Dialkyl β-Chlorovinyl Phosphates. A Proposed Scheme to Predict the Products of the Action of Base with Dialkyl α-Hydroxyphosphonic Esters

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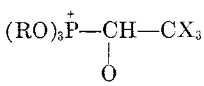
The reaction of α-halo aldehydes with phosphorus esters was originally believed to proceed by the Michaelis-Arbuzov reaction to yield compounds of structure I.[1] It now has been shown that the reaction products are II, the isomeric dialkyl β-halovinyl phosphates.[2]

X = Halogen or H

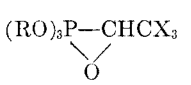
$(RO)_2P(O)CX_2CHO$ I

$(RO)_2P(O)OCH = CX_2$ II



$(RO)_3\overset{+}{P}-\underset{\underset{-}{O}}{CH}-CX_3$

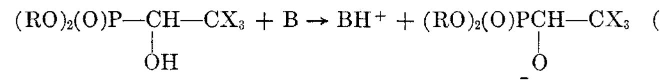
III



$(RO)_3\overset{\diagdown\quad\diagup}{P-CHCX_3}\ O$

IV

Kharasch and Bengelsdorf[2f] have proposed that the reaction proceeds by a nucleophilic attack of the phosphorus atom on the carbonyl carbon atom to give III; this is followed by a further nucleophilic attack of the negatively-charged oxygen atom on the neighboring positively-charged phosphorus atom. A halide ion is concomitantly displaced to yield the vinyl ester, II.



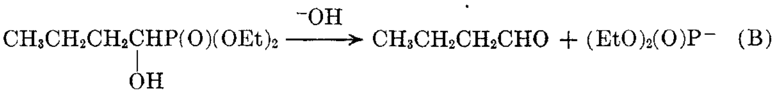
$$(RO)_2(O)P-\underset{OH}{CH}-CX_3 + B \rightarrow BH^+ + (RO)_2(O)P\underset{\underset{-}{O}}{CH}-CX_3 \quad (A)$$

V VI

Allen and Johnson[2e] have proposed a three-membered ring structure, IV, as a reaction intermediate. The difficulty with IV is that the phosphorus atom forms five *singly*-covalent bonds, of which four are to oxygen atoms; this represents a less likely situation in organophosphorus chemistry than does III. An even less probable anion-cation addition complex has been suggested by Perkow, *et al.*[2d] The experimental results of the latter can readily be correlated by assuming III as the intermediate.

In addition, a structure similar to III, also explains the basic dehydrohalogenation of dialkyl α-hydroxy-β-halophosphonates, V, to yield II. Eqn. A reveals that the removal of a proton from V, gives an intermediate VI, which can also undergo the rearrangement to the vinyl ester, as does III.

The question now arises as to whether the rearrangement of α-hydroxyphosphonic esters to dialkyl vinyl phosphates, in the presence of base, is a general reaction. It is here proposed that the course of the reaction will depend upon the nature of the group —X in $(RO)_2(O)PCHOHCX_3$. If —X is an atom, or group of atoms, capable of leaving as an anion, then the rearrangement to a vinyl phosphate should occur. If —X is not such a group, then the α-hydroxyphosphonate should revert to the original starting materials, aldehyde and dialkyl phosphonate. Mosher[3] has already shown that, under alkaline conditions, the reversion of α-hydroxyphosphonates to the aldehyde and dialkyl phosphonate is quantitative. For example,



$$CH_3CH_2CH_2\underset{OH}{CH}P(O)(OEt)_2 \xrightarrow{^-OH} CH_3CH_2CH_2CHO + (EtO)_2(O)P^- \quad (B)$$

For the vinyl rearrangement to occur, in this case, a hydride ion would have to be released; such a process is energetically unfavorable.

