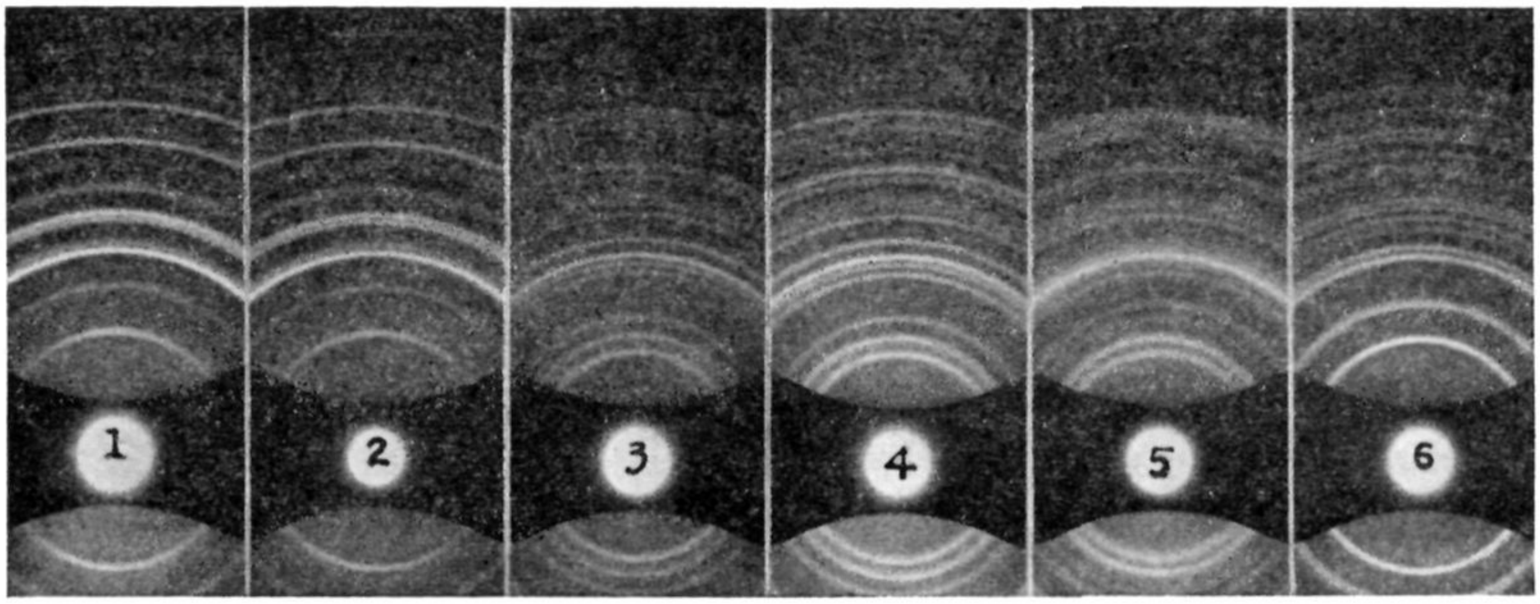
Representative X-ray diffraction patterns of crystalline hydrochlorides.

Fig. 1 Fig. 2 Fig. 3 Fig. 4 Fig. 5 Fig. 6



Ib-Form-B
Cryst. from
isopropyl alcohol

Sample No. 1.
Cryst. from
CH_3OH

Ib-Form-A.

Sample No. 2.
(Mixt. of Ia and b),
Cryst. from CH_3OH

Ia

tified by mixture melting points and X-ray diffraction patterns as nearly pure Ib hydrochloride. The next fraction (sample no. 2) was shown to be a mixture of Ib and Ia hydrochlorides by X-ray diffraction patterns (Fig. 5). In similar experiments without added hydrogen chloride Ia was recovered and was identified in the form of the base by mixture melting points; and similar experiments (without added hydrogen chloride) were carried out with similar results on Ia hydrochloride which had been freshly precipitated from an ether solution of Ia by hydrogen chloride, washed with dry ether and used directly without drying (these samples had retained very little if any free hydrochloric acid).

