In summary, two unusual examples of formation of electronically excited products from electronically excited precursors are reported. Each reaction is characterized by an unexpected propensity to form triplet rather than singlet products.[13]

(13) After submission of this manuscript, Professor Josef Michl, Department of Chemistry, University of Utah, informed us that he has made MO calculations which suggest that photochemical valence isomerizations of the naphthvalene to naphthalene type should be adiabatic. We are very grateful to Professor Michl for preprints of his work on this subject. We also wish to thank Professor Lionel Salem, University of Orsay, for some stimulating discussions concerning adiabatic excited state reactions.

(14) NATO Postdoctoral Fellow, 1971–1972.

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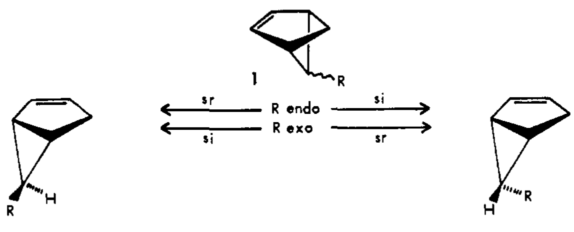
Forbidden 1,3-Sigmatropic Rearrangements[1]

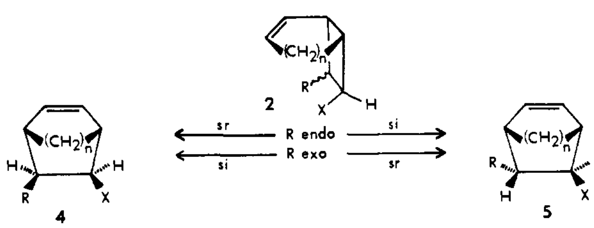
Sir:

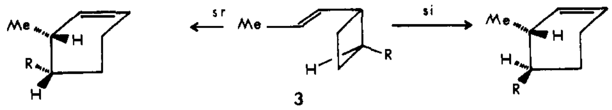
To conserve orbital symmetry, a thermal suprafacial 1,3-sigmatropic rearrangement of carbon must occur with inversion of configuration of the migrating group.[2-5] It has been assumed that when some extrasymmetric factor (for example, a steric blockade of inversion[4b]) forces retention, a nonconcerted diradical mechanism prevails. However, recent theoretical speculations[6] suggest that subjacent orbital effects may stabilize the "forbidden" concerted transition state relative to the nonconcerted one and thereby permit violations of the conservation rule.

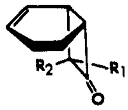
The present paper reports four new rearrangements in the bicyclo[4.2.0]octene series (**2**, $n = 2$), which exemplify a type of reactant structure intermediate between those with a freely rotating allylic migration framework (*e.g.*, **3**) and those in which a rigid ring system sharply restricts the conformational possibilities (*e.g.*, **2**, $n = 1$, and **1**). The pattern of stereospecificities now observed in the series **1**, **2**, and **3** suggests the occurrence of forbidden concerted reactions under subjacent orbital control.

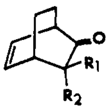
Alcohols **2** (R = *endo*-Me, X = OH, $n = 2$), **2** (R = *exo*-Me, X = OH, $n = 2$), **4**, and **5** (R = Me, X = OH) are obtained from the corresponding ketones **6**, **7**, **8**, and **9**, the *endo*-methyl[4.2.0]ketone **6** being the major cycloadduct from the 1,3-cyclohexadiene–methyl ketene reaction.[7–10] Lanthanide-induced nuclear magnetic resonance shifts (LIS), supported by spin decoupling experiments and infrared measurements, establish the stereochemical relationships of hydroxyl to methyl and hydroxyl to olefin in the alcohols and hence in the reactants (**2**, R = *endo*- or *exo*-Me, X = OAc or OSiMe$_3$, $n = 2$) and products (**4** and **5**, R = Me, X = OAc or OSiMe$_3$, $n = 2$).[11,12]











6, R_1 = H; R_2 = Me **8**, R_1 = H; R_2 = Me
7, R_1 = Me; R_2 = H **9**, R_1 = Me; R_2 = H

The rates of gas-phase pyrolysis of the reactants are not affected by added glass surface. Table I shows the ratios of rates of formation of products by the forbidden suprafacial-retention (sr) and allowed suprafacial-inversion (si) pathways[13] as determined by kinetic analysis[14] and/or by extrapolation of the product ratio to zero time. The allowed si reaction predominates in the "unblocked" series, but in the "blocked" series, especially in **2** (n = 1 or 2), the endo substituent interferes with the somersault required for this process, and rearrangement occurs with a large contribution from the forbidden sr pathway.

