and concentrated. There resulted a viscous yellow oil boiling at 280–285° (2 mm.). The yield was 4.4 g. or 84.1%.

Anal. Calcd. for $C_{16}H_{13}O_2Br$: C, 60.5; H, 4.1; $—OCH_3$, 9.8. Found: C, 60.8; H, 4.0; $—OCH_3$, 10.0.

o-**Bromophenylglyoxylic Acid.**—This acid was purified by several crystallizations from methyl alcohol and water. The thin colorless needles melted over a range with decomposition as reported by Russanow. For a concentration of 0.03449, molecular conductivity 266.21, and conductivity at infinite dilution 348, the ionization constant at 25° was calculated to be 8.6×10^{-2}.

Summary

The preparation and properties of a new diketone are herein reported in connection with a discussion of the methylation of alpha diketones.

WASHINGTON, D. C. RECEIVED APRIL 24, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 140]

The Hydroxylation of the Double Bond[1]

BY NICHOLAS A. MILAS AND SIDNEY SUSSMAN

The use of osmium tetroxide and chlorates for the addition of hydroxyl groups to the double bond[2] is limited to aqueous solutions, and, at times, to specialized conditions. Similarly, organic peracids which have been used for this purpose are not of general applicability.[3] During the past year and a half we have been engaged in the preparation of tertiary alkyl peroxides and hydroperoxides, and found that anhydrous solutions of hydrogen peroxide and tertiary butyl alcohol are stable at room temperature for long periods of time. Such solutions, however, are perfectly inert toward olefinic double bonds, but in the presence of a small amount of osmium tetroxide, likewise dissolved in anhydrous tertiary butyl alcohol, a reaction proceeds smoothly to yield almost invariably a glycol. For example, from ethylene we obtained ethylene glycol; from tetramethylethylene, pinacol; from cyclohexene, adipic acid; from the ethyl esters of crotonic, maleic and fumaric acids, the corresponding dihydroxy esters. Table I shows some of the quantitative results obtained.

TABLE I

Olefinic substance	Main product	% yield
Isobutylene	Isobutylene glycol	37.6
Trimethylethylene	Trimethylethylene glycol	37.8
Allyl alcohol	Glycerol	60.2
Cinnamic acid	Phenylglyceric acid	56.2
Crotonic acid	Dihydroxybutyric acid	53.8
Maleic acid	Mesotartaric acid	30.3
Fumaric acid	Racemic acid	48.3

While our work was under way Criegee[4] published recently some preliminary results using osmium tetroxide and hydrogen peroxide in ethyl ether, and obtained aldehydes as his main products. In the present research, however, all of the unsaturated substances tried yielded glycols, although in certain cases the latter oxidized further to yield small amounts of by-products. We are now actively engaged in this field and hope to publish in the near future a more extended investigation.

Experimental

Preparation of the Reagent.—To 100 cc. of 30% hydrogen peroxide (Albone C) was added 400 cc. of pure tertiary butyl alcohol and the solution treated with small portions of anhydrous sodium sulfate whereby two layers separated out. The alcohol layer, which contained most of the hydrogen peroxide, was removed and dried with anhydrous sodium sulfate and finally with anhydrous calcium sulfate (Drierite). A solution of 6.32% hydrogen peroxide in tertiary butyl alcohol was obtained, giving a recovery of 93.8%. This solution can easily be concentrated by vacuum distillation of the alcohol at room temperature to any desired concentration without any loss of the peroxide provided an all-glass apparatus is employed. When hydrogen peroxide solutions of this sort were allowed to stand at room temperature for over six months, only a small decrease in hydrogen peroxide concentration was noticed.

The Catalyst.—Osmium tetroxide (Merck osmic acid) dissolves readily in tertiary butyl alcohol and the solution is perfectly stable provided no isobutylene is present, otherwise most of the osmium tetroxide is readily reduced into an insoluble black colloidal oxide which is a very active catalyst for the decomposition of hydrogen peroxide. In aqueous solutions osmium tetroxide destroys hydrogen peroxide in a very short time, whereas in anhydrous tertiary butyl alcohol it decomposes the latter to the extent of 20% in one month's time.

