the original p orbital are hardly affected. The allyl ψ_2 orbital does not mix with the p orbital, and although ψ_1 and ψ_3 both mix with p, the interactions approximately cancel each other. Similar conclusions emerge from a corresponding treatment of reactions in which the migrating group retains configuration and rearranges either by an allowed antarafacial or a forbidden suprafacial one.[7]

In most geometries corresponding to the forbidden transition state of Figure 1, there is substantial overlap between the migrating p orbital and the orbital on the center carbon of the allyl system. This further depresses the energy of the subjacent level (to $2.56\beta_0$ if the interaction is assumed equal to the nearest-neighbor interactions) and reinforces the effect.

Subjacent orbital control of the transition state geometry normally would not be expected to become important until steric factors became unfavorable to the operation of Woodward–Hoffmann control. However, it must be kept in mind that even in the most favorable cases known, the allowed suprafacial inversion 1,3-sigmatropic transition state is only slightly preferred experimentally, the geometric distortions needed to achieve it being very severe.[8] Consequently, it should not be difficult to present steric or other extrasymmetric obstacles to its achievement and thereby bring the forbidden concerted reaction to the fore.[9] In such circumstances, the assumptions of equal interaction terms used to derive the orbital energies in Figure 1 become quite unsatisfactory, but perturbation theory provides a more realistic comparison of the two types of stabilization. Applied to the rearrangement of methylenecyclobutane for example, a Hückel-like perturbation calculation with resonance integrals assumed proportional to overlap and overlap integrals[10] evaluated from assumed molecular geometry yields stabilization energies of 2.9–5.8 (first order) and 1.6–3.2 kcal/mol (second order) for the allowed and forbidden reactions, respectively. The calculations are too crude to permit a prediction on the stereochemistry of the rearrangement but clearly suggest that the allowed and forbidden pathways are closely balanced in energy.

It may well be that the subjacent orbital effect plays an important role in facilitating the forbidden pathway in the rearrangements of thujene,[11] 2-cyano-3-methylethylidenecyclopropane,[12] and *trans*-1,2-dipropenylcyclobutanes.[13] In the latter two cases, steric factors do not heavily favor either the forbidden or allowed kind of motion. In several examples constructed to make the allowed pathway sterically difficult (1,3 rearrangements of *endo*-7-methylbicyclo[3.2.0]hept-2-enes[8c,14] and bicyclo[4.2.0]oct-2-enes[15]), it is now clear that rearrangement occurs not with the stereorandomness expected if the reactive sites were widely separated, but rather with high symmetry-forbidden stereospecificity (88% for one member of the series[8c,14] and 93–94% for the rest[15]).

Acknowledgment. We are indebted to Professor W. von E. Doering for helpful discussions.

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[7] Very similar arguments apply to electrocyclic reactions. For example, the transition state for the cyclobutadienoid forbidden reaction (disrotatory opening of cyclobutene) also has a stabilized subjacent level, the behavior of which may be seen by consultation of Figure 11 in the paper by H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

[8] (a) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5303 (1967); (b) J. A Berson, *Accounts Chem. Res.*, **1**, 152 (1968); (c) 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June 13–17, 1971, Abstracts, p 28.

[9] Our conclusions are based upon one-electron considerations. It is not inconceivable that the important two-electron energies characteristic of open shells[5c] could reverse, in certain cases, the ordering of the nonconcerted and forbidden transition state energies

[10] We are grateful to W. Jorgensen for values of the atomic integrals.

[11] W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, **27**, 2005 (1971).

[12] W. von E. Doering and L. Birladeanu, *ibid.*, submitted for publication.

[13] J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, submitted for publication.

[14] J. A. Berson and G. L. Nelson, *ibid.*, **92**, 1096 (1970).

[15] J. A. Berson and R. Holder, submitted for publication.

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Aliphatic Semidiones. XXI. Isomerization of Bicyclo[2.2.1]hept-5-ene-2,3-semidiones to Bicyclo[3.2.0]hept-2-ene-5,6-semidiones[1]

Sir:

An interest in the possibility of long-range interaction of nonconjugated π-electron systems led us to attempt the synthesis of **2**. Since α-hydroxy ketones in basic DMSO usually yield the semidione,[2,3] we prepared **1a** and **1b** by the addition of benzoyl nitrite[4] to norbornadiene and 1-methylnorbornadiene.[5] Hydrolysis of the first formed benzoyloxy nitrimines[6] gave **1** (a, $R_1 = R_4 = H$;[5] **b**, $R_1 = CH_3$, $R_4 = H$; **b′**, $R_1 = H$, $R_4 = CH_3$).[7]

Treatment of **1a** with potassium *tert*-butoxide in DMSO in a flow system[8] gave an unstable semidione detectable from ~1 to 20 sec after mixing, whose esr spectrum was inconsistent with the symmetry of **2a** (Chart I) but which was consistent with bicyclo[3.2.0]hept-2-ene-5,6-semidione (**3a** or **4a**).[9]

Addition of acetoxyketene[10] to cyclopentadiene yielded **5a**. Pure samples of the endo isomer[7] (the major adduct) and exo isomer[7] yielded the same esr spectra as observed for the paramagnetic reaction product from **1a**.

