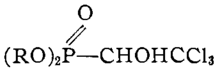
TABLE II

O,O-DIALKYL 2,2-TRICHLORO-1-HYDROXYETHYLPHOSPHONATES,



$(RO)_2\overset{O}{P}\text{—}CHOHCCl_3$

R	Yield, %[9]	M.p., °C.	Formula	Phosphorus, % Calcd.	Phosphorus, % Found	Chlorine, % Calcd.	Chlorine, % Found
CH_3	54	78–80	$C_4H_8Cl_3O_4P$	12.03	12.11	41.32	41.86
C_2H_5	74	55–56	$C_6H_{12}Cl_3O_4P$	10.93	10.96	37.52	37.20
C_3H_7	56	68–70.5	$C_8H_{16}Cl_3O_4P$	10.01	10.00	34.37	34.55
i-C_3H_7	54	105–106.5	$C_8H_{16}Cl_3O_4P$	10.01	10.12	34.37	34.24
C_4H_9	Not purified	Liquid $n^{25}D$ 1.4718	$C_{10}H_{20}Cl_3O_4P$	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 Chromatograms[1]

BY R. L. METZENBERG AND H. K. MITCHELL

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Buchanan, Dekker and Long[2] 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 KIO_4 (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 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, Nα-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.

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[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).

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

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

BY MELVIN S. NEWMAN AND F. JAMES EVANS, JR.[1]

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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

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[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.

that a study of the effect of various cations would lead to synthetic improvements in this typical S_N2 reaction.

When 2-ethylhexyl bromide was treated for two hours with absolute alcoholic solutions of metal alkoxides at reflux 2-ethyl-1-hexene and ethyl 2-ethylhexyl ether were formed in a ratio of about 2/1. The results recorded in Table I indicated that under these conditions the nature of the cation had no appreciable effect on the product composition. We were able to account for about 75–80% of the starting bromide with reasonably good duplication of results. Our conclusion is that the slight trend noted is not significant. Possibly more accurate work would reveal a significant trend but we decided to drop this study as it did not seem profitable to pursue it further.

TABLE I

PRODUCTS OF REACTION OF 1.5 *N* C_2H_5OM WITH 2-ETHYLHEXYL BROMIDE

Expt.	Olefin, %	Ether, %	Unreacted bromide, %	Ratio[a] olefin/ether
Li-1	42.0	18.8	15.3	
Li-2	46.0	19.6	16.2	2.29
Na-1	51.3	24.5	5.4	
Na-2	51.7	24.5	5.7	2.10
K-1	50.4	24.8	6.0	
K-2	50.2	25.1	5.1	2.02

[a] Average of two experiments. In all experiments 350 ml. of 1.5 *N* ethoxide in ethanol and 0.249 mole of 2-ethylhexyl bromide were used. A non-volatile residue of 9% by weight was obtained in each experiment.

Experimental

Absolute ethanol[3] was used in all experiments. 2-Ethylhexyl bromide, b.p. 65–67° at 5 mm., $n^{25}D$ 1.4520–1.4532, was used; the same batch in all experiments.

Ethyl 2-Ethylhexyl Ether.—Several hours was needed for 12.5 g. of sodium to dissolve in a solution of 70 g. of 2-ethyl-1-hexanol in 100 cc. of benzene. To this solution was added 77 g. of diethyl sulfate in 50 cc. of benzene. The reaction mixture became quite viscous and an additional 150 cc. of benzene was added. After one hour the reaction mixture was treated with ethanol and water. The crude product, b.p. 70–80° at 25–30 mm., had a disagreeable odor which was only removed from the desired narrower boiling range material, b.p. 55–56° at 6 mm., by heating with sodium for several hours. Redistillation afforded a material, b.p. 53–54° at 5 mm., which had the same index of refraction, 1.4099 at 28°, for four 5-g. cuts. The yield is not significant as attention was paid to securing very pure material.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.9; H, 14.0. Found: C, 76.0; H, 13.8.

