R = C_2H_5) is cleaved by a catalytic amount of dissolved sodium at 145–175° to yield 2-ethyl-1-butanol (IV, R = C_2H_5) in 58% yield. It may be that the same mechanism is operative in the diol reaction with sodium hydroxide and water as in the diol reaction with dissolved sodium.

Experimental

N.m.r. spectra were by Dr. L. D. Colebrook.

Materials.—Baker analytical reagent grade sodium hydroxide and sodium sulfite were used. Commercially available 2,2-diethyl-1,3-propanediol was recrystallized before use, m.p. 62–63° (lit.[6] m.p. 61.0–61.6°).

Reaction of 2,2-Diethyl-1,3-propanediol with Sodium Sulfite and Sodium Hydroxide.—To a three-neck, 100-ml., round-bottom flask equipped with a dropping funnel, stirrer, and condenser was added 15.8 g. (0.125 mole) of sodium sulfite, 15.0 g. (0.375 mole) of sodium hydroxide, and 2.3 g. (0.125 mole) of distilled water. 2,2-Diethyl-1,3-propanediol (16.6 g., 0.125 mole) was added to the dropping funnel. The flask was flushed with nitrogen to remove most of the atmospheric oxygen. Stirring was begun, and the flask was heated at 140° in an oil bath. The dropping funnel was heated with an infrared lamp until the diol liquefied. When the flask reached 140°, the liquid diol was added dropwise over a 7-hr. period. After addition was complete, the reaction mixture was maintained at 140° for 1 hr. before it was allowed to cool slowly to room temperature.

The solidified reaction mixture was dissolved in 125 ml. of distilled water and extracted with three 25-ml. portions of 30–60° petroleum ether. The combined petroleum ether extracts were washed with 25-ml. portions of 3 N hydrochloric acid, distilled water, 5% sodium bicarbonate, and distilled water. The petroleum ether solution was dried over anhydrous magnesium sulfate, filtered, and reduced in volume on a rotary evaporator. Fractional distillation gave 7.3 g. of material boiling at 147° (lit.[7] b.p. 149°), n^{24}D 1.4195 (lit.[7] n^{25}D 1.4200). The 3,5-dinitrobenzoate had m.p. 50–51°[8] (lit.[9] m.p. 51°).

Reaction of the cyclic sulfite of 2,2-diethyl-1,3-propanediol[10] with sodium hydroxide and water was carried out in the same manner.

(6) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **70**, 948 (1948).

(7) R. W. Freedman and E. I. Becker, *J. Org. Chem.*, **16**, 1701 (1951).

(8) The melting point of the 3,5-dinitrobenzoate derivative of 2-ethyl-2-methyl-1-butanol (II, R = C_1H_5) prepared in this laboratory was found to be 65–67° (lit.[9] m.p. 51°).

(9) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(10) For preparation, see L. P. Kyrides, *J. Am. Chem. Soc.*, **66**, 1006 (1944).

Structure of Indene-1(3)-carboxylic Acid

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The action of carbon dioxide on indenylmagnesium,[1] -sodium,[2,3] or -lithium[4,5] always gives the same indenecarboxylic acid. This acid was considered in the earlier literature[3] and also more recently[5] to be 1-indenecarboxylic acid (I, R = H). As the infrared spectrum

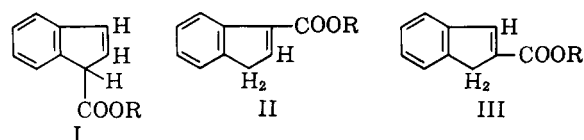(1) C. Courtot, *Ann. chim.* (Paris), [9] **4**, 83 (1915).

(2) R. Weissgerber, *Ber.*, **44**, 1440 (1911).

(3) W. S. Knowles, J. A. Kuck, and R. C. Elderfield, *J. Org. Chem.*, **7**, 374 (1942).

(4) N. H. Cromwell and D. B. Capps, *J. Am. Chem. Soc.*, **74**, 4448 (1952).

(5) R. Meier, *Chem. Ber.*, **86**, 1483 (1953).

indicated an α,β-unsaturated acid, other authors assigned the structure of 3-indenecarboxylic acid (II, R = H) to this product.[6,7]

The acid, which had been prepared for other purposes, was transformed into the methyl ester. The n.m.r. spectrum of the ester and of the methyl ester of 2-indenecarboxylic acid (III, R = CH_3) was determined. It shows unequivocally that structure II should be preferred. In both compounds, the methylene protons at δ 3.43 (II, R = CH_3) or 3.58 (III, R = CH_3) are split by the olefinic proton with J = 2 c.p.s.[8] In compound III, the latter shows up as a triplet at δ 7.63, whereas in II it is found at 7.33. It should be noted that in II, one aromatic proton is shifted towards low field (δ 8.03) owing to the nearby presence of the $COOCH_3$ group.

