

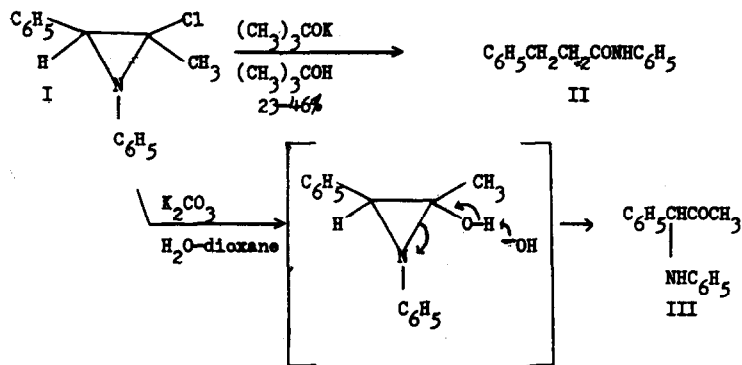
AN AZIRIDINE REARRANGEMENT

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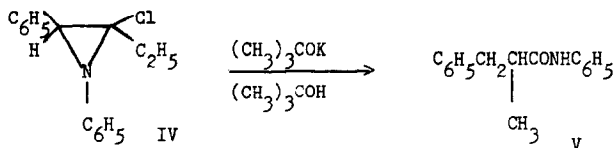
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It was recently shown that monochloroaziridines undergo facile nucleophilic displacement without rupture of the three-membered ring.<sup>(3)</sup> A variety of nucleophiles could be employed successfully including sterically undemanding bases such as ethoxide, cyanide and thiophenolate. In contrast to these results, we would like to report an unusual rearrangement which results when cis-3-chloro-3-methyl-1,2-diphenylaziridine (I) is refluxed for 90 minutes with an excess of a hindered base, potassium t-butoxide, in t-butanol. The product, which formally represents the replacement of Cl by OH, was identified as hydrocinnamanilide (II).<sup>(4)</sup> A simple displacement of Cl<sup>-</sup> by OH<sup>-</sup> could, in fact, be observed under different conditions and this product (III) bore no resemblance to II.<sup>(5)</sup>

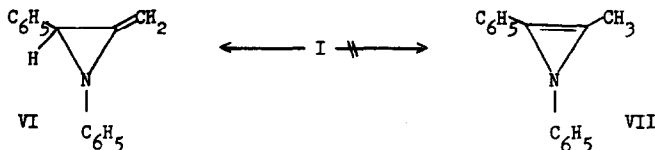


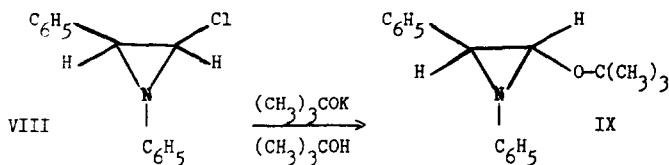
In order to determine the fate of the methyl carbon in I, it was effectively "labeled" by synthesizing the ethyl analog (IV)<sup>(7)</sup> of I and subjecting it to the above conditions. The product, V,<sup>(8)</sup> clearly indicates that the methyl carbon in I eventually becomes the  $\alpha$  carbon of II.



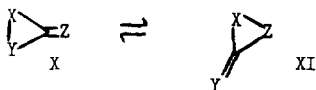
Treatment of I with  $(\text{CH}_3)_3\text{COK}$  in  $(\text{CH}_3)_3\text{COD}$  yielded a product which had incorporated deuterium to the extent of 95% at the  $\alpha$  position and 90% at the  $\beta$ .<sup>(10)</sup> A control experiment showed that II exchanged 95+% of its  $\alpha$  hydrogens and none of its  $\beta$  hydrogens under the rearrangement conditions. Therefore, in addition to accounting for the relative arrangement of the carbon atoms in I and II, any acceptable mechanism for this transformation must include intermediates which are capable of exchanging the original benzylic proton and abstracting a second.

