Tetrahedron, 1958, Vol. 4, pp. 197-200. Pergamon Press Ltd., London

NOTES

Esters containing phosphorus—XVI*

A new colour reaction for the detection and estimation of dialkyl phosphites

(*Received* 26 *June* 1958)

THE formation of a colour on treatment of a solution of *m*-dinitrobenzene in acetone with alkali was first observed by Janovsky.[1] This reaction has been extended by several workers[2,3,4] to a wide range of aromatic nitro-compounds and of compounds containing the >CH—CO— grouping, and has many uses both as a qualitative test[5] and for the quantitative analysis of, for instance, aromatic nitro-compounds,[6] creatinine,[7] digitoxin[8] and various carbonyl compounds.[9] During the course of our investigations into certain aspects of the chemistry of peroxidase and of phosphorous esters,[10] we have recently observed that acetone can be replaced by one of several dialkyl phosphites, when a blue or purple colour is usually obtained. This affords a further illustration of the similarity of dialkyl phosphites to carbonyl compounds, demonstrated for example in recent years by the many instances of base-catalysed addition of phosphites to carbonyl functions, a reaction formally analogous to the aldol condensation.

Further investigation has shown us that the colours are produced most rapidly with dialkyl phosphites in aqueous sodium hydroxide, but that they then become brown and soon fade. It has been found convenient to carry out the reaction in a saturated solution of sodium bicarbonate, when dialkyl phosphites give fairly stable colours, in contrast to acetone and similar compounds, which give little or no coloration under these conditions. A representative selection of dialkyl phosphites ($[RO]_2POH$, R = methyl, ethyl, *iso*propyl, *tert.*-butyl, benzyl, *cyclo*hexyl, 1-ethylpropyl, 1-carbethoxyethyl, 3-methylbutyl or 1:3-dimethylbutyl) has been examined; all have given positive reactions. A wide variety of substituted *m*-dinitrobenzenes may be used, but the reagent of choice is 3:5-dinitrobenzoic acid, which has the advantage of solubility in aqueous media and the property of intense colour formation. The test is sensitive to a phosphite concentration of 1 : 10,000.

Most other classes of organo-phosphorus compounds do not give this reaction, but substances (such as diethyl α-hydroxyethylphosphonate, diethyl phosphorochloridite, and tetraethyl pyrophosphite), which readily undergo cleavage to dialkyl phosphites on treatment with alkali, can be detected. Diethyl phosphorocyanidate gives a brown solution similar to that produced by the action of inorganic cyanide on 3:5-dinitrobenzoic acid. The reaction is also given by a number of compounds (*cyclo*pentadiene, pyrrole, nitromethane, etc.) which form anions under alkaline conditions, but the colorations are usually quite unlike the blue or purple hues formed by phosphites.

The reaction can be used for the quantitative determination of dialkyl phosphites by a colorimetric method. The following procedure combines simplicity of apparatus and operation with reasonable accuracy. The sample of phosphite (1 mg or more) is diluted with water to 1·0 ml, and

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* Paper XV. B. B. Hunt and B. C. Saunders, *J. Chem. Soc.* 2413 (1957).

[1] J. V. Janovsky and L. Erb, *Ber. Dtsch. Chem. Ges.* **19**, 2155 (1886).

[2] M. J. Newlands and F. Wild, *J. Chem. Soc.* 3686 (1956).

[3] F. Reitzenstein and G. Stamm, *J. prakt. Chem.* **81**, 167 (1910).

[4] T. Canbäck, *Farm. Revy* **48**, 217, 234, 249 (1949).

[5] F. G. Mann and B. C. Saunders, *Practical Organic Chemistry* (3rd Ed.) pp. 216, 261, 293. Longmans, Green, London (1952).

[6] F. L. English, *Analyt. Chem.* **20**, 745 (1948).

[7] J. J. Carr, *Analyt. Chem.* **25**, 1859 (1953).

[8] T. Canbäck, *Svensk Farm. Tid.* **51**, 261 (1947).

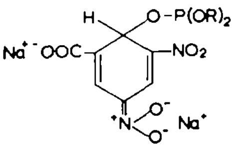
[9] T. Canbäck, *Farm. Revy* **46**, 802 (1947).

[10] B. C. Saunders and B. P. Stark, *Tetrahedron* **4**, 169 (1958).

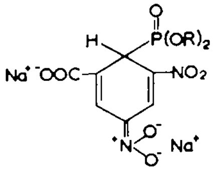
a solution of 3:5-dinitrobenzoic acid (0·5 gm) in saturated aqueous sodium bicarbonate (10 ml) is added with shaking. After a suitable interval (40 min-3 hr) the solution is compared in a visual colorimeter with a standard solution containing an arbitrary amount of phosphite. The amount of phosphite present in the sample is obtained by comparison of the colorimeter reading with a calibration curve of readings from tubes containing known amounts of phosphite, measured against the same standard after the same time. Modifications may sometimes be necessary for individual phosphites.

The coloration of dialkyl phosphites with 3:5-dinitrobenzoic acid in the presence of alkali is not due to hydrolysis products (e.g. monoalkyl phosphite) since sodium monobenzyl phosphite fails to respond to the test, whereas diphenylphosphinous acid (Ph_2POH, which is incapable of undergoing hydrolysis) gives a positive reaction.

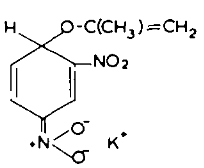
The nature of the coloured compounds formed by dialkyl phosphites is not yet clear. Since the reaction can be carried out in the presence of only traces of water if a strong organic base be substituted for alkali, it seems possible that compounds of the types (I) or (II) may be present, analogous to the quinonoid adducts (III) described by Gitis[11] in his work on the reaction with acetone.



(I)



(II)



(III)

A reaction rather similar to the Janovsky test is that in which sodium iodide is added to a solution of an aromatic nitro-compound in acetone or certain other solvents.[12] We have now found that in this test also, acetone can be replaced by a dialkyl phosphite; the colours obtained are similar to those produced in the presence of acetone. As in the case of acetone, the colours are bleached by the addition of water; free iodine is apparently not present.

Finally it may be mentioned that addition of dilute alkali to a mixture of a dialkyl phosphite and aqueous sodium nitroprusside gives generally a red or orange colour. Similar colours are given by acetone and related compounds.[4]

Further investigations into the mechanism, specificity and uses of these reactions are proceeding.

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[11] S. S. Gitis, *Zh. obshch khim.* **27**, 1894 (1957).
[12] R. W. Shellman, *J. Org. Chem.* **22**, 818 (1957).

Esters containing phosphorus—XVII*

Detection and estimation of dialkyl phosphites in the presence of trialkyl phosphites

(*Received* 15 *August* 1958)

WE have recently recorded[1] that dialkyl phosphites and certain related compounds produce intense purple colours with alkaline solutions of 3:5-dinitrobenzoic acid.† Most trialkyl phosphites also give colours, probably because they undergo some dealkylation under these conditions. It has been

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* Paper XVI: B. C. Saunders and B. P. Stark, *Tetrahedron* **4**, 197 (1958).

† It is considered convenient to designate the reaction involving colorations with 3:5-dinitrobenzoic acid under alkaline conditions as the 3:5-DB test.

[1] B. C. Saunders and B. P. Stark, *Tetrahedron* In press (1958).