white ammonium salt[9] was collected, washed with ether, and dried *in vacuo*, yielding 4.59 g. of the crude product.

A modification of the procedure of Weinstock[10] was used for the conversion of cyclopropanecarboxylic acid-1-*d* to cyclopropylamine-1-*d*. The unpurified ammonium cyclopropanecarboxylate-1-*d* prepared above was dissolved in 12.5 ml. of water, and 0.4 g. of triethylamine in 30 ml. of dioxane was added. This was cooled in ice, and a solution of 6.3 g. (0.058 mole) of ethyl chloroformate in 23 ml. of dioxane was added slowly. After stirring for 70 min. with ice cooling, 4.3 g. (0.066 mole) of sodium azide in 12.5 ml. of water was added dropwise with stirring. After 30 min., the two layers were separated and the aqueous layer was extracted with 60 ml. of toluene. Addition of toluene to the other layer caused water to separate; it was removed and the organic phase was washed with saturated sodium chloride solution. The combined organic layers were dried with anhydrous magnesium sulfate and molecular sieve. Ethanol (4.0 g., 0.087 mole) and triethylamine (0.1 g.) were mixed with the dried solution. This was then added dropwise with stirring to a flask heated to 105–110° equipped with a condenser cooled with ice–salt. Heating was continued for 4 hr. Removal of the solvent yielded 4.84 g. of a yellow oil (cyclopropylethylurethan).

The urethane was hydrolyzed by heating for 5 hr. with 6 g. of potassium hydroxide in 6 ml. of water and 8 ml. of ethylene glycol. This was carried out under nitrogen with stirring, and the amine distilled out as formed. The crude product was purified by reaction with oxalic acid in ether followed by two recrystallizations from absolute alcohol, giving a 13% yield (1.359 g.) of cyclopropylamine-1-*d* hydrogen oxalate, m.p. 123.5–124.5°. An additional 0.124 g., melting at 120–124°, was obtained by concentrating the mother liquors. Analysis of the product by n.m.r. (D_2O, 60°) shows two singlets at δ 0.62 and 4.78; the integration shows 94.4 ± 2.8% deuterium substitution on C-1.

Deamination of Cyclopropylamine-1-*d*.—A portion (0.440 g., 2.97 mmoles) of the cyclopropylamine-1-*d* hydrogen oxalate prepared above was dissolved in 3.6 ml. of water and chilled in an ice-bath. Sodium nitrite (0.32 g., 4.6 mmoles) dissolved in 0.45 ml. of water was added over 1 hr. The system was kept in ice for an additional 3 hr. until gas evolution had nearly ceased. The reaction mixture was then saturated with potassium carbonate, filtered, and extracted with eight 10-ml. portions of benzene. The benzene solution was dried with anhydrous magnesium sulfate, and 0.63 g. (2.57 mmoles) of *p*-phenylazobenzoyl chloride and 0.41 g. (5.14 mmoles) of pyridine were added. The mixture was allowed to stand for 5.5 hr., then refluxed for 12 hr. After cooling in ice, 0.18 g. (10 mmoles) of water in a few milliliters of acetone was added and the mixture was stirred for 1 hr. The solvent was then removed, and the product was twice recrystallized from ethanol. A 44% yield (0.346 g.) was obtained of allyl-2-*d* *p*-phenylazobenzoate: m.p. 67.5–68.5°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.81 μ; n.m.r. ($CDCl_3$), δ = 4.13 (singlet, two methylene protons), 4.65 (multiplet, two vinyl protons), and 6.7–7.6 p.p.m. (aromatic protons). Integration of the n.m.r. spectrum showed 89.7 ± 5.1% deuterium substitution. Mixture melting point with an authentic sample prepared from allyl alcohol and *p*-phenylazobenzoyl chloride[11] showed no depression. An analysis was obtained for the undeuterated derivative.

Anal. Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.08; H, 5.33; N, 10.51.

A second deamination similarly yielded allyl-2-*d* *p*-phenylazobenzoate with 90 ± 7% deuterium substitution.

