ture.[10] The mixture was then thoroughly blended by further grinding together, placed in a Perkin-Elmer potassium bromide evacuable die, and pressed under approximately 25,000 p.s.i. (gauge) for 3 min. Spectral measurements were made using the disk holder described by Waggoner[11] with a similarly prepared 400 mg. potassium bromide disk for a blank.

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(10) The final compositions of the disks were: 0.05 mg. of *p*-bromoacetophenone, 0.3 mg. of nitrosobenzene, 0.2 mg. of 3-phenacylideneoxindole, each in 400 mg. of potassium bromide.

(11) W. H. Waggoner, *Chemist-Analyst*, **48**, 80 (1959).

Cyclic Ether Formation by Bis[(1-hydroxyethyl)cyclopentadienyl]iron

EUGENE C. WINSLOW AND EDWARD W. BREWSTER

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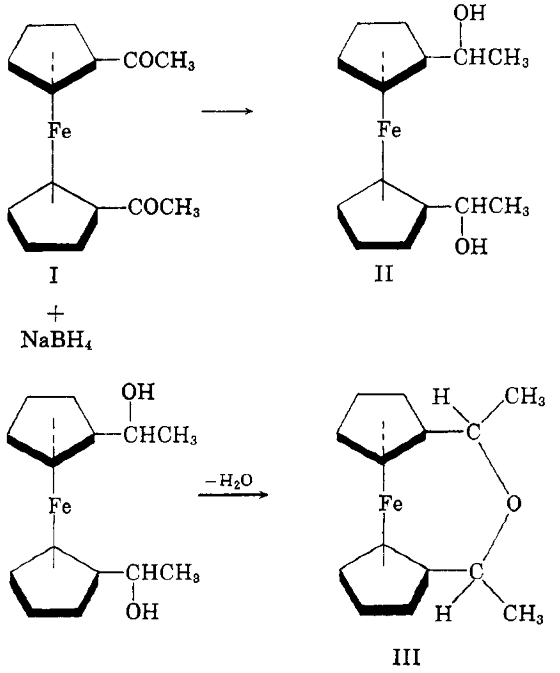
The preparation of divinylferrocene was attempted in this laboratory by the use of diacetylferrocene (I) as a starting material. This was reduced to form bis [(1-hydroxyethyl) cyclopentadienyl]iron (II). This compound was previously reported as melting at 69–71°.[1] Infrared data and other evidence indicate that the compound produced by reduction of diacetylferrocene with sodium borohydride in this laboratory is in fact bis[(1-hydroxyethyl)cyclopentadienyl]iron II and has a melting point of 105–106°.

The attempted dehydration of this dialcohol (II) produced a cyclic ether (III) between the side chains of the two cyclopentadiene rings of ferrocene rather than the desired divinyl ferrocene.

The infrared spectrum of II shows a strong hydroxy bond at 3.10 μ. The carbonyl bond is absent in the spectrum. Additional significant bonds appears at 7.35, 7.60, 9.10, and 12.41 μ. The infrared spectrum of the cyclic ether III shows a disappearance of the hydroxyl bonds. An ether bond at 8.8 μ can be cited as evidence for a cyclic ether. Other bonds appear at 7.68, 9.36, 9.88, 11.95, and 12.35 μ.



EXPERIMENTAL

Diacetylferrocene was prepared by following the procedure of Woodward (2).

Preparation of bis[(1-hydroxyethyl)cyclopentadienyl]iron. In a liter one-neck flask, fitted with a reflux condenser, was placed 27.0 g. (0.0985 mole) of diacetyl ferrocene, 7.56 g. (0.2 mole) of sodium borohydride, and 200 ml. of isopropyl alcohol. The mixture was refluxed for 5 hr. on a steam bath.

The solution was then evaporated to dryness by means of an air stream and water was added to the residue to hydrolyze the salt formed in the reaction. The product was then extracted with ether. The ether was removed and a yellow crystalline solid was obtained, which was recrystallized from methanol The yield was 14.4 g. (53.4%), m.p. 105–106°.

Anal. Calcd. for $C_{14}H_{18}O_2$ Fe: C, 61.31; H, 6.57. Found: C, 61.36; H, 6.72.

Preparation of 1,1'-diethyl-α,α'-epoxybiscyclopentadienyliron (II)(III). In a 1-l. flask, fitted with a reflux condenser, was placed 27.0 g. (0.0985 mole) of diacetylferrocene, 7.56 g. (0.2 mole) of sodium borohydride, and 200 ml. of isopropyl alcohol. The mixture was refluxed for 5 hr. on a steam bath.

