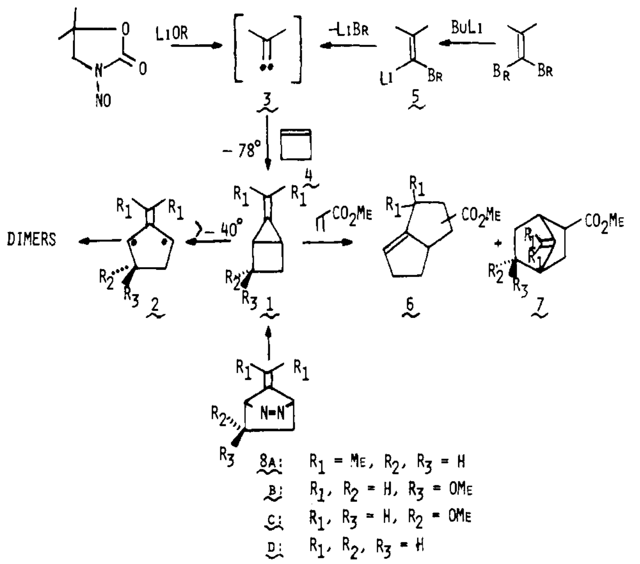
Scheme I



2.[13] In either case, the 5-isopropylidenebicyclo[2.1.0]pentane molecule **1a** owes its existence to the low *A* factor. For example, a "normal" *A* factor of 10^{14} combined with the E_a of 13 kcal/mol would result in a half-life of ~1 s at −80 °C.

TMM dimerizations do not commonly accompany thermal methylenecyclopropane rearrangements in other systems.[11,12,14] This fact and the observation[15] that molecular oxygen does not affect the course of the rearrangement suggest that under the usual pyrolysis conditions of high temperature, the triplet TMM, although it is probably the ground state,[16] is not involved. The sharply different behavior of the 5-alkylidenebicyclo[2.1.0]pentanes (**1**) could be rationalized if the Arrhenius plots for intersystem crossing (low *A* factor, low E_a) and stereomutation (higher *A* factor and higher E_a) were not parallel. The much lower temperatures at which reaction occurs in the **1** series then would make the two rates approach each other and would permit intersystem crossing to compete more effectively.

Thermal reversion of triplet **2a** to the bicyclic hydrocarbon **1a** apparently does not occur in crystalline diazene **8a** as host, since the intensity of the electron paramagnetic resonance (EPR) signal follows the Curie Law between 14 and 268 K.[16b] As the present work shows, the upper end of this range includes temperatures at which reaction **1a** → triplet **2a** is fast in fluid medium. It follows that either the crystalline environment greatly retards the unimolecular **2a** → **1a** reaction or, alternatively, the energy[17] of the triplet biradical is substantially lower than that of the bicyclic hydrocarbon.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We are also grateful to the National Science Foundation (CHE-76-00416) and the National Institute of General Medical Sciences (GM-23375) for research support, and to the Biotechnology Resources Program of the National Institutes of Health (RR-798) for its support of the Southern New England High Field NMR Facility. We especially thank Mr. Peter Demou for technical assistance.

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(1) J. A. Berson, C. D. Duncan, and L. R. Corwin, *J. Am. Chem. Soc.*, **96**, 6175 (1974).

(2) J. A. Berson, C. D. Duncan, G. C. O'Connell, and M. S. Platz, *J. Am. Chem. Soc.*, **98**, 2358 (1976).

(3) M. S. Platz, D. R. Kelsey, J. A. Berson, N. J. Turro, and M. Mirbach, *J. Am. Chem. Soc.*, **99**, 2009 (1976).

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(5) J. A. Berson, *Acc. Chem. Res.*, **11**, 446 (1978).

(6) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Am. Chem. Soc.*, **93**, 1544 (1971).

(7) M. S. Platz and J. A. Berson, *J. Am. Chem. Soc.*, **98**, 6743 (1976).

(8) M. Lazzara, J. J. Harrison, M. Rule, and J. A. Berson, *J. Am. Chem. Soc.*, following paper in this issue.

(9) The major isomer (75%) of the two 2-methoxy-5-methylenebicyclo[2.1.0]pentanes formed in the photolysis of **8c**.

(10) We have been concerned that these reactions may be catalyzed by oxygen or metallic species. The kinetic samples are carefully degassed by repeated freeze-pump-thaw cycles. The rate constants determined on solutions of **1a** and **1b** that have been prewashed with disodium ethylenediaminetetracetate solution are identical within experimental error with those obtained on unwashed solutions. Whether the rates are affected by the magnetic field of the NMR spectrometer is unknown.

