

## FRAGMENTATION REACTION OF AZIRIDINIUM YLIDS

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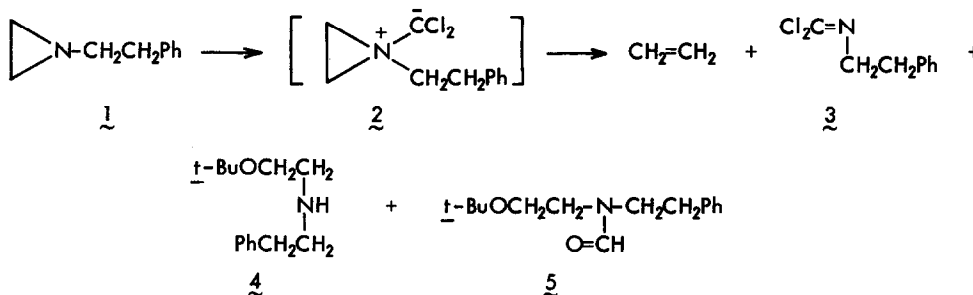
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Despite the very extensive study currently being devoted to the development of aziridine chemistry, little information is available on aziridine ylid derivatives (1).

In view of this, aziridinium ylids may be of particular interest, and to investigate the properties of aziridinium ylids, we have studied the reactions of dichlorocarbene with aziridine derivatives and wish to report here a stereospecific fragmentation reaction observed.

N-Phenethylaziridine 1 prepared by the reaction of ethylenimine and styrene (2) was dissolved in *n*-pentane or ether and an excess of potassium *t*-butoxide was suspended in the solution at 0°. No reaction occurred at this stage, but on the addition of chloroform the reaction immediately took place. After the reaction ceased, quenching with water and distillation of the mixture gave three products, 3, 4 and 5, in yields of 20%, 9% and 30% respectively.

During the reaction, the generated ethylene was collected and identified by conversion to its dibromo derivative. The yield of ethylene was 43%. The structure of compound 4 was deduced from elemental analysis and the nmr spectrum ( $\tau$  2.75, s 5H; 6.5, t 2H; 7.20, m 6H; HCl salt mp 173-175°) and product 5 was identified in the comparison with authentic sample\* (bp 120°/1 mmHg, 1675 cm<sup>-1</sup> (N-C=O)).

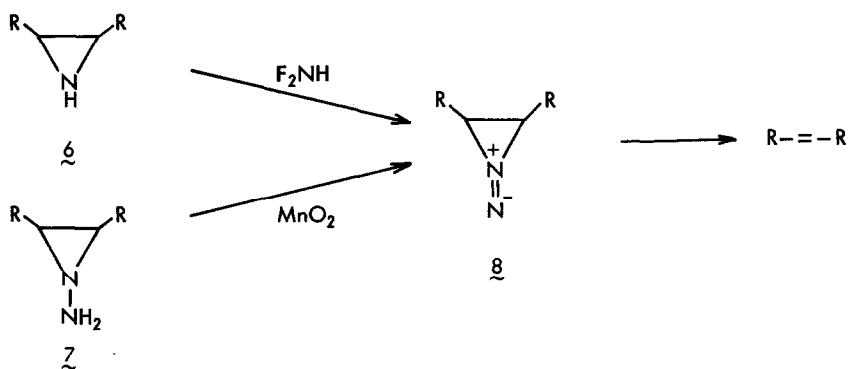


\* Authentic sample was prepared from 4 on the reaction with acetic formic anhydride.

Compound 3 (bp 60-62°/1 mmHg) showed a strong absorption band at 1655  $\text{cm}^{-1}$  attributed to C=N, and its nmr spectrum showed signals at  $\tau$  6.1 (t 2H) and 6.9 (t 2H) corresponding to two  $\text{CH}_2$  groups. Compound 3 was readily converted to phenethylamine hydrochloride by contact with a moist atmosphere, and it gave ethyl phenethylaminoformate with ethanol in good yield. These amine derivatives were identified by comparison with authentic samples. \*\*

In general, the reaction of amino compounds with carbene proceeds through the formation of ammonium ylid intermediates (3). In our reaction, though the formation of azetidine, which would be expected in Steven's rearrangement of ylid was not observed (3), it is reasonable to consider the formation of aziridinium ylid 2 as a reaction intermediate, and the formation of 5 by attack of butoxide ion on the ring carbon atom of 2 supports this. Generation of ethylene and 3 may be understood as arising from fragmentation of an ylid intermediate, and the low yield of latter may be attributed to its instability under the reaction conditions.

