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A GENERAL SYNTHESIS OF 2H-AZIRINES FROM OLEFINS. FUSED AZIRINES. Alfred Hassner and Frank W. Fowler

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Azirines, simplest of the nitrogen heterocycles, have received little attention.² Possibly this is because there has been reported no synthesis that has proven to be of general applicability.³ The generality of the synthetic routes reported in the literature has been limited either because of the unavailability of the necessary intermediates^{3c} or the instability of most azirines to the reaction conditions.^{3a-b}

We wish to report that 2H-azirines can be synthesized in good yield from olefins according to the following scheme:



The recent discovery in this laboratory of the stereospecific addition of IN_3 to olefins presents a convenient method for the synthesis of iodo azides I.⁴ We now find that dehydrohalogenation of I takes place stereospecifically <u>trans</u> leading to vinyl azides II, indicating a directive effect of the azido function.⁵ However, <u>trans</u> \emptyset -iodo azides derived from cyclopentene and cyclohexene (ie. IV and VI) give, upon elimination, allyl azides V and VII respectively. Here the stereoelectronic preference for trans elimination to the allyl azide appears to be greater than the conju-

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gative effect of the vinyl azide. In an eight membered ring, where the possibility exists for <u>trans</u> elimination to the <u>trans</u> olefin, we have observed that treatment of 1-azido-2-iodocyclooctane VIII or 3-azido-4-iodocylooctene X gives the vinyl azide IX and XI respectively. All vinyl azides are characteristically yellow with a strong C-C stretching frequency near 1650 cm⁻¹ in contrast to the colorless allyl azides which show only weak C-C absorption. The nmr spectra of vinyl azides II indicate a deshielding effect by the azide group toward the <u>cis</u> vinyl hydrogen. Thus, <u>cis</u> 2-azido-2-butene (II, R,R":CH₃, R':H) the vinyl proton absorbs at 4.927, whereas in the <u>trans</u> isomer (II, R,R':CH₃, R':H) it absorbs at 5.347.



Either photolysis or pyrolysis of vinyl azides II gives the 2H-azirines III in good yield. We prefer photolysis rather than pyrolysis as a path leading to 2H-azirines since it has been reported that pyrolysis of IId gives much polymerization 3c and we have observed little polymerization with photolysis. ⁶ All azirines are colorless liquids having an unpleasant odor.

To date no fused azirine has been reported although an attempt to synthesize one has been made.³ This could be attributed to the unavailability of the prerequisite intermediate or to the fact that increased strain energy might prohibit the isolation of such bicyclic systems. We have had only partial success in the synthesis of an azirine fused to a 5 or 6 membered ring, e.g. indane; the crude unstable products showed strong characteristic absorption near 1750 cm⁻¹ but no pure material was obtained. Photolysis was generally incomplete and much polymerization occurred. However, 2H- **Azirines** fused to eight membered rings can be prepared readily by the above method. Azirine XII is a stable colorless liquid, b.p. $76^{\circ}/20$ mm, that exhibits a strong band at 1760 cm⁻¹; impure XII readily polymerizes on standing. The structures of azirines XII and XIII were confirmed by reduction to the





aziridines which were characteriged.

In fact, we have discovered that reduction of 2H-azirines with lithium aluminum hydride proceeds in a highly stereospecific manner to give, in good yield <u>cis</u> aziridines XVII indicating that hydride attack at the C=N in azirines is sterically controlled.



This reaction sequence not only allows for the stereospecific synthesis of aziridines from readily available trans olefins⁷ but also permits the <u>con-</u> <u>version of a mixture of cis and trans olefins into a cis aziridine exclu-</u> sively. <u>Trans aziridines can be obtained by diborane reduction of α , \emptyset -iodo azides derived from trans olefins.^{4,8}</u>

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