Tetrahedron Letters No.2, pp. 109-112, 1971. Pergamon Press. Printed in Great Britain.

RING EXPANSIONS AND RING CONTRACTIONS VIA NITRENIUM IONS[1]

Paul G. Gassman* and Arnaldo Carrasquillo
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

(Received in USA 17 November 1970; received in UK for publication 8 December 1970)

The nitrenium ion has been shown to be a valuable new species of intermediate which is involved in a variety of reactions.[2] Wagner-Meerwein rearrangements,[3] π-routes to azabicyclics,[4] and the concerted ring cleavage of N-chloroaziridines[5] are only a few of the many types of reactions in which divalent electron-deficient nitrogen serves as the crucial intermediate. At this time we wish to report the prototypes of reactions which involve ring expansions and ring contractions _via_ nitrenium ion precursors.

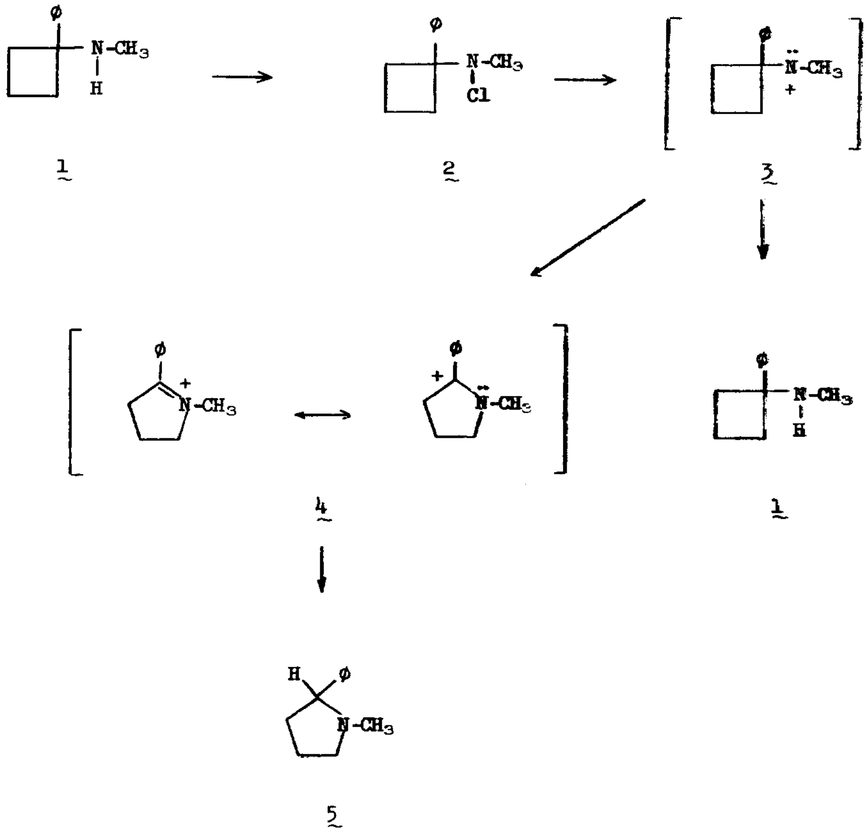
We have found that the generation of a nitrenium ion adjacent to a small ring, such as cyclobutane, results in expansion of the four-membered ring to a five-membered ring containing nitrogen in a reaction reminiscent of the Demjanov rearrangement in carbonium ion chemistry. We also wish to report that when the nitrogen of a small heterocyclic, such as an azetidine, is converted to a nitrenium ion, products are formed which are most consistent with the ring contraction of the azetidine to an aziridine.

When 1-phenyl-N-methylcyclobutylamine (1) was treated with commercial sodium hypochlorite solution, it was quantitatively converted to 2. Addition of a methanolic solution of silver trifluoroacetate to a methanolic solution of 2 resulted in an im-

