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THE REACTION OF EPOXIDES WITH DIMETHYL SULFOXIDE

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Previously, we reported that the oxidation of epoxides by dimethyl sulfoxide in the presence of catalytic amount of boron trifluoride produced α-hydroxy ketones (1). By the employment of boron trifluoride, however, the product was contaminated with its dimer or polymer as the by-product.

We now wish to report a new method of converting epoxides to α-hydroxy ketones. The oxidation proceeded by passing air through the dimethyl sulfoxide solution of epoxide in an excellent result. Its mode of reaction was found to be different from that of earlier method.

A solution of epoxide (0.1 mole) in 40 ml. of dimethyl sulfoxide was heated on a steam bath for 30 hours by passing air gently through a solution. The mixture poured into water, extracted with chloroform, and evaporated the dried extracts. The residue, which did not contain the polymer, was purified by recrystallization or distillation. By this general procedure, phenacyl alcohol and 2-hydroxycyclohexanone were prepared from styrene oxide and cyclohexene oxide in yields of 92% and 65%,

respectively. 2-Hydroxycyclohexanone obtained hereof was not contaminated with its dimer. Both two α-hydroxy ketones were identical with the authentic samples. 1-Hydroxy-2-octanone (I), b.p. 70-76°/6 mm., was derived from 1,2-epoxyoctane in 72% yield. Compound (I) was converted to 1-acetoxy-2-octanone, which was identified with the authentic sample (2).

The consumption of oxygen was not observed during the oxidation. In one run, dimethyl sulfide was obtained in 71% yield under conditions which produced phenacyl alcohol in 88% yield. These data support to designate dimethyl sulfoxide as the oxidant. Next, no oxidation occured in the absence of oxygen. In a second run, a solution of styrene oxide (0.01 mole) and t-butyl hydroperoxide (0.001 mole) in 4 ml. of dimethyl sulfoxide was heated on a steam bath for 10 hours under oxygen-free conditions. Phenacyl alcohol and dimethyl sulfide were obtained in 44% and 37% yields, respectively. While, styrene oxide was recovered in 48% yield. From these results, it seems likely that this reaction initially produces radical.

The oxidation of epoxides by dimethyl sulfoxide in the presence of boron trifluoride proceeded in oxygen-free conditions. Therefore, it may be said that the earlier method proceeds via an ion, or at least with a strong polarized form of epoxide as the intermediate.

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