g.), and the reaction mixture brought to 250° as rapidly as possible (*ca.* 30 min.). Samples of the mixture were removed starting when the reaction temperature was reached and at regular intervals during the reaction. These samples were analyzed by liquid-liquid partition chromatography using a chloroform–butanol-1 solvent system on a silica bed.[5,6]

The 2,6-dioxocyclohexanepropionic acid was eluted after 120 ml. and the unchanged glutaric acid after 240 ml. The quantity of the particular acid eluted was determined by titration of the elutate with alcoholic sodium hydroxide. The identities of the eluted fractions were indicated by addition of known samples to test columns. In addition, the eluted acid fractions from the reaction samples were retained and the sodium salts prepared. The infrared spectra of these individual sodium salts in potassium bromide were determined by the method of Struthers and Childers[7] and compared with the spectra of the sodium salts of the pure acids to unequivocally confirm the identities of the fractions.

It was noted that samples from the initial phases of the reaction contained an extra elution peak at 90 ml. which was present in neither the reactant glutaric anhydride nor in samples taken at the end of the reaction. The eluate after titration was retained and the infrared spectrum of the sodium salt was obtained as described above. The spectrum of the salt of the extra elution peak was found to be identical to that of the sodium salt of δ-oxoazelaic acid prepared by acid hydrolysis of 2,6-dioxocyclohexanepropionic acid. It can be concluded from this that δ-oxoazelaic acid or more probably its dilactone derivative is an isolable intermediate in the formation of 2,6-dioxocyclohexanepropionic acid from glutaric anhydride.

After the reaction had reached completion, the reaction mixture was distilled using a spinning band column (1/2" × 4'). The 2,6-dioxocyclohexanepropionic acid lactone of purity sufficient to determine the melting point was not obtained due to the partial hydrolysis to the acid. However, by a combination of the morpholine titration for anhydride[4] and a total acid titration with caustic, a molecular weight of 169 was determined. This agrees within the error of the method with the calculated value of 166. Further indication of the anhydride nature of the lactone is seen by the reaction with *p*-toluidine. The reaction occurs in cold acetone solution. The derivative was found to be the monotoluidide, m.p. 177–178°.

Anal. Calcd. for $C_{18}H_{19}NO_3$: Neut. equiv. 273; N, 5.14. Found: Neut. equiv. 277; N, 5.07.

A portion of the distillation fraction containing the 2,6-dioxocyclohexanepropionic acid lactone (b.p. 188° at 20 mm.) was dissolved in hot water. The acid thus formed was allowed to crystallize from solution and was recovered by filtration. The melting point of the acid was 187–188°; lit.[8] m.p. 188°, semicarbazide; 282° dec., lit.[8] m.p. 278°.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.8; H, 6.5; Found: C, 59.0; H, 6.6.

The bis-2,4-dinitrophenylhydrazone was a deep red-violet solid melting at 105–107°.

Anal. Calcd. for $C_{21}H_{22}N_8O_{10}$: N, 20.5. Found: N, 21.5.

As would be expected from the enol structure, an aqueous solution of the acid gave a bright red-violet color with ferric chloride. The neutral equivalent was found to be 92, which again confirms the dibasic character of this highly enolized carboxylic acid.

Preparation of dimethyl ether-ester derivative of 2,6-dioxohexanepropionic acid. The dimethyl ether-ester derivative was prepared by heating a methanolic solution of 2,6-dioxocyclohexanepropionic acid in a reaction flask to about 100–110°. Methanol was dropped in below the surface of the liquid. The methanol addition was continued until the distillate from the reaction was water-free. The reaction product was distilled using a spinning band column similar to that used in the distillation of the lactone. A distillation flat occurred at 167° at 5 mm.

Anal. Calcd. for $C_{11}H_{16}O_4$: Sapon equiv., 106. Found, 104.

Preparation of δ-oxoazelaic acid. A sample of 5 g. of 2,6-dioxocyclohexanepropionic acid was refluxed for 3 hr. in 50 ml. of 12*N* aqueous hydrochloric acid. At the end of the reaction period, most of the solution was boiled off and the product allowed to crystallize. The crystals obtained had a melting point of 107–109° and formed a semicarbazide melting at 182.5–183.59° dec.[9] No attempt was made to determine the yield of the hydrolysis reaction.