(11) J. J. Gajewski and S. K. Chow, *J. Am. Chem. Soc.*, **99**, 5696 (1977).

(12) W. R. Roth and G. Wegener, *Angew. Chem., Int. Ed. Engl.*, **14**, 758 (1975).

(13) Compare the low *A* factor (log *A* = 9.1) observed in the ring closure of the parent triplet TMM to methylene cyclopropane: M. Chow and P. Dowd, *J. Am. Chem. Soc.*, **99**, 6438 (1977).

(14) (a) J. A. Berson in "Rearrangements in Ground and Excited States", P. de Mayo, Ed., Academic Press, in press; (b) J. J. Gajewski in "Mechanisms of Molecular Migrations", Vol. 4, B. Thyagarajan, Ed., Wiley-Interscience, 1971, p 1.

(15) W. von E. Doering and S. Buchwalter, unpublished observations cited by W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2096 (1975).

(16) (a) R. Baseman, D. W. Pratt, M. Chow, and P. Dowd, *J. Am. Chem. Soc.*, **98**, 5726 (1976); (b) M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter, and J. A. Berson, *ibid.*, **98**, 5725 (1976).

(17) Strictly, the argument applies to the free energies, but the similarity of the *A* factor for closure of a model TMM triplet[13] to that found here for ring opening **1a** → **2a** justifies its extension to the enthalpies.

(18) H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 526 (1964).

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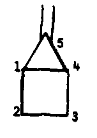
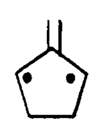
Stereoisomerization by Bridgehead Double Inversion and Olefinic Torsion in 5-Alkylidenebicyclo[2.1.0]pentanes

Sir:

An accompanying study[1] reports the thermal ring opening of 5-alkylidenebicyclo[2.1.0]pentanes (**1**) to trimethylenemethanes (TMMs) of the 2-alkylidenecyclopenta-1,3-diyl group (**2**). We now describe experiments that help to define the energy surface of these reactions and provide information relevant to the question of negative bond dissociation energies.

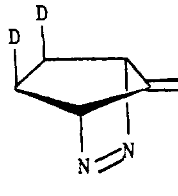


1

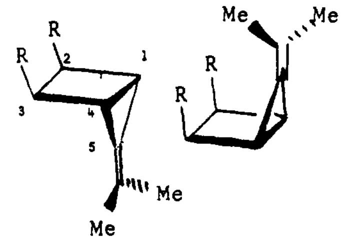


2

Fused-ring methylenecyclopropanes undergo bridgehead double inversion and geometric isomerization about the exocyclic double bond. These reactions are exemplified in the 6-alkylidene bicyclo[3.1.0]hexanes,[2,3] which are ring homologous with structure **1**. Detection of the corresponding double inversion process in derivatives of **1** requires substituents, preferably deuteriums, on the ring. However, irradiation at 350 nm of 7-isopropylidene-5,6-*exo,exo*-dideuterio-2,3-diazanorbornene (**3**)[4] in CD_2Cl_2 at −78 °C gives not the desired stereospecifically labeled 7-isopropylidenebicyclo[2.1.0]pentane but instead a mixture of 50% each of the two double epimers **4** and **5**, as determined by the equal intensities of the *exo-* and *endo*-methylene proton signals (δ 1.46 and 2.17 or vice versa) in the NMR spectrum[5] of the product at −80 °C.



3



4,5: R = D

6: R = H

Scheme 1 outlines the synthesis of the diazene 5-*exo*-methoxy-2,3-diaza-7-methylenenorbornene (**7a**) and its counterpart **7b**, which is stereospecifically deuterated[6] on the exocyclic double bond. The double labeling in the latter compound permits the simultaneous observation of bridgehead inversion and exocyclic olefinic torsion.

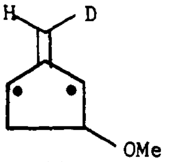
^{1}H NMR spectroscopic examination (Bruker HX-270) of the solution obtained by photolysis (350 nm, −78 °C) of **7b** in $CDCl_3$-$CFCl_3$ or toluene-d_8 shows the presence of two 5-alkylidenebicyclopentanes, **9** (75%) and **10** (25%)[7] (Scheme II). The individual exocyclic methylene proton resonances of both isomers can be discerned directly in toluene-d_8 or by addition of the lanthanide shift reagent, $Eu(fod)_3$, to the $CDCl_3$-$CFCl_3$ solution.

