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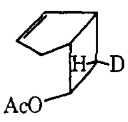
Steric Prohibition of the Inversion Pathway. A Test of the Orbital Symmetry Prediction of the Sense of Rotation in Thermal Suprafacial 1,3-Sigmatropic Rearrangements[1]

Sir:

Inversion of configuration of the migrating group occurs in thermal suprafacial 1,3-sigmatropic rearrangements of bicyclo[3.2.0]hept-2-enes when the *exo* substituent is deuterium (**1**)[2,3] or methyl (**2**).[4] If this is a consequence of special stabilization of the transition state in an "allowed" concerted process,[2–5] the interchange of the C-7 methyl and hydrogen of reactant **2** (Scheme I) logically should produce drastic changes in behavior.



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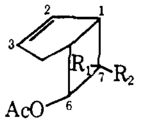
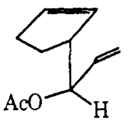


2, $R_1 = H$, $R_2 = Me$
3, $R_1 = Me$, $R_2 = H$



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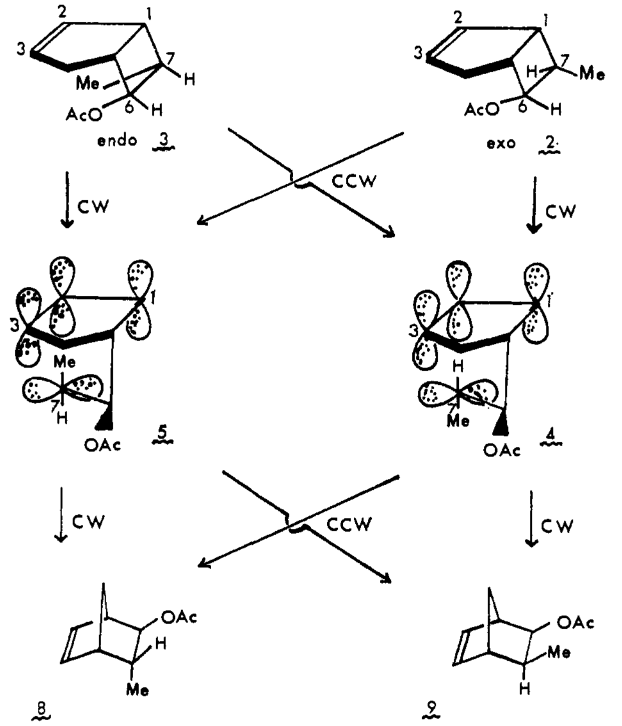
In the transition states (or intermediates) for inversion (**4** and **5**), the migrating group and its substituents would lie in a plane (or approximately so) that is perpendicular to the plane of the five-membered ring containing the allyl system. This would produce severe steric repulsion, especially in the array **5**, where the larger group (Me) is *inside*. Moreover, since it is the *back lobe* of the migrating carbon (C-7) of the reactant that must bond to C-3,[2,3,5] the approach to the transition state and the path from it to product would be by way of a *clockwise* (CW) rotation of C-7 about the C-6–C-7 axis. In reactions proceeding by this rotational mode, the increment of strain energy between the reactant and the transition state caused by methyl–ring repulsions would be larger for the case *endo*-methyl reactant (**3**) → *inside* methyl transition state (**5**) than for the case *exo*-methyl (**2**) → *outside* methyl (**4**). Conversely, if the rotations were for some reason contra orbital symmetry (counterclockwise, CCW), the situation would be reversed, since such rotations would relieve methyl–ring repulsive strain in the *endo*-methyl reactant and increase it in the *exo*.[6]

Scheme I



It follows that the rate of rearrangement with configurational inversion in the CW mode should be substantially greater from *exo*-methyl reactant (**2**) than that from *endo*- (**3**) ($k_{\mathrm{inv}}(exo) > k_{\mathrm{inv}}(endo)$), whereas inversion by the CCW path should lead to $k_{\mathrm{inv}}(endo) > k_{\mathrm{inv}}(exo)$. We now report experiments that show $k_{\mathrm{inv}}(exo) > k_{\mathrm{inv}}(endo)$.

