

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.

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[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

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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 solution⁴ 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 acids⁶ 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 aldoximes⁷ because, under the conditions used to effect the elimination of water, a considerable portion of the β -aldoxime is converted into the α -isomer.⁸

The rate of conversion⁵ of β -3,4-methylenedioxybenzaloxime 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-methoxybenzaloxime apparently is converted into the α -isomer within four hours. Since practically pure α -benzaloxime is often obtained as an oil, the products recovered after four hours from both α - and β -benzaloximes 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

(1) This paper is from a portion of a thesis presented by Earl Jordan in partial fulfillment 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-methylenedioxybenzaloxime (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 -benzaloximes 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 quantities.

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

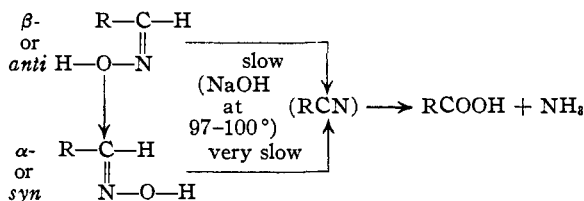
(8) This is in agreement with the results reported by Brady and Goldstein, *J. Chem. Soc.*, 1959 (1927).

TABLE I
PERCENTAGE YIELDS OF PRODUCTS FROM BENZALDOXIMES AND 2 N SODIUM HYDROXIDE AT 97-100°

Oxime	M. p., °C.	Time	Recovered oxime		Acid			Total yield, %
			%, yield	M. p., °C. crude prod.	%, yield	M. p., °C. crude prod.	Authentic m. p., °C.	
α -3,4-Methylenedioxy-	110	15 min.	84	110	Trace			84
α -3,4-Methylenedioxy-	110	90 min.	90	108-110	3	224	228	93
α -3,4-Methylenedioxy-	110	4 hrs.	78	109-110	5	225	228	83
α -3,4-Methylenedioxy-	110	12 hrs.	74	110	21	220-222	228	95
β -3,4-Methylenedioxy-	146	15 min.	87	124-127	5	224-225	228	92
β -3,4-Methylenedioxy-	146	60 min.	68	100-102	16	227-228	228	84
β -3,4-Methylenedioxy-	146	90 min.	62	110 ^a	31	225	228	93
β -3,4-Methylenedioxy-	146	4 hrs.	53	110 ^a	37	225	228	90
β -3,4-Methylenedioxy-	146	12 hrs.	41	110 ^a	58	224-226	228	99
α -Benzal-	35	4 hrs.	87	Oil	10	121	121	97
β -Benzal-	132	4 hrs.	52	Oil	38	121	121	90
α -4-Methoxy-	64	4 hrs.	89	64	8	179-180	184	97
β -4-Methoxy-	133	4 hrs.	59	64 ^a	39	182	184	98
α -3-Nitro-	123	90 min.	96	123	Trace			96
β -3-Nitro-	123	90 min.	26	116	62	137-139	140	88
α -Furfuraldoxime	75-76	90 min.	67	47-50	18	115-118	132-134	85
β -Furfuraldoxime	89-91	90 min.	38	48-50	49	132-133	132-134	87

^a Melting point of α -isomer.

2 N sodium hydroxide solution are heated at 97-100° may be represented by the scheme⁹



In order to show that the formation of carboxylic acid is brought about by the presence of alkali, β -3,4-methylenedioxybenzaloxime was heated at 97-100° with water alone for four hours, and in a solution of dioxane and water for ninety minutes. No nitrile or carboxylic acid could be isolated in either case; the only change observed was the conversion of a portion of the β -aldoxime to the α -isomer.

Experimental

Approximately 2 g. of aldoxime was dissolved in 50 cc. of 2 N sodium hydroxide and heated on a boiling water-bath (97-100°). In cases in which considerable acid was produced, ammonia was readily detected in the vapors.

(9) For references to the evidence supporting these configurations of aldoximes, see note 2.

After a designated time the solution was cooled and saturated with carbon dioxide. The oxime which precipitated was filtered through a sintered glass crucible. The filtrate was extracted with ether to remove the oxime in solution. The filtrate was then acidified with hydrochloric acid and the precipitated carboxylic acid filtered off; the filtrate was extracted with ether. The products were dried and weighed; they were identified by the mixed melting point method. No other products were found.

Blanks were run with β -3,4-methylenedioxybenzaloxime at 97-100°: (a), after four hours with water, 99% oxime (m. p. 138-140°) was recovered; (b), after ninety minutes in water-dioxane solution, 95% oxime (m. p. 99-101°) was recovered.

Summary

1. Certain β -aldoximes with 2 N sodium hydroxide at 97-100° are slowly converted into mixtures of carboxylic acids and the corresponding α -aldoximes. The latter are more slowly changed to carboxylic acids.

2. These results indicate that a β -aldoxime eliminates water to form nitrile more readily than its α -isomer; presumably, the nitrile undergoes hydrolysis in the presence of hot alkali to form the corresponding carboxylic acid and ammonia.

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