem. Soc.*, 2036 (1956)].