A conventional interpretation of the sr component as a nonconcerted diradical reaction is difficult to support on kinetic or stereochemical grounds. For example, the rate of rearrangement with inversion (k_{inv})

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(1) The support of this work by the National Science Foundation (GP-33909X) and by the National Institute of General Medical Sciences (GM-16962) is gratefully acknowledged.

(2) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(4) (a) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5303 (1967), (b) *ibid.*, **92**, 1096 (1970).

(5) (a) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968); (b) Abstracts, American Chemical Society 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June 13–17, 1971, p 28; (c) G. L. Nelson, Ph.D. Dissertation, University of Wisconsin, 1969.

(6) (a) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972); (b) J. A. Berson, *Accounts Chem. Res.* **5**, 406 (1972).

(7) The stereochemistry **6** is strongly suggested by many analogies.[8-10]

(8) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **92**, 4618 (1970).

(9) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970).

(10) W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966); *Tetrahedron*, **23**, 4251 (1967).

(11) R. W. Holder, Ph.D. Dissertation, Yale University, 1972.

(12) The assignments in the cases of **4** and **5** (n = 2, R = Me, X = OH) are confirmed by a fit of the LIS data to structural parameters: M. R. Willcott, R. E. Davis, and R. W. Holder, *J. Amer. Chem. Soc.*, submitted for publication.

(13) Antarafacial reaction is precluded by the structure of the reactants in **1** and **2** (n = 1 or 2).

(14) Since an epimerization interconverting the *endo*-methyl and *exo*-methyl isomers **2** (R = *endo*- or *exo*-Me, X = OSiMe$_3$, n = 2) competes with the sigmatropic rearrangement, the data are fitted to the kinetic scheme by a numerical integration procedure using a program and subroutine for the Runge-Kutta method kindly supplied by Professor Martin Saunders and Mr. Peter Dervan.[15]

(15) See J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 267, 269 (1973); P. B. Dervan, Ph.D. Dissertation, Yale University, 1972.

Table I. Stereospecificities in Pyrolytic 1,3-Sigmatropic Rearrangements

Reactant	R	X	n	Rate ratio (sr/si)	Ref
		Unblocked			
1	*exo*-OAc			Low[b]	*c*
1	*exo*-Me			0.005	*d*
2	*exo*-D	OAc	1	0.053	4a, 5
2	*exo*-Me	OAc	1	0.1	4b, 5
2	*exo*-Me	$OSiMe_3$	2	0.42	*a*
2	*exo*-Me	OAc	2	0.45	*a*
3	*trans*-C_3H_5			0.85	*e*
3	*cis*-C_3H_5			0.97	*e*
		Blocked			
1	*endo*-Me			0.45	*d*
2	*endo*-Me	OAc	1	7	4b, 5
2	*endo*-Me	OAc	2	12	*a*
2	*endo*-Me	$OSiMe_3$	2	15	*a*

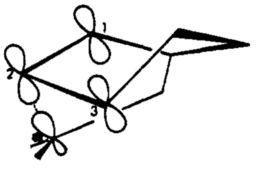
[a] This work. [b] Only the si product was reported. [c] S. Masamune, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969). [d] W. R. Roth and A. Friedrich, *Tetrahedron Lett.*, 2607 (1969). [e] J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 269 (1973).

of 7-*exo*-methylbicyclo[3.2.0]hept-2-en-6-*endo*-yl acetate (**2**, $n = 1$, R = *exo*-Me, X = OAc) is greater than the rate of rearrangement with retention (k_{ret}) from the *endo*-methyl analog (**2**, $n = 1$, R = *endo*-Me, X = OAc), as might be expected if the *exo*-methyl compound but not the *endo*-methyl one were rearranging concertedly. However, the rate factor is only 7, hardly an impressive driving force. Also, the stereospecificities, factors of 10 favoring inversion in the *exo*-methyl isomer and 7 favoring retention in the *endo*-methyl compound, provide little support for a sharp discontinuity in mechanism.