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Cleavage of 2,2-Dialkyl-1,3-diols[1]

Ronald L. Heidke[2] and William H. Saunders, Jr.[3]

Department of Chemistry, University of Rochester, Rochester, New York

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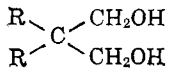
It has been reported that 2,2-dialkyl-1,3-propanediols (I) react with sodium sulfite, sodium hydroxide, and water at 140° to yield 2,2-dialkylpropanols (II).[4] It was further reported that the corresponding cyclic sulfites (III) react with sodium hydroxide and water at 140° to yield the same 2,2-dialkylpropanols (II).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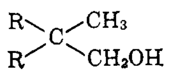
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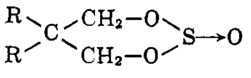
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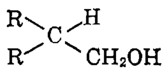
IV

We were interested in this reaction as a synthetic method for 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5). Accordingly, 2,2-diethyl-1,3-propanediol (I, R = C_2H_5) was added to sodium sulfite, sodium hydroxide, and water at 140° as described by Crowdle, *et al.*[4] Distillation of the reaction product gave a 63% yield of 2-ethyl-1-butanol (IV, R = C_2H_5) instead of the expected 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5). The corresponding cyclic sulfite (III, R = C_2H_5) also reacted with sodium hydroxide and water at 140° to yield 2-ethyl-1-butanol (IV, R = C_2H_5). 2-Ethyl-2-methyl-1-butanol (II, R = C_2H_5) was not obtained under any of the reaction conditions that were tried.

Identification of the distilled reaction product was made by boiling point, refractive index, 3,5-dinitrobenzoate derivative, and infrared and n.m.r. spectra. The infrared spectrum of the alcohol obtained from the diol reaction was identical with the infrared spectrum of commercially available 2-ethyl-1-butanol (IV, R = C_2H_5) but was substantially different from the infrared spectrum of 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5) prepared in this laboratory by another method.

The integrated n.m.r. spectrum of the alcohol product with a trace of added acid showed one hydroxyl proton as a singlet at τ 5.2, two hydroxymethylene protons as a doublet at 6.6, and eleven protons as a multiplet at higher field. This multiplet consisted mainly of an A_3B_2 spectrum which would be expected for two ethyl groups. The fact that the hydroxymethylene protons appeared as a doublet indicated the presence of a proton on an α-carbon. 2-Ethyl-1-butanol (IV, R = C_2H_5) has such a proton, whereas 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5) does not.

For comparison, the n.m.r. spectra of several derivatives of 2-ethyl-2-methyl-1-butanol (II, R = C_2H_5) prepared in this laboratory showed the two hydroxymethylene protons as a singlet (*i.e.*, no protons of an α-carbon) and 13 protons as a multiplet at higher field. The multiplet at higher field consisted of the sharp singlet expected for the unsplit methyl group superimposed on the A_3B_2 spectrum expected for two ethyl groups.

The cleavage of 2,2-dialkyl-1,3-propanediols (I) at elevated temperatures and under strongly basic conditions to 2,2-dialkylethanols (IV) has been previously reported.[5] Specifically, 2,2-diethyl-1,3-propanediol (I,

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(1) This work was supported by the Army Research Office (Durham).

(2) Du Pont Teaching Fellow, 1962–1963.

(3) Sloan Foundation Fellow.

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$R = C_2H_5$) 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.

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Structure of Indene-1(3)-carboxylic Acid

A. MELERA, M. CLAESEN, AND H. VANDERHAEGHE

Varian AG Research Laboratories, Zurich, Switzerland, and Rega Institute, University of Louvain, Belgium

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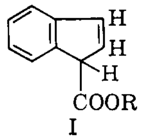
The action of carbon dioxide on indenylmagnesium,[1] -sodium,[2,3] or -lithium[4,5] always gives the same indenecarboxylic acid. This acid was considered in the earlier literature[3] and also more recently[5] to be 1-indenecarboxylic acid (I, R = H). As the infrared spectrum indicated an α,β-unsaturated acid, other authors assigned the structure of 3-indenecarboxylic acid (II, R = H) to this product.[6,7]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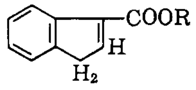
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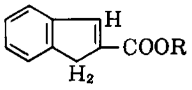
III

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.

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