We believe that this rearrangement is initiated by  $(\text{CH}_3)_3\text{COK}$  abstraction of HCl to give the methylene aziridine VI. This methylene aziridine is presumably favored over its endocyclic isomer (VII) by the unfavorable electronic characteristics of VII and the non-planar arrangement of the Cl-C<sub>3</sub>-C<sub>2</sub>-H bonds in I. In support of this presumption, we have observed that VIII gives IX as the only spectroscopically recognizable product.<sup>(11)</sup>

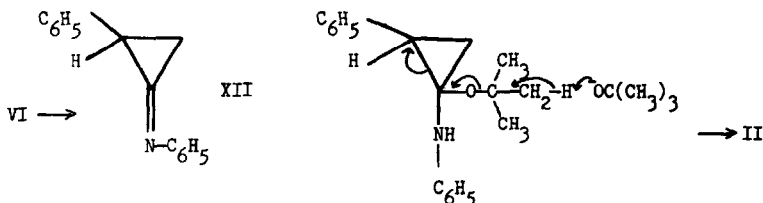




Compounds of the general structure X are known to be susceptible to thermal X-Y bond cleavage<sup>(12)</sup> and/or isomerization.<sup>(13)</sup> By an isomerization



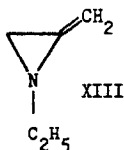
of this type, VI would yield XII and thus form all the skeletal bonds (plus one) required in the final product. From XII, a series of relatively straightforward steps could lead to the final product.<sup>(14)</sup> If this scheme is correct, XII appears to be the most likely candidate for exchange of the original benzylic proton.



Of greatest general interest in this proposed scheme is the X  $\rightarrow$  XI type isomerization. Any formulation of a detailed mechanism involving a discrete diradical and/or zwitterion intermediate (as opposed to a concerted valence-tautomerization) suggests that the rate and possibly the mechanistic type could be quite sensitive to the nature of X, Y and Z as well as their substituents. Substituent effects have already been noted where X, Y and Z = C.<sup>(13)</sup> In the case of X = C, Y = N, and Z = O, the isomerization is apparently complete in ten minutes at 75°.<sup>(15)</sup> It must also be anticipated that the ability to detect the isomerization depends on the relative stabilities of X and XI as

well as the ease with which each may be (irreversibly) transformed to other products.

The above is pertinent to our observation that XIII<sup>(16)</sup> can be recovered from  $(\text{CH}_3)_3\text{COH} - (\text{CH}_3)_3\text{COK}$  solutions at reflux (1 1/2 hours) or 190° (3/4 hour; with some decomposition).



We are currently attempting to assess the effects of substituents on the rate, equilibria and scope of these isomerizations.

#### REFERENCES

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- (2) Smith, Kline and French Co., Philadelphia, Pennsylvania.
- (3) J. A. Deyrup and R. B. Greenwald, *J. Am. Chem. Soc.*, 87, 4538 (1965).
- (4) Infrared and n.m.r. spectroscopic methods allowed the initial identification. The sample was then compared and shown identical to an authentic sample.<sup>(5)</sup> Other products could not be isolated from the reaction mixture.
- (5) W. Dieckmann, J. Hoppe and R. Stein, *Chem. Ber.*, 37, 4627, (1904).
- (6) R. B. Greenwald, Ph.D. thesis, Harvard University, 1965.
- (7) This compound was prepared according to a previously described procedure<sup>(3)</sup> in which ethyllithium was substituted for methyllithium. The product, which had spectral characteristics fully consistent with IV, could not be crystallized or distilled and was, therefore, used without further purification.
- (8) This material was identical to an authentic sample.<sup>(9)</sup>
- (9) S. Shinya, *Nippon Nogei-Kagaku Kai Shi*, 29, 91 (1955); *Chem. Abstr.*, 53, 1228a (1959).
- (10) As determined by its n.m.r. spectrum.

- (11) Although this material could not be obtained in crystalline form, its n.m.r. spectrum was in agreement with the assigned structure.
- (12) W. B. Hammond and N. J. Turro, *J. Am. Chem. Soc.*, 88, 2880 (1966).
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- (14) Alternatively, XII could be attacked by hydroxide formed from trace amounts of water in the reaction mixture.
- (15) J. C. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, 86, 746 (1964).
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