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The Epoxidation of 1-Acetoxycyclohexene and the Rearrangement of 1-Acetoxy-1,2-epoxycyclohexane[1]

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The product obtained from the reaction of perbenzoic acid with 1-acetoxycyclohexene is shown to have the properties and characteristics of 1-acetoxy-1,2-epoxycyclohexane. This product, however, is not the same as that claimed by Mousseron and Jacquier[4] as 1-acetoxy-1,2-epoxycyclohexane. The product undergoes thermal rearrangement to 2-acetoxycyclohexanone; this rearrangement occurs slowly even at room temperature. The infrared characteristics are given.

As the result of some work on the oxidation of cyclohexene in acetic anhydride solution,[2] it was considered necessary to prepare and characterize by infrared spectroscopy the three structurally isomeric acetoxyepoxycyclohexanes. The first preparation undertaken was that of 1-acetoxy-1,2-epoxycyclohexane, since the enol ester from which it is prepared is easily made[3] and because the directions for its preparation are given in the literature. Thus, Mousseron and Jacquier[4] report the preparation of 1-acetoxy-1,2-epoxycyclohexane by the perbenzoic acid oxidation of 1-acetoxycyclohexene.

In following the directions given by Mousseron and Jacquier, however, startlingly different results were obtained. It was found that the type of product obtained from the reaction of perbenzoic acid with 1-acetoxycyclohexene at 0° depended on the temperature at which isolation was carried out. That is, when the crude product of reaction was fractionally distilled at 15 mm., as suggested by Mousseron and Jacquier, the fractions obtained were for the most part a mixture of a liquid and a solid. The solid was found to be 2-acetoxycyclohexanone.

The formation of 2-acetoxycyclohexanone in the distillate was avoided by fractionally distilling the crude product at 1 to 3 mm. with the pot temperature kept as low as possible. By so doing a liquid product was obtained which had all the characteristics of 1-acetoxy-1,2-epoxycyclohexane, but whose physical properties were quite different from those given by Mousseron and Jacquier. It showed none of the reactions characteristic of hydroxyl and carbonyl groups. It was readily converted to 2-acetoxycyclohexanone at 110°. Reduction of the liquid product with lithium aluminum hydride gave a mixture of the *cis-* and *trans-*1,2-cyclohexanediols. Hydrolysis by 5% hydrochloric acid occurred quickly on shaking and was exothermic; the products were acetic acid and the dimer of 2-hydroxycyclohexanone. The molar refraction of the liquid product, 38.22, agreed with the calculated value for the epoxy ester, 38.04. It must be pointed out, however, that the molar refraction of Mousseron and Jacquier's compound, calculated from their data, is 38.2, also in agreement with the expected value for the epoxy ester.

The product obtained in the present work shows all the properties of an epoxide of an enol ester. In particular the thermal rearrangement to 2-acetoxycyclohexanone is analogous to similar rearrangements found by Gardner[5] in the tetralone and benzsuberone systems, and by others[6,7] in the steroid systems. In fact not only was the product easily rearranged to 2-acetoxycyclohexanone at 110°, but it also rearranged slowly at room temperature.

Finally, the infrared absorption spectrum of the product had strong peaks at 11.32 and 12.22 μ, and a strong doublet at 12.88 and 13.0 μ, all of which are attributable to the epoxy group.

We believe, therefore, that the product obtained by us is 1-acetoxy-1,2-epoxycyclohexane and that it exhibits the simplest case of rearrangement of enol ester epoxides so far known. We are unable to account for the difference between the properties of Mousseron's epoxide and the one described here without resorting, perhaps, to the possibility that a *cis*-epoxide has been prepared in one case and a *trans*-epoxide in another. This possibility is so remote that we are obliged to consider the alternative possibility that the compound obtained by Mousseron was not 1-acetoxy-1,2-epoxycyclohexane. It does not appear, from their data, that their product was 2-acetoxycyclohexanone.

The nature of this rearrangement in other simple enol esters is being studied.

