68.7°. The infrared spectrum showed a strong band at 1740 cm.$^{-1}$ (δ lactone).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.81.

Behavior of the lactone of cis-3-hydroxycyclohexanecarboxylic acid in concentrated sulfuric acid. Fifteen grams of the lactone of *cis*-3-hydroxycyclohexanecarboxylic acid was dissolved in 50 ml. of concd. sulfuric acid and allowed to stand at room temperature for 48 hr. At the end of this period the opaque brown mixture was poured into water and continuously extracted with ether. The extracts were dried, evaporated, and the product fractionally distilled. The main fraction, b.p. 115° (8 mm.) weighing 4.2 g. (28%) was obtained and proved to be the lactone of *cis*-4-hydroxycyclohexanecarboxylic acid. One crystallization from ether-pentane yielded 3.3 g. of lactone melting over a range to 124°. Crystallization of a small sample gave material of m.p. 127–128°, (lit.[12] m.p. 126–128°). The infrared spectrum was identical with that of an authentic sample of *cis*-4-hydroxycyclohexanecarboxylic acid lactone.[13]

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Preparation of Methyl β-Hydroxybutyrate from Propylene Oxide, Carbon Monoxide, Methanol, and Dicobalt Octacarbonyl

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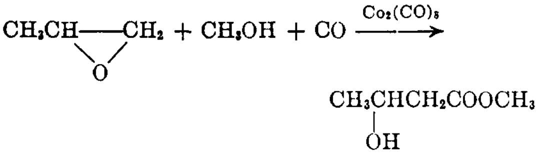
Received October 18, 1960

The oxo reaction[1] is a well known method for converting olefins to aldehydes or alcohols by hydroformylation, using carbon monoxide, hydrogen, and a cobalt catalyst. When water, alcohols, or amines are used as the source of hydrogen,[2] the products are acids, esters, and amides, respectively. This paper reports the results from the reaction of propylene oxide with methanol and carbon monoxide in the presence of dicobalt octacarbonyl under the conditions of temperature and pressure used in oxo syntheses.

Very little has been published concerning the reaction of the epoxy structure with carbon monoxide. Hamada, Baba, and Hagihara[3] treated ethylene oxide with carbon monoxide and hydrogen in toluene using dicobalt octacarbonyl as catalyst and obtained a mixture of products all of which resulted from the reaction of the oxide with hydrogen only. Lenel[4] reported that in the oxo reaction, epoxides other than ethylene oxide gave rise to mixtures of isomers which proved extremely difficult to separate. Seon and Leleu[5] claimed the preparation of monoethylene glycol hydracrylate from ethylene oxide, carbon monoxide, and water and of mixtures of hydracrylates by replacing the water with alcohols. Apparently nothing has been reported concerning the reaction of unsymmetrical epoxides with carbon monoxide.

Propylene oxide in methanol as solvent reacted with carbon monoxide in the presence of preformed dicobalt octacarbonyl to give predominantly methyl β-hydroxybutyrate.



$$CH_3CH(O)CH_2 + CH_3OH + CO \xrightarrow{Co_2(CO)_8} CH_3CH(OH)CH_2COOCH_3$$

I

Under the conditions used, minor amounts of 1-methoxy-2-propanol and 2-methoxy-1-propanol were also formed together with very small amounts of unidentified hydroformylation products, one of which is probably methyl crotonate. Table I presents the reaction conditions and results of several typical runs.

In addition to the products shown, gas chromatographic analysis indicates that traces of methyl β-hydroxyisobutyrate may have been produced in some of these experiments. Larger scale runs support this, but in no case could the isobutyrate consist of more than 5% of the total ester formed. Polymeric material derived from the condensation of the hydroxyester or the polymerization of propylene oxide was not found; neither was the formation of any monopropylene glycol hydroxybutyrate noted.

The structure of I was proved by the identity of its infrared spectrum and the melting point of its amide to the corresponding data from authentic methyl β-hydroxybutyrate. In addition, oxidation of I with potassium dichromate yielded methyl acetoacetate, also identified by infrared spectra and the preparation of comparison of suitable derivatives. Confirmation of the structure of I was also made by comparison of its gas chromatogram to that of authentic hydroxybutyrate.

Identification of the two methoxypropanols was made by means of their retention times determined from gas chromatograms and by infrared spectra. Data procured by both of these methods were identical to those obtained from the two propanols when synthesized by an independent route.