Analytical Methods.—In order to estimate the composition of mixtures of 2-ethylhexyl bromide and ethyl 2-ethylhexyl ether obtained from reaction mixtures, a composition–index of refraction curve was constructed by mixing weighed amounts of the components and determining the index.

2-Ethyl-1-hexene was determined by titration with bromine in acetic acid.[4] Values for the bromine number of about 108 were obtained in acetic acid and chloroform. The correct value of 143 was obtained only when 5 ml. or more of ethyl alcohol was added. The percentage of olefin found in various fractions of the reaction mixture was calculated by dividing the bromine number found by 143. Tests on all of the suspected impurities showed that they did not interfere or give blanks.

Bromine analyses of certain non-volatile residues were made by the Umhoefer method.[5] 2-Ethylhexyl bromide gave the theoretical value.

TABLE II

COMPOSITION–INDEX OF REFRACTION AT 28° OF MIXTURES OF 2-ETHYLHEXYL BROMIDE AND ETHYL 2-ETHYLHEXYL ETHER

Wt. % of bromide	$n^{28}D$	Wt. % of bromide	$n^{28}D$
0.00	1.4099	15.48	1.4148
3.48	1.4112	25.25	1.4177
4.94	1.4116	40.35	1.4230
8.53	1.4128	46.50	1.4248
13.37	1.4140		

General Procedure.—After several preliminary experiments to determine appropriate concentration, reaction time and method of working up the products, the following procedure was adopted: In a 1-liter, 3-necked flask equipped with stirrer, reflux condenser with calcium chloride drying tube, and dropping funnel was placed 350 ml. of a 1.5 *N* solution of the appropriate metallic ethoxide. This solution was brought to reflux temperature and 48.0 g. (0.25 mole) of 2-ethylhexyl bromide added in five minutes. Stirring at reflux temperature was continued for two hours. The reaction mixture was then cooled and treated with dilute sulfuric acid. The layers were separated and the aqueous layer salted out with sodium bromide and extracted with ether. No attempt was made to dry the combined organic layers at this point because of the large amount of ethanol present. The organic solution was fractionated and ether collected to a temperature of 35°. An intermediate cut and some of the ethanol was then collected from 35 to 78°. This intermediate cut contained an azeotrope of ethanol and 2-ethyl-1-hexene boiling at 74°. The olefin in this cut was titrated with a solution of bromine in acetic acid and the percentage of olefin present thus determined. Most of the ethanol was then fractionated from the remaining material. The residue, which now contained only a small amount of alcohol, consisted of two layers which were separated and the aqueous layer salted out with sodium bromide and extracted with ether. The combined organic layers were then dried over sodium sulfate. After fractionation of the ether, the residual material was dried at 5 mm. at room temperature and weighed. This residual material was then analyzed for bromine and the amount of non-volatile material present determined by distillation at 5 mm. The amount of ethyl 2-ethylhexyl ether present was determined by subtracting the amount of 2-ethylhexyl bromide and non-volatile material from the weight of the original residue and also by using the index of refraction–composition diagram (Table II). The values obtained by the two methods checked within 2 to 5%.

In each of the six experiments reported in Table I there remained about 9% (by weight) of non-volatile residue containing less than 1% of bromine.

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(3) R. H. Manske, THIS JOURNAL, **53**, 1104 (1931).

(4) K. Uhrig and H. Levin, *Ind. Eng. Chem., Anal. Ed.*, **13**, 90 (1941).

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Isolation of a New Fraction from Wool Wax Acids

BY JACK RADELL, ABNER EISNER AND E. T. DONAHUE

RECEIVED APRIL 1, 1954

By the saponification of wool wax and the isolation of the acid fraction free of all alkali-insoluble material, it has been possible to separate chromatographically from the "acid" fraction a non-acidic material which apears to be a lactone of molecular formula $C_{20}H_{33}O_2$ representing 12% of the acid fraction. This material gave negative tests for nitrogen by the soda lime test, for unsaturation using bromine in carbon tetrachloride and for aldehyde or ketone using 2,4-dinitrophenylhydrazine reagent. Additional efforts to saponify this material and obtain an unsaponifiable fraction were unsuccessful. Infrared examination of the lactone fraction dis-