

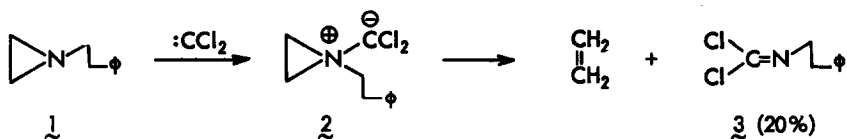
FRAGMENTATION REACTION OF AZIRIDIUM YLIDS. II.

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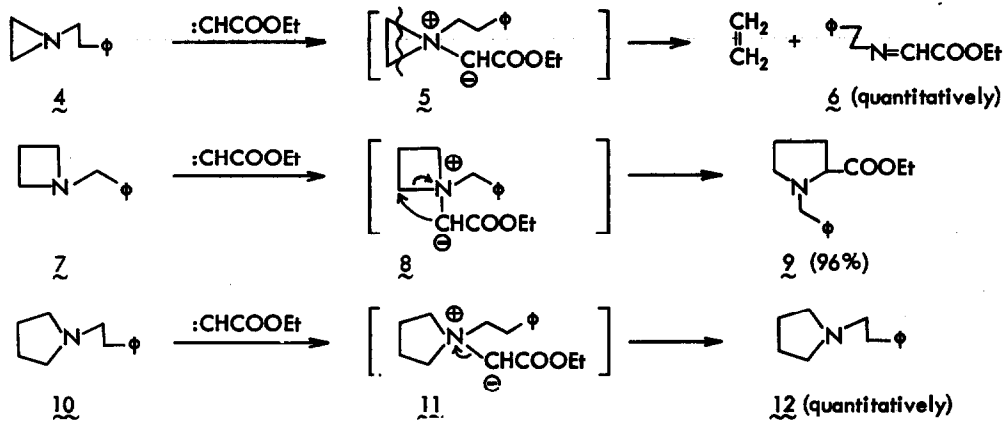
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Steven's rearrangement is one of the most common reactions for the degradation of quarternary ammonium ylids. In an earlier study however we observed that the quarternary aziridinium ylid **2** gave no detectable product due to Steven's rearrangement, instead a characteristic fragmentation occurred as shown below.¹

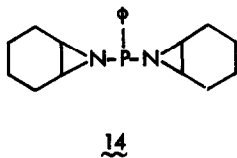
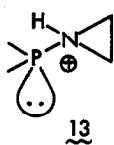


We now wish to report the reactions between carbene and 3, 4 or 5 membered cyclic imines, in which the course of the reaction is completely depended on their ring size. We will also give a brief discussion of the biological significance of aziridine derivatives recently used as insect chemosterilants.



When a mixture of 1-phenethylaziridine **4**, ethyl diazoacetate, and a catalytic amount of $\text{Cu}(\text{AcAc})_2$ was heated at 70-80°, a vigorous reaction occurred and the product **6** was given in quantitative yield,² no other product being observed. This result clearly shows that fragmentation is the only reaction of

aziridinium ylid. Under similar conditions the four membered ring compound, 1-benzylazetidine 7 afforded 9 as the sole product in 96% yield, showing that reaction proceeded exclusively with Steven's rearrangement. On the other hand, the five membered ring compound, 1-phenethylpyrrolidine 10 under the same reaction conditions was recovered with no reaction taking place. When benzophenone was present in the solution, however, the generation of ylid intermediate 11 was indicated by the formation of a complicated product.³ These results illustrate that there are three kinds of mechanism for the degradation of ylids 5, 8, and 11. An important factor determining the course of the reaction is probably the amount of strain energy released. We are at present investigating this in detail.



The electronic structures of protonated amino-phosphine 13 strongly resemble that of aziridinium ylid 5. We therefore tried the fragmentation reaction of 13 system, using compound 14.⁴

When the compound was heated at 70° in perchloric acid or with Dowex 50W anion exchange resin in water, formation of the corresponding olefin, cyclohexene, was clearly observed, though in only a few percent yield. The result clearly shows that the fragmentation reaction is applicable to ylid analogue such as 13. Because aziridine derivatives which carry a phosphorus or sulphur atom on the ring nitrogen atom generally have a strong mutagenic action,⁵ they are attracting much interest in the biological field. If the *in vivo* decomposition of these aziridine derivatives on the enzyme surface takes place with initial proton attack and in the absence of an anion which leads to ring cleavage, then the fragmentation reaction may have important significance in the mechanism of the chemosterilant action of these compounds.

REFERENCES

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