Since rearrangement products **8** and **9** suffer retro-Diels–Alder reaction at different rates (**9** > **8**) under the pyrolysis conditions (decalin solution at 290°), pyrolysis of each reactant **2** and **3** is carried only to a few per cent conversion so as to minimize fractionation.[7] The **9**:**8** ratios observed are therefore lower limits for the ratios of rearrangement rates. The pyrolysis of *exo*-methyl compound **2** at 290° gives predominant inversion (**9**:**8** $\geqslant$ 9.3), in sharp contrast to that of *endo*-methyl epimer **3**, which gives predominant retention (**9**:**8** $\geqslant$ 7.2).[8,9] Moreover, no observable trace of

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(1) This work was supported in part by grants from the National Science Foundation (Grant No. GP-6212X) and the National Institutes of Health (Grant No. AM-07515).

(2) J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5503 (1967).

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(6) The hypothetical CCW mode involves severe uncoupling of orbitals, so that the transition state might well have a geometry quite different from that in the CW mode. This does not materially affect the argument.

(7) A side reaction consumes most of **3**, 82% of the 7% total product from a low-conversion run being the monocyclic diene **6**, derived by shift of a methyl hydrogen. At longer reaction times, **6** undergoes further change, perhaps by Cope rearrangement, although we have not established this.

(8) All four products are identified by isolation (vpc) and spectroscopic comparison with samples synthesized independently.[4b] Synthesis and identification of reactants **2** and **3**[4b] will be described in a full paper.

(9) We have considered the possibility that the rearrangement passes over a stereochemically indeterminate diradical in the case of both *exo*- and *endo*-methyl-labeled reactants **2** and **3**, and that the observed predominance of *cis*-product **9** from each merely results from a preference for closure of the diradical to *cis-exo* (**9**) rather than *trans* (**8**) product. This possibility seems remote. It would require that the predominant inversion, very similar to that in **2**, observed in the deuterium-labeled system (**1**),[2] be ascribed to an entirely different cause, since no such preference can exist there. Moreover, one can make a reasonable guess that the ratio of rates of formation of **9** *vs.* **8** from the alleged diradical should be similar to this ratio determined from competition experiments on the Diels–Alder reaction of cyclopentadiene with the propenyl acetates. The transition states of the latter processes (regardless of whether one or two bonds are being formed) bear a close *geometric* resemblance to those for closure of the diradical. At 300°, the observed Diels–Alder ratio **9**:**8** is 0.25, but the rearrangement ratio **9**:**8** is about 7–10. The alleged diradical in question as the sole intermediate in the rearrangement provides no obvious explanation for the 40-fold discrepancy.

epimerization of *exo*- to *endo*-methyl reactant ($\mathbf{2} \nrightarrow \mathbf{3}$) occurs in the pyrolysis of **2**, whereas the reverse process ($\mathbf{3} \rightarrow \mathbf{2}$) is readily detectable in the case of **3** and occurs about 60% as fast as the rearrangement of **3** to **9** and **8**.

These observations are compatible with a change in mechanism for the major portion of the carbon rearrangement, from a largely concerted one in the case of *exo*-methyl reactant **2** to a diradical pathway in *endo* compound **3**. The principal observable reactions of the diradical intermediate, formed by C-7–C-1 cleavage of **3**, are recyclization with retention of configuration at the migration terminus to give *cis-exo* product **9** and recyclization after rotation about C-6–C-7 to give epimerization product **2**.[10,11]

The ratio $k_{\text{inv}}(exo)/k_{\text{inv}}(endo)$ is given by the product of two ratios: (i) the overall[7] pyrolysis rate ratio (0.8) and (ii) the ratio of the fractions of total product obtained with inversion (91:1.4). The minimum value of $k_{\text{inv}}(exo)/k_{\text{inv}}(endo)$ is 54.

The present results indicate that the configuration-inverting transition state from *endo*-methyl reactant **3** is sterically too strained to permit the electronically "allowed" concerted process to occur. They also clearly define as CW the sense of the configuration-inverting motion in the rearrangement of *exo*-methyl reactant **2**. Although we would greet proposed alternatives with interest, we presently consider "orbital symmetry" control of the geometry of the transition state an attractive explanation of these findings.

