are the five adamantyl systems, though isomers **7**, **8**, and **9** do emerge in the correct order of stability. (iv) The strain energy of diamantane is larger than expected. Using our $\Delta H_f°$ (g) values and the Schleyer and Allinger strain-free increments, we obtain strain energies of 15.5 and 7.7 kcal mol^{-1} for diamantane and adamantane, respectively. Thus the former is almost exactly twice as strained as the latter. It appears, therefore, that both force fields require some reparameterization.

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On the Isomerization of Pentacoordinated Molecules

Sir:

The isomerizations of a pentacoordinated molecule, MABCDE, with five different ligands have been extensively discussed. Unless all six atoms are coplanar, such a molecule can have no symmetry element other than the identity. Several authors[1] have pointed out that interconversions among the 20 possible isomers can be classified formally in terms of five different types or "modes" of rearrangement: two axial ligands exchange (aa), an axial and an equatorial ligand exchange (ae), an axial and two equatorial ligands exchange cyclically (aee), two independent axial-equatorial exchanges take place simultaneously (aesae), or two axial and two equatorial ligands exchange cyclically (aeae). Both the Berry mechanism[2] and the turnstile mechanism[3] lead to the mode aeae, but the view appears to be held[1] that the other modes must be seriously considered.

At the risk of laboring the obvious we wish to point out here that the first four modes are only to be considered as formal possibilities and may safely be excluded in any discussion of the detailed mechanisms. This is clear from a consideration of the topological properties of the coordination polyhedra;[4] that is, we ignore metrical aspects. We may choose the vertices of the coordination polyhedra either at the atoms bonded to M or at the ends of the five unit vectors that originate at M and lie along the bond directions. Either way, only three topologically distinct kinds of polyhedra are possible: (a) trigonal bipyramid or hexahedron (six triangular faces); (b) tetragonal pyramid or pentahedron (four triangular faces and one quadrilateral face); (c) the degenerate polyhedron with all five vertices in a plane.[4] Since there is no symmetry we shall refer to these as the hexahedral, pentahedral, and planar forms to avoid the symmetry connotations associated with the more familiar names. If the five vectors from M to the vertices A-E remain distinct, that is, no two bond directions ever coincide in the course of the rearrangement, then clearly any interconversion of one hexahedral isomer into another has to pass either through an intermediate pentahedral form or through an intermediate planar form. This follows because the edges that are not common to the polyhedra of the initial and final states must disappear, that is, become diagonals of planar faces, in the intermediate. Single-step mechanisms involving an intermediate pentahedral form are associated exclusively with the aeae mode (Figure 1); hence any single-step mechanism associated with the first four modes must involve an intermediate planar form. The first four modes can, of course, correspond to multistep processes involving pentahedral intermediates, but this is equivalent to replacing them by a sequence of aeae steps. An example is shown in Figure 1.

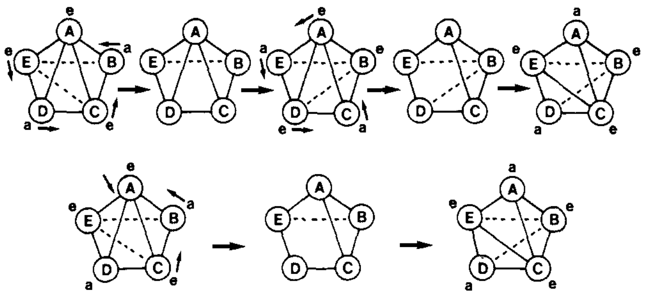

Figure 1. (1-3): an aeae rearrangement proceeding in a single step through a pentahedral intermediate. (6-8), an aee rearrangement proceeding through a single intermediate. Since the intermediate has two quadrilateral faces sharing two edges it must be planar. (1-5), the same aee rearrangement proceeding through two aeae steps.

The conclusion we draw from this is that while five rearrangement modes are formally possible, the chemical improbability of planar intermediates eliminates four of these as serious possibilities, leaving only details of possible aeae mechanisms (Berry and turnstile, for example) to be explained further.

Since a pentahedral form must occur somewhere along the reaction path for all chemically feasible rearrangements, it would appear that the most economical procedure for mapping the reaction pathway by quantum mechanical calculations might be to find the most stable pentahedral form and to proceed from there.

Exactly analogous arguments apply to interconversions between the 30 possible pentahedral isomers, which must proceed either through hexahedral intermediates or through planar ones.

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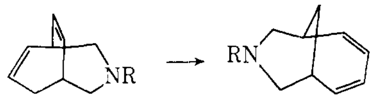
A Remarkably Facile 1,3-Sigmatropic Suprafacial Shift with Retention of Stereochemistry. Catalysis of Carbon-Carbon Bond Migration by an Amide Ion Substituent

Sir:

Since Woodward and Hoffmann[1] in 1965 first announced the principle of the conservation of orbital symmetry in concerted reactions, there have been refinements of the theory and the presentation of alternative schemes for discussion of pericyclic reactions.[2,3] One modification or clarification of the Woodward-Hoffmann rules[1] involves the allowed stereochemistry of 1,3 shifts, where it appears two concerted pathways can be available.[2a,3] A fine balance of opposing electronic and steric effects suggests that when migration by an electronically favored suprafacial inversion (si) pathway is sterically prohibited, the suprafacial retention (sr) pathway can proceed in a concerted manner. Herein we report a novel example of the sr 1,3 shift[5,6] in which a dramatic effect on reaction energetics results from hydrogen atom removal on a nitrogen substituent adjacent to the migrating center.[5]

The *N*-benzyl[7] (**1b**) and *N*-carbomethoxy[8] (**1d**) derivatives of 3-azabicyclo[3.3.2]deca-6,9-diene (**1a**) have been purified by GLPC. Therefore, it was surprising when introduction of amine **1a** into a GLPC injector port heated to 250° (column temperature[10] 120°) was followed by isolation of only amine **2a**[11] (90% recovery), the product of 1,3-sigmatropic rearrangement. Even more surprising, if amine **1a** in either diethyl ether or *n*-pentane was treated with methyllithium at 30° after 1 min a complete conversion to amine **2**[12] (90% recovery) resulted.

