

TABLE II

R	Yield, % ^a	M.p., °C.	Formula	Phosphorus, %		Chlorine, %	
				Calcd.	Found	Calcd.	Found
CH ₃	54	78-80	C ₄ H ₈ Cl ₃ O ₄ P	12.03	12.11	41.32	41.86
C ₂ H ₅	74	55-56	C ₆ H ₁₂ Cl ₃ O ₄ P	10.93	10.96	37.52	37.20
C ₃ H ₇	56	68-70.5	C ₈ H ₁₆ Cl ₃ O ₄ P	10.01	10.00	34.37	34.55
<i>i</i> -C ₃ H ₇	54	105-106.5	C ₈ H ₁₆ Cl ₃ O ₄ P	10.01	10.12	34.37	34.24
C ₄ H ₉	Not purified	Liquid <i>n</i> _D ²⁵ 1.4718	C ₁₀ H ₂₀ Cl ₃ O ₄ P	9.07	9.17	31.14	31.83

duced. The entire mass solidified, giving a quantitative yield of crude product. The crude product, after being crystallized several times from petroleum ether containing a little benzene, melted at 78-80°.

Other dialkyl esters were prepared in the same manner. Their properties, yields and analyses are given in Table II.

(9) Yield of recrystallized ester based on dialkyl hydrogen phosphite, Yields of crude product were essentially quantitative for all homologs.

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Detection of Periodate-oxidizable Compounds on Paper Chromatograms¹

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Buchanan, Dekker and Long² have reported a method, based on periodate oxidation, for the detection of various glycols and nucleosides on chromatograms. The procedure outlined below is less specific, but is simpler and, in our experience, more sensitive.

Experimental

Preparation of the Chromatogram.—Whatman #1 Filter Paper was used. In some solvent systems, soluble periodate-reacting materials in the paper migrate just behind the solvent front and interfere with the detection of compounds of high *R_f* value. This problem can be eliminated by washing the paper with the solvent to be used before applying the spots.

Solvent Systems.—Use of phenolic solvents interferes with the sensitivity of the method, as does use of buffered solvents.

Detection of Periodate-oxidizable Compounds.—The chromatogram is dried thoroughly to remove any acid or base remaining after development. It is then sprayed very lightly and evenly with aqueous KIO₄ (0.01 *M*), air-dried at room temperature for 8-10 minutes, and then sprayed with a solution of 35% saturated sodium tetraborate containing 0.8% KI, 0.9% boric acid and 3% soluble starch, boiled to bring the starch into solution.

On areas of the chromatogram not having any periodate-oxidizable substances, periodate reacts with iodide ion to liberate iodine, which in turn gives a blue color with the starch; but wherever periodate has been reduced to iodate ion, iodine is not liberated, and no color is observed. Therefore, white spots are seen on a blue background.

Optimum contrast is usually observed about 10 minutes after the second spraying. The spots are not permanent, but may readily be photographed by interposing the wet chromatogram between two sheets of glass, placing it over a sheet of high contrast printing paper, exposing to light, and developing the print. This has the added advantages of

(1) This work was supported in part by a National Science Foundation Predoctoral Fellowship.

(2) J. G. Buchanan, C. A. Dekker and A. G. Long, *J. Chem. Soc.*, 3162 (1950).

increasing the contrast somewhat, and giving dark spots on a light background.

Discussion.—The specificity seems to be essentially that of the well known periodate reaction.³ Of compounds tested, tartaric acid, xylose, glucose, sucrose, mannitol, inositol, quinic acid, chlorogenic acid, shikimic acid, glucuronolactone, ascorbic acid, serine, threonine, methionine, cystine, tryptophan, riboflavin, adenosine, guanosine, inosine, xanthosine, cytidine, uridine, catechol, phloroglucinol, gallic acid, *β*-phenylserine, anthranilic acid and protocatechuic acid show periodate-reducing power. Very weak reactions were given by histidine, tyrosine, aspartic acid, *trans*-cinnamic acid, benzoic acid and *o*-coumaric acid. Compounds which gave no detectable reaction were arginine, ornithine, proline, leucine, isoleucine, lysine, asparagine, glycine, alanine, glutamic acid, *N*α-acetylkynurenine, phenylalanine, glutathione, chloromycetin, guanine, hypoxanthine, xanthine, cytosine, uracil, thymine, thymidine, uric acid, mandelic acid, *p*-hydroxybenzoic acid and vanillin.

Anthranilic acid, gallic acid, chlorogenic acid and cystine were observed to give transient yellow or orange colors after the periodate reagent. Malic acid, citric acid and fumaric acid gave dark spots, probably by exceeding the buffer capacity of the second reagent and causing iodate to react with iodide.

Under conditions of optimum sensitivity, the method will give a barely detectable spot with 0.25 μg. of inositol, or its equivalent in periodate reducing power. The limiting factor appears to be the reaction of the periodate with the paper itself.

(3) E. L. Jackson, "Organic Reactions," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 341.

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Concerning the Reaction of Lithium, Sodium and Potassium Ethoxide in Ethanol with 2-Ethylhexyl Bromide

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The chemical literature describes many cases in which the variation of the inorganic cation affects the nature of the product or the rate of its formation.² We were interested in this aspect of the Williamson reaction, especially with regard to the ratio of ether to olefin formed. It was hoped

(1) Taken from the Ph.D. Thesis of F.J.E., 1952.

(2) See O. L. Brady and J. Jakobovits, *J. Chem. Soc.*, 767 (1950), for literature references and discussion.