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[1] Application of Electron Spin Resonance Spectroscopy to Studies of Valence Isomerization. IV. Work supported by a grant from the National Science Foundation.

[2] G. A. Russell and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 744 (1964).

[3] G. A. Russell and P. R. Whittle, *ibid.*, **89**, 6781 (1967).

[4] L. Francesconi and U. Cialdea, *Gazz. Chim. Ital.*, 34 (I), 435 (1904).

[5] Private communication from Dr. T. R. Sharpe, Du Pont Experimental Station.

[6] G. A. Boswell, *J. Org. Chem.*, **33**, 3699 (1968).

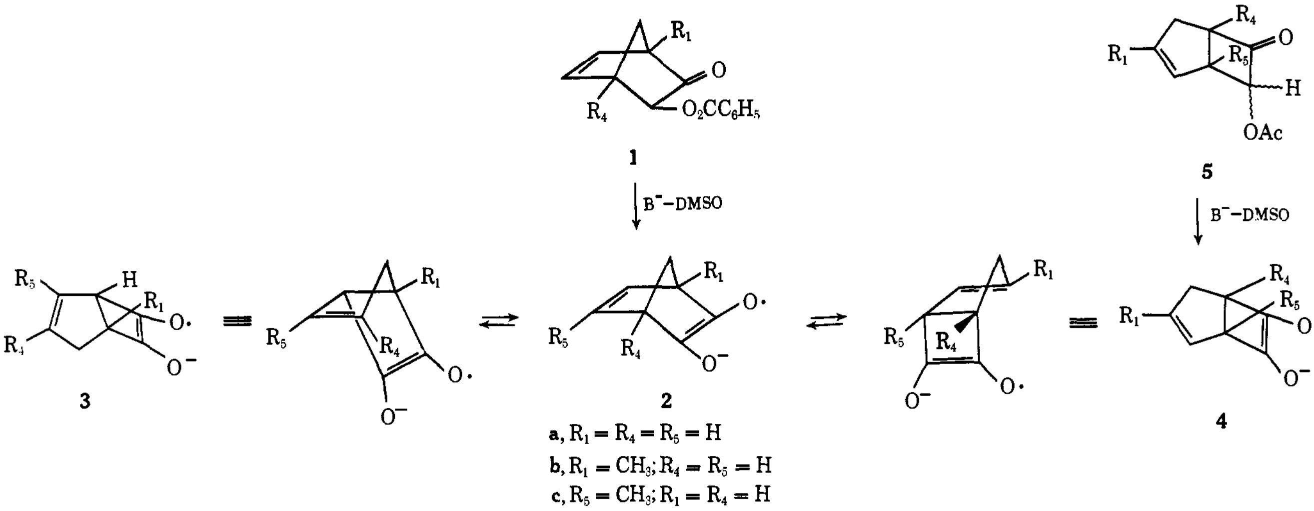
[7] Identification based on pmr, ir, elemental analysis, or high-resolution mass spectra.

[8] G. A. Russell and R. L. Blankespoor, *Tetrahedron Lett.*, 4573 (1971).

[9] For example, INDO calculations using a logical set of bond lengths and a dihedral angle of 120° between planar rings gave values of $a_a{}^H = 10.2$, $a_b{}^H = 9.1$, $a_c{}^H = 1.5$, $a_d{}^H = -0.44$, $a_e{}^H = -0.47$, and $a_f{}^H = 0.2$ G (unpublished results with Mr. C. Chung). The positive sign of $a_c{}^H$ indicates that $\pi-\pi$ overlap is not the predominant delocalization mechanism since the negative value of $Q_{CH}{}^H$ predicts a negative sign of $a_c{}^H$ for homoconjugation. Similar calculations for **2** lead to small negative values for $a_{vinyl}{}^H$ indicating that in **2** homoconjugation predominates over spin polarization mechanisms.