The solution was then evaporated to dryness by means of an air stream and 100 ml. of water containing 5 ml. of glacial acetic acid was added to the residue to hydrolyze the salt formed in the reaction. The product was extracted with ether. The ether was evaporated and a yellow crystalline solid was obtained. The product was recrystallized from methanol. The yield was 11.2 g. (44.5%), m.p. 95–96°.

Anal. Calcd. for $C_{14}H_{16}O$ Fe: C, 65.52; H, 6.25. Found: C, 65.53; H, 6.42.

Acknowledgment. This work was carried out as a portion of work on a contract with the U. S. Army Quatermaster Corps.

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(1) R. J. Graham *et al.*, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

(2) R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

Preparation of 2,6-Dioxocyclohexanepropionic Acid and δ-Oxoazelaic Acid from Glutaric Anhydride

RALPH F. GILBY, JR.

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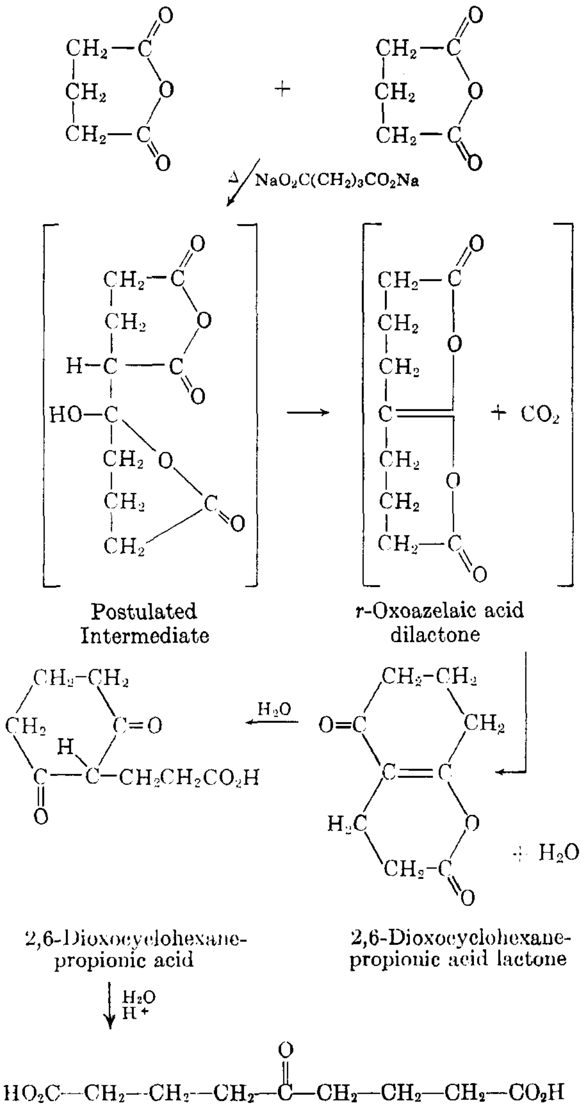
The preparation of δ-oxoazelaic acid (5-oxononanedioic acid) from disodioacetone dicarboxylic



ester and β-iodopropionic acid[1] or from the intermolecular Claisen condensation of glutarate esters[2] has been reported. Both methods require the use of alkali metal catalysts. 2,6-Dioxocyclohexanepropionic acid (3-(2,6-dioxocyclohexyl) propanoic acid) can be prepared by heating δ-oxoazelaic acid, preferably under reduced pressure[1,2] or by the condensation of dihydroresorcinol and ethyl acrylate.[3]

In the course of our work on the dehydration of glutaric acid to glutaric anhydride, a new synthesis for either 2,6-dioxocyclohexanepropionic acid or δ-oxoazelaic acid has been found. This method involves the bimolecular condensation of glutaric anhydride. While no catalyst is required, small quantities of an alkali glutarate (*e.g.*, 0.5% sodium glutarate) increase the rate significantly.

The reaction proceeds by a Claisen condensation followed by the splitting out of carbon dioxide to form the dilactone of δ-oxoazelaic acid. The latter compound is definitely an intermediate. It has been isolated in the reaction product from the initial phase of the reaction and identified by the infrared spectrum of the sodium salt. Further heating causes rearrangement and dehydration to the lactone of 2,6-dioxocyclohexanepropionic acid.[1,2]

At 250° the maximum conversion of 2,6-dioxocyclohexanepropionic acid was obtained after about two hours. No further decrease in reactant was observed after this period. Further heating resulted in lower yields due to decomposition of the product.