In addition to the preparation of diethyl β-chlorovinylphosphate, which now appears in the literature[2b,e] dibutyl β-chlorovinyl phosphate was synthesized; like diethyl[2f] and dimethyl β,β-dichlorovinyl phosphate,[4] it reacted slowly with 2,4-dinitrophenylhydrazine to give the 2,4-dinitrophenylosazone of glyoxal.

EXPERIMENTAL

Materials. Dichloroacetaldehyde was prepared from the amorphous polymeric Westvaco material by heating it with sulfamic acid; the aldehyde distilled at 87–88°. Trialkyl phosphites were obtained from the Virginia-Carolina Chemical Corporation and were distilled before use. Triethyl phosphite, b.p. 83–85°/20, n_D^{20} 1.4130; tributyl phosphite, b.p. 78–82°/0.5, n_D^{20} 1.4318.

Tributyl phosphite—Dichloroacetaldehyde. Tributyl phosphite (23.3 g., 0.092 mole) was slowly added to dichloroacetaldehyde (11.29 g., 0.1 mole) immersed in an ice-bath

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[1] (a) Bengelsdorf, Ph.D. dissertation, University of Chicago, 1951; (b) Arbuzov and Alimov, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 530 (1951); (c) Ladd and Harvey, U. S. Patent 2,597,938 (1952); (d) Ladd and Harvey, U. S. Patent 2,631,162 (1953); (e) Bengelsdorf, 124th National Meeting American Chemical Society, Chicago, Illinois, 1953, page 10-O.

[2] (a) Perkow, *Chem. Ber.*, **87**, 755 (1954); (b) Barthel, Alexander, Giang, and Hall, *J. Am. Chem. Soc.*, **77**, 2424 (1955); (c) Lorenz, Henglein, and Schrader, *J. Am. Chem. Soc.*, **77**, 2554 (1955); (d) Perkow, Krockow, and Knoevenagel, *Chem. Ber.*, **88**, 662 (1955); (e) Allen and Johnson, *J. Am. Chem. Soc.*, **77**, 2871 (1955); (f) Kharasch and Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

[3] R. A. Mosher, Ph.D. dissertation, University of Chicago, 1950. The reaction of a dialkyl phosphonate with an aliphatic or aromatic aldehyde to give the corresponding dialkyl α-hydroxyphosphonates, V, was first studied by Mosher and by Craig and Hester, U. S. Patent 2,485,573, October 25, 1949; *Chem. Abstr.*, **44**, 3005h (1950).

[4] Mattson, Spillane, and Pearce, *J. Agr. Food Chem.*, **3**, 319 (1955).

to moderate the vigorous reaction. The reaction then was heated to evolve butyl chloride. Distillation of the residue gave dibutyl β-chlorovinyl phosphate (b.p. 96°/0.5, n_{D}^{25} 1.4392, 85% yield).

Anal. Calc'd for $C_{10}H_{20}ClO_4P$: Cl, 13.0, P, 11.4. Found: Cl, 12.8; P, 11.3.

A mixture of 0.5 g. of the ester, 1 g. of 2,4-dinitrophenylhydrazine, 2 ml. of conc'd hydrochloric acid, and 25 ml. of ethanol were refluxed for 10 minutes, filtered, and the filtrate was allowed to stand. Dark violet-red prisms of the 2,4-dinitrophenylhydrazine (m.p. 196–197° dec., lit. m.p. 198° dec.) were deposited. The filtrate, after removal of the unreacted hydrazine, then deposited a small amount of orange-red crystals of glyoxal 2,4-dinitrophenylosazone, m.p. 324° dec., lit. m.p. 328°. Both the derivative and an authentic osazone sample give the same intense royal-blue color when treated with ethanolic sodium hydroxide.

Triethyl phosphite—Dichloroacetaldehyde. Diethyl β-chlorovinylphosphate was prepared as described above.[2b,e] B.p. 61°/0.5, 112°/8, n_{D}^{25} 1.4342, 66% yield.