The representative X-ray diffraction patterns given in Figs. 1–6 are contact prints and were obtained by the powder wedge technique in a cylindrical camera with a 7.16 cm. radius exposed to radiation from a copper target X-ray tube with a nickel oxide filter giving essentially Cu K_α radiation.

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The Preparation and Properties of Diethylene Glycol Diacetate

BY SHOU CHU LIANG,[1] R. W. WALKER AND N. R. TRENNER

In connection with another investigation, a quantity of pure diethylene glycol diacetate was required, and consequently we followed the work of previous authors.[2,3] An examination of the properties of the products so obtained revealed that they were of unsatisfactory purity, whereupon the more satisfactory methods described below were developed. The physical properties of the pure diethylene glycol diacetate thus obtained were found sufficiently different from those reported by the earlier investigators to warrant publication.

Several methods of preparation were tried. Application of the classical esterification procedure, *i. e.*, refluxing diethylene glycol with glacial acetic acid in the presence of concd. sulfuric acid, yielded no diacetate. The diester, however, was obtained by a Schotten–Baumann reaction using diethylene glycol in the presence of pyridine with either acetic anhydride or acetyl chloride. Diethylene glycol monoacetate was obtained in all cases, but it was not isolated in pure form.

It has been found that acetic acid, formed during the preparation, must not be removed from the diacetate by alkali extraction for the diester was found to be extremely sensitive to bases. Thus, if a solution of the diester is shaken with aqueous potassium hydroxide (3 *N*) at room temperatures for a short time, the diester is hydrolyzed to the monoester.

It was not found possible to separate the mono- and diacetates very well by fractional distillation under vacuum as they formed a constant boiling mixture. The diacetate could be isolated, however, by extracting with ether from an aqueous solution of the mixture of the two esters. The monoester is more hydrophilic and remains in the aqueous phase.

Diethylene glycol diacetate is hygroscopic. When pure and dry, it melts at 18°. On standing in air, the melting point gradually lowers as the diester absorbs moisture from the atmosphere and finally drops to below 0°.

Quite unexpectedly, the diacetate is completely miscible with water. This is very different from the behaviors of structurally similar compounds such as ethyl acetate, diethyl ether and 1,4-butanediol diacetate.

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(1) Present address: 31 Lambton Road, Ottawa, Canada.

(2) L. H. Cretcher and W. H. Pittenger, THIS JOURNAL, **47**, 165 (1925).

(3) M. Macleod, *J. Chem. Soc.*, 3092 (1928).

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.

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.

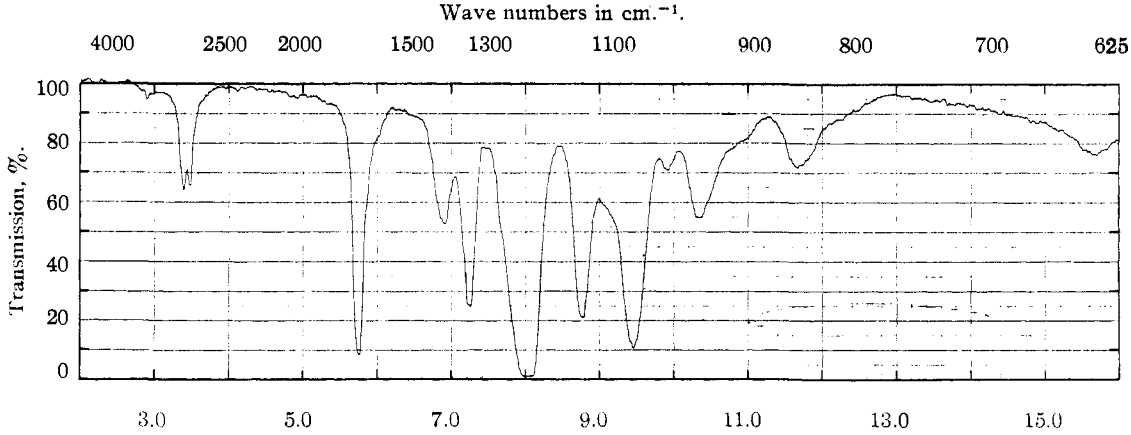

Fig. 1.—Diethylene glycol diacetate oil film.

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.

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