Communications TO THE EDITOR

The Oxidation of Epoxides by Dimethyl Sulfoxide. A Simple Synthesis of α-Hydroxy Ketones[1]

Sir:

Dimethyl sulfoxide reacts with primary and secondary alkyl halides and tosylates to yield the corresponding aldehydes and ketones respectively.[2–6]

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 α-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[7] b.p. 71°/7 mm. This substance was further identified (1) by comparison of its infrared spectrum with that reported,[7] (2) by the formation of its osazone,[7,8] m.p. 218° dec., and (3) by its solidification to a variable melting range mixture of monomer and dimer.[7,9] In one run, dimethyl sulfide, b.p. 36–38°, was obtained in 60% yield by distillation of the reaction mixture prior to work-up.

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

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

Contribution No. 1080
Department of Chemistry
University of Pittsburgh
Pittsburgh 13, Pa.

Theodore Cohen
Tadakazu Tsuji

Received February 10, 1961

---

[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.

[2] N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. W. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957).

[3] N. Kornblum, W. J. Jones, and G. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959).

[4] H. R. Nace and J. J. Monagle, *J. Org. Chem.*, **24**, 1792 (1959).

[5] M. M. Baizer, *J. Org. Chem.*, **25**, 670 (1960).

[6] I. M. Hunsberger and J. M. Tien, *Chem. & Ind.*, 88 (1959).

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

[8] H. Adkins and A. G. Rossow, *J. Am. Chem. Soc.*, **71**, 3836 (1949).

[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 β- and α-epoxides would be expected to yield, respectively, 5α-cholestan-2β-ol-3-one and 5α-cholestan-3α-ol-2-one. These are presumably converted *via* a common enol intermediate to the more stable[10] hydroxyketone actually isolated.

[12] E. T. Stiller and O. Rosenheim, *J. Chem. Soc.*, 353 (1938).

[13] R. E. Marker and L. Plambeck, Jr., *J. Am. Chem. Soc.*, **61**, 1332 (1939).

The Reaction of Aminomethyltrimethylsilane with Nitrous Acid[1]

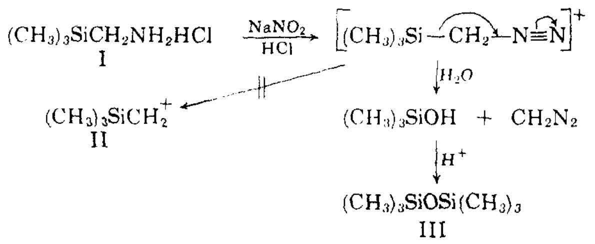
Sir:

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[2] 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)].



The striking contrast between this reaction and the reaction of neopentylamine[3] may be attributed to the ease of nucleophilic attack through the *d*-orbitals of the silicon.

To a solution of 25.0 g. (0.18 mole) of aminomethyltrimethylsilane hydrochloride[4] and 37.0 g. (0.53 mole) of sodium nitrite in 200 ml. of water, 100 ml. of 6*N* hydrochloric acid was added dropwise with cooling. After the addition had been completed (2 hr.), the mixture was heated at reflux for an hour. The mixture was extracted with ether, the ethereal extracts washed with base to remove any nitrous acid also extracted and then concentrated by distillation. Fractional distillation yielded 7.8 g. (56%) of hexamethyldisiloxane (III), b.p. 98–100°, n_D^{21} 1.3765 [lit.,[5] b.p. 99–100°, n_D^{20} 1.3772]. The infrared spectra of this material and of an authentic sample of hexamethyldisiloxane were identical. Gas phase analysis (5′ Silicone column, T = 100°) of the concentrated ethereal extracts prior to distillation indicated the absence of hydroxymethyltrimethylsilane,[6] *sym*-tetramethyldiethyldisiloxane,[7] and chloromethyltrimethylsilane.[8] Each of these compounds was prepared independently and could be easily distinguished from hexamethyldisiloxane in gas chromatographic analysis. Aminomethyltrimethylsilane hydrochloride and sodium nitrite, in the absence of acid, do not react.