This interpretation was confirmed by double resonance experiments at 100 Mc. Irradiation of the doublet at δ 3.43 of II (R = CH_3), while observing the triplet at 7.33, simplifies the latter to a singlet and *vice versa*. Similar irradiation of the triplet at δ 7.63 of III (R = CH_3) simplifies the doublet at 3.58 into a singlet and *vice versa*.

The formation of II instead of I may be explained by the ready isomerization of indene in alkaline medium.[14] The isomerization of 1-benzyl or 1-benzhydrylindene to the 3-substituted derivative by alcoholic KOH has been described before.[15] Recent studies have shown that 1-alkylindenes are isomerized already under the influence of organic amines.[11,12] The formation of indene-3-carboxylic acid by reaction of carbon dioxide with an organometallic derivative of indene can be explained assuming that, under the alkaline conditions used, structure II is the more stable one.

Experimental

Methyl Ester of Indene-3-carboxylic Acid.—Indene-3-carboxylic acid was prepared by carbonation of indenylsodium[2,3] or indenyllithium.[4] The acid (2 g., m.p. 159–161°) was treated with a slight excess of an ethereal solution of diazomethane. After washing with potassium bicarbonate solution and water and drying, the ethereal solution was evaporated and the residue was distilled under reduced pressure. The liquid (1.65 g.) distilled at 155–156° (23 mm.). Weissgerber[2] gives b.p. 153–165° (23 mm.). The product gave one peak when examined by gas chromatography at 150° using diethyleneglycol succinate as stationary phase.

(6) A. C. Cope, J. E. Meili, and D. W. H. MacDowell, *J. Am. Chem. Soc.* **78**, 2557 (1956).

(7) P. Yates and R. W. Robb, *ibid.*, **79**, 5760 (1957).

(8) A spin coupling constant of 1.7 to 2.0 c.p.s. between the olefinic proton and the methylene protons has been found in 2-butenolide[9] and in methylindenes.[10-12]

(9) M. P. Cava, B. Weinstein, W. R. Chan, L. J. Maynes, and L. F. Johnson, *Chem. Ind.* (London), 167 (1963).

(10) A. M. Weidler, B. Mathiasson, and G. Bergson, *Arkiv. Kemi*, **21**, 187 (1963).

(11) G. Bergson and A. M. Weidler, *Acta Chem. Scand.*, **17**, 862 (1963).

(12) A. M. Weidler, *ibid.*, **17**, 2724 (1963).

(13) A. R. Hawdon and I. J. Lawrenson, *Chem. Ind.* (London), 1960 (1963).

(14) C. F. Koelsch and R. A. Scheiderbauer, *J. Am. Chem. Soc.*, **65**, 2311 (1943).

(15) C. Courtot, *Ann. chim.* (Paris), [9] **5**, 52 (1916).

Methyl Ester of Indene-2-carboxylic Acid.—Indene-2-carboxylic acid was prepared by hydrolysis of diethyl indene-2,3-dicarboxylate, obtained by treatment of diethyl benzyloxalacetate with cold sulfuric acid.[16] The acid (3 g.) was esterified with diazomethane in ethereal solution. The solid (2.9 g.), obtained by evaporation of the organic solvent, was purified by crystallization in petroleum ether (b.p. 60–80°) and by sublimation *in vacuo*, m.p. 82–83.5°. The product was homogeneous by gas chromatography and could be separated from methyl indene-3-carboxylate on the above mentioned column.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.73; H, 5.76.

The n.m.r. and double resonance spectra in deuteriochloroform were obtained on a Varian Associates H. R. 100 spectrometer using the method of Johnson.[17]

(16) J. Bougault, *Compt. rend.*, **159**, 745 (1914).

(17) L. F. Johnson, "Varian Technical Information Bulletin," Vol. III, No. 3, 5, 1962.

A Convenient Preparation of Methanol-*d*[1]

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The α-hydrogens of esters are conveniently exchanged with methanol-*d* (CH_3OD) as the solvent, but a good preparation of this alcohol has been lacking.

Among the methods used previously are the hydrolysis of dimethyl oxalate with D_2O and sodium carbonate,[3] the exchange of methanol with D_2O,[4] the hydrolysis of trimethyl borate with D_2O,[5] and the reaction of sodium methoxide or magnesium methoxide with D_2O.[6] We have used most of these methods and have also utilized the acid-catalyzed hydrolysis of 2,2-dimethoxypropane.[7]

None of these methods is really satisfactory, especially for the preparation of reasonable quantities of methanol-*d* of high isotopic purity. Such objections do not apply to the preparation described below.

