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CONSERVATION OF INTERMEDIATE POSITIONAL INTEGRITY IN THE DEAMINATION OF 1-d-3-ISOPROPYLCYCLOBUTYLAMINE; ABSENCE OF CYCLOPROPYLCARBINYL DEGENERACY

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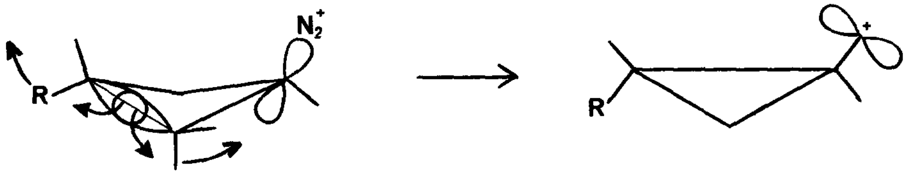
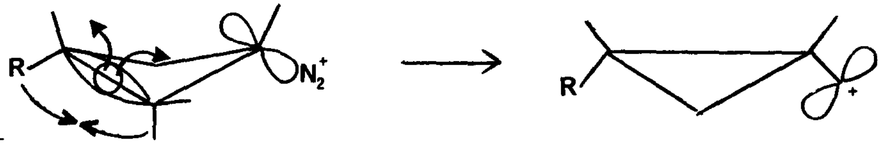
Recent evidence has provided new insight into cyclobutane carbonium ion rearrangements as examples of concerted orbital overlap processes which proceed with conservation of orbital symmetry (1), and are very sensitive to steric factors. It has been shown that in the case of deamination of 3-isopropyl- (2) and 3-methylcyclobutylamine (3), differences in cis and trans product distribution are correlated with conformational facilitation of bond overlap motions in the cyclobutyldiazonium intermediates. Analogous results have been obtained in solvolysis of 3-isopropylcyclobutyl brosylates (4)*. Similar conclusions have been independently drawn by Wiberg and coworkers in their study of solvolysis of fused ring cyclobutyl derivatives (5). Thus, the major trans pathway is represented in I by disrotatory C_2-C_3 orbital opening (6) followed by C_1-C_3 overlap; a process

I



II



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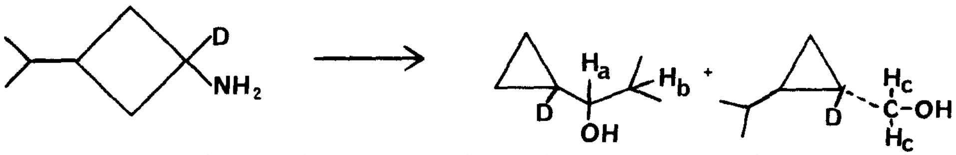
*As in the case of the 3-isopropyl group, the 3-methyl group results in a which is retarded for cis intermediate (II) by developing R-H oppositions. The premise was presented (2) that cyclobutyldiazonium cation was the branching point for products, and was converted directly to cyclopropylcarbinols or carbonium ion precursors without the intervention of bicyclobutonium ions. We now report complete confirmation of this rationale in the deamination of specifically deuterated 3-isopropylcyclobutylamine.

The amine, consisting of cis and trans isomers and labeled in the 1-position, was deaminated in the same fashion as the unlabeled amine (2). Products were separated by vpc, and the deuterium label located by nmr comparison with undeuterated compound. Major trans product trans-(2-isopropylcyclopropyl)carbinol is stereospecifically produced, while isopropylcyclopropylcarbinol, the major cis product, results for both isomers. These products were quantitatively labeled as indicated. Clearcut and specific disappearance of the furthest downfield



cyclopropane proton integral resonance in each case was noted. H_a was simplified from an ABX quartet (J = 5.5, 7 cps) to a simple doublet exhibiting coupling only to H_b (J = 5.5). H_c was simplified from a doublet (J = 7) to a singlet without discernible splitting.

The singular position of deuterium in the trans-(2-isopropylcyclopropyl)carbinol obtained is consistent with the concerted genesis proposed. However, more revealing is the labeling in the isopropylcyclopropylcarbinol. It was pointed out (2) that this product could arise from either an intermediate 2-isopropylcyclopropylcarbinyl cation, or via a synchronous 1,2-hydride shift and C_3-C_2 bond migration; the latter viewpoint was espoused. However, the present results clearly eliminate this alternative for both isomers, and unequivocally point to the former route.

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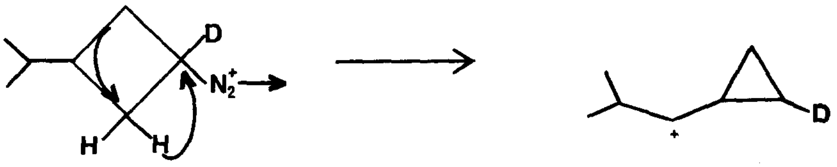
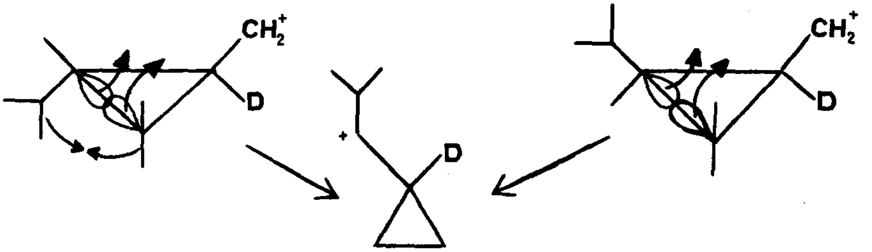
rate ratio favoring the trans isomer in brosylate solvolysis (I. Lillien and L. Handloser, unpublished work). A similar effect is noted with the 3-t-butyl group (P. von R. Schleyer, private communication).

The hydride shift path can only lead to differently labeled product as shown below. On the other hand, transformation of intermediate cis-(2-isopropylcyclopropyl)carbinyl cation to isopropylcyclopropylcarbinyl cation occurs with less steric opposition than in the case of the trans isomer, in which isopropyl-H repulsive interaction ensues as a result of orbital movement, accounting for the larger proportion of this product for cis-3-isopropylcyclobutylamine.





Trans Cis

Positional degeneracy in cyclopropylcarbinyl cation reactions has been often observed in labeling experiments (7-11), and has formed part of the basis of original bicyclobutonium ion proposals (12); and more recently was used in support of a symmetrical bicyclobutonium ion intermediate concept (13). It has been widely assumed to be an invariable concomitant of rearrangements in this system; indeed it has been referred to as a "main characteristic" of the cyclopropylcarbinyl cation (13). The present work, therefore, represents the first reported instance of specific retention of a positional label in a cyclobutane carbonium ion reaction proceeding to or through the cyclopropylcarbinyl cation. These results clearly support the picture of concerted rearrangement sans intervention of "nonclassical" intermediates, for the case of cyclobutane deamination. The question of scrambling in the analogous solvolysis is being examined.

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