J. Org. Chem. **1981**, *46*, 3767–3768 **3767**

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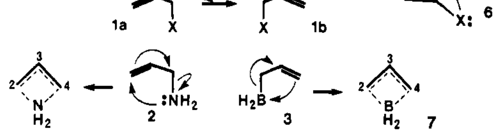
Received March 10, 1981

(1,3)-Sigmatropic Shifts of Allylamine and Allylborane. Flexible Models for Possible Pseudopericyclic Reactions

Summary: The degenerate 1,3-shift rearrangements of allylamine and allylborane have been mapped by the PRDDO method. It is shown that the former is neither pericyclic nor pseudopericyclic in character, but that the latter conforms to the pseudopericyclic concept when it is recognized that a general feature of electron-deficient sigmatropic migrations is the existence of polycyclic transition-state binding.

Sir: Unimolecular allylic rearrangements for simply substituted propene derivatives have traditionally been characterized by two mechanistic polar extremes. Ion pair formation accompanied by internal return has been invoked when the substituent X (**1a**/**1b**) is a good leaving group.[1] Concerted migration with inversion or the intervention of biradicals is demonstrable when carbon is the migrating atom.[2] Recently Lemal and co-workers proposed an alternative to the concerted pericyclic shift for certain cases in which the migrating atom X bears either a lone electron pair or a vacant orbital. Specifically, concerted rearrangements proceeding through a cyclically delocalized transition state in which nonbonding orbitals at X exchange roles with bonding orbitals at the same center have been designated as "pseudopericyclic".[3] The arrows in **2** and **3** depict the concept for X = NH_2 and BH_2 and imply the involvement of six and four electrons, respectively, in the delocalized transition states.



By means of approximate ab initio PRDDO calculations, we have previously shown that degenerate allylic rearrangement in the geometrically constrained 5-X-bicyclo[2.1.0]pent-2-ene system **6** is best described as a pericyclic 1,3-shift unaccompanied by lone-pair participation at X. The calculated and experimentally correlatable variations in relative reaction rates were interpreted on the basis of transition-state structure.[4] In order to probe the nature of the cyclic transition state under conditions providing for maximum involvement of the nonbonding orbitals at X, we have evaluated the concerted migration in the more flexible, simple allylic system **1** for X = NH_2 and BH_2. While we are aware of only two cases of a 1,3-nitrogen shift,[5] dialkylboranes undergo rearrangement readily with energy barriers ranging $\Delta H^{\ddagger} = 10–15$ kcal/mol.[6]

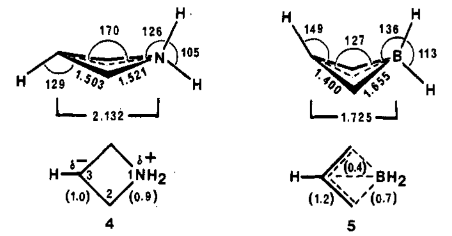


Figure 1. The PRDDO optimized C_s midpoints in the 1,3-shifts of allylamine and allylborane. Bond distances are given in angstroms and bond angles in degrees. Structures **4** and **5** represent the overall binding based on the molecular geometries and the parenthetical APS indices.

The allyl ground states, $CH_2{=}CHCH_2X$, were fully geometry optimized by means of the PRDDO method[7] with no constraints. The corresponding cyclic complexes were treated similarly under the assumption of C_s symmetry (Figure 1). Linear synchronous transit (LST) pathways[8] were constructed between the endpoints (e.g., **2**/**4** and **3**/**5**). The allylamine transformation exhibited an intervening maximum and was therefore subjected to additional path-constrained optimizations. The resulting PRDDO reaction pathway $\mathbf{3} \rightarrow \mathbf{4} \rightarrow \mathbf{3'}$ accommodates the nitrogen-containing four-membered ring as an intermediate surrounded symmetrically by barriers of 4.7 kcal/mol. The final QST[8] pathways exhibit overall barriers of 98 and 11 kcal/mol for X = NH_2 and BH_2, respectively.

Can the computed reaction surfaces be characterized as pseudopericyclic? Electronic reorganization from allyl-X to the C_s cycles has been monitored by following the Armstrong–Perkins–Stewart (APS) bond indices[9] and both canonical (CMO) and Boys' localized (LMO) molecular orbitals along the QST pathways. For X = NH_2 the APS valency of the amine nitrogen varies from 3.0 to 3.7 as $CH_2{=}CHCH_2NH_2$ cyclizes to **4**. Simultaneously, C_3 builds up negative charge ($-0.02 \rightarrow -0.45$) and the N–C bond orders change from 1.01/0.01 to 0.89/0.89. The near-full N–C bond formation is likewise reflected in the optimized length of 1.521 Å for the C_s intermediate (Figure 1). The latter is best formulated as a nearly flat azetidinium ylide with the carbanion center located at C_3. The transition state leading into the zwitterion is unsymmetrical and characterized by a weakened C=C bond (1.381 Å) and a developing N–C bond (1.771 Å). Thus the PRDDO 1.3-shift in **1** (X = NH_2) is distinguished by neither pericyclic nor pseudopericyclic delocalization but rather corresponds to two discrete steps initiated by the attack of NH_2: at the terminal allyl carbon. The C=C π electrons are thereby transformed into a carbanionic lone pair at C_3, giving **4**. Subsequently, analogous to the elimination of a quaternary ammonium salt, ylide **4** decomposes by cleavage of the alternate N–C bond. An obvious experimental entry onto the rearrangement surface is suggested. The very large calculated barrier to cyclization may stem in part from PRDDO's inflexible basis set and the lack of diffuse orbitals for properly handling the carbanion center