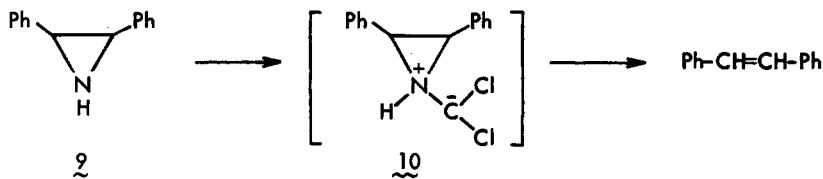
Freeman and Graham reported the preparation of an isomeric pair of azamines 8 ( $\text{R} = \text{CH}_3$ ) from cis- and trans-dimethylaziridine 6 ( $\text{R} = \text{CH}_3$ ) by reaction with difluoroamine and they observed that the con-



version to olefin was stereospecific (4). More recently, however, Carpio and Kirkley reported the reverse phenomenon in the fragmentation of 8 ( $\text{R} = \text{cis Ph}$ ) which was derived from 7 ( $\text{R} = \text{cis Ph}$ ) under oxidation conditions (5). The stilbene was formed with a loss of stereospecificity and they proposed a two-step process involving phenyl stabilization of the radical.

\*\* Product 3 was also appeared in the reaction of 1 with  $\text{PhHgCCl}_3$ -benzene at 80°,  $\text{LiCCl}_3$ -THF or  $\text{LiCCl}_3$ -tetramethylethylenediamine at low temperature. These results indicate the formation of 3 was attributed to the reaction of 1 with carbene.

It thus seemed to us of interest to examine the stereochemistry of olefins formed from the fragmentation of aziridinium ylids, so we next carried out the fragmentation reaction using cis- and trans-2,3-diphenylaziridine 9 (6).



Treatment of cis- and trans-9 under the conditions described above, produced stilbene in yields of 30% respectively. Direct vpc analysis of the reaction mixture using n-octadecane as internal reference showed that a mixture of 95.5% cis- and 4.5% trans-stilbene were produced from cis-9 and >99% trans-stilbene from trans-9. Thus neither the stilbenes produced nor starting material 9 were isomerized under the reaction conditions. We can rationalized the results by postulating that aziridinium ylid fragmentations mainly occur through a mechanism involving a concerted cheletropic reaction with retention of configuration (7). Phenyl stabilization of the radical is not important in the fragmentation of 9. Our conclusions also throw light upon the mechanism of the reaction between phenyl(bromo-dichloromethyl)mercury and diisopropylcarbodiimide or phenyl isocyanate, recently reported by Seyferth and his-coworkers (8). These reactions may proceed through the formation and the fragmentation of aziridinium ylid intermediates to the products, N-dichloromethyleisopropylamine or 1-phenyl-2,2,3,3-tetrachloroaziridine respectively.

Similar observations have been made on the fragmentation of 1-(2-octyl)aziridine, 1-(exo-2-benzonorbonyl)aziridine, and the other aziridine derivatives, these will be published shortly.

#### REFERENCES

1. Recently, the fragmentation of aziridin N-oxides were reported. J. E. Baldwin, A. K. Bhatnagar, S. C. Choi and T. J. Shortridge, J. Am. Chem. Soc. 93, 4082 (1971).
2. H. Yoshida and K. Naito, Kogyo Kagaku Zasshi 55, 455 (1952).
3. G. Wittig and G. Felleitschin, Ann. 555, 133 (1944); P. Miginiac, Bull. Soc. Chim. Fr. 2000 (1962); A. W. Johnson, "Ylid Chemistry," Academic Press (N. Y. & London), 1966, p 251.
4. J. P. Freeman and W. H. Graham, J. Am. Chem. Soc. 89, 1761 (1967).
5. L. A. Carpino and R. K. Kirkley, J. Am. Chem. Soc. 92, 1784 (1970).

6. A. Hassner, G. J. Matthews and F. W. Fowler, J. Am. Chem. Soc. 91, 5046 (1969).
7. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press (N. Y. & London), 1970, p 152.
8. D. Seyferth, R. Damrauer, H.-M. Shih, W. Tronich, W. E. Smith and J. Y.-P. Mui, J. Org. Chem. 36, 1786 (1971).