Anal. Calc'd for $C_6H_{12}ClO_4P$: Cl, 16.5; P, 14.4. Found: Cl, 15.9; P, 14.1.

The ester gives a positive Tollens' and Beilstein's test. It does not react with ferric ion or Schiff's reagent; after prolonged boiling with Fehling's solution, a bright purple-red precipitate is deposited, quite unlike the usual brick-red cuprous oxide.

The infrared spectrum, as determined in a Perkin-Elmer Model 21 with a 0.0494-mm. cell, revealed strong olefinic absorption bands at 3.26 and 6.11μ. Absorption in the 10.4μ region, and the lack of an absorption in the 14μ region, indicates, but does not verify, that the vinyl ester is of the *trans* configuration.

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Color Test. Part III. A Color Test for 2-Methylchromones with *m*-Dinitrobenzene and Its Significance for Taxonomic Work

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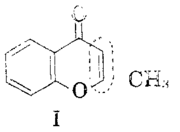
Lately, it has been pointed out[1] that the power of 2-methylchromones to condense with aromatic aldehydes may be explained by considering these chromones as vinylogs of acetophenone (*cf.* I). The



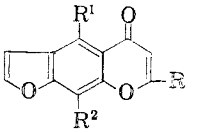
I

application of this principle to the chemistry of γ-pyrones has now led to the discovery of a most sensitive color test. Bittó[2] has shown that an alcoholic solution containing acetophenone (or acetone) and *m*-dinitrobenzene gives an intense violet-red color on addition of alkali. We found that a deep violet color was developed when the test was applied to 2-methylchromones, and also to 2,6-dimethylpyrone which may be regarded as a vinylog of acetone. The importance of the methyl group in position 2 for this color test is stressed, since chromones (γ-pyrones) which have no methyl group in this position do not give the color. This test, however, is frequently inconclusive in the case of 2-methylchromones containing a phenolic hydroxyl group; this may be due to the fact that many of these chromones dissolve in alkali with color. Demethylated khellin (IIc) a yellow substance for example, dissolves in alkali with a reddish-brown color.[3] One can overcome this difficulty by methylation or acetylation of the phenolic groups before carrying out the test. This new micro test may be regarded as supplementary to the color test described by Schönberg and Sina[4] but it is more sensitive and quicker.

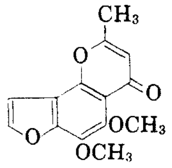
TABLE I

Compounds Giving a Positive Test

2,6-Dimethylpyrone.
2-Methylchromone.
2,6-Dimethylchromone.
2,3,7-Trimethylchromone.
2-Methyl-1,4-α-naphthopyrone.
Visnagin (IIa).
Khellin (IIb).
iso-Khellin (III).
5,7-Dimethoxy-6-formyl-2-methylchromone.
5-Acetoxy-7-methoxy-2,6-dimethylchromone (eugenitin acetate).



IIa: $R = CH_3$; $R^1 = OCH_3$; $R^2 = H$
IIb: $R = CH_3$; $R^1 = R^2{=}OCH_3$
IIc: $R = CH_3$; $R^1 = R^2{=}OH$
IId: $R = CH_2OH$; $R^1 = OCH_3$; $R^2 = H$



III

TABLE II

Compounds Giving a Negative Test

Benzalacetophenone.
2,6-Diphenylpyrone.
3-Methylchromone.
Flavone.
α-Naphthoflavone.
2-Styrylchromone.
2-Styrylvisnagin.
Khellol (IId).
Coumarin.
Xanthotoxin.
Imperatorin.

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[1] Schönberg, Sidky, and Aziz, *J. Am. Chem. Soc.*, **76**, 5115 (1954).

[2] von Bittó, *Ann.* **269**, 377 (1892).

[3] Schönberg and Sina, *J. Am. Chem. Soc.*, **72**, 3396 (1950).

[4] Schönberg and Sina, *J. Chem. Soc.*, 3344 (1950).