Anal. Calcd. for $C_9H_{14}O_5$: Neut. equiv., 101: C, 53.5; H, 6.9. Found: Neut. equiv., 101.5; C, 53.8; H, 7.0.

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Oxidation of Glycidaldehyde by Alkaline Hydrogen Peroxide

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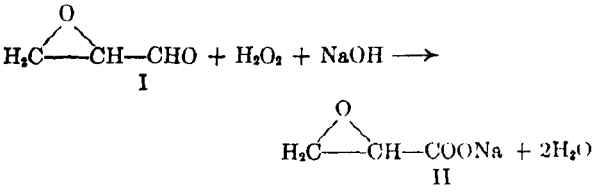
The efficient conversion of glycidaldehyde (I) to sodium glycidate (II) has been accomplished through use of hydrogen peroxide under controlled *p*H. Thus, a solution of glycidaldehyde in 1.1



molar equivalents of dilute hydrogen peroxide was treated with sodium hydroxide solution at 30–45° at such a rate as to maintain a *p*H of 9. Reaction was complete in less than one hour to give crystalline sodium glycidate hemihydrate in 65% yield.

While the sodium salt has apparently not been prepared before, potassium glycidate was recently described.[1] There, glycerol α-monochlorohydrin was oxidized by nitric acid over a period of several days to give β-chlorolactic acid. This was treated with potassium hydroxide to give the salt of the epoxy acid.

In the present work, glycidic acid of 93% purity (titration for oxirane oxygen) was obtained in

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80% recovery by ether extraction of the solution resulting from treatment of aqueous sodium glycidate with dilute nitric acid at −5°. Further purification was achieved by distillation followed by recrystallization. Pure glycidic acid is a crystalline hygroscopic solid melting at 36–38° and having a pK_a of 3.4.

Hydration of the epoxide group of sodium glycidate was accomplished in dilute aqueous solution at reflux for eight hours. Treatment of the resulting solution with calcium chloride led to the precipitation of calcium glycerate in 83% overall yield.

EXPERIMENTAL

Sodium glycidate hemihydrate. Procedure A. To a 1-l., five-neck, round bottom flask equipped with stirrer, dropping funnel, thermometer, and *p*H electrodes connected to a Beckman *p*H meter, was added 108 g. (1.50 moles) of anhydrous glycidaldehyde.[2] With stirring and ice bath cooling at 35–40° was added 1.60 moles of 30% hydrogen peroxide over a 10-min. period. The wet ice bath was then replaced with an efficient Dry Ice–acetone bath, and a solution of 60 g. (1.50 moles) of sodium hydroxide in 200 ml. of water was added as rapidly as possible at 40–45° and an initial *p*H of 8.5–9.0. After part of the alkali had been added, it was possible to control the *p*H at 9.0 ± 0.1. After completion of the addition (*ca.* 30 min.), the mixture was allowed to stir for an additional 15 min. The final *p*H was about 7.

The reaction mixture was concentrated at 100 mm. and <40° by means of a circulating evaporator.[3] When the volume had been reduced to about 250 ml., the concentrate was diluted with 1600 ml. of ethanol. Sodium glycidate hemihydrate started to precipitate immediately. After 12 hr. in the cold, the solid product was recovered by filtration, washed with ethanol, and vacuum-dried at room temperature. The weight of white crystalline product was 115 g. (65% yield). Titration for oxirane oxygen indicated a minimum purity of 94%.

Anal. Calcd. for $C_3H_3O_3Na \cdot {}^1/_2H_2O$: Oxirane oxygen, 13.4. Found: Oxirane oxygen, 12.6.[4]

The salt was best recrystallized by dissolving 10.0 g. in 20 ml. of water and adding this solution to 200 ml. of boiling ethanol. On cooling to room temperature there was recovered 8.0 g. having a minimum purity of 98%.