---

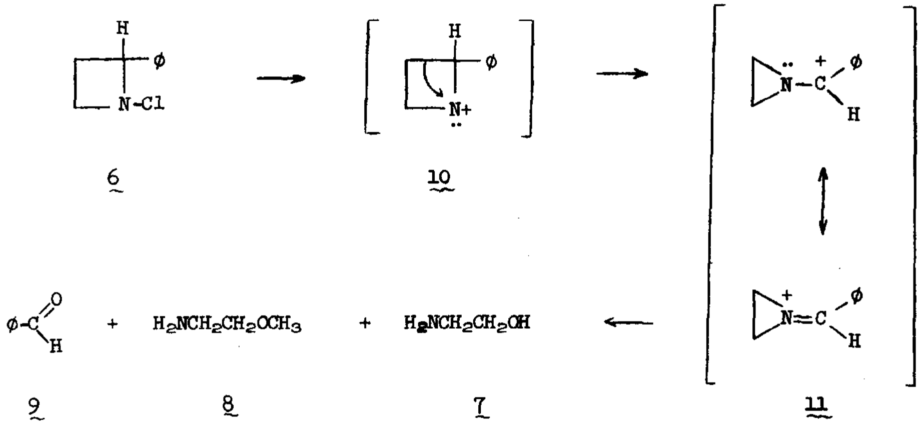
*Alfred P. Sloan Research Fellow, 1967-1969.

Fellow of the Economic Development Administration of Puerto Rico mediate exothermic reaction and precipitation of silver chloride. Workup at this stage gave 1 and an unstable intermediate which decomposed on attempted purification.



It was felt that this unstable component was best represented by 4. The singlet nitrenium ion 3 could either spin invert to give a triplet nitrenium ion which would give 1 by hydrogen abstraction,[6] or 3 could undergo a ring expansion to incorporate nitrogen into the ring. In order to prove this hypothesis, the total reaction mixture was neutralized with sodium methoxide and reduced with sodium borohydride. In this way we obtained a 36% yield of 5[7] and a 24% yield of 1.[8] The structure of 5 was substantiated by comparison with an authentic sample.[9] This provided conclusive evidence for the expansion of carbocyclic rings to adjacent nitrenium ion centers.

When N-chloro-2-phenylazetidine (6) was treated with methanolic silver trifluoroacetate, rapid precipitation of silver chloride was again observed. Hydrolysis and



neutralization of the reaction mixture followed by addition of benzoyl chloride gave 67% of benzaldehyde (9, isolated as its 2,4-dinitrophenylhydrazone), 39% of the benzamide of 8, and 36% of benzoate-benzamide of 7. The extensive fragmentation of 6 under solvolytic conditions is best explained in terms of a ring contraction *via* the nitrenium ion 10 to give the aziridinium salt 11. Hydrolysis of the C=N linkage of 11 should give benzaldehyde and the protonated aziridine which would be expected to open under the reaction conditions to give the mixture of 7 and 8 (accounting for 75% of the starting material). An alternate course would involve opening of the three-membered ring, followed by hydrolysis of the imine linkage.

The observation of both ring expansions and ring contractions *via* nitrenium ion precursors indicates added versatility for divalent electron-deficient nitrogen in the synthesis of heterocyclics. In addition, the specific ring contraction of 6 exemplifies a unique degradative scheme for azetidines.

We are currently investigating both the scope and limitations of ring expansions and ring contractions of nitrenium ions.

Acknowledgment. We are indebted to the National Cander Institute of the Public Health Service for Grant CA-07110 which supported this investigation.

References

1. Paper XV in a series on The Chemistry of Nitrenium Ions. For the previous paper in this series see P. G. Gassman and J. Dygos, Tetrahedron Letters, in press.
2. For a review of the reactions of nitrenium ions see P. G. Gassman, Accounts of Chem. Res., **3**, 26 (1970).
3. P. G. Gassman and R. L. Cryberg, J. Amer. Chem. Soc., **91**, 2047 (1969).
4. P. G. Gassman, F. Hoyda, and J. Dygos, ibid., **90**, 2716 (1968).
5. P. G. Gassman, D. K. Dygos, and J. E. Trent, ibid., **92**, 2084 (1970).
6. For a discussion of spin inversion of nitrenium ions see P. G. Gassman and R. L. Cryberg, ibid., **91**, 5176 (1969).
7. Based on unrecovered **1**, this represents a 47% yield of the ring expanded product, **5**, for the three step procedure of chlorination, rearrangement, and reduction.
8. Catalytic reduction of the reaction mixture over palladium on carbon gave 35% of **5** and 19% of **1**.
9. L. D. Quin and G. L. Roof, J. Org. Chem., **27**, 4451 (1962).