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(1) A preliminary report of this work was presented before the research conference, M. I. T., December 13, 1935.

(2) (a) Milas and Terry, THIS JOURNAL, **47**, 1412 (1925); (b) Terry and Milas, *ibid.*, **48**, 2647 (1926); (c) Milas, *ibid.*, **49**, 2005 (1927).

(3) (a) Milas and Cliff, *ibid.*, **55**, 352 (1933); (b) Milas and McAlevy, *ibid.*, **56**, 1219 (1934).

(4) Criegee, *Ann.*, **522**, 75 (1936).

Isobutylene Glycol from Isobutylene.—The isobutylene was prepared by the dehydration of tertiary butyl alcohol with oxalic acid. To 4.3 g. (0.0768 mole) of isobutylene dissolved in 36.3 g. of tertiary butyl alcohol was added 39.3 cc. (0.0768 mole) of 6.62% hydrogen peroxide reagent. The mixture was cooled in an ice-bath and to it added 0.75 cc. of a 0.5% solution of osmium tetroxide in tertiary butyl alcohol, and allowed to stand overnight at 0°. The reaction was complete on the following day when the mixture was fractionated and the fraction boiling at 176–178° collected; yield, 2.6 g. or 37.6% of the theoretical. This had a density of 0.999 at 25°. The boiling point and density of isobutylene glycol are recorded in the literature[5] as 176–178° and 1.003 at 20°, respectively.

Trimethylethylene Glycol from Trimethylethylene.—To 7 g. (0.1 mole) of trimethylethylene[6] (b. p. 38.3–38.4°) were added 48.4 cc. (0.1 mole) of 7.03% hydrogen peroxide reagent and 1 cc. of the osmium tetroxide solution catalyst, and the mixture allowed to stand at room temperature for twenty-four hours. At the end of this time the reaction was complete; the mixture was then fractionated whereby 2.9 g. of trimethylethylene was recovered and a fraction boiling at 175° collected; yield, 2.3 g. or 37.8% of the theoretical. This had a density of 0.992 at 25°. The boiling point and density of trimethylethylene glycol are recorded in the literature[7] as 176–178° and 0.989 at 25°, respectively.

Glycerol from Allyl Alcohol.—To 6.1 g. (0.105 mole) of allyl alcohol (Eastman Kodak Company) were added 54.6 cc. (0.1 mole) of 6.3% hydrogen peroxide reagent and 1 cc. of the osmium tetroxide solution catalyst. The reaction mixture warmed up considerably and had to be cooled under running water. At the end of three hours the peroxide was completely consumed and the reaction mixture subjected to fractionation to remove the solvent, the catalyst and the unreacted allyl alcohol (1.7 g.). The glycerol obtained amounted to 4.2 g. or 60.2% of the theoretical. The glycerol was definitely identified as the tribenzoyl ester which was prepared in pyridine from benzoyl chloride and the product obtained. It had a m. p. of 69°. Balbiano[8] gives the m. p. of this derivative as 71–72°.

Phenylglyceric Acid from Cinnamic Acid.—To 3.7 g. (0.025 mole) of cinnamic acid (Eastman Kodak Company) were added 13.6 cc. (0.025 mole) of 6.3% hydrogen peroxide reagent and an equal volume of tertiary butyl alcohol. The mixture was cooled in an ice-bath, to it added 2 cc. of the osmium tetroxide solution catalyst, and allowed to stand overnight at 0°. The reaction was complete on the following day when the solvent was removed by vacuum distillation and the residue taken up with water. The unchanged cinnamic acid (2.4 g.) was removed by filtration and the filtrate distilled under reduced pressure when a semi-solid residue separated out; yield 0.9 g. or 56.2% of the amount of cinnamic acid consumed. The semi-solid phenylglyceric acid was not crystallized, but was found to have a neutralization equivalent of 190 which is in close agreement with the theoretical value of 182 for phenylglyceric acid.