This method involves the hydrolysis of commercially available dimethyl carbonate. However, in one experiment a mixture of 800 g. of dimethyl carbonate, 20 g. of D_2SO_4 and 196 g. of D_2O required 3 weeks of refluxing for complete reaction. The reaction rate could undoubtedly be increased by using more acid, but a separate preparation of D_2SO_4 is an important limitation. This inconvenience was avoided by an *in situ* preparation of the acid catalyst using dimethyl sulfate since hydrolysis of this ester is rapid. The experimental procedure below uses quantities such that reaction is complete in 3 days of refluxing. A somewhat larger ratio of dimethyl sulfate could undoubtedly be used but a too rapid hydrolysis rate should be avoided because of the evolution of CO_2.

(1) This research was supported in part by a grant from the National Science Foundation.

(2) (a) National Institutes of Health Postdoctoral Fellow, 1963–1964; (b) National Science Foundation Summer Cooperative Predoctoral Fellow, 1964.

(3) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

(4) K. Wiberg, *J. Am. Chem. Soc.*, **77**, 5987 (1955).

(5) C. G. Swain and M. M. Labes, *ibid.*, **79**, 1084 (1957).

(6) C. G. Swain, J. T. McKnight, and V. P. Kreiter, *ibid.*, **79**, 1088 (1957).

(7) F. R. Jensen, unpublished results.

Since diethyl carbonate and diethyl sulfate are also available commercially, a similar preparation of ethanol-*d* should be feasible.[8]

Experimental

Dimethyl carbonate (Eastman White Label), 400 g. (4.44 moles), and deuterium oxide (Bio-rad Labs., Richmond, Calif.), 100 g. (5.00 moles), were placed in a carefully dried 1-l. one-necked flask. Dimethyl sulfate (Eastman practical grade), 16 g. (0.13 mole), was added and the flask was attached to two reflux condensers arranged in series (initial rapid evolution of carbon dioxide may entrain some liquid). The flask contents were heated to reflux with provision for moisture exclusion. After 72 hr. the disappearance of the carbonyl stretching frequency of dimethyl carbonate in the infrared indicated that the reaction was complete. The methanol-*d* was distilled directly from the reaction flask through a 30-cm. Vigreux column. One further distillation from a small amount of sodium sufficed to yield 275 g. (8.34 moles, 94% yield) of gas chromatographically pure (Carbowax 20M column) methanol-*d*, b.p. 66–66.5°.

The amount of deuterium substitution was obtained conveniently from the n.m.r. spectrum[9] of methanol-*d*. The area under the hydroxyl peak was compared with one of the two peaks due to C^{13} splitting. From the relative intensities, the methanol-*d* was found to contain 98.6 ± 0.4% deuterium.

(8) NOTE ADDED IN PROOF.—This preparation has now been carried out successfully. Because of a slower hydrolysis rate, double the quantity of diethyl sulfate is convenient.

(9) A Varian A-60 nuclear magnetic resonance spectrometer was used.

Stability of the Carbon–Phosphorus Bond in Trichloromethylphosphonate Esters. Ether Formation in Reactions with Alcohols and Phenols

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Esters of phosphonic acids containing a trichloromethyl group attached to phosphorus are sensitive to alkali, liberating chloroform,[1] but it is now generally accepted that in the absence of alkali the C–P bond is stable. The reaction of trichloromethylphosphonate esters with primary amines was believed at first to be a case of C–P bond scission,[2] but later work,[3] which has been amply substantiated,[4] showed that the products were not amides but amine salts, the esters behaving in this reaction as alkylating agents. The products of the reaction of diethyl trichloromethylphosphonate with aniline, for example, were N-ethylaniline and the aniline salt of ethyl hydrogen trichloromethylphosphonate.[3,4]

More recently, the reaction of diethyl trichloromethylphosphonate with ethanol was examined to determine

(1) I. S. Bengelsdorf, *J. Am. Chem. Soc.*, **77**, 6611 (1955).

(2) G. Kamai, *Dokl. Akad. Nauk SSSR*, **55**, 219 (1947); *Chem. Abstr.*, **41**, 5863 (1947). A similar behavior was implied for ethyl phenyltrichloromethylphosphinate by G. Kamai, *Zh. Obshch. Khim.*, **18**, 443 (1948); *Chem. Abstr.*, **42**, 7723 (1948).

(3) (a) A. Ya. Yakubovich and V. A. Ginsburg, *Dokl. Akad. Nauk SSSR*, **82**, 273 (1952); *Chem. Abstr.*, **47**, 2685 (1953); (b) A. Ya. Yakubovich and V. A. Ginsburg, *Zh. Obshch. Khim.*, **24**, 1465 (1954); *Chem. Abstr.*, **49**, 10834 (1955).

(4) (a) K. C. Kennard and C. S. Hamilton, *J. Am. Chem. Soc.*, **77**, 1156 (1955); (b) C. E. Griffin, *Chem. Ind.* (London), 415 (1958); (c) Tzeng-Shou Tung and Shyh-Tsong Chern, *Hua Hsüeh Hsüeh Pao*, **24**, 30 (1958); *Chem. Abstr.*, **53**, 3113, 2114s (1959).