[10] Generated from acetoxyacetyl chloride by the procedure of W. T. Brady and E. F. Hoff, Jr., *J. Org. Chem.*, **35**, 3733 (1970).

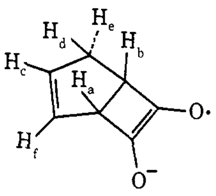
Chart I. Semidiones and Precursors



a, $R_1 = R_4 = R_5 = H$

b, $R_1 = CH_3; R_4 = R_5 = H$

c, $R_5 = CH_3; R_1 = R_4 = H$



4a (enantiomer of **3a**)

$a_a^H = 12.3, a_b^H = 10.1, a_c^H = 2.0,$
$a_d^H = a_e^H = 0.5, a_f^H = 0.2$ G

Treatment of **1b** or **1b′** with base and DMSO in the flow system gave a single semidione whose esr spectrum indicated the presence of a single α-cyclobutane hydrogen, $a^H = 13.1$ G. Considerable fine structure was present in the spectrum but it has not been completely resolved. This result is consistent with the interpetation that the initially formed **2b** readily isomerized to **3b** in preference to **4b**. To further test this rationalization, and to explore the possibility of the reverse reaction (**3**, **4** → **2**), acetoxyketene was added to a mixture of 1- and 2-methylcyclopentadiene. Pure samples of **5b**[7,11] and **5c**[7,11] were isolated by glpc and converted to their semidiones by base and DMSO. Acetoxy ketone **5b** yielded only a single semidione whose spectrum consisted of a 13.1-G doublet with unresolved fine structure, identical with the spectrum observed from **1b** or **1b′**. This result strongly supports the conclusion that a rapid reversible isomerization between **2**, **3**, and **4** occurs. Apparently **3b** is more stable than **4b** because of nonbonded interactions.

Acetoxy ketone **5c** gave rise to a mixture of semidiones, assigned to **4c** ($a^H = 1.75$, 12.9 G) and **3c** ($a^H = 9.75$, 12.8 G) whose ratio depended on the flow rate with short reaction periods favoring the unrearranged **4c**.

Since rearrangements similar to **2** $\rightleftarrows$ **3** or **4** have not been recorded in the pyrolysis of norbornadiene,[12] it appears that the presence of the unpaired electron (added to the HOMO of the parent dione) is required.

The rearrangement may be analogous to the photochemical conversion of norbornenones to bicyclo[3.2.0]hept-2-en-7-ones[13-15] and the photoisomerization of 1,4,4-trimethyl[3.2.0]hept-6-en-2-one to 4,4,6-trimethylbicyclo[3.2.0]hept-6-en-2-one[16] for which diradical intermediates have been postulated after promotion of an electron to π^* of the ketone function.[13] Facile scission of an α carbon–carbon bond in **2**, **3**, or **4** could also explain the short chemical lifetimes of the semidiones observed in this work. On the other hand a concerted 1,3-sigmatropic rearrangement of **2** $\rightleftarrows$ **3** or **4** is possible as in the thermal isomerization of bicyclo[3.2.0]hept-2-enes to norbornenes.[17] A one-step interconversion of **3** $\rightleftarrows$ **4** although possible does not seem likely.

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(11) For **5b**, $J_{12} = 3$ Hz. For **5c**, $J_{45} = 3.0$, 6.5, $J_{57} = 3.1$ Hz. These coupling constants are in agreement with those reported for other bicyclo[3.2.0]hept-2-en-6-ones: W. F. Erman, *J. Amer. Chem. Soc.*, **89**, 3828 (1967); W. F. Erman, R. S. Treptow, P. Bakuzis, and E. Wenkert, *ibid.*, **93**, 657 (1971).

(12) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).

(13) D. I. Schuster, M. Axelrod, and J. Auerbarh, *Tetrahedron Lett.*, 1911 (1963).

(14) D. E. Bays and R. C. Cookson, *J. Chem. Soc. B*, 226 (1967).

(15) This process appears to be reversible under certain conditions and may occur thermally; private communication from Dr. P. W. Schiess, University of Basel.

(16) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).

(17) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

Variation of Stoichiometry with Solvent in a Lanthanide Nuclear Magnetic Resonance Shift Reagent Complex[1]

Sir:

One reason for the considerable recent interest in lanthanide nmr chemical shift reagents is the proposed use of "bound" chemical shifts (Δ_B) in determination of molecular configuration, since molecular geometry is directly reflected in the Δ_B values. The first step in such analyses must be to obtain an accurate measure of Δ_B from concentration dependence of the induced shift, δ. It has recently been shown that Δ_B values may be obtained most easily and reliably from a plot of $[S]_0$

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