Dihydroxybutyric Acid from Crotonic Acid.—To 4.3 g. (0.05 mole) of crotonic acid (Eastman Kodak Company) was added 27.2 cc. (0.05 mole) of 6.3% hydrogen peroxide reagent. The mixture was cooled in an ice-bath and to it added 1 cc. of the osmium tetroxide solution catalyst, and allowed to stand overnight at 0°. The reaction was complete on the following day when the solvent was removed by distillation under reduced pressure, and the residue taken up with water. The unchanged crotonic acid was then extracted with chloroform following the method of Braun.[9] When the chloroform was evaporated 2.7 g. of unchanged crotonic acid was recovered. The aqueous portion was evaporated under reduced pressure and yielded 1.2 g. of a thick sirup; yield, 53.8% of the amount of crotonic acid consumed. This had a neutralization equivalent of 122, which is in close agreement with the calculated value of 120 for dihydroxybutyric acid.

Mesotartaric Acid from Maleic Acid.—To 2.9 g. (0.025 mole) of maleic acid (Eastman Kodak Company) were added 27.2 cc. (0.05 mole) of 6.3% hydrogen peroxide reagent, 2 cc. of the osmium tetroxide solution catalyst, and the mixture was allowed to stand overnight at room temperature. The reaction was complete on the following day when the solvent was removed under reduced pressure and the residue dissolved in water. The solution was then made ammoniacal, heated to boiling and treated with excess 10% calcium chloride solution, whereby the calcium oxalate and mesotartrate precipitated out. This precipitate was removed, dried and weighed; yield, 1.9 g. To remove the calcium mesotartrate, the precipitate was extracted with 20% sodium hydroxide solution. This separation yielded 1.2 g. of calcium mesotartrate and 0.7 g. of calcium oxalate. The calcium mesotartrate was further purified by reprecipitation and analyzed.

Anal. Calcd. for $C_4H_4O_6Ca \cdot 3H_2O$: Ca, 16.53. Found: Ca, 16.28.

The filtrate from the calcium precipitation was treated with three volumes of 95% alcohol, and the calcium maleate, which precipitated out, collected, dried and weighed; 2.1 g., equivalent to 1 g. of unreacted maleic acid. From these results the yield of mesotartaric acid was calculated to be 30.3% and that of oxalic acid 14.6% of the maleic acid consumed in the reaction. Obviously the mesotartaric acid formed from maleic acid oxidizes further to oxalic acid.

Racemic Acid from Fumaric Acid.—To 2.9 g. (0.025 mole) of fumaric acid prepared from furfural[2c] were added 27.2 cc. (0.05 mole) of 6.3% hydrogen peroxide reagent, 2 cc. of the osmium tetroxide solution catalyst, and the mixture was allowed to stand for two days at 0°. The solvent was then removed under reduced pressure, the residue taken up with a small volume of water and the unreacted fumaric acid (1.7 g.) removed by filtration. The filtrate yielded 0.3 g. of calcium oxalate precipitated in acetic acid solution, and 1.3 g. of calcium racemate precipitated in ammoniacal solution. These correspond to 9.9% yield of oxalic acid and 48.3% yield of racemic acid. The calcium racemate was then analyzed for calcium.

Anal. Calcd. for $C_4H_4O_6Ca \cdot 4H_2O$: Ca, 15.38. Found: Ca, 15.26.

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(5) Nevole, *Bull. soc. chim.*, [2] **27**, 63 (1877).

(6) Furnished through the courtesy of Dr. George Thomson.

(7) Krassuski, *Chem. Centr.*, **73**, 1, 628 (1902).

(8) Balbiano, *Ber.*, **36**, 1573 (1903).

(9) Braun, THIS JOURNAL, **51**, 228 (1929).

Summary

1. It has been found that hydrogen peroxide in anhydrous tertiary butyl alcohol and in the presence of osmium tetroxide reacts with olefinic substances to yield glycols as the main products.

2. Ethylene glycol, isobutylene glycol, trimethylethylene glycol, pinacol, glycerol, phenylglyceric acid, dihydroxybutyric acid, mesotartaric acid and racemic acids have been obtained from their corresponding olefinic substances.

