

looked this publication¹ and the statement in our publication, "Posternak did not report, however, the preparation of allomucic acid," does a grave injustice to Dr. Posternak. After having read his paper no one can doubt Dr. Posternak's claim of priority of the preparation of allomucic acid.

(1) Posternak, *Helv. Chim. Acta*, **18**, 1283 (1935).

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RECEIVED FEBRUARY 27, 1937

Hydrogen-Deuterium Exchange in Acetate Solution

BY SYLVESTER LIOTTA AND VICTOR K. LA MER

In the course of a study of acetate-ion catalyzed reactions in heavy water, it became necessary to determine the extent of the exchange between the hydrogens of the methyl group and the deuterium of the solvent. From the results of early investigations^{1,2,3} little or no exchange was to be expected, while from later work^{4,5} varying degrees of exchange could be expected, depending upon temperature and time of contact.

Heavy water (d^{25}_{25} 1.1000, approximately 93% D) was purified by distillation *in vacuo* to remove possible catalysts. Anhydrous sodium acetate was added to produce a 10% solution. After standing for two weeks in a Pyrex vessel at 25–30°, the solvent was recovered by distillation *in vacuo*. The density was redetermined by filling the same pycnometer. Sodium acetate and acetic anhydride were then added to make a final concentration of 10% and 1%, respectively. After two weeks at 25–30°, the solution was neutralized with caustic soda and the same procedure repeated.

Solvent before addn. of sodium acetate, g.	10.5417
Solvent after first distn., g.	10.5413
Solvent after second distn., g.	10.5420

If any exchange occurs either in slightly acid or slightly alkaline solution at room temperature it is exceedingly slow.

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RECEIVED FEBRUARY 24, 1937

- (1) Bonhoeffer, *et al.*, *Z. physik. Chem.*, **B23**, 171 (1933).
- (2) Lewis and Schutz, *THIS JOURNAL*, **56**, 493 (1934).
- (3) Klar, *Z. physik. Chem.*, **B26**, 335 (1934).
- (4) Hall, Bowden and Jones, *THIS JOURNAL*, **56**, 750 (1934).
- (5) Wynne-Jones, *Chem. Rev.*, **17**, 115 (1935). Results of Turkevich. Table 3, 200 hrs. at 80° yields 85% exchange.

An Improved Method for Synthesizing Isobutyl Ethyl Ether

BY E. M. MARKS, DAVID LIPKIN AND BERNARD BETTMAN

According to Cerchez¹ aliphatic ethers can be synthesized from alkyl sulfates and magnesium alcoholates. In several instances he obtained yields of 60–70%. In preparing isobutyl ethyl ether by this method from diethyl sulfate and magnesium isobutylate, we obtained the product in only about 30% yield.

By substituting sodium for magnesium in the Cerchez method we have succeeded in raising the yield of isobutyl ethyl ether to 70%. Experimental conditions for optimum results are as follows: 93 g. (1.25 mole) of anhydrous isobutyl alcohol is placed in a 500-ml. round-bottomed flask fitted with a reflux condenser and 12.5 g. (0.54 mole) of sodium added. The mixture is allowed to react until refluxing has ceased, after which it is heated in an oil-bath at 120–130° for two and three-quarters hours. At the end of this time a portion of the sodium remains undissolved. The mixture is then cooled to 105–115° and 77.1 g. (0.5 mole) of pure diethyl sulfate added gradually during a two-hour period. Reaction is vigorous and steady refluxing takes place during addition of the sulfate. After all has been added, refluxing is continued for two hours. The reaction mixture is then permitted to cool to room temperature (overnight) after which an equal weight of crushed ice is added, followed by a slight excess of dilute sulfuric acid. The ether is then steam-distilled out of the flask, separated from the aqueous portion of the distillate, given three equal-volume washes of 30% sulfuric acid, to remove most of the unreacted isobutyl alcohol, washed twice with water and dried over anhydrous potassium carbonate. The dried product is then refluxed over sodium ribbon for three hours to remove all traces of alcohol and finally is distilled through a precision fractionating column of the type recommended by Podbielniak.² The yield of isobutyl ethyl ether was 70%, based on diethyl sulfate. The boiling point, density and refractive index of our ether agreed with the recorded values³ within the experimental error.

Several variables in this synthesis have been studied. (1) If the isobutyl alcohol is not dried rigorously, the yield of ether is reduced to

- (1) Cerchez, *Bull. soc. chim.*, **43**, 762 (1928).
- (2) Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, **5**, 135 (1933).
- (3) Norris and Rigby, *THIS JOURNAL*, **54**, 2088 (1932).