In the bicyclo[4.2.0]octenyl series, the absolute rate, k_{ret}, from **2** ($n = 2$, R = *endo*-Me, X = $OSiMe_3$) is actually greater than k_{inv} from the *exo*-methyl counterpart **2** ($n = 2$, R = *exo*-Me, X = $OSiMe_3$), the ratio being about 3.1 at 320°. Moreover, the preferences for retention in both *endo*-methyl compounds (**2**, $n = 2$, R = *endo*-Me, X = OAc or $OSiMe_3$), factors of 12 and 15, respectively, also are greater than the preferences for inversion in the *exo*-methyl counterparts (factors of 2.2 and 2.4, respectively, for **2**, $n = 2$, R = *exo*-Me, X = OAc or $OSiMe_3$). Thus, in these cases, a concerted mechanism seems to fit the experimental facts for the formally forbidden reaction at least as well as for the allowed one.

Table I also reveals a strong dependence of the sr/si ratio on reactant structure. In both the "unblocked" and "blocked" series, the forbidden sr reaction steadily increases in relative importance as the reactant changes in the order bicyclo[2.1.1]hexenyl (**1**) < bicyclo[3.2.0]heptenyl (**2**, $n = 1$) < bicyclo[4.2.0]octenyl (**2**, $n = 2$) < monocyclic (**3**).

The hypothesis that both the allowed inversion and forbidden retention reactions are concerted permits a straightforward analysis of the ordering of the sr/si ratios. As has been emphasized elsewhere,[6] overlap between the front lobe of the migrating carbon and the suprafacial lobe of C_2 of the allylic framework strongly stabilizes the transition state of the forbidden concerted sr pathway. This overlap should be very sensitive to geometric factors. Molecular models clearly show that the greater flexibility introduced by the extra methylene group of the bicyclo[4.2.0]octenyl reactants makes possible a conformation and an sr transition state derived from it (**10**) in which overlap of the relevant orbital lobes at C_2 and the migrating carbon (C*) is more favorable than in the corresponding transition states from the rigid bicyclo[3.2.0]heptenyl reactants (**11**), and much more favorable than in the bicyclo[2.1.1]hexenyl cases (**12**). The monocyclic cases (**3**) should permit optimum overlap of this type, in agreement with the observation that in the unblocked series they show the highest sr/si ratio (Table I).



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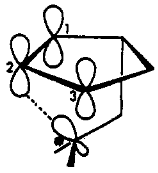

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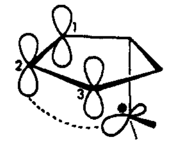

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[16] National Science Foundation Graduate Fellow (No. 8700-35-45821), 1968-1972.

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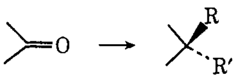
New Synthetic Reactions. Geminal Alkylation

Sir:

The creation of a fully substituted carbon center with controlled stereochemistry presents a general yet unsolved problem in organic synthesis. The ready availability of the carbonyl group makes it highly desirable to be able to convert a carbonyl carbon to a quaternary center as represented by eq 1. Two recent



(1)

approaches involve the use of the thio-Claisen rearrangement[1] and organolithium addition to ketene thioacetals.[2] We wish to report a new approach to this problem based upon the spiro annelation procedure.[3]

We have previously reported the facile synthesis of cyclobutanones from carbonyl partners by the condensation with diphenylsulfonium cyclopropylide.[3] This reaction proceeds with a high degree of stereoselectivity. Thus, treatment of 4-*tert*-butylcyclohexanone with this sulfur ylide followed by rearrangement of the intermediate oxaspiropentane with $Eu(fod)_3$ produced only the spiro cyclobutanone **1** uncontaminated by its isomer.[4,5] Similarly, the spiro cyclobu-

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[1] E. J. Corey and J. I. Shulman, *J. Amer. Chem. Soc.*, **92**, 5522 (1970).

[2] P. F. Jones and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 526 (1972); F. A. Carey and A. S. Court, *J. Org. Chem.*, **37**, 1926 (1972); D. Seebach, B. T. Gröbel, A. K. Beck, M. Braun, and K. H. Geiss, *Angew. Chem., Int. Ed. Engl.*, **11**, 443 (1972); D. Seebach, *Synthesis*, **1**, 17 (1969).

[3] B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **93**, 3773 (1971); M. J. Bogdanowicz and B. M. Trost, *Tetrahedron Lett.*, 887 (1972).

[4] Proof of stereochemistry was based upon conversion to a γ-butyrolactone with hydrogen peroxide and subsequent reduction to a tetrahydrofuran. The latter was synthesized independently; see M. J. Bogdanowicz and B. M. Trost, *Tetrahedron Lett.*, in press.

[5] All new compounds have satisfactory analytical and spectroscopic data to support the assignments.