[Contribution from the Shell Development Co.]

Reactions of Hydrogen Peroxide. IV. Sodium Tungstate Catalyzed Epoxidation of α,β-Unsaturated Acids

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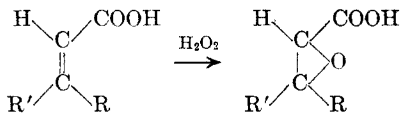
Maleic, fumaric, and crotonic acids, materials which are very resistant to attack by peroxyacetic and peroxybenzoic acids, have been efficiently converted to their corresponding epoxides in yields of 77, 50, and 50%, respectively, by means of hydrogen peroxide and sodium tungstate catalyst at *p*H 4–5.5.

The epoxidation of an α,β-unsaturated acid by the usual reagent such as peroxybenzoic or peroxyacetic acid is generally very slow; this is attributed to the electron-withdrawing effect of the carboxyl group directly attached to the ethylenic double bond.[1]

When higher temperatures are used in order to obtain practical reaction rates, hydroxylation rather than epoxidation is the end result.[2]

In the present work, maleic, fumaric, and crotonic acids were epoxidized with hydrogen peroxide by using sodium tungstate catalyst and maintaining the *p*H in the range 4–5.5. These acids had been *hydroxylated* earlier[3] by means of tungstic acid catalyst; however, no attempt was made in those cases to control the *p*H of the reaction so as to retard hydrolysis of the intermediate epoxide.



	Yield[4]
R = COOH, R′ = H,	77%
R = H, R′ = COOH,	50%
R = H, R′ = CH_3	50%

Maleic acid reacted extremely rapidly with hydrogen peroxide and 2 mole % of catalyst, only 1.5 hr. being required for complete reaction at 65°. Disodium *cis*-epoxysuccinate was obtained in quantitative yield and was 95% pure by titration for oxirane oxygen. The free acid was best prepared from the barium salt by means of ethereal sulfuric acid[5a]; use of the sodium salt led to considerably lower recoveries of pure acid. *cis*-Epoxysuccinic acid has been prepared before, by the chlorohydrination route[3] as well as by the action of alkaline hydrogen peroxide on hydroquinone or *p*-benzoquinone.[6]

Fumaric acid, with only 2 mole % of catalyst, was epoxidized to the extent of only 25% after 1.5 hr. at 65°; continued reaction resulted in a substantial amount of epoxide hydrolysis. In order to obtain a practical rate of epoxidation, it was necessary to employ 10 mole % of catalyst; there was then obtained a crude disodium *trans*-epoxysuccinate (heavily contaminated with sodium tungstate) which, by titration for oxirane oxygen, contained epoxy product in an amount corresponding to a yield of 86%. The free epoxy acid was again secured by treatment of its barium salt with sulfuric acid in ether. *Trans*-epoxysuccinic acid has been prepared before *via* the chlorohydrination of fumaric acid.[5]

Crotonic acid reacted somewhat more readily than fumaric; however, 10 mole % of catalyst was again required in order to limit the reaction time and moderate hydration of the epoxide linkage. The yield of epoxide by titration of the reaction mixture was 80%; however, difficulty was encountered in isolating free acid and the yield of material having a purity of 87% was 57%. Essentially pure 2,3-epoxybutyric acid was obtained in 30% yield based on crotonic acid charged. This epoxy acid has been prepared earlier by allowing crotonic acid to react with peroxybenzoic acid for three months,[7] *via* hypochlorination of crotonic acid,[7] and by the hypobromite oxidation of crotonaldehyde.[8a]

This epoxidation procedure has also been applied to materials other than α,β-unsaturated acids and with particular success to allylic alcohols.[8b] Simple olefinic compounds, however, have been found to be of lesser reactivity. For example, 2-heptene, a compound that is readily attacked by organic peroxyacids,[1] underwent only 66% re-

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(1) D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947).

(2) G. S. Myers, *J. Am. Chem. Soc.*, **73**, 2100 (1951); J. English, Jr., and J. D. Gregory, *J. Am. Chem. Soc.*, **69**, 2120 (1947).

(3) M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949); J. M. Church and R. Blumberg, *Ind. Eng. Chem.*, **43**, 1780 (1951); R. P. Linstead, L. N. Owen, and R. F. Webb, *J. Chem. Soc.* 1218 (1953).