Anal. Calcd. for $C_3H_3O_3Na \cdot {}^1/_2H_2O$: C, 30.3; H, 3.4; Na, 19.3; oxirane oxygen, 13.4 Found: C, 30.3; H, 3.4; Na, 19.1 oxirane oxygen, 13.1.[4]

Procedure B. To the same flask was added 100 ml. of water and 1.10 moles of 30% hydrogen peroxide. With stirring and cooling at 30–35° was added dropwise 72 g. (1.0 mole) of glycidaldehyde. A solution of 40 g. (1.0 mole) of sodium hydroxide in 150 ml. of water was then added dropwise at 30–35° at such a rate as to maintain a *p*H of 8.5–9.0. After about one half of the alkali had been added, the *p*H was controlled at 9.0 ± 0.1. Alkali addition was complete in 1.25 hr. and stirring was continued for 15 min. longer as the *p*H fell to 7–8.

The reaction mixture was concentrated under vacuum at 15–20° to a volume of 150–200 ml. Some crystalline sodium salt precipitated. Dilution with 1500 ml. of ethanol then afforded 78 g. (65%) of sodium glycidate hemihydrate having an oxirane oxygen content of 12.7.[4]

Glycidic acid from sodium glycidate hemihydrate. A solution of 23.8 g. (0.20 mole) of sodium salt in 50 ml. of water was stirred at −5° as 37 ml. of 5.17*N* nitric acid (0.19 equiv.) was added dropwise over 1 hr. The resulting solution was saturated with ammonium sulfate and extracted with ten 75-ml. portions of ether. After drying over magnesium sulfate, the combined ether extract was concentrated on the steam bath until the internal temperature reached 45°. This concentrate was then pumped at 2 mm. pressure to a constant weight of 13.3 g. (80% yield) of colorless liquid. A minimum purity of 93% was indicated by titration for oxirane oxygen.

Anal. Calcd. for $C_3H_4O_3$: oxirane oxygen, 18.2; neut. equiv., 88. Found: oxirane oxygen, 16.8;[4] neut. equiv., 93.

Claisen distillation of an 11.3 g. portion gave 4.3 g. of distillate, b.p. 55–60° (0.5 mm.), n_D^{25} 1.4424, and 6.9 g. of polymeric residue. Analysis of the glycidic acid indicated a minimum purity of 97% (found: oxirane oxygen, 17.6; neut. equiv., 89).

In another experiment, carried out as above except that 2*N* sulfuric acid was used in place of nitric acid, there was obtained a 53% over-all recovery of distilled glycidic acid. Its purity was 94% by titration for oxirane oxygen. That material, on crystallization from benzene-hexane, gave analytically pure glycidic acid, m.p. 36–38°.

Anal. Calcd. for $C_3H_4O_3$: C, 40.9; H, 4.6. Found: C, 40.8; H, 4.6.

Calcium glycerate. A solution of 10.0 g. (0.084 mole) of sodium glycidate hemihydrate in 100 ml. of water was allowed to reflux for 8 hr. To the warm solution was then added a solution of 5.1 g. (0.046 mole) of calcium chloride in 25 ml. of water. The clear solution, on standing at 50°, deposited crystals which, on filtration, washing with 50% alcohol and drying, amounted to 7.4 g. of calcium glycerate dihydrate. An additional 2.5 g. was recovered from the original mother liquor for a total yield of 83%.

Anal. Calcd. for $C_6H_{10}O_8 \cdot 2H_2O$: C, 25.2; H, 4.9; Ca, 14.0; H_2O, 12.6; α-glycol value, 0.70 mole/100 g. Found: C, 25.0; H, 5.0; Ca, 13.9; H_2O, 13.9; α-glycol value, 0.70 mole/100 g.[5]

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A Case of Nonstereospecificity in the Simmons-Smith Procedure for Preparation of Cyclopropanes[1]

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In connection with studies of the unimolecular isomerization of cyclopropanes, we have attempted the preparation of the *trans*-dideutero (I), all *cis* (II), and *cis*-dideutero-*trans*-methyl (III) isomers of 1,2-dideutero-3-methylcyclopropane. Use of the Simmons-Smith reaction appeared feasible since addition to 1,2-disubstituted olefins proceeds stereospecifically to yield 1,2-disubstituted cyclopropanes of corresponding configuration.[3] In our

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