produces conglomerates, as opposed to racemates, spectral distinctions are not expected.

(17) The ammonium sodium tartrates exhibit spectra similar to those obtained for tartaric acid. The ammonium sodium salts of (+)-**1** and of the racemate of (±)-**1** exhibit double carbonyl absorptions which are chemically shifted relative to each other; the salt of (+)-1 exhibits an α-carbon doublet, while that of (±)-1 exhibits a broad single absorption. Both resonances for the ammonium sodium salt of **2** are narrow, single signals indicating that a crystalline modification is adopted in which the carbonyls and α-carbon atoms are symmetry equivalent. (An alternate explanation of the observed spectrum is possible: symmetry nonequivalent groups can exhibit accidental isochrony.[3,4]) To our knowledge the crystal structure of *meso*-ammonium sodium tartrate is unknown.

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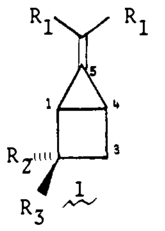
5-Alkylidenebicyclo[2.1.0]pentanes. On the Question of a Negative Bond Dissociation Energy

Sir:

The 5-alkylidenebicyclo[2.1.0]pentanes (general structure **1**) are of special interest because their large ring strain and their relationship to relatively stable trimethylenemethanes (TMMs) of structure **2**[1-6] may conspire to produce a carbon-carbon bond (C-1–C-4) with a negative dissociation energy. In this paper, we report the preparation and properties of four members of the class, **1a–d**.



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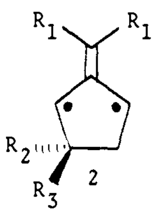


2

a: R_1=Me, R_2,R_3 = H

b: R_1,R_2 = H; R_3 = OMe

c: R_1,R_3 = H; R_2 = OMe

d: R_1,R_2,R_3 = H

The first of two synthetic approaches (Scheme I) modifies the previously reported[6] addition of dimethylvinylidene (**3**) to cyclobutene (**4**), which under the earlier conditions (isolation of the products above room temperature) gave low yields of dimers of the TMM **2a**. We now find that addition of cyclobutene to **3** generated by thermal decomposition of ethereal 1-lithio-1-bromo-2-methylpropene (**5**)[18] at −78 °C forms a solution, which, when treated with methyl acrylate and allowed to warm to room temperature, gives the characteristic adducts[1,2] **6** and **7**. This suggests that the species produced in the **3** + **4** reaction persists at −78 °C for at least several minutes, a property expected of the bicyclopentane **1a** but not of its biradical counterpart **2a**.

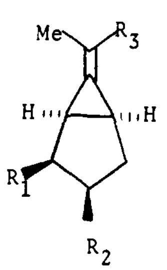
Compound **1a** is formed in virtually quantitative yield by photolysis (>350 nm) of the diazene **8a** in CD_2Cl_2, $CDCl_3$-$CFCl_3$, or toluene-d_8 solutions at −78 °C. The 270-MHz nuclear magnetic resonance (NMR) spectrum, observed at −80 °C, shows six equivalent allylic CH_3 protons (δ 1.74), two equivalent bridgehead protons (1.99), and two pairs of equivalent methylene protons (1.46 and 2.17). These features require a structure of C_s rather than C_{2v} symmetry and demonstrate that **1a** is not in rapid equilibrium (NMR time scale) with the biradical **2a** at −80 °C.

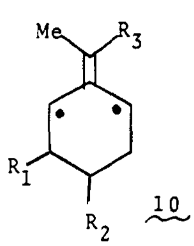
Efficient photochemical formation of **1a** is the fortunate consequence of a "thermal window". The species is unstable at higher temperatures (see below), and product studies[2] have suggested that photolysis of **8a** at much lower temperatures in immobilized media gives not **1a** but rather the triplet ground state of the biradical **2a**, which is known[7] to dimerize rapidly in fluid solution. In qualitative confirmation, we now find that photolysis of **8a** in toluene-d_8 (mp −95 °C) at −196 °C and NMR examination of the solution carefully warmed to −80 °C shows the alkylidenebicyclopentane **1a** to be only a minor component, the major products (~80%) being the TMM dimers of **2a**.

