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SELECTIVE OZONATION OF N-SUBSTITUTED AZIRIDINES.

Yoshikatsu Ito,* Hisao Ida, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

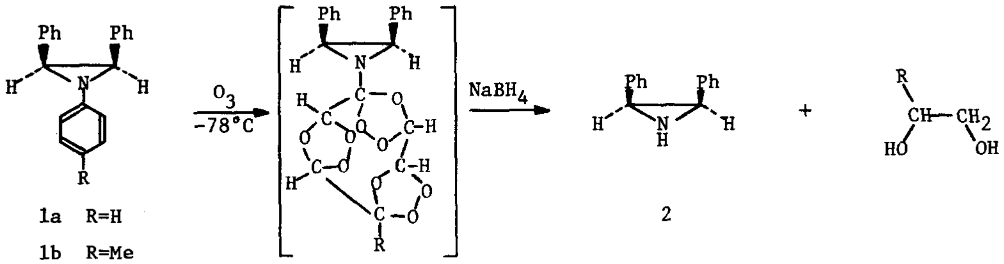
Ozonation of N-alkylated aromatic amines usually results in the formation of a complex mixture of products derived from α-oxidation of the alkyl side-chains as in case of alkylamines, but no products from cleavage of the aromatic ring were isolated.[1] According to the report of Baldwin, et al.,[2] the ring hydrogens of N-*tert*-butylaziridine appear stable to the attack of ozone, since it gives only the N-oxide. In order to gain more insight on the mechanism of amine ozonation,[3] we studied the reaction of N-aryl- and N-alkylaziridines **1** and found that ozone attacks selectively on the N-substituent but not on the aziridine ring.

An ozone-oxygen stream (1.5 g of O_3/hr) was passed through a solution of **1a** in methylene chloride (10 ml, 10^{-2}M) at -78°C until all of the starting material was consumed (usually 2 hr). A colorless solution thus obtained turned brown on warming up to room temperature indicating a complex decomposition, and the only isolable product was benzaldehyde (ca. 10 % yield). However, treatment of the colorless solution with a large excess of sodium borohydride suspended in methanol at -78°C afforded *cis*-2,3-diphenylaziridine (**2**) in quantitative yield and ethyleneglycol (18 %).[4] The results indicate that a thermally unstable intermediate is formed in the ozonation of **1a**. An NMR spectrum was taken with the colorless solution (at -65°C) obtained by the ozonation of **1a** in methylene chloride-d_2 showing three broad bands at δ (TMS) 3.8 (2H, $NC\underline{H}$), 5.7 (5H, $OC\underline{H}O$), and 7.4 (10H, $C_6\underline{H}_5$). These peaks disappeared within a few minutes at 0°C with the appearance of many unidentified peaks.

Quite analogous results were obtained in the ozonation of **1b**,[5] the ozonized mixture from which showed NMR peaks at δ 1.6 (3H, $C\underline{H}_3$), 3.8 (2H), 5.5 (4H), and 7.3 (10H) at -65°C and afforded **2** (80 %), ethyleneglycol (6 %), and propyleneglycol (3 %)[4] on borohydride reduction. Both of the intermediates obtained from **1a** and **1b** were found to react with three equivalents of trimethylphosphite or dimethylsulfide to give the corresponding oxide, indicating that they have three peroxidic bonds in each aziridine unit. We can now formulate the intermediates as triozonides or polymeric ozonides.

Ozonation of an N-n-butyl analog 1c at -78°C followed by the borohydride reduction of the ozonized mixture gave 2 (37 %) and an N-butyrylaziridine 3[5] (33 %). When the ozonized mixture was warmed up to room temperature, 3 (8 %), a urea derivative 4[5] (14 %), benzaldehyde (15 %), and butyraldehyde (20 %) were obtained. Except benzaldehyde, the formation of all the products can be rationalized in terms of α-oxidation on the butyl side-chain.

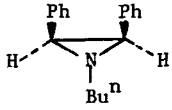
It may be concluded from the above results that the C-H bonds on an aziridine ring are remarkably stable to the attack of ozone. In sharp contrast, N,N-dibenzylaniline, an acyclic analog of 1a, was found to react with ozone ten times faster than 1a and 1b, affording benzaldehyde (78 %) and N-benzylaniline (20 %) indicative of the predominant α-oxidation of the benzyl side chain. The reason of this dramatic change in reactivity and selectivity is not clear at present.



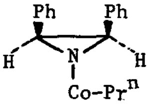
1a R=H
1b R=Me

or polymeric ozonide

2



1c



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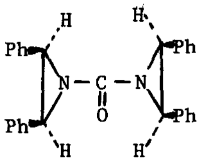

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References and Footnotes

1. E. Keinan and Y. Mazur, J. Org. Chem., 42, 844 (1977); G. H. Kerr and O. Meth-Cohn, J. Chem. Soc. (C), 1971, 1369; A. B. Shapiro, A. V. Osipova, L. A. Skripko, S. D. Razumovskii, and E. G. Rozantsev, Izv. Akad. Nauk SSSR, Ser. Khim., 1971, 1086; P. Kolsaker and D. Meth-Cohn, Chem. Commun., 1965, 423.
2. J. E. Baldwin, A. K. Bhatnager, S. C. Choi, and T. J. Shortridge, J. Am. Chem. Soc., 93, 4082 (1971).
3. P. S. Bailey, J. P. Carter, Jr., and L. M. Southwick, J. Org. Chem., 37, 2997 (1972) and references cited therein.
4. Products were isolated by TLC and/or GLC. Ethyleneglycol and propyleneglycol were isolated as their diacetates.
5. All new compounds gave satisfactory microanalytical and spectral data.

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