Both isomers show partial stereochemical scrambling of the deuterium to the same extent; the ratio (R) of the exocyclic methylene resonances is 2.0 in each case. This is consistent with a common intermediate (plausibly a singlet TMM) which can suffer exocyclic torsion in competition with two modes of ring closure. From the data given, it is possible to deduce the ratio of rate constants for achievement of a randomized syn-anti stereochemistry (k_s) and ring closure (k_9, k_{10}) from the intermediate as $k_s/(k_9 + k_{10}) \sim 2$, and $k_9/k_{10} \sim 3$, where k_9 and k_{10} refer to products **9** and **10**.[8]

At −60 °C, the minor isomer **10** rearranges to the major one with a half-life of ~30 min. During rearrangement, no further scrambling of the deuterium label in **10** can be observed by NMR, although it must be stated that, because the available starting mixture contains only 25% **10** which is already 50% scrambled, the experiment cannot sensitively detect further scrambling in the **10** → **9** rearrangement.

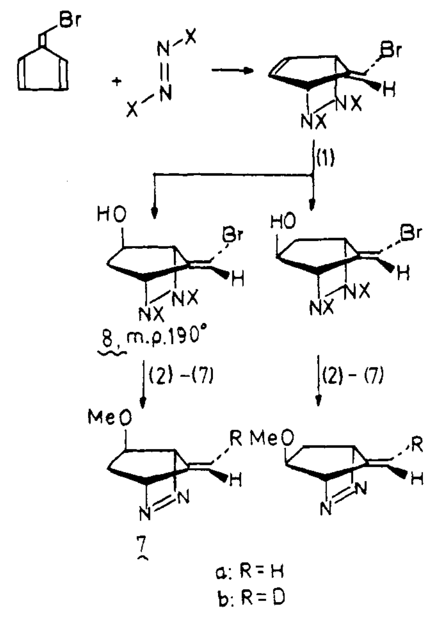
At −40 °C, the deuterium label of **9** undergoes syn-anti scrambling with a half-life of ~15 min ($k \simeq 7 \times 10^{-4}\ s^{-1}$).[9] Finally, as is described elsewhere,[1] **9** suffers ring opening and dimerization at temperatures above +5 °C.

The rate of syn-anti deuterium scrambling in **9** and **10** corresponds to $\Delta G^{\ddagger} \sim 17$ kcal/mol. On the assumption that $\Delta S^{\ddagger}$ is near zero, this gap may be equated to an upper limit of the enthalpy difference between a 5-methylenebicyclopentane and the corresponding bisected form of a singlet TMM, **11**. If the singlet-triplet energy separation in **11** is about the same as that calculated[10] from theory (14 ± 3 kcal/mol) for the parent trimethylenemethane, the C-1-C-4 bond dissociation energy in compounds **9** and **10**, defined as the enthalpy difference between the ground states[11] of the covalent and biradicaloid forms, must be close to zero. Both this work and the accompanying study[1] suggest that the concept of a covalent C-1-C-4 bond in 5-alkylidenebicyclopentanes may have only kinetic, not thermodynamic, significance.



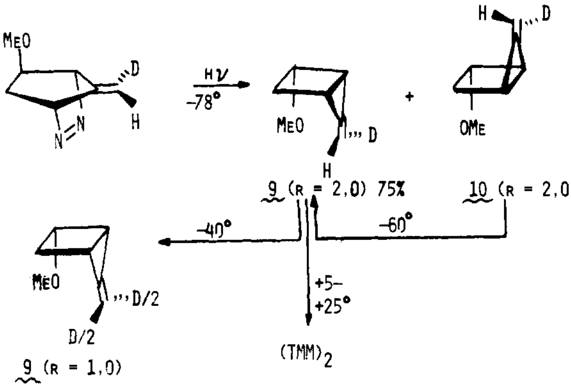
11

Scheme I[a]



[a] Method (X = CO_2CH_3): (1) B_2H_6, then H_2O_2, NaOH; (2) separation; (3) NaH, MeI; (4) *t*-BuLi, then EtOD; (5) Et_2O, aqueous KOH; (6) aqueous HCl; (7) O_2.

Scheme II



(R = INTENSITY RATIO OF ANTI TO SYN METHYLENE PROTONS)

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We are also grateful to the National Science Foundation (CHE-76-00416) and the National Institute of General Medical Sciences (GM-23375) for research support, and to the Biotechnology Resources Program of the National Institutes of Health (RR-798) for its support of the Southern New England High Field NMR Facility. We especially thank Mr. Peter Demou for technical assistance.