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(10) The relative rates of rearrangement of **2** and **3** do not permit **2** to be a significant intermediate in the formation of **9** from **3** at low conversion.

(11) Conceivably, **2** may originate in cleavage of the C-6–C-7 bond of **3** and not the C-7–C-1 bond, but it seems unlikely that α-acetoxy activation would be superior to allylic activation.[12]

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(13) This investigation was supported in part by National Institutes of Health Predoctoral Fellowship 5-F1-GM-33,023-03 from the National Institute of General Medical Sciences.

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Utilization of Steric Compression to Assign the Absolute Configuration and Ring Conformation of Some Transition Metal Complexes

Sir:

In recent years in the field of transition metal stereochemistry considerable research has been undertaken to determine the absolute configuration and ring conformation of transition metal complexes. The assignments are generally made by analysis of the ORD or CD spectra of the complex[1] or by X-ray determination of its structure.[2] Recently, however, nuclear magnetic resonance (nmr) has been utilized to determine the absolute configuration of the cobalt(III) complexes with the ligand ethylenediamine-N,N′-di-L-α-propionic acid (LL-EDDP) in terms of the magnetic anisotropy of the C–N bond.[3] Nuclear magnetic resonance has also confirmed the absolute configuration of the cobalt(III) complexes containing *l*-propylenediamine and ethylenediamine-N,N′-diacetic acid (EDDA),[4] and trends in the chemical shifts of the methyl signals of certain propylenediamine complexes of cobalt(III) and platinum(IV) have been related to the absolute configuration of these complexes.[5] These assignments made use of the different electronic environments of certain protons in the two diastereomers.

In coordination compounds containing organic ligands, there are several ways in which the electronic environment about a proton can be influenced by intramolecular interactions. These include anisotropy effects from bonds within the molecules,[6] involvement of the metal d-electron system on the ligand substituents,[7] and van der Waals interaction or steric compressions.[8] Utilizing the last-mentioned effect of steric compression we have examined the absolute configurations and ring conformations of some cobalt(III) complexes.

This effect, which has been observed in certain organic molecules,[9] is produced when a hydrogen atom is forced into proximity of some other atom in the molecule. The proton involved in the compression is found to resonate at a lower field than when the compression is absent. For the complexes under study the distance between the two nuclei involved in the compression is 2–3 Å which results in a shift of 0.1–0.3 ppm. A shift of similar magnitude was observed by Terrill and Reilley[10] in connection with the *trans*-1,2-cyclohexanediamine-N,N′-tetraacetatocobalt(III) cation and was assumed to be in part due to steric compression.

We have prepared a series of bis(amino acid) complexes of cobalt(III) containing optically active amino acids and find that it is possible to assign the absolute configuration of these complexes using nmr steric compression. The compounds synthesized were *trans*-(O)-$[\mathrm{Co(en)(AA)_2}]^+$ and *trans*-(O)-$[\mathrm{Co(en)(AA)(gly)}]^+$ (Table I) which were prepared from the reaction of the optically active amino acid (AA) with either $[\mathrm{Co(en)(AA)(H_2O)Cl}]^+$ or $[\mathrm{Co(en)gly(H_2O)Cl}]^+$[11] and separated from the various *cis* isomers by ion-exchange chromatography. The compounds were characterized by their elemental analyses and visible absorption spectra which exhibited bands at 360 and 533 mμ with a shoulder at 450 mμ characteristic of *trans*-$\mathrm{CoO_2N_4}$ complexes. The diastereomers were separated on a cation-exchange resin and distinguished by the sign of the dominant component of the CD spectrum in the first spin-allowed d–d transition region.

The relative arrangement of the α protons in the two diastereomers is seen in Figure 1. In these compounds one would expect that the amino acid ring would not be planar but slightly puckered, placing the substituent on the amino acid in a equatorial position and forcing the α proton into a position adjacent to the amino pro-

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