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OLEFIN SYNTHESIS *VIA* THE STEREOSPECIFIC DEAMINATION OF AZIRIDINES

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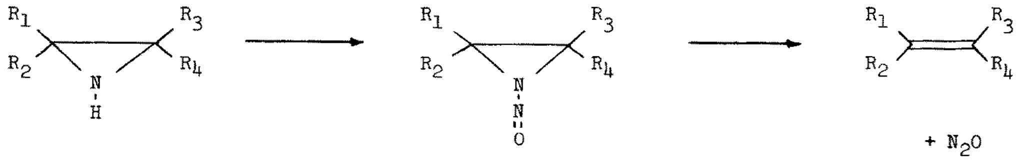
It has been shown by Clark[2] that the deamination of aziridines under nitrosating conditions proceeds stereospecifically to the corresponding olefin of retained stereochemistry (Equation 1).[3]

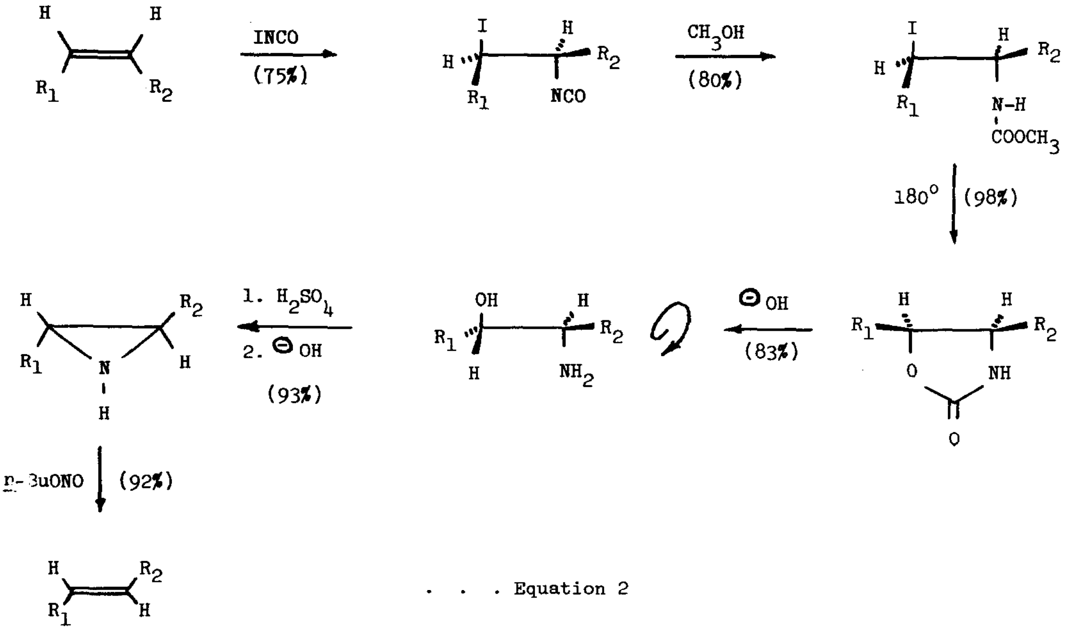


. . . Equation 1

However, as deamination in the majority of cases would result in the regeneration of the olefin that was the basis for the original aziridine synthesis, the reaction has eluded serious consideration as a synthetic method. We have now examined several select methods of aziridine synthesis (including the as yet unreported stereospecific addition of Grignard reagents to azirines) that avoid the problem of starting material regeneration and found that they do represent satisfactory routes to aziridines of predictable geometry. Nitrosative deamination was effected with *n*-butyl nitrite containing a small amount of added triethylamine.

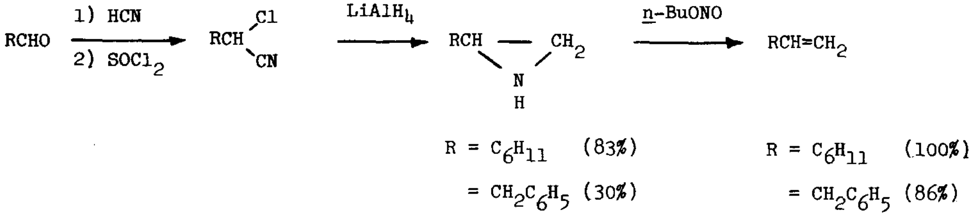
One new application of the aziridine deamination is the interconversion of *cis*-*trans* isomers of olefins. The method that was developed utilized Hassner's preparation of vicinal amino alcohols,[4] a Wenker's aziridine synthesis,[5] followed by an alkyl nitrite deamination (Equation 2).