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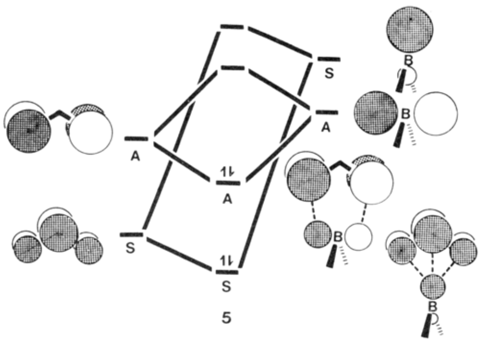

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Figure 2. A qualitative PMO orbital correlation diagram for the allylborane automerization transition-state **5** derived by interaction of the allyl and BH_2 fragments. Both the symmetric (S) and antisymmetric (A) MO's describing the bonding to boron are stabilized. The S combination necessarily incorporates cross-ring bonding.

at C_3. Nonetheless, we take the large barrier as a qualitative reflection of the difficulty to concerted rearrangement apparently experienced by allylamines.[5]

To obtain some insight into the possibility for pseudopericyclic behavior in the amine system, we constructed an optimized PRDDO–ST pathway in C_s symmetry from the cyclic intermediate **4** to separated NH_2 and allyl radicals via SCF–CI and GVB–CI calculations.[10] Although the energy varies little, the nitrogen lone pair utilization is rapidly dissipated. At $r(N–C) = 1.69$ and 1.92 Å, for example, the APS valencies at N and the N–C bond orders have fallen to 3.5/0.68 and 3.1/0.50, characteristic of pseudopericyclic and pericyclic transition states, respectively. The molecular orbitals of the latter point are just those expected for a genuine pericyclic shift. This result suggests the existence of a very restricted range of transition-state geometries for which the postulated pseudopericyclic character can be expected to be manifested when nitrogen is the migrating atom. The situation is reminiscent of the geometrical determination of transition-state character found for the rearrangements of bicyclies **6**,[4] where only pericyclic-shift intermediate structures are geometrically accessible.

The single step, concerted rearrangement of allylborane **3** via transition-state **5**, exhibits a change in the valency of boron from 3.1 (at **3**) to 3.8 (at **5**) accompanied by a B–C bond order variation from 1.01/0.03 to 0.73/0.73. In this case, C_3 (**5**) develops only a slight positive charge (–0.01 → 0.13) in accord with a transannular B–C_3 bond order of 0.37 and a charge at boron of –0.23. The optimized C_s transition state (Figure 1), in contrast to the nitrogen analogue, is strongly puckered such that the B–C_3 distance is only 1.725 Å (vs. $r(B–C_2) = 1.553$ Å for PRDDO-optimized allylborane). Pentacoordination at boron, a well-known tendency for this element,[11] is clearly signified. The excellent agreement between the calculated energy barrier for **3** (11 kcal/mol) and the observed $\Delta H^{\ddagger}$ values for dialkylallylboranes (10–15 kcal/mol[6]) is undoubtedly fortuitous. Nevertheless, the much reduced energy requirement for cyclization of **3** relative to **2** can be attributed to the additional cross-ring bonding in the former. Previous workers have clearly recognized the concerted nature of the 1,3-boron migration, though they have consistently depicted the transition state as a monocyclic entity (e.g., **7**).[6]

In contrast to the NH_2 analogue, the transition-state **5** is cyclically delocalized (cf. the APS bond orders in Figure 1). Moreover, a clear pseudopericyclic interchange of orbital roles is indicated in the localized MO framework. Specifically, the bonding to boron in **5** is described by a symmetrically related pair of B,C_2,C_3 and B,C_4,C_3 three-center LMO's. When **5** is converted to **3** (or **3′**) the first (or second) such LMO transforms into the B–C_2 (or B–C_4) bond orbital, while the second (or first) gives rise to the C=C π bond and simultaneously liberates the formally vacant p orbital on boron.

The BH_2 automerization would thus seem to conform to the pseudopericyclic model. A difficulty arises, however, because Lemal and co-workers have defined the concept in terms of a "(mono)cyclically delocalized transition state",[3a] whereas **5** is bicyclically delocalized. Nevertheless, the borane rearrangement in our view can be regarded as pseudopericyclic. This assessment is based on a consideration of the shape of the "orbital interchange" LMO's. On the NH_2 pathway, pure two-center N–C_2 and N–C_4 orbitals are found in **4**. As a result, two full N–C bonds are reflected, C_3 carries a localized electron lone pair, and cyclic delocalization is absent; the rearrangement is not pseudopericyclic. Two center B–C_2 and B–C_4 LMO's might also arise in the transition state for the BH_2 reaction, but C_3 would then carry a formally vacant orbital and a formal positive charge. In fact, the B–C_2, B–C_4 LMO's diffuse onto C_3, producing cyclic delocalization *together with and inseparable from* a strong cross-ring B–C_3 interaction. Figure 2 illustrates an equivalent description in the alternative canonical (delocalized) MO framework in terms of the interaction of the S and A group orbitals of allyl and BH_2 in **5**. Hence, *a pseudopericyclic interchange of orbital roles via a cyclically delocalized transition state necessitates a strong transannular interaction when the nonbonding orbital in question is empty.*

Our investigations of this concept continue. In particular, the differences among and between first and second row shift species and the question of d orbitals are being taken up.

Acknowledgment. We are grateful to the Danish Natural Science Research Council for generous provision of computer facilities (J.nr.11-0923).

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Received February 20, 1981

A New Protocol for Stereocontrolled Lactone Annulation

Summary: Through regiocontrolled alkylation of cyclopentanone enolates with methyl 4-bromo-3-methoxycrotonate, base-promoted cyclization, and ketalization, α,β-unsaturated esters having a diquinane molecular framework are produced. Controlled reduction of the