(4) Yields of purified acids; the yields of sodium salts were 95, 86, and 80%, respectively, calculated from titration for oxirane oxygen.

(5) (a) R. Kuhn and F. Ebel, *Ber.*, **58B**, 919 (1925); (b) Y. Inoue, M. Hamada, and S. Asano, *J. Agr. Chem. Soc. Japan*, **19**, 17 (1943); *Chem. Abstr.*, **45**, 8980, (1951); (c) J. Timmermans, P. Machtelinckx, and J. Mokry, *Bull. chim. soc. Belg.*, **60**, 424 (1951).

(6) E. Weitz, H. Schobbert, and H. Seibert, *Ber.*, **68B**, 1163 (1935).

(7) G. Braun, *J. Am. Chem. Soc.*, **52**, 3185 (1930).

(8)(a) A. A. Kaufmann, U. S. Patent **1,858,551** (May 17, 1932). (b) G. J. Carlson, J. R. Skinner, C. W. Smith, and C. H. Wilcoxen, Jr., (to Shell Development Co.) U.S. Patent **2,833,787**(May 6, 1958).

action in 6 hr. at 65° (10 mole % of catalyst) to give (by titration for oxirane oxygen) a 55% yield of epoxide based on hydrogen peroxide reacted. There was also observed a considerable loss of peroxide due to decomposition during the lengthy reaction period.

It is possible, indeed probable, that the relatively high reactivity of α,β-unsaturated acids is due to the formation of an intermediate cyclic complex involving substrate and inorganic peroxyacid. The elucidation of this reaction mechanism is the subject of a continuing study.

EXPERIMENTAL[9]

Disodium cis-epoxysuccinate. To a 1-liter, 5-neck, round-bottom flask equipped with stirrer, thermometer, and dropping funnel was charged a filtered solution of 116 g. (1.0 mole) of maleic acid (E. K. Co.) in 300 ml. of distilled water. To this was added a solution of 60 g. (1.5 moles) of sodium hydroxide in 100 ml. of water. The heat of neutralization caused a rise in temperature to about 70°. To the warm solution was added 6.6 g. (0.02 mole) of sodium tungstate dihydrate (Baker and Adamson). Standard *p*H electrodes were inserted into the solution and 1.2 mole of 30% hydrogen peroxide was added in one portion.[10] The strongly exothermic reaction was held at 63–65° by cooling with an ice bath for about 15 min. during which time the *p*H fell from about 5.5 to 4.[11] In order to maintain the *p*H at a minimum of 4, a solution of 0.5 mole of sodium hydroxide in 100 ml. of water was added dropwise as needed throughout the remainder of the reaction. After an additional hour at 65°, iodometric titration indicated the consumption of 1.02 moles of hydrogen peroxide, and the solution was cooled to 40° and treated with the remainder of the sodium hydroxide solution. After vacuum concentration[12] at 40° to a volume of about 300 ml., the residual liquid was poured with stirring into 1.5 liters of acetone to precipitate 176 g. (100%) of disodium *cis*-epoxysuccinate.

Anal. Calcd. for $C_4H_2O_5Na_2$: oxirane oxygen, 9.1. Found: oxirane oxygen, 8.6.[13]

The *barium salt* was prepared from sodium salt by the addition of a solution of the latter to a molar equivalent of barium chloride dissolved in hot water (33 g. per 100 ml.). The recovery of barium *cis*-epoxysuccinate dihydrate was essentially quantitative.

Anal. Calcd. for $C_4H_2O_5Ba\cdot 2H_2O$: C, 15.8; H, 2.0. Found: C, 15.3; H, 2.1.

cis-Epoxysuccinic acid. The procedure employed was a modification of that used by Kuhn and Ebel.[5a] A suspension of 152 g. (0.50 mole) of barium salt and 30 g. of anhydrous magnesium sulfate in 750 ml. of ether was stirred at 0–5° and treated dropwise over 1 hr. with a solution of 49 g. of sulfuric acid in 200 ml. of ether. After an additional hour at 5–10°, the mixture was allowed to stir overnight at room temperature. After removal of barium sulfate by filtration, the filtrate was dried over magnesium sulfate and concentrated under vacuum to a constant weight of 51 g. (77%), m.p. 148–149°; reported[5a] m.p. 149°.