It is noteworthy that although the reaction sequence appears formidable, the actual experimental execution is much less of a challenge.[6] For the specific conversion of cis to trans-2-octene (R_1 = CH_3, R_2 = n-C_5H_{11}) an overall yield of 41% was realized.[7]



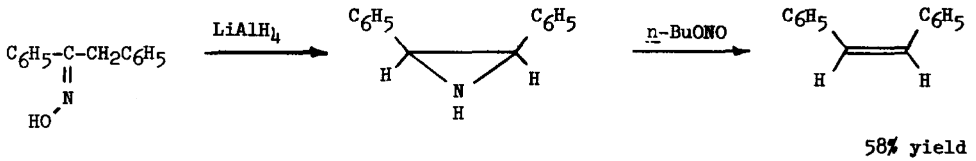
. . . Equation 2

The reported lithium aluminum hydride reduction of α-chloronitriles[8] was investigated as an alternate route to the synthesis of terminal methylene compounds from aldehydes. By this procedure heptaldehyde (R = C_6H_{11}) and phenylacetaldehyde (R = $C_6H_5CH_2$-) were converted into 1-octene and allylbenzene respectively (Equation 3).



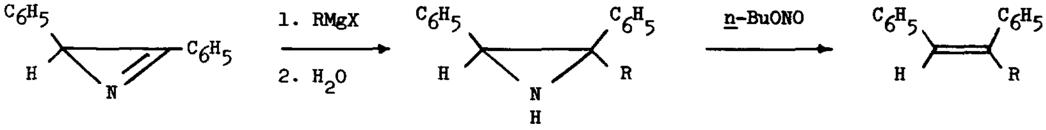
. . . Equation 3

The stereospecific reduction of ketoximes to cis aziridines[9] was utilized to prepare cis-2,3-diphenylaziridine which (upon deamination) generated cis stilbene (Equation 4). If this reaction sequence is translated to other systems, an entry is provided for the synthesis of thermodynamically less stable cis olefins.



. . . Equation 4

However, as the limiting step in the olefin synthesis appeared to be the preparation of the aziridine, an alternate method of aziridine synthesis was developed. The new method, which proceeds in high yield, is based on the addition of Grignard reagents to azirines[10] (Equation 5). The direction of addition is such as to give only the product derived from attack at the least hindered side of the azirine.[11] Deamination gives the corresponding olefin.



R = CH_3 (80%)
= C_2H_5 (100%)
= C_6H_5 (100%)

R = CH_3 (87%)
= C_2H_5 (83%)
= C_6H_5 (73%)

. . . Equation 5

We are examining further the azirine addition-aziridine deamination procedure as a method for stereospecific olefin synthesis.

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[1] Taken in part from the dissertation submitted by S. Y. Lee in partial fulfillment of the requirements for the M.S. Degree, University of Minnesota, 1968.

[2] R. D. Clark and G. K. Helmkamp, J. Org. Chem., **29**, 1316 (1964).

[3] The stereochemical course of the mild and selective deamination with n-butyl nitrite was established (as in Equation 1) by reacting *n*-butyl nitrite with *cis* and *trans*-2-methyl-3-*n*-pentyl aziridine to give respectively *cis* and *trans*-2-octene in high yield. None of the other isomer was detected by vapor-phase chromatography.

[4] A. Hassner, M. E. Lorber and C. Heathcock, J. Org. Chem., **32**, 540 (1967).

[5] P. A. Leighton, W. A. Perkins and M. L. Renquist, J. Amer. Chem. Soc., **69**, 1540 (1947).

[6] Two isomers were noted by thin-layer chromatography for the isocyanate through amino-alcohol. The stereochemical argument is still valid if R_1 = *n*-C_5H_{11} and R_2 = CH_3 and accordingly, only a single aziridine was observed.

[7] Yields throughout this communication are expressed as isolated yields of olefins possessing the physical and spectral properties of the isomers shown.

[8] K. Ichimura and M. Ohta, Bull. Chem. Soc. Japan, **40**, 432 (1967).

[9] K. Kotera and K. Kitahonoki, Organic Synthesis, John Wiley and Sons, New York, 1968, p. 20.

[10] S. Eguchi and Y. Ishnii, Bull. Chem. Soc. Japan, **36**, 1434 (1963).

11 The stereochemical results are in significant agreement with those observed for:

The reaction of Grignard's with ketoximes, A. Laurent and A. Muller, Tetrahedron Lett., **19**, 759 (1969).

The reduction of azirines with lithium aluminum hydride, A. Hassner and F. W. Fowler, J. Org. Chem., **90**, 2869 (1968).