TABLE I

COMPARISON OF PHYSICAL DATA ON DIETHYLENE GLYCOL DIACETATE

	Cretcher and Pittenger	Macleod	Liang, Walker and Trenner
Melting point, °C.	....	Viscous oil	18° (cor.)
Boiling point, °C.	148° (26 mm.)	110–135° (16 mm.)	142° (12 mm.)
Specific gravity	d^{15}_{15} 1.1078	d^{20}_{20} 1.123	d^{25}_{25} 1.1081
Refractive index	....	n^{20}D 1.4348	n^{25}D 1.4323
Solubility in water	....	....	Completely miscible

Some of the physical properties of diethylene glycol diacetate have been determined. A comparison of our data with those reported in the literature is given in Table I.

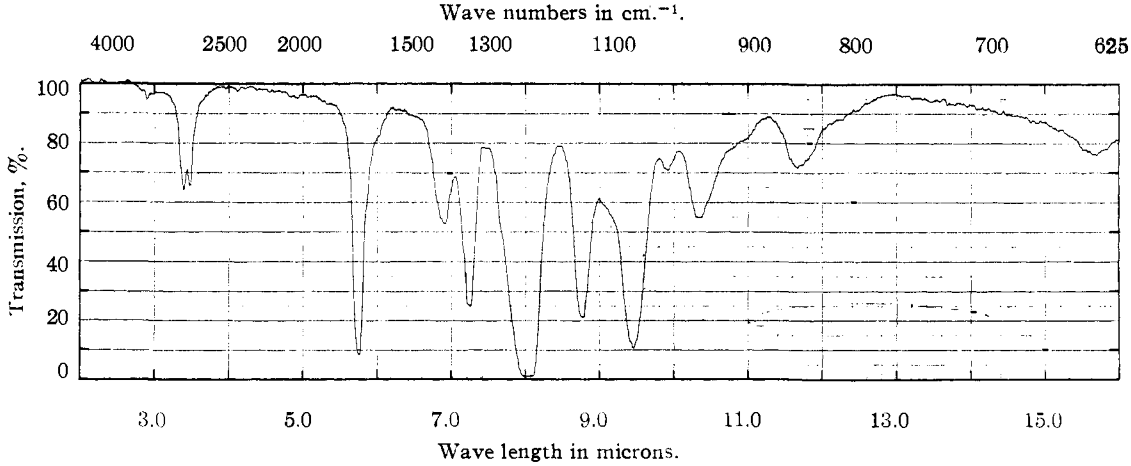

Fig. 1.—Diethylene glycol diacetate oil film.

The infrared absorption spectrum is presented in Fig. 1. In connection with the infrared spectrum of our preparation, attention is called to the complete absence of any significant absorption band in the 2.8–3.1 μ region, indicative of the absence of both water and monoacetate. The ester carbonyls are represented by the strong 5.75 μ band, the C–O bonds in the ester groups by the strong 8.05 μ band and the C–O–C ether linkage by the strong 9.45 μ band.

Experimental

Materials Used.—The diethylene glycol was obtained from Carbide and Carbon Chemicals Corporation. This was redistilled and only the portion boiling above 150° was used. Acetyl chloride and acetic anhydride were of Merck reagent grade. The pyridine was the ordinary stock reagent.

Preparation.—I. To 200 ml. of the redistilled diethylene glycol was added 200 ml. of pyridine. One kilogram of acetic anhydride was added in portions. The mixture was then refluxed for six hours during which its color darkened appreciably. About three-quarters of the total volume was distilled off before the boiling point reached 160°. The portion remaining was cooled and dissolved in water. Diethylene glycol diacetate was then separated from the monoacetate and most other materials by extracting with ether. The ethereal extract was partially dried with sodium sulfate and the ether removed by evaporation. The impure diacetate was then vacuum distilled and foreign materials removed in the forerun before a constant boiling point was attained. About 300 g. of the diacetate was then distilled over representing a 75% yield.

II. When acetyl chloride was used, a molal ratio of 10:3 of acetyl chloride to diethylene glycol proved effective. Less than one hour of refluxing was used and a 70% yield was obtained isolating as above.

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.53; H, 7.37. Found: C, 50.32; H, 7.44.[4]

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[4] The authors wish to express their appreciation to Mr. R. N. Boos and his associates for these analytical results.

The Degradation of Propionic Acid[1]

BY VICTOR LORBER AND MARGARET COOK

Carson, *et al.*,[2] have described a method for the partial degradation of propionic acid using dichromate as the oxidant. Equivalent yields of carbon dioxide and titrable acidity, presumably acetic acid, were reported. When $CH_3CH_2C^{14}OOH$ was degraded in this manner, C^{14} was present only in the carbon dioxide. It was concluded that the carbon dioxide arose only from the carboxyl group of the propionic acid, according to the reaction $CH_3CH_2C^{14}OOH \rightarrow CH_3COOH + C^{14}O_2$.

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[1] This work was supported in part by a grant from the American Cancer Society upon recommendation of the Committee on Growth of the National Research Council, and in part by a grant from the Prentiss Foundation. The radiocarbon used was obtained on allocation from the U.S. Atomic Energy Commission.

[2] S. F. Carson, J. W. Foster, S. Ruben and H. A. Barker, *Proc. Natl. Acad. Sci.*, **27**, 229 (1941).