Anal. Calcd. for $C_4H_4O_5$: Neut. equiv., 66.0; oxirane oxygen, 12.1 Found: Neut. equiv., 66.4; oxirane oxygen, 11.7.[13]

Epoxidation of fumaric acid. The epoxidation was carried out essentially as above (E. K. Co. fumaric acid, recrystallized from water) except for the use of 10 mole % of sodium tungstate instead of 2 mole %. After 3 hr. at 65° and 1 hr. at 75–80°, the solution was processed as above to yield 222 g. of a mixture containing sodium tungstate and 0.86 mole of disodium *trans*-epoxysuccinate (titration for oxirane oxygen[13]). The *barium salt* was prepared as above, 108 g. being obtained from 84 g. of crude sodium salt. The 108 g. was suspended in 500 ml. of ether containing 5 ml. of water and treated as above wth a solution of 37 g. of sulfuric acid in 100 ml. of ether. After stirring overnight, the salt was removed by filtration and the filtrate concentrated to a volume of about 200 ml. and diluted with two volumes of petroleum ether (40–60°). The solid product thus obtained was collected by filtration and washed with more petroleum ether. An additional amount was secured by again stirring the recovered barium sulfate overnight with 500 ml. of ether and repeating the isolation procedure. The combined weight of epoxy acid thus obtained was 30 g. (60% yield based on fumaric acid) m.p. 207–209°; reported m.p. 209°[5a] and 208–209°.[5b]

Anal. Calcd. for $C_4H_4O_5$: Neut. equiv., 66.0; oxirane oxygen, 12.1. Found: Neut. equiv., 65.2; oxirane oxygen, 9.5.[13]

In view of the low value for oxirane oxygen, a 5.8-g. sample was heated in 50 ml. of water to 80°, cooled to room temperature, and filtered to remove 0.9 g. of insoluble solid (probably crude fumaric acid). Concentration of the filtrate afforded 4.9 g. of purified *trans*-epoxysuccinic acid, *instantaneous* m.p. 233° (reported[5c] *instantaneous* m.p. 232°), neut. equiv., 66.0; oxirane oxygen, 11.1.[13]

2,3-Epoxybutyric acid. One mole (86 g.) of crotonic acid (E. K. Co., recrystallized, m.p. 71–72°) was added to a solution of 20 g. (0.50 mole) of sodium hydroxide in 250 ml. of water. This solution was filtered into a 1-liter flask equipped as above, warmed to 55°, and treated with 33 g. (0.10 mole) of sodium tungstate dihydrate. To the stirred mixture, 1.30 moles of 30% hydrogen peroxide was added dropwise over 5 min. The reaction temperature was held at 63–65° by cooling and the *p*H held above 4 by dropwise addition of 30% alkali as needed. After 1 hr. at the same temperature, the mixture was cooled and titrated for oxirane oxygen;[13] a yield of 80% was indicated. Sulfuric acid (30%) was added dropwise to a *p*H of 2.5 and the epoxy acid was isolated by saturating with ammonium sulfate, extracting with five 200-ml. portions of ether and drying over magnesium sulfate. After removal of the ether *in vacuo* there remained 58 g. (50% yield allowing for purity) of crystalline epoxy acid; the purity was 87% by titration for oxirane oxygen.[13] A 50-g. sample, on recrystallization from 150 ml. of benzene, gave 26 g. of purified 2,3-epoxybutyric acid, m.p. 84.5–85°; reported m.p. 88.5°[7] and 84°.[8]

Anal. Calcd. for $C_4H_6O_3$: Neut. equiv., 102; oxirane oxygen, 15.7. Found: Neut. equiv., 103; oxirane oxygen, 15.1.[13]

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[9] All melting points are corrected.

[10] In larger scale runs the peroxide was added dropwise over 0.3–0.5 hr.

[11] The drop in *p*H can be attributed to the formation of a considerably stronger acid: pK_2 for *cis*-epoxysuccinic acid is 3.92 as against pK_2 of 6.5 for maleic acid; *Cf.* A. Wasserman, *Helv. Chim. Acta,* **13,** 207 (1930).

[12] A circulating evaporator was used; see *Ind. Eng. Chem., Anal. Ed.,* **16,** 754 (1944).

[13] A sample was allowed to stand overnight in 0.1*N* hydrochloric acid saturated with magnesium chloride; the mixture was back-titrated with 0.1*N* sodium hydroxide to the bromcresol purple end point.