References and Notes

(1) M. Rule, M. G. Lazzara, and J. A. Berson, *J. Am. Chem. Soc.*, preceding paper in this issue.

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(4) J. A. Berson, D. M. McDaniel, and L. R. Corwin, *J. Am. Chem. Soc.*, **94**, 5509 (1972).

(5) Double epimerization must be slow on the NMR time scale even at the higher temperatures required[1] to cause ring opening of **6**, because the disappearance of the NMR signals is not accompanied by any detectable site exchange, which would average the exo and endo proton chemical shifts.

(6) The syn stereochemistry of the OMe and D groups of **7b** follows from the assumptions that methylation of the OH and metalation-deuteration of the Br of the precursor **8** occur with retention of configuration, combined with the assignment of the syn stereochemistry to **8** by a single-crystal X-ray

analysis (paper in preparation), for which we are indebted to Professor Richard Adams and Ms. Nancy Golembeski.

(7) (a) The stereochemical assignment of the major isomer as **9** and the minor one as **10** is arbitrary and could be reversed without effect on the present study. The configurations are assigned here by NMR chemical shift differences analogous to those observed in the 2-methoxybicyclo[2.1.0]pentanes.[7b,c] (b) E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, **89**, 7133 (1967); (c) *ibid.*, **91**, 6766 (1969).

(8) This analysis of the partition of the photochemical intermediate is based on the unproven assumption that loss of N_2 gives a singlet TMM with intact deuterium stereochemistry as the first product. Other mechanisms compatible with the data may be imagined.

(9) Although we consider the data for toluene-d_8 solution to be more reliable, the rate constant in $CDCl_3$–$CFCl_3$–Eu(fod)$_3$ is approximately the same.

(10) (a) D. M. Hood, H. F. Schaefer, III, and R. M. Pitzer, *J. Am. Chem. Soc.*, **100**, 8009 (1978). Cf., however, (b) M. P. Conrad, R. M. Pitzer, and H. F. Schaefer, III, *ibid.*, **101**, 2245 (1979); (c) M. S. Platz and J. A. Berson, *ibid.*, **99**, 5178 (1977); (d) P. Dowd and M. Chow, *ibid.*, **99**, 6438 (1977).

(11) The evidence that TMM **11** has a triplet ground state consists of the observations of a long-lived triplet signal, when **7a** is irradiated in a glassy matrix at 77 K,[12] and a typical dilution effect[13] in cycloaddition reactions of the TMM with olefins.

(12) We thank Mr. E. F. Hilinski for this experiment.

(13) Compare (a) J. A. Berson, L. R. Corwin, and J. H. Davis, Jr., *J. Am. Chem. Soc.*, **96**, 6177 (1974); (b) J. A. Berson, C. D. Duncan, and L. R. Corwin, *ibid.*, **96**, 6175 (1974).

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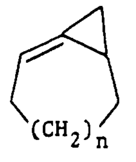
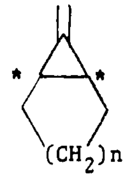
Mechanisms of Dimerization and Rearrangement of a Bicyclo[3.1.0]hex-1-ene

Sir:

Bicyclo[3.1.0]hex-1-ene (**1a**) and 5-methylenebicyclo[2.1.0]pentane (**2a**) are hypothetically related through a common trimethylenemethane (TMM) biradical **3**. Members of the **2a** series seem to be so precariously balanced on the edge of covalency that their bridge bond (C*–C*) may have a negative dissociation energy (DE); that is, the (triplet) ground state of the biradical may be more stable than the bicyclic hydrocarbon.[1,2]



1a: n = 0
b: n = 1



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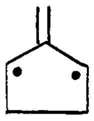
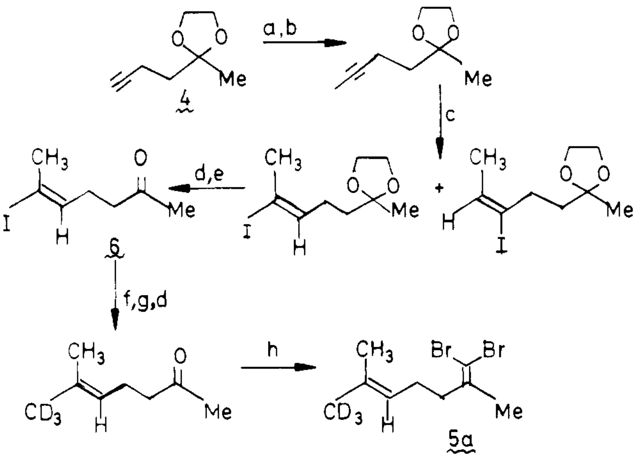