Experimental[8]

Dry solutions of perbenzoic acid in chloroform were made as needed by the method of Braun.[9] The perbenzoic acid concentration was determined iodimetrically. 1-Acetoxycyclohexene[3] was distilled at reduced pressure and had b.p. 72° (15 mm.), $n^{25}\text{D}$ 1.4560.

Peroxidation Leading to 2-Acetoxycyclohexanone.—To a dry solution of perbenzoic acid (0.2 mole) in 300 ml. of chloroform at 0° standing over anhydrous sodium sulfate was added in one portion 31 g. (0.22 mole) of 1-acetoxycyclohexene. The solution was stirred at 0° for 8 hr. at which time most of the perbenzoic acid had been used. The sodium sulfate was removed by filtration and the solution was washed twice with 20% sodium carbonate solution, twice with water and dried over sodium sulfate in the refrigerator. The dried solution was freed of solvent at 31°. The residue was divided into two portions. One portion was fractionally distilled at 2 mm. to give two liquid fractions, 6 g., of 1-acetoxy-1,2-epoxycyclohexane, b.p. 47–48°, $n^{25}\text{D}$ 1.4475 to 1.4478. The second portion was

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[2] H. J. Shine and R. H. Snyder, A.C.S. Meeting, New York, 1957, Abstracts p. 78-P.

[3] I. V. Machinskaya, *J. Gen. Chem. U.S.S.R.*, **22**, 1205 (1952).

[4] M. Mousseron and R. Jacquier, *Bull. soc. chim. France*, 698 (1950).

[5] P. D. Gardner, THIS JOURNAL, **78**, 3421 (1956).

[6] A. H. Soloway, W. J. Considine, D. K. Fukushima and T. F. Gallagher, *ibid.*, **76**, 2941 (1954).

[7] N. S. Leeds, D. K. Fukushima and T. F. Gallagher, *ibid.*, **76**, 2943 (1954).

[8] Analyses by Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y.

[9] G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 431.

then added to the still pot and distillation was continued at 13 mm. to give first some liquid fractions containing a white solid and last some fractions consisting in solid only. In all, five fractions were collected over the range b.p. 82–114°, n^{25}_{D} 1.4494 to 1.4588, the last two of which, 8.8 g., solid, had b.p. 113–114°, n^{25}_{D} 1.4580 to 1.4588. Recrystallization of the solid from petroleum ether gave 2-acetoxycyclohexanone, m.p. 34–35°, n^{37}_{D} 1.4526; 2,4-dinitrophenylhydrazone, m.p. 169.5–171°; literature values 35–36°[10] and 167–168°.[11] Elemental analyses of the keto acetate and its 2,4-dinitrophenylhydrazone were in excellent agreement with the calculated values.

Peroxidation Leading to 1-Acetoxy-1,2-epoxycyclohexane (I).—Using a solution of 0.3 mole of perbenzoic acid in 300 ml. of chloroform and 43.5 g. (0.31 mole) of 1-acetoxycyclohexene as above and fractionally distilling the product at 2 mm. there were obtained seven fractions, 26.7 g., 55% yield, 1-acetoxy-1,2-epoxycyclohexane, b.p. 44–48°, n^{25}_{D} 1.4471 to 1.4476. The three center fractions, I, b.p. 48°, n^{25}_{D} 1.4475, d^{25} 1.0945, were combined and used for identification work. Mousseron and Jacquier[4] give b.p. 115° (15 mm.), n^{25}_{D} 1.4620, d^{25} 1.126.

Anal. Calcd. for $C_8H_{12}O_3$ (I): C, 61.50; H, 7.76. Found: C, 61.90; H, 7.66.

Reduction with Lithium Aluminum Hydride.—Four grams of I in anhydrous ether was reduced with 2 g. of lithium hydride at room temperature followed by a 10-min. reflux. Decomposition with ice, continuous extraction with ether for 72 hours and evaporation of the sodium sulfate dried ether solution gave a white solid. Extraction of the solid with ethyl acetate and concentration of the ethyl acetate solution gave 3.2 g., m.p. 73–90°. This solid was found to be a mixture of *cis*- and *trans*-cyclohexandiols.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.14. Found: C, 62.09; H, 10.16.