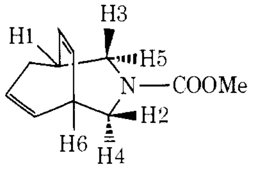


1a, R = H
b, R = CH_2Ph
c, R = COOPh
d, R = COOMe

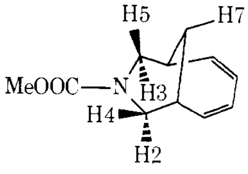
2a, R = H
b, R = CH_2Ph
c, R = COOPh
d, R = COOMe
e, R = COPh

To study rearrangement stereochemistry amine **1a** was synthesized[13] with one deuterium atom selectively distributed among the positions α to nitrogen. Selectively labeled **1a** was then rearranged to labeled **2a** and the fate of the label during rearrangement was determined by ^1H NMR integration (Table I). Because of conformational mobility of **1**, dihedral angle relationships do not reveal whether H2/H3 or H4/H5 is the exo pair. However, the deuterated methylurethanes[8] **1d** and **2d** could be used to assign H3 of **1d**, and thence from coupling data all protons α to nitrogen. First, the endo proton H3 in **2d** was assigned by its W-plan[15] coupling with the bridge proton H7. Second, the exo proton H3 of **1d** has not undergone stereomutation during rearrangement so it has been transformed into endo proton H3 of **2d.** It then follows since **2d** has 92% of the label at the endo H2/H3 positions that the most deuterated shift position of **1d** at δ 2.79 (58% D) must correspond to exo proton H3.

Table I. Partial ^1H NMR (100 MHz) and Deuterium (D) Labeling[a] Analysis of 1d and 2d



1d



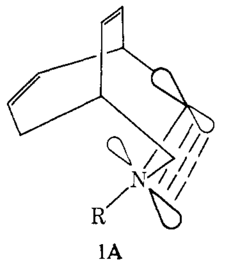
2d

	1d		2d		Reaction path,[f] calcd %-one D for 2d		
Proton	Shift (δ)[b]	D (%)[c,d]	Shift[e] (δ)	D (%)	sr	rac (sr + si)	si
H2	2.73[g]	35 ± 3	4.09[k]	92[m] (90)[n]	93	77	62
H3	2.79[g]	58	(4.09)				
H4	3.02[h,i]	3.5	2.85[l]	8[m] (10)[n]	7	23	38
H5	3.36[h,j]	3.5	(2.85)				

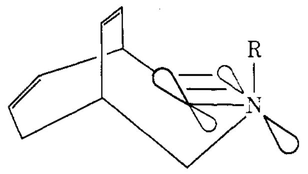
[a] Standard deviations were used to determine the most probable error $\delta y/y = [(\delta a/a)^2 + (\delta b/b)^2 + \ldots]^{1/2}$. ^1H NMR of the phenyl carbamate derivatives 1c and 2c confirmed these results. [b] Benzene-d_6, 76°. [c] H2 + H3 = 93 ± 3%, the ratio (H2 + H3)/(H4 + H5) was determined via relative ^1H NMR peak areas. [d] The H2/H3 ratio was determined from relative ^1H NMR peak heights; J. A. Dale and H. S. Mosher, *J. Am. Chem. Soc.*, 90, 3732 (1968). [e] $CDCl_3$, 76°. [f] sr, si = suprafacial retention and inversion, respectively, rac = racemization. [g] d, *J* = 14 Hz. [h] Broad. [i] Irradiation of H6 (δ 2.51) collapses H4 to a d, *J* = 14 Hz. [j] Irradiation of H1 (δ 2.00) collapses H5 to a d, *J* = 14 Hz. [k] d, *J* = 13 Hz. [l] dd, *J* = 4 Hz, 13 Hz. [m] H2 + H3 = 92 ± 1% from 1a and methyllithium in ether or pentane. [n] H2 + H3 = 90 ± 2%, GLPC of 1a at 250° injection temperature.

Comparison of the situs of deuterium label of **1d** determined by ^1H NMR integration with the predicted deuterium label for various stereochemical possibilities (Table I) indicates net retention of stereochemistry (sr) during thermal or methyl lithium catalyzed sigmatropic rearrangement. The yield and stereochemical data, while consistent with a concerted mechanism, does not exclude stepwise ionic or radical pathways.[16] Error limits of the data do allow for contribution from random processes of 46% (77% sr, 23% si) during thermal rearrangement and 29% (85% sr, 15% si) during base catalyzed rearrangement of **1a.**

The most favorable overlap of the lone pair on nitrogen with the migrating σ bond results when R is exo in the N-anti conformation **1A** and R is endo in the N-syn conformation **1B.**[18] In both these conformations a substituent group, R = CH_2Ph or COOMe, is in the sterically more crowded position and should as observed raise the transition state energy relative to R = H. Removal of the nitrogen substituent



1A



1B