

# Communications TO THE EDITOR

## The Oxidation of Epoxides by Dimethyl Sulfoxide. A Simple Synthesis of $\alpha$ -Hydroxy Ketones<sup>1</sup>

Sir:

Dimethyl sulfoxide reacts with primary and secondary alkyl halides and tosylates to yield the corresponding aldehydes and ketones respectively.<sup>2-6</sup>

We should now like to report that epoxides can also be oxidized by dimethyl sulfoxide if catalytic quantities of boron trifluoride are present. In accord with the results obtained with halides and tosylates, the products are  $\alpha$ -hydroxy ketones and dimethyl sulfide. Although the same reaction occurs in the absence of catalyst, much longer reaction periods are required and the yields are seriously reduced. A sample procedure is described.

A solution of 10.0 g. (0.102 mole) of cyclohexene oxide and 0.12 ml. of boron trifluoride etherate in 40 ml. of dimethyl sulfoxide (predried by azeotropic distillation with benzene) was heated on a steam bath for 22 hr. Additional portions (0.06 ml. and 0.04 ml.) of catalyst were added at the end of 15 and 20 hr., respectively. The reaction mixture was poured into ice water and extracted with chloroform. Evaporation of the dried extracts and distillation of the residue furnished 8.8 g. (76% yield) of 2-hydroxycyclohexanone as a colorless oil, b.p. 83–85°/13 mm.; reported<sup>7</sup> b.p. 71°/7 mm. This substance was further identified (1) by comparison of its infrared spectrum with that reported,<sup>7</sup> (2) by the formation of its osazone,<sup>7,8</sup> m.p. 218° dec., and (3) by its solidification to a variable melting range mixture of monomer and dimer.<sup>7,9</sup> In one run, dimethyl sulfide, b.p. 36–38°, was obtained in 60% yield by distillation of the reaction mixture prior to work-up.

(1) This work was sponsored by the United States Air Force under Contract No. AF 49(638)-788 monitored by the AF Office of Scientific Research of the Air Research and Development Command.

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(7) J. C. Sheehan, R. C. O'Neill, and M. A. White, *J. Am. Chem. Soc.*, **72**, 3376 (1950).

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In a similar manner, both 2 $\beta$ ,3 $\beta$ -epoxy-5 $\alpha$ -cholestane and 2 $\alpha$ ,3 $\alpha$ -epoxy-5 $\alpha$ -cholestane (dioxane was required as a co-solvent in the latter case) gave 5 $\alpha$ -cholestane-3 $\beta$ -ol-2-one,<sup>10</sup> m.p. 105.5–107°, in yields of 55% and 45%, respectively.<sup>11</sup> In addition, both epoxides afforded 5 $\alpha$ -cholestane-2,3-dione,<sup>12</sup> m.p. 138–140° (11% and 19%, respectively) and 5 $\alpha$ -cholestane-2 $\beta$ ,3 $\alpha$ -diol,<sup>13</sup> m.p. 200–201° (10% and 5%, respectively).

Phenacyl alcohol was prepared in 57% yield from styrene oxide by the same procedure.

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(9) An apparently pure sample of dimer, m.p. 151–152°, has been obtained by recrystallization of this mixture from acetone. Its elemental analysis, determined molecular weight, infrared spectrum and its ready conversion to the osazone of the monomer are all consistent with the dimeric structure.

(10) J. C. Sheehan and W. F. Erman, *J. Am. Chem. Soc.*, **79**, 6050 (1957).

(11) Assuming diaxial ring opening by dimethyl sulfoxide, the  $\beta$ - and  $\alpha$ -epoxides would be expected to yield, respectively, 5 $\alpha$ -cholestan-2 $\beta$ -ol-3-one and 5 $\alpha$ -cholestan-3 $\alpha$ -ol-2-one. These are presumably converted via a common enol intermediate to the more stable<sup>10</sup> hydroxyketone actually isolated.

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## The Reaction of Aminomethyltrimethylsilane with Nitrous Acid<sup>1</sup>

Sir:

The well known reaction of nitrous acid and aliphatic amines is characterized by products resulting from an intermediate carbonium ion. We wish to report that the reaction of aminomethyltrimethylsilane hydrochloride (I) and nitrous acid results in silicon-carbon bond cleavage. Apparently diazomethane, rather than nitrogen, is the leaving group. No products which would result from carbonium ion II<sup>2</sup> could be detected.

(1) This work was supported by a grant (NSF-G14554) from the National Science Foundation.

(2) The conversion of chloromethyltrimethylsilane to ethyldimethylchlorosilane with aluminum chloride is postulated as proceeding through II [F. C. Whitmore, L. H. Sommer, and J. R. Gould, *J. Am. Chem. Soc.*, **69**, 1976 (1947)].