A positive test[12] with periodic acid was obtained, while oxidation in benzene solution by lead tetraacetate gave adipaldehyde; 2,4-dinitrophenylhydrazone, m.p. 236.5–237° (nitrobenzene).

The infrared absorption spectrum of the solid in a Nujol mull had the identical characteristics of the spectrum (Nujol) of a 1:1 mixture of authentic *cis*-[13] and *trans*-1,2-cyclohexanediol.[14] The melting point of the authentic *cis*-diol was 96–98° and that of the *trans*-diol was 102–104°. The literature values are 96° and 101.5–103°. A 1:1 mixture of the two had m.p. 70–83°.

Hydrolysis with 5% Hydrochloric Acid.—Three ml. of 5% hydrochloric acid was added to 4.3 g. of I. Shaking the immiscible liquids caused much heat to be evolved and a single phase solution to be formed. A portion of this gave no derivative when treated with 2,4-dinitrophenylhydrazine. The solution was neutralized with sodium hydroxide and extracted continuously with ether for 21 hours. The aqueous portion was boiled with a solution of *p*-bromophenacyl bromide in ethanol to give the ester of acetic acid, m.p. 82°. The ether solution was dried and evaporated to give a viscous liquid which, on standing, solidified to a powdery white solid, 1.5 g., m.p. 107–117°. A repetition of this hydrolysis gave a product, m.p. 117–121°. Repeated recrystallization from acetone did not improve the melting point.

The product which was expected from the hydrolysis of I was 2-hydroxycyclohexanone. The nature of the product obtained from each of the two hydrolyses corresponded with that of the readily formed dimer of 2-hydroxycyclohexanone.[15,16] The difference in the melting points of the two hydrolysis products is consistent with the range of 93 to 130° reported[16] for different samples of dimer. The identity of the solid hydrolysis product was confirmed by analysis and by the preparation of the 2,4-dinitrophenylosazone.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83. Found: C, 62.80; H, 8.75.

Treatment of the solid with a highly acid solution of 2,4-dinitrophenylhydrazine readily gave the orange-red derivative. Crystallization from hot ethyl acetate gave m.p. 221–222° dec. An authentic specimen of the dimer was prepared by the sodium carbonate hydrolysis of 2-bromocyclohexanone.[10] The dimer had m.p. 121–122°, and gave the 2,4-dinitrophenylosazone, m.p. 220–221° dec., literature[16] 221° dec.

Rearrangement at 110°.—A sample of I was sealed in a glass vial under nitrogen and kept at 105 to 115° for 2 hr. On cooling, the tube contents solidified, giving 2-acetoxycyclohexanone, m.p. 35°; 2,4-dinitrophenylhydrazone, m.p. 168–169°.

Rearrangement at Room Temperature.—Freshly prepared samples of 1-acetoxy-1,2-epoxycyclohexane were stored at room temperature in the dark. The samples slowly isomerized over a period of 34 days to 2-acetoxycyclohexanone, as found by periodic recording of refractive indices and infrared absorption spectra. Similar samples stored in the refrigerator did not isomerize.

Infrared Spectra.—The absorption spectra were recorded with a Perkin–Elmer single-beam spectrometer, model 212. Liquid I was used in a 0.025-mm. cell with sodium chloride windows. The spectra were recorded, similarly, of 3-acetoxycyclohexene (liquid), 1-acetoxycyclohexene (liquid), cyclohexyl acetate (liquid), cyclohexanone (liquid) and 2-acetoxycyclohexanone (supercooled liquid). By comparison of the spectrum of I with these and by observing the diminution and final disappearance of peaks when Compound I slowly isomerized to 2-acetoxycyclohexanone it was possible to allocate the following peaks in the spectrum of I to the epoxy group: singlets at 11.32 and 12.22 μ, and a doublet with peaks at 12.88 and 13.0 μ. Patterson[17] gives peaks at 11.22 and 12.31 μ for 1,2-epoxycyclohexane.

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