Evidence for the release of diazomethane is indirect. An attempt to remove it from the reaction mixture by co-distillation with ether was unsuccessful. However, distillation of the acidic aqueous reaction mixture yielded methanol (gas phase chromatography identification using a 10′ Carbowax column at T = 102°). Also, in one run, when 3,5-dinitrobenzoic acid was added to the reaction mixture, a 43% yield of methyl 3,5-dinitrobenzoate was isolated, m.p. 107–108° [lit.,[9] m.p. 107°].

The scope of this reaction and its possible use as an alternate route for the synthesis of diazoalkanes are now under investigation.

Dept. of Chemistry
San Jose State College
San Jose, Calif.

Ralph Fessenden
Francis J. Freenor

Received February 15, 1961

---

[3] M. Freund and F. Lenze, *Ber.*, **24**, 2150 (1891).

[4] L. H. Sommer and J. Rockett, *J. Am. Chem. Soc.*, **73**, 5130 (1951).

[5] R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).

[6] J. L. Speier, B. F. Daubert, and R. R. McGregor, *J. Am. Chem. Soc.*, **70**, 1117 (1949).

[7] C. Eaborn, *J. Chem. Soc.*, 2755 (1949).

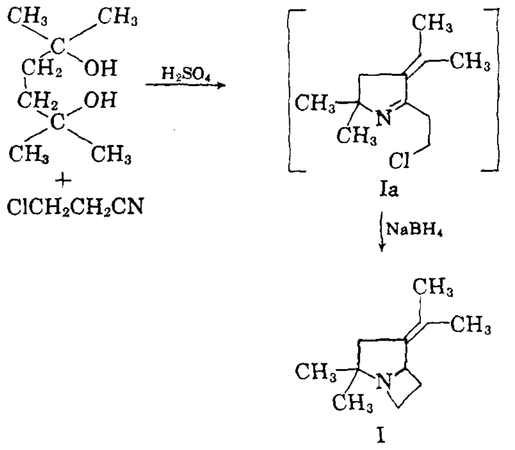
[8] Purchased from Peninsular ChemResearch Corp., Gainesville, Fla.

[9] R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, Third Ed., 1948, p. 226.

A New Approach to Polycyclic Bases. I. The 1-Azabicyclo[3.2.0]heptane System[1]

Sir:

We wish to report a novel procedure for the preparation of polycyclic bases from acyclic starting materials which does not require the isolation of intermediates. The method involves the treatment of ditertiary glycols with ω-chloronitriles in concentrated sulfuric acid followed by the reduction of the resulting C=N link with sodium borohydride and then the addition of alkali to induce intramolecular alkylation. As a result of this technique, we were able to obtain 2,2-dimethyl-4-isopropylidene-1-azabicyclo[3.2.0]heptane (I) a derivative of a hitherto unreported bicyclic system.



The formation of I illustrates a further example of a new and general route to *N*-heterocycles which have, to date, led to 1-pyrrolines, 5,6-dihydropyridines,[2] dihydro-1,3-oxazines,[3] dihydro-1,3-thiazines, 2-thiazolines,[4] and bis(*N*-heterocycyl)alkanes.[5]

The 1-azabicyclo[3.2.0]heptane(I) was prepared in 60% over-all yield based on the dimethylhexanediol. The intermediate 2-chloroethyl-1-pyrroline (Ia) was formed when 3-chloropropionitrile was treated with 2,5-dimethyl-2,5-hexanediol in cold concentrated sulfuric acid. This compound was

---

[1] This study is supported by funds granted from the National Institutes of Health (RG-6248) and the Greater New Orleans Cancer Association.

[2] A. I. Meyers and J. J. Ritter, *J. Org. Chem.*, **23**, 1918 (1958).

[3] A. I. Meyers, *J. Org. Chem.*, **25**, 145 (1960).

[4] A. I. Meyers, *J. Org. Chem.*, **25**, 1147 (1960).

[5] A. I. Meyers, *J. Org. Chem.*, **25**, 2231 (1960).