At higher temperatures, **1a** is converted into dimers of the TMM **2a** with a half-life at −40 °C of ~20 min. Qualitatively, the unsubstituted 5-methylenebicyclo[2.1.0]pentane (**1d**), prepared by photolysis of **8d**[4] in $CDCl_3$-$CFCl_3$ at −78 °C, is less stable than **1a**, since conversion of **1d** into the corresponding TMM dimers has a comparable rate at −65 °C. On the other hand, one of the two stereoisomers of the methoxy compound (**1b** or **1c**[8,9]) decomposes to dimers at an appreciable rate only above 0 °C. The origin of these apparent substituent effects remains to be elucidated.

Compounds **1a** and **1b** (or **1c**[8,9]) decompose to dimers in $CDCl_3$ or CD_2Cl_2-$CFCl_3$ solutions with strict first-order kinetics. The products are the same as those produced when the corresponding diazenes **8a**[6] and **8c** are pyrolyzed (>60 °C). The disappearance of the bicyclic monomer is followed by NMR spectroscopic observation at 270 MHz of the strong allylic CH_3 signals (**1a**) or of the $=CH_2$ signals (**1b**). Practical considerations prevent the study of a wide temperature range, but the Arrhenius parameters E_a = 13.2 kcal/mol, log A = 9.2 (A in seconds) for **1a**, and E_a = 16.9 kcal/mol, log A = 9.8 for **1b** (or **1c**[9]) are based upon measurements at four temperatures each, spanning −50 to −30 °C for **1a** and +5 to +25 °C for **1b** (or **1c**). Statistical analysis suggests error limits of ±1 kcal/mol in E_a and ±1 unit in log A.[10]

The observed A factors (corresponding to about −16 eu in $\Delta S^{\ddagger}$) are extremely low for a thermal unimolecular methylenecyclopropane pyrolysis. By contrast, the thermal stereomutations of the ring-homologous 6-alkylidenebicyclo[3.1.0]hexanes **9a**[11] and **9b**,[12] which occur in the temperature range 160–200 °C and are believed to involve TMM intermediates **10**, have log A values of 14.5 and 13.5, respectively.





10

9a: R_1,R_3 = Me; R_2 = H

b: R_1,R_3 = H; R_2 = Me

The low A factors observed in the 5-alkylidenebicyclo[2.1.0]pentane pyrolyses may signify a spin-forbidden transition state, either (i) in a direct bicyclopentane → triplet reaction, presumably involving a crossing of energy surfaces, or (ii) in the second, rate-determining step of a sequential mechanism bicyclopentane **1** → singlet **2** → triplet

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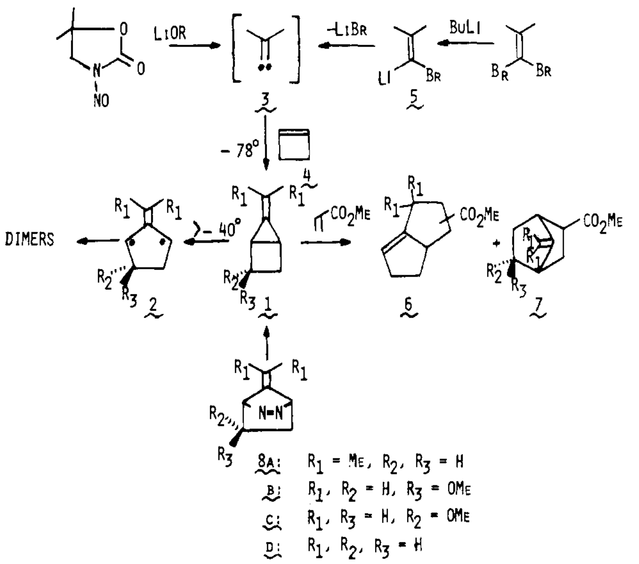
Scheme I



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 $\sim$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.

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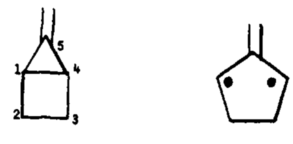
Stereoisomerization by Bridgehead Double Inversion and Olefinic Torsion in 5-Alkylidenebicyclo[2.1.0]pentanes

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.

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