The 2,6-dioxocyclohexanepropionic acid may be separated from the reaction mixture by distillation of the lactone under reduced pressure. Esterification followed by distillation of the ester is also a means of separation. However, the high temperature required will reconvert a portion of the ester to the lactone. The acid can be formed by hydrolysis of the lactone in either acidic or basic media.

Because of the presence of a highly enolized tertiary hydrogen between two carbonyl groups in addition to one carboxyl group, 2,6-dioxocyclohexanepropionic acid reacts as a dibasic acid. The enol group etherifies under conditions required for the esterification of a carboxylic acid, thus giving an ether-ester which has the characteristics of a diester.

This dibasic characteristic is also illustrated in the reaction of 2,6-dioxocyclohexanepropionic acid lactone with morpholine in the determination of anhydride concentration.[4] The lactone acts as a cyclic anhydride giving a monomorpholide by direct reaction.

Reaction of 2,6-dioxocyclohexanepropionic acid with 55% nitric acid at 75° proceeds rapidly yielding mole for mole of succinic acid plus 0.8 mole for mole of glutaric acid (over-all yield 90%).

Even though δ-oxoazelaic acid or its dilactone is formed as an intermediate in the preparation of 2,6-dioxocyclohexanepropionic acid, it is difficult to separate the compound from the reaction mixture without forming 2,6-dioxocyclohexanepropionic acid lactone. The best method for obtaining δ-oxoazelaic acid of good purity is to hydrolyze 2,6-dicyclohexanepropionic acid in 15–20% hydrochloric acid for three to five hours.[2] The δ-oxoazelaic acid formed can then be crystallized from the reaction mixture.

EXPERIMENTAL

Preparation of 2,6-dioxocyclohexanepropionic acid. Two hundred fifty grams of glutaric anhydride (96.5%)[4] was placed in a 500-ml. round bottom flask fitted with an air-cooled reflux condenser. Sodium glutarate was added (1.25

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[1] H. Von Pechmann and N. V. Sidgwick, *Ber.*, **37**, 3816 (1904).

[2] F. Sorm, *Collection Czech, Chem. Commun.*, **12**, 150 (1947), *Chem. Abstr.*, **41**, 4775 (1947).

[3] H. Stetter and M. Coenen, *Chem. Ber.*, **87**, 869 (1954).

[4] J. B. Johnson and G. L. Funk, *Anal. Chem.*, **27**, 1464 (1955).

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 $C_{16}H_{19}NO_3$: 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.[2] m.p. 188°, semicarbazide; 282° dec., lit.[8] m.p. 278°.

Anal. Calcd. for $C_9 10_{12}O_4$: 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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(5) T. Higuchi, N. C. Hill, and G. B. Corcoran, *Anal. Chem.*, **24**, 491 (1952).

(6) C. J. Marvel and R. D. Rands, *J. Am. Chem. Soc.*, **72**, 24742 (1950).

(7) G. W. Struthers and E. Childers, *Anal. Chem.*, **27**, 757 (1955).

(8) F. Beilstein, *Handbuch der Organische Chemie*, Springer, Berlin, 1931, Volume 10, page 794.

(9) F. Beilstein, *Handbuch der Organische Chemie*, Springer, Berlin, 1931, Vol. 3, p. 816.

Oxidation of Glycidaldehyde by Alkaline Hydrogen Peroxide

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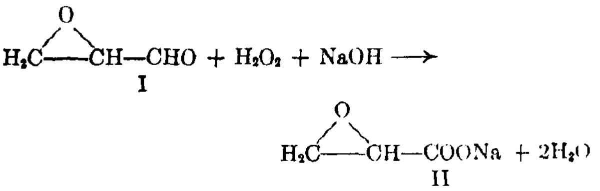
The efficient conversion of glycidaldehyde (I) to sodium glycidate (II) has been accomplished through use of hydrogen peroxide under controlled *p*H. Thus, a solution of glycidaldehyde in 1.1 molar equivalents of dilute hydrogen peroxide was treated with sodium hydroxide solution at 30–45° at such a 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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(1) N. F. Blau, J. W. Johnson, and C. G. Stuckwisch, *J. Am. Chem. Soc.*, **76**, 5106 (1954).