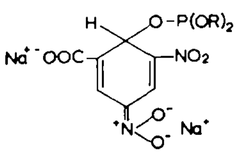
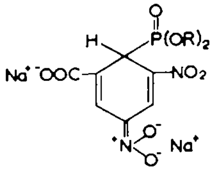
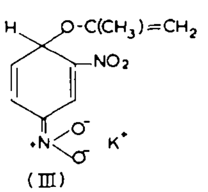
a solution of 3:5-dinitrobenzoic acid (0·5 gm) in saturated aqueous sodium bicarbonate (10 ml) is added with shaking. After a suitable interval (40 min–3 hr) the solution is compared in a visual colorimeter with a standard solution containing an arbitrary amount of phosphite. The amount of phosphite 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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University Chemical Laboratory
Lensfield Road
Cambridge, England

B. C. SAUNDERS
B. P. STARK

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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

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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).

found possible, however, to devise a method for the estimation of dialkyl and trialkyl phosphites in the presence of one another. The basis of this method is that the trialkyl esters react quantitatively with iodine to form dialkyl phosphoroiodidates (which do not respond to the 3:5-DB test), whereas the dialkyl esters do not react appreciably.[2] Thus, a rough estimation of the amount of trialkyl phosphite present can be obtained by titration with iodine. Addition of alkaline 3:5-dinitrobenzoate to the mixture thus obtained then permits colorimetric determination of the dialkyl phosphite. The method given below has been found suitable with mixtures of triethyl and diethyl phosphites, and is clearly capable of extension to other esters.

During our survey of the applicability of the 3:5-DB test to a wide range of compounds of different types, we have observed that a few inorganic anions give marked colours with 3:5-dinitrobenzoic acid. In 10 per cent sodium hydroxide solution, the most pronounced colours are those given by cyanide (red-brown, stable to acids), arsenite (red, unstable to acids), and sulphite (red, unstable to acids). Inorganic sulphides, persulphates, dithionites, and iodides, which give less distinct colours, interfere. Most other inorganic anions have negative reactions. Thiosulphates do not respond to the test, except after preliminary treatment with mineral acid (to liberate the sulphite) and then with alkali. Arsenite and sulphite can be distinguished by virtue of the fact that the latter, but not the former, gives a pink or red colour with 3:5-dinitrobenzoic acid in aqueous sodium bicarbonate solution, or in aqueous ammonia-ammonium sulphate solution (cf. Rothera's test for acetoacetate).[3] It is worthy of note that Feigl[4] has used potassium cyanide in acidic solution as a reagent for the detection of *m*-dinitro-compounds.

As an illustration of the use of this reaction with inorganic anions, we present a colorimetric method for the estimation of inorganic arsenite, and a method for the detection of arsenite on paper chromatograms.

The 3:5-DB test with inorganic ions may be summarised as follows. Preliminary work shows that the test may be of some use in the detection of cyanide, arsenite, and sulphite (see Table 1).

TABLE 1

Anion	3:5-dinitrobenzoic acid in 10% NaOH	3:5-DB test in $NH_3/(NH_4)_2SO_4$
Cyanide	Red-brown, stable to mineral acids.	Red-brown
Sulphite	Red, becoming faint yellow on addition of mineral acid.	Pink
Arsenite	Red, becoming weak yellow on addition of mineral acid.	No colour
Sulphide	Deep red, soon succeeded by brown and then yellow colour, with yellow precipitate. Bleached by acids, with evolution of H_2S.	brown-yellow
Persulphate	Slightly yellower than control test. Yellow in acid.	Very faint yellow
Dithionite	Yellower than control; yellow precipitate. Faint yellow in acid.	Pink
Iodide	Slightly more yellow than control; weak yellow in acid.	Weak yellow
Most other anions tested	No change in alkali.	No change.

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[2] H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.* 921 (1945).
[3] A. C. H. Rothera, *J. Physiol.* 37, 491 (1908).
[4] F. Feigl, *Spot Tests* Vol. II, p. 125. Elsevier (1954).

EXPERIMENTAL

Estimation of diethyl phosphite in the presence of triethyl phosphite

The mixture is dissolved in ether (2 ml), and the solution cooled to 0°; a solution of iodine (10% in ether) is now added until a faint yellow colour persists. The volume of iodine solution added is noted. The mixture is shaken at room temperature for 45 min with a solution of 3:5-dinitrobenzoic acid (0·5 g) in saturated aqueous sodium bicarbonate solution (10 ml). 5 ml of the aqueous layer are then diluted to 20 ml, the diluted solution left for a further 10 min, and then compared with an arbitrary standard as previously described.[1] The colorimeter reading is compared with a calibration curve as before,[1] to give the concentration of diethyl phosphite.

Colorimetric estimation of inorganic arsenite

The procedure necessary is essentially the same as that previously described for dialkyl phosphites,[1] except that the 3:5-dinitrobenzoic acid should be dissolved in 10 per cent sodium hydroxide solution rather than in sodium bicarbonate. The method is suitable for the estimation of 10 mg or more of sodium arsenite; the dilution limit is ca. 1:200.

Detection of inorganic arsenites on paper chromatograms

The arsenite (ca. 50–100 μg) is applied to Whatman No. 1 filter paper, and an ascending chromatogram run overnight, with butan-1-ol saturated with 20 per cent aqueous acetic acid as solvent.[5] The paper is then dried and sprayed with a 5 per cent solution of 3:5-dinitrobenzoic acid in 10 per cent aqueous sodium hydroxide solution. Red spots (R_F 0·43) appear after a few minutes at room temperature, or more rapidly on warming.

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B. C. SAUNDERS
B. P. STARK

University Chemical Laboratory
Lensfield Road
Cambridge, England

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[5] M. Lederer, Unpublished experiments, quoted in E. Lederer and M. Lederer, *Chromatography* p. 339. Elsevier (1953).