CAMBRIDGE, MASSACHUSETTS RECEIVED MAY 27, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

Conversion of Aldoximes to Carboxylic Acids by Means of Hot Alkali. The Elimination of Water from Aldoximes

BY EARL JORDAN[1] AND CHARLES R. HAUSER

The common statement that a β-aldoxime loses water to form a nitrile more readily than its α-isomer has been based presumably on the well-known fact that, in the presence of certain reagents, as for example acetic anhydride followed by alkali, the β-aldoxime forms nitrile, whereas the α-isomer usually gives only negligible amounts of this product. Under these conditions, however, the nitrile is *not* formed by the elimination of water from the β-aldoxime; the latter is first converted to its acetyl derivative which eliminates acetic acid to form nitrile.[2] Apparently there has been no direct evidence that in general, a β-aldoxime loses water more easily than its α-isomer.[3]

In this paper it is shown that certain β-aldoximes in 2 N sodium hydroxide solution[4] at 97–100° are slowly converted into mixtures of the corresponding carboxylic acids, ammonia and the α-aldoximes;[5] the latter are more slowly converted into carboxylic acids. The yields of acid and oxime isolated after certain periods of time are given in Table I. It can be seen that after the same periods of time the yields of acid obtained from β-aldoximes are higher than those from the α-isomers. Since these carboxylic acids[6] are probably formed by the hydrolysis of intermediate nitriles produced from the aldoximes by elimination of water, β-aldoximes apparently *do* lose water more readily than their α-isomers; however, this reaction is not recommended for distinguishing a pair of geometrically isomeric aldoximes[7] because, under the conditions used to effect the elimination of water, a considerable portion of the β-aldoxime is converted into the α-isomer.[5]

The rate of conversion[5] of β-3,4-methylenedioxybenzaldoxime into the α-isomer under these conditions is roughly indicated by the melting points of the products recovered after various periods of time. Evidently, complete conversion of the β-aldoxime to the α-isomer requires from sixty to ninety minutes. Likewise, β-4-methoxybenzaldoxime apparently is converted into the α-isomer within four hours. Since practically pure α-benzaldoxime is often obtained as an oil, the products recovered after four hours from both α- and β-benzaldoximes are probably almost pure α-aldoxime. On the other hand, both α- and β-furfuraldoxime apparently are converted into a mixture of the two isomers.[8]

The changes occurring when benzaldoximes in

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(1) This paper is from a portion of a thesis presented by Earl Jordan in partial fulfilment of the requirements for the Ph.D. degree at Duke University.

(2) For a recent discussion of this reaction see Hauser and Jordan, THIS JOURNAL, **57**, 2450 (1935); Hauser and Sullivan, *ibid.*, **55**, 4611 (1933).

(3) This has been pointed out by Brady, *Science Progress*, **29**, 485 (1935). In this connection it should be mentioned that Hantzsch and Lucus [*Ber.*, **28**, 748 (1895)] have reported that β-mesitylaldoxime with hot alkali gives nitrile whereas the α-isomer is stable under similar conditions; also, Hantzsch [*ibid.*, **24**, 47 (1891)] has reported that β-thiophenaldoxime with hot sodium carbonate gives nitrile. For references to the thermal decomposition of aldoximes see Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., N. Y., 1929, p. 659.

(4) Aldoximes in alkaline solutions are quite stable at room temperatures. See Freudenberg, "Stereochemie," Vol. VII, 1933, p. 987. In this Laboratory β-3,4-methylenedioxybenzaldoxime (m. p., 146°), after being kept in 2 N sodium hydroxide solution at 30° for thirty-six hours was recovered in a yield of 93% melting at 133–135°; the α-isomer melts at 110°.

(5) It is well known that there is a tendency for the β-benzaldoximes to revert to the α-isomers. See Freudenberg, "Stereochemie," Vol. VII, 1935, p. 988.

(6) It does not seem possible that the carboxylic acids could have been produced by a Cannizzaro reaction since no benzyl alcohol has been found; moreover, in certain cases, the total yields of carboxylic acid and aldoxime recovered amounts to over 90% of the theoretical quantitatives.

(7) These isomers are more readily distinguished by the reactions of their acetyl derivatives with bases; see references 2 and 3.

(8) This is in agreement with the results reported by Brady and Goldstein, *J. Chem. Soc.*, 1959 (1927).