Hydroxylation and Epoxidation of Double Bonds with Disuccinoyl Peroxide

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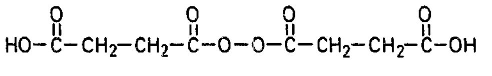
Disuccinoyl peroxide (1) has been described as a source of monopersuccinic acid which has been used to hydroxylate alkenes in a two-stage sequence[1]. Described here is the direct hydroxylation of alkenes with disuccinoyl peroxide.



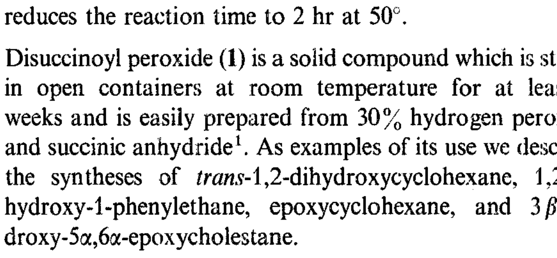
$$HO-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

1

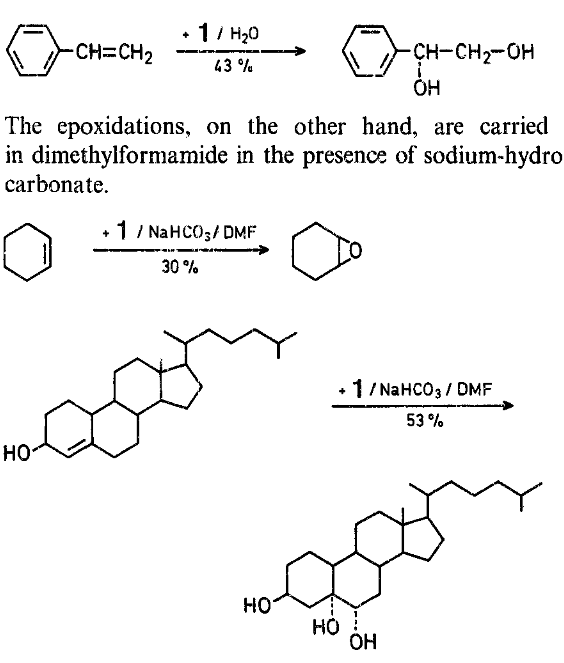
Epoxidation of limonene has been described utilizing disuccinoyl peroxide but the reaction time was inconveniently long[2]. Addition of sodium hydrogen carbonate reduces the reaction time to 2 hr at 50°.

Disuccinoyl peroxide (1) is a solid compound which is stable in open containers at room temperature for at least 6 weeks and is easily prepared from 30% hydrogen peroxide and succinic anhydride[1]. As examples of its use we describe the syntheses of *trans*-1,2-dihydroxycyclohexane, 1,2-dihydroxy-1-phenylethane, epoxycyclohexane, and 3β-hydroxy-5α,6α-epoxycholestane.

The hydroxylations are carried out in a vigorously stirred suspension of the olefin and **1** in water containing a detergent.



The epoxidations, on the other hand, are carried out in dimethylformamide in the presence of sodium-hydrogen carbonate.



trans-1,2-Dihydroxycyclohexane:

Disuccinoyl peroxide (5.0 g, 21 mmol), cyclohexene (1.5 g, 17 mmol), Tergitol 15-S-9 (15 mg), and water (15 ml) were vigorously stirred for 2 hr at 40–50°. The resultant mixture was neutralized with sodium-hydrogen carbonate and extracted with ether/ethyl acetate 1:1 (3×25 ml). The combined extracts were dried with sodium sulfate, the solvent was evaporated, and the residue recrystallized from ethyl acetate; yield: 1.0 g (55%); m.p. 101° (Ref.[3], m.p. 101.5–103°). The I.R. spectrum of the colorless crystalline product was identical with that of an authentic sample.

1,2-Dihydroxy-1-phenylethane:

The same procedure was used as above except that the reaction time was 4 hr and the product was recrystallized twice from benzene; yield: 1.1 g (43%); m.p. 65–66° (Ref.[1], m.p. 67–68°). The I.R. spectrum of the colorless crystals was identical with that of an authentic sample.

Epoxycyclohexane:

Disuccinoyl peroxide (5 g, 21 mmol), cyclohexene (1.4 g, 0.017 mmol), sodium hydrogen carbonate (8.5 g, 0.1 mmol), and dimethylformamide (15 ml) were stirred for 2 hr at 50°. Then water (85 ml) was added and the mixture was shaken until the evolution of carbon dioxide ceased. The mixture was extracted with petroleum ether (3×25 ml), the combined extracts were dried with sodium sulfate, and the solvent was removed under reduced pressure; yield: 0.5 g (30%). The colorless liquid product exhibited an I.R.-spectrum identical to that of a reference sample[4].

A two-stage procedure using monopersuccinic acid prepared as described previously[1] and utilized under the same reaction conditions as described above gave a yield of 45%.

3β-Hydroxy-5α,6α-epoxycholestane:

Cholesterol (3.4 g, 8.8 mmol) was dissolved in chloroform (10 ml) and added to disuccinoyl peroxide (3.1 g, 13 mmol) and sodium-hydrogen carbonate (5.0 g, 60 mmol) in dimethylformamide (8 ml). The mixture was stirred for 2.5 hr at 50°. The work-up was the same as for cyclohexene oxide with the exception that the product was extracted with chloroform and recrystallized twice from 88% aqueous acetone; yield: 1.9 g (53%); m.p. 137–138°; $[\alpha]_D^{25}$: $-46°$ (Ref.[5], m.p. 141–143°; $[\alpha]_D^{25}$: $-46°$).

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