3

By analogy to the next higher homologous pair, **1b** and **2b**, in which the isomer (**1b**) with the endocyclic double bond is of much higher energy,[3] one might predict the energy ordering **1a** > **2a**. With reference to the TMM **3**, **1a** therefore might be even more likely than **2a** to embody a bond with a negative DE. In this paper, we report some reactions of a putative member of the **1a** series which tend to confirm the **1a** > **2a** order of energies.

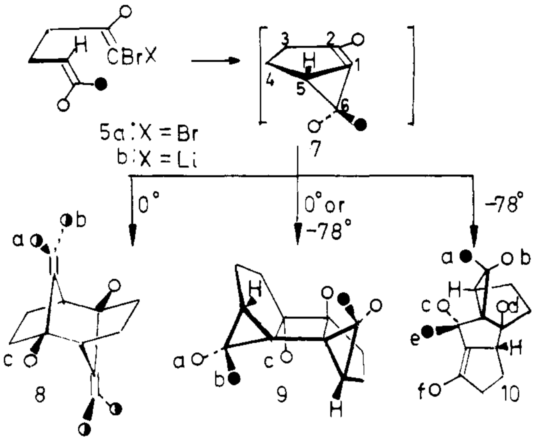
Scheme I outlines the synthesis of 1,1-dibromo-2-methyl-6-*trans*-trideuteriomethylhepta-1,5-diene (**5a**) from the known[4a] acetylenic ketal **4**. The key step is the hydrozirconation[4b]-iodination sequence leading to compound **6**. Although not highly regiospecific, this step gives **6** and ultimately **5a** with complete (>95%) stereospecificity, as judged by integration of the NMR signals of the geminal allylic methyl groups. Undeuterated **5a** (CH_3 instead of CD_3) shows resonances at δ 1.68 and 1.61. The δ 1.68 absorption disappears completely in **5a**.

Scheme I[a]



[a] Methods: (a) $LiNH_2/NH_3$ (l)/THF, −78 °C; (b) MeI, 0 °C, THF; (c) $Cp_2Zr(H)Cl$, PhH, 4 h, then I_2, following a general procedure of ref 4b; (d) H_3O^+; (e) separation by GC; (f) $HOCH_2CH_2OH$, TsOH, PhH; (g) CD_3Li, 5% CuBr, following a general procedure of ref 4c; (h) CBr_4, Ph_3P, $PhCH_3$, 12 h, 110 °C, following a general procedure of ref 5, modified.

Scheme II



As has been previously reported in the unlabeled series,[6,7] α-elimination from 1-halo-1-lithio-2,6-dimethylhepta-1,5-dienes leads to two major types of products derived from a trimethylbicyclo[3.1.0]hex-1-ene (**7**, Scheme II, ● = ○ = ◑ = CH_3): (i) a mixture of dimers of the trimethylenemethane (TMM) **11**, among which is the crystalline, highly symmetrical compound **8**, and (ii) the symmetrical [2 + 2] dimer **9**. The latter product predominates at low temperature. We now find that the reaction mixture generated from **5a** and MeLi in Et_2O at −78 °C also contains ~5% a third dimer which can be isolated by gas chromatography (GC) on a 15% OV-17 column. This compound, assigned structure **10** by its spectroscopic properties,[8] is clearly related to the analogue **10** (H instead of Me groups a, b, c, e) obtained[7] from 1,1-dibromo-2-methylhexa-1,5-diene under similar conditions.

Metalation of stereospecifically deuterated **5a** (Scheme II, ● = CD_3, ○ = CH_3, ◑ = $CD_3/2$) gives via **5b** stereospecifically deuterated **9** and **10**. At normal isotopic abundance, **9** shows three different six-proton methyl-group NMR resonances (Bruker HX-270) at δ 1.16, 1.03, and 0.99, but **9**-d_6 generated from **5b**-d_3 shows two six-proton singlet absorptions at δ 1.16 and 1.03 but no absorption at δ 0.99. This suggests that carbenoid cyclization of **5b** onto the isopropylidene group is stereospecific (presumably cis), and that the intermediate