The results in Table I indicate that the reaction occurs over a fairly wide range of conditions but highest yields are obtained by heating at 130° for about four hours with an initial carbon monox-

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TABLE I

REACTION OF PROPYLENE OXIDE WITH METHANOL AND CARBON MONOXIDE[a]

Run	Initial CO Pressure P.S.I.	Temp.	Time, Hr.	Methyl β-Hydroxybutyrate Yield, %	1-Methoxy-2-propanol Yield, %	2-Methoxy-1-propanol Yield, %
1	3500	190	2	21.6	1.8	1.9
2	3500	130	2	25.6	0.8	0.8
3	3500	130	4	40.3	0.9	0.7
4	3500	130	6	35.7	0.8	2.5
5	3500	110	2	27.5	0.7	1.2
6	3500	110	4	20.8	3.0	6.1
7	6000	130	4	29.7	4.0	4.4
8	2500	130	2	21.6	2.6	2.9
9	1500	130	2	20.8	1.8	2.2
10	800	130	2	20.8	0.1	0.4

[a] Propylene oxide = 1.0 mole; CH_3OH = 250 ml., $Co_2(CO)_8$ = 10 g.

ide pressure of 3500 p.s.i. The yields given in the table do not take into account any propylene oxide which may have been lost during venting and flushing the reactor, nor any recovered with the excess methanol after the reaction. Work not yet completed indicates that some of the propylene oxide unconverted to ester appears as a low-boiling by-product. Increasing or decreasing the carbon monoxide pressure decreases the maximum yield of ester obtained. A similar phenomenon has been observed in the hydroformylation of olefins[1]; however, unlike the oxo reaction with olefins, carbonylation to form all possible isomeric products does not occur in the propylene oxide–carbon monoxide–methanol reaction. In contrast, carbon monoxide adds to propylene oxide to give almost exclusively the normal ester. The factors and mechanism that cause this directive effect are not known, but investigation of them may provide information on the mechanism of the oxo reaction also.

EXPERIMENTAL[6]

The reactor used for all the high-pressure experiments was an Aminco rocker-type autoclave having a 1-l. void with stainless steel liner and equipped with heating mantle and an automatic temperature and pressure recorder. Carbon monoxide (C.P.) was obtained from the Matheson Co., Inc., East Rutherford, N.J., and propylene oxide from Distillation Products and Union Carbide. Dicobalt octacarbonyl was prepared from cobalt carbonate (Baker & Adamson) by published procedures.[1] Infrared spectra were recorded on a Beckman IR-5 equipped with sodium chloride optics. A Perkin-Elmer Fractometer, Model 154B, was used for all gas chromatography work.

Methyl β-hydroxybutyrate via propylene oxide. For a typical run as shown in Table I, 1 mole (58 g.) of propylene oxide in 250 ml. of methanol was charged into the reactor and approximately 10 g. of dicobalt octacarbonyl in 100 ml. of petroleum ether (b.p. 30–60°) were added. The reactor was sealed and flushed twice with nitrogen and once with carbon monoxide. Carbon monoxide was then added to a pressure of 3500 p.s.i. and rocking started. The gas pressure always dropped two or three hundred pounds at this point, but the reactor was then repressured to 3500 p.s.i., heated to reaction temperature and held there for the desired length of time. No break in the recorded temperature or pressure curve was ever observed during the course of the heating to indicate that a reaction had occurred, but after the specified time, the reactor was cooled, vented, flushed, and the contents removed by aspiration. Any unchanged propylene oxide, excess methanol and petroleum ether, and low boiling products were removed by distillation and the liquid residue distilled under vacuum. Redistillation gave methyl β-hydroxybutyrate, b.p. 50–52°/2–3 mm., 173–174°/1 atm. (lit.[7] b.p. 67–68.5°/13 mm.). Yields are recorded in Table I.

Anal. Calcd. for $C_5H_{10}O_3$: C, 50.9; H, 8.5. Found: C, 50.6; H, 8.7.

The infrared spectrum had bands at 3436 cm.$^{-1}$ and 1718 cm.$^{-1}$ corresponding to hydroxyl and carbonyl groups.[8] The spectrum and also the retention time on a Perkin-Elmer gas chromatograph column with substrate "A" were identical with those of authentic methyl β-hydroxybutyrate.

The amide, prepared by allowing 1 g. of the ester to stand 48 hr. in liquid ammonia, had m.p. 83–84°. (lit.[9] m.p. 84–87° and 83–84°[10])

Anal. Calcd. for $C_4H_9O_2N$: C, 46.6; H, 8.7; N, 13.6. Found: C, 46.7; H, 8.9; N, 13.6.

A mixed melting point with the amide of authentic methyl β-hydroxybutyrate gave no depression and the infrared spectra of the two compounds were identical.

The forerun from the redistillation always contained small amounts of the isomeric 1-methoxy-2-propanol and 2-methoxy-1-propanol, identified from the fact that their retention times from analysis by gas chromatography exactly matched those of the two authentic methoxypropanols. Infrared spectra obtained by solvent-trapping the effluent from the chromatograph column at appropriate intervals were also identical to the spectra of the standard alcohols.

Oxidation of methyl β-hydroxybutyrate. Methyl β-hydroxybutyrate (10 g., 0.085 mole) prepared *via* propylene oxide, and potassium dichromate (22 g., .075 mole), in 10 ml. of water were placed in a flask, cooled to 10°, and a mixture of 23 g. of concd. sulfuric acid and 6 ml. of water added dropwise with stirring. Addition was complete in about an hour and the solution was then stirred at room temperature overnight. The next day, water was added, the mixture extracted with ether, and the ether dried and evaporated. The crude methyl acetoacetate was treated with 2,4-dinitrophenylhydrazine[11] to yield a 2,4-dinitrophenylhydrazone,

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m.p. 109–110° (lit.[12] m.p. 110°), which gave no depression in a mixed melting point with the 2,4-dinitrophenylhydrazone of authentic methyl acetoacetate.