During the course of a study of the metabolism of propionic acid, an effort was made to use the dichromate method in the degradation of propionic acid. $CH_3C^{14}H_2COOH$ and $C^{14}H_3C^{13}H_2$-$COOH$, prepared by established synthetic methods essentially as outlined elsewhere,[3] were degraded. The partition coefficient[4] for the isotopic acids agreed with theory within experimental error. The distribution of isotope in the latter compound was verified by conversion to lactate, *via* α-bromination, and stepwise degradation of the lactate by established procedures.[5,6]

Conversion of the isotopic propionic acids to carbon dioxide and acetic acid was accomplished using the dichromate oxidation of Carson, *et al.*[2] Titrable acid and carbon dioxide could be obtained in equivalent yields, but the carbon dioxide, as shown in Table I, contained isotope from both the α- and β-carbons of the propionate. The acid fraction from the dichromate oxidation was removed from the reaction mixture by steam distillation. A small aliquot of the free acid, when fractionated by silica gel chromatography,[7] was found to have at least two components.[8] The remainder was neutralized with barium hydroxide, evaporated to dryness, and further degraded by pyrolysis[9] and sodium hypoiodite.[10] The reactions undergone by the acetic acid present in this fraction may be summarized

TABLE I

DEGRADATION OF SYNTHETIC ISOTOPIC PROPIONIC ACID

		Isotope concentration in the degradation fractions[a]		
Type of propionic acid	Type of isotope	CO_2 ("carboxyl" carbon of propionate)	$BaCO_3$ (α-carbon of propionate)	CHI_3 (β-carbon of propionate)
$CH_3C^{14}H_2COOH$	C^{14}	61	184	0
$C^{14}H_3C^{13}H_2COOH$	C^{13}	0.12	0.58	0
	C^{14}	152	0	494

[a] C^{13} values are given in atom per cent. excess and C^{14} values in counts/min./mg. of carbon.

$$Ba(COOCH_3)_2 \xrightarrow[\text{vacuum}]{500-520\,°} BaCO_3 + CH_3COCH_3$$

$$CH_3COCH_3 \xrightarrow{NaOI} CHI_3 + CH_3COOH$$

The barium carbonate arises from the carboxyl group of the acetic acid and should correspond to the α-carbon of the original propionic acid. The iodoform is formed from the methyl group of the acetic acid and should correspond to the β-carbon of the propionic acid. The distribution of isotope in these fractions, shown in Table I, is in line with these expectations. It should be pointed out that the carboxyl group of any unreacted propionic acid would be converted to barium carbonate during the pyrolysis.

From the foregoing data the following conclusions may be drawn: (a) The carbon dioxide arising from the dichromate oxidation of propionic acid described by Carson, *et al.*,[2] does not come solely from the carboxyl group of the acid, as supposed by these authors, but contains appreciable carbon from the α- and β-positions of the propionic acid. (b) The equivalence which may be obtained between carbon dioxide and titrable acid produced in the reaction is fortuitous. (c) The acetic acid produced in the reaction appears to arise from the α- and β-carbons of propionic acid, as proposed by Carson, *et al.*[2]

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[3] H. G. Wood, "Cold Spring Harbor Symposia on Quantitative Biology," **13**, 201 (1948).

[4] O. L. Osburn, H. G. Wood and C. H. Werkman, *Ind. Eng. Chem., Anal. Ed.*, **8**, 270 (1936).

[5] H. G. Wood, N. Lifson and V. Lorber, *J. Biol. Chem.*, **159**, 475 (1945).

[6] N. Lifson, V. Lorber, W. Sakami and H. G. Wood, *ibid.*, **176**, 1263 (1948).

[7] S. R. Elsden, *Biochem. J.*, **40**, 252 (1946).

[8] The two components which were eluted from the silica gel column migrated at rates comparable to those observed for acetic and propionic acids. The conditions of the test, however, were not well enough standardized to render the results acceptable for purposes of identification. The faster component, presumed to be unreacted propionic acid, made up about 20%, by titration, of the total acid eluted in the two fractions.

[9] A. V. Grosse and S. Weinhouse, *Science*, **104**, 402 (1946).

[10] L. F. Goodwin, THIS JOURNAL, **42**, 39 (1920).

The Reaction of Hydroquinone with Ethyl Chloroacetate

BY CARL M. MOSER

In an attempt to find a more convenient synthesis of homogentisic acid (hydroquinone-2-acetic acid), the boron fluoride catalyzed alkylation of hydroquinone with ethyl chloroacetate was investigated in the hope that C-alkylation might predominate. A survey of the literature did not reveal any previous alkylation of phenolic compounds with alkyl halides catalyzed by boron fluoride. Hennion and Kurtz[1] investigated the boron fluoride catalyzed alkylation of benzene and toluene with alkyl halides and found that reaction at atmospheric pressure proceeds only in the presence of small quantities of polar catalysts, and the highest yields are obtained with tertiary and benzyl halides.

From the boron fluoride catalyzed alkylation of hydroquinone with ethyl chloroacetate an oily mixture was obtained. After alkaline hydrolysis of the oily mixture, two acids of m. p. 248° and 150° were obtained. The higher-melting acid could be esterified with ethanol in the presence of boron fluoride–ether complex as catalyst, and this ester proved to be identical with diethyl hydroquinone-O-diacetate (III) previously synthesized by Carter and Lawrence.[2] The higher melting acid was thus proved to be I. The melting point of the lower melting acid was in close proximity to that reported for both homo-

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[1] Hennion and Kurtz, THIS JOURNAL, **65**, 1001 (1943).

[2] Carter and Lawrence, *J. Chem. Soc.*, **77**, 1226 (1900).