Methyl β-hydroxybutyrate. β-Butyrolactone was prepared according to Johansson's[9] method of heating a well stirred aqueous solution of sodium β-bromobutyrate at 40° for 6 hr. with chloroform, replacing the chloroform several times during the heating period. The solution was maintained basic to bromthymol blue by addition of 10% sodium hydroxide as needed. The combined chloroform solutions were dried, the solvent evaporated, and the β-butyrolactone (55%) distilled under vacuum, b.p. 58–59°/15 mm. (lit.[9] b.p. 54.4–55/10 mm.). A carbonyl band at 1818 cm.$^{-1}$ confirmed the presence of the lactone structure[8] and hydrolysis[13] with methanolic sodium hydroxide at 0° followed by neutralization by dilute hydrochloric acid gave methyl β-hydroxybutyrate (54%), b.p. 56–58°/7 mm. (lit.[7] b.p. 67–68.5°/13 mm.).

The amide, prepared as above, had a m.p. of 84–85° (lit.[9] m.p. 84–87° and 83–84°[10]).

1-Methoxy-2-propanol and 2-methoxy-1-propanol. Propylene oxide (1 mole, 58 g.) and 250 ml. of methanol were heated to 130° in a sealed system[14] under a nitrogen atmosphere and held at this temperature for 2.5 hr. The reaction product was then removed and stripped of excess methanol and unchanged propylene oxide. Fractionation of the residue on an 18-in. Widmer column gave 24.6 g. of 1-methoxy-2-propanol, b.p. 53–55°/50 mm., 116–119°/1 atm. (lit.[15] b.p. 118–119°/1 atm.) and 9.8 g. of 2-methoxy-1-propanol, b.p. 58–59°/50 mm., 127–129°/1 atm. (lit.[15] b.p. 130°/1 atm.). The 2,4-dinitrobenzoate[11] of 1-methoxy-2-propanol melted at 73–76° (lit.[15] m.p. 83.5–85°). The same derivative prepared from authentic 1-methoxy-2-propanol (Dowanol PM) had a melting point of 74–77° and did not depress the melting point of the original material. Analysis by gas chromatography did not reveal any impurities in the authentic 1-methoxy-2-propanol and its infrared spectrum was the same as that of the compound prepared above.

2-Methoxy-1-propanol gave a 2,4-dinitrobenzoate which had m.p. 93–95° (lit.[15] m.p. 95.5–97°).

Acknowledgment. The authors would like to thank the Diamond Alkali Company for their support of this work.

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Catalytic Hydrogenation of *cis*-6,7-Epoxyoctadecanoic Acid

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Received July 27, 1960

The catalytic hydrogenation of 9,10-epoxyoctadecanoic acid and certain of its esters results in the selective formation of the 10-hydroxy derivative.[2–5] It was postulated that this reaction proceeds by a mechanism involving an oxonium ion intermediate and its specificity was attributed to the influence exerted at both the oxirane center and the catalyst surface by the electrophilic —COO— group.[4] More recently the hydrogenation of 9,10-epoxyoctadecyl acetate was investigated and it was found that 9- and 10-hydroxy isomers were formed in equimolar proportions.[6] The difference in results in these two instances was attributed to the relative positions of the oxirane centers with respect to the —COO— groups. It appeared of interest, therefore, to investigate the catalytic hydrogenation of a long chain epoxy acid in which the oxirane center was not situated at the 9,10-position. Accordingly, the catalytic hydrogenation of *cis*-6,7-epoxyoctadecanoic acid, obtained by epoxidation of petroselinic (*cis*-6-octadecanoic) acid, was investigated.

Attempts to hydrogenate alcoholic solutions of *cis*-6,7-epoxyoctadecanoic acid at room temperature and 20–30 pounds pressure employing either Raney nickel, Adams' catalyst, or 5% palladium on calcium carbonate were unsuccessful. However, under identical conditions it was found that hydrogenation could be readily effected through use of 10% palladium on carbon. It was also found that the theoretical amount of hydrogen was absorbed during quantitative hydrogenation[7] employing acetic acid as solvent and 10% palladium on carbon as catalyst. In general, the rate of hydrogenation of *cis*-6,7-epoxyoctadecanoic acid in ethanolic solution employing either 5 or 10% of 10% palladium on carbon catalyst was comparable to that observed for other long chain epoxides. However, in one experiment employing 10% of 10% palladium on carbon catalyst more than the theoretical quantity of hydrogen was absorbed and hydrogenation was complete in twelve minutes whereas several hours were generally required for complete hydrogenation.

The identity of the hydroxy acids resulting from the abnormally rapid hydrogenation and those from

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