J. Am. Chem. Soc. 1982, 104, 2209–2216

Synthesis and Thermolysis of 5-Alkylidenebicyclo[2.1.0]pentanes. Generation and Dimerization of Trimethylenemethane Triplet Biradicals by Bond Rupture of Strained Hydrocarbons

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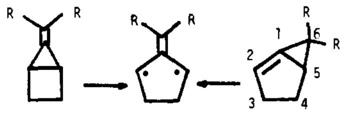
Abstract: The synthesis of 5-isopropylidenebicyclo[2.1.0]pentane (**4**) is accomplished in quantitative yield when 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene (**15**) is photolyzed in CD_2Cl_2 solution at −78 °C. Hydrocarbon **4** undergoes thermal dimerization to the trimethylenemethane dimers **7**–**10** in about 3 h at −53 °C. The kinetics of the dimerization are first order, a finding which is consistent with unimolecular rate-determining conversion of **4** to a reactive intermediate. Dimer then can be formed either by combination of two molecules of the intermediate or by attack of a molecule of the intermediate on a molecule of the bicyclopentane **4**. The Arrhenius preexponential term for the thermolysis is $\sim 10^9$, corresponding to $\Delta S^\ddagger \sim -16$ eu. The low A factor probably arises from a rate-determining step in which a forbidden transition from the singlet to the triplet energy surface occurs. The dissociation energy of the bridge bond of **4** probably is negative, that is, the triplet biradical **11-T** is more stable than the bicyclic hydrocarbon.

Cleavage of a single carbon–carbon bond hypothetically converts a member of the 5-alkylidenebicyclo[2.1.0]pentane (**1**) or bicyclo[3.1.0]hex-1-ene (**3**) series to a 2-alkylidenecyclopentane-1,3-diyl (**2**).[1] Although the latter derivatives of the trimethylenemethane biradical[2] have triplet ground states,[3] the chemistry of a transient singlet species can be separated from that of the triplet.[4–7] It has been difficult to decide whether the reactive form of the "singlet" actually is a true non-Kekulé compound,[8] that is, a biradical (**2** with paired electrons), or instead is better formulated as either of the bicyclic compounds **1** or **3**. Examination of the chemistry of authentic examples of these hitherto unknown hydrocarbons obviously is of crucial importance to the resolution of this mechanistic question. Moreover, the hydrocarbons **1** and **3** generate special interest in their own right because their large ring strain and their relationship to a stable biradical may conspire to produce carbon–carbon bonds (C-1–C-4 of **1**, C-5–C-6 of **3**) with negative dissociation energies.

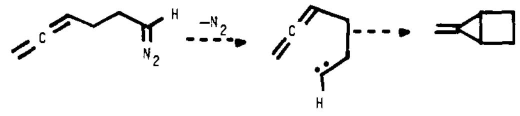


1 2 3

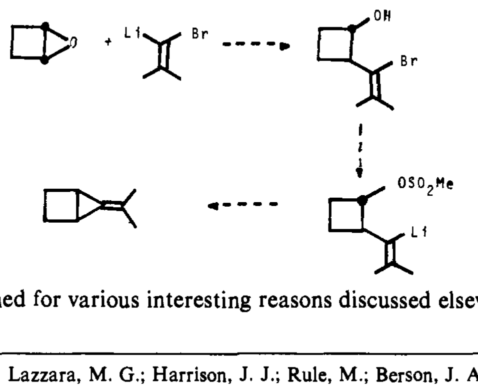
The present paper[7] describes the first syntheses of 5-alkylidenebicyclo[2.1.0]pentanes and some of their properties. Four accompanying papers report further mechanistic studies on these substances[9] and the generation and transformations of bicyclo[3.1.0]hex-1-enes.[10] The completion of these tasks allows us to make an experimental connection between the TMMs observed by direct spectroscopic means[1,2] and the TMM species widely discussed[11] as intermediates in the thermal rearrangements of methylenecyclopropanes. It also provides the basis for the identification of the characteristic chemistry of both types of bicyclic compound (**1** and **3**), for a distinction between their behavior and that of the singlet biradical **2-S**, and for an energetic ordering of these three species and the fourth member of this family, the triplet biradical **2-T**.

Synthetic Routes to 5-Alkylidenebicyclo[2.1.0]pentanes. Of the several formal approaches to the target bicyclic structure, we have explored five. The first three (Methods A, B, and C) were abandoned for various interesting reasons discussed elsewhere[12]

Method A



Method B



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[1] Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.

[2] For a review of acyclic TMM derivatives, see: Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242.

[3] Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725.

[4] (a) Berson, J. A.; Corwin, L. R.; Davis, J. H. *J. Am. Chem. Soc.* **1974**, *96*, 6177; (b) Berson, J. A.; Duncan, C. D.; Corwin, L. R. *Ibid.* **1974**, *96*, 6175.

[5] Berson, J. A.; Duncan, C. D.; O'Connell, G. C.; Platz, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 2358.

[6] (a) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276. (b) Duncan, C. D.; Corwin, L. R.; Davis, J. H.; Berson, J. A. *Ibid.* **1980**, *102*, 2350.

[7] Preliminary communication: Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7091.

[8] As far as we know, the actual term "non-Kekulé compound" was used first by Dewar ((a) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; p 233). The concept itself had origins in writings by Longuet-Higgins ((b) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265), who called attention to "an alternant hydrocarbon with no classical structure of the (Kekulé) type" and even earlier in the work of Clar, Hückel, and Müller ((c) Clar, E. "Aromatische Kohlenwasserstoffe"; Springer: Berlin, 1941; p 311. (d) Hückel, E. *Z. Phys. Chem. Abt. B* **1936**, *34*, 339. (e) Müller, E.; Müller-Rudloff, I. *Justus Liebigs Ann. Chem.* **1936**, *517*, 134). More recently, we have used it to cover a broader meaning, a molecule that "contains enough atoms but not enough bonds to satisfy the standard rules of valence" ((f) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron*, in press).

[9] (a) Lazzara, M. G.; Harrison, J. J.; Rule, M.; Berson, J. A. *J. Am. Chem. Soc.*, accompanying paper in this issue. (b) Lazzara, M. G.; Harrison, J. J.; Rule, M.; Berson, J. A. *Ibid.* **1979**, *101*, 7092.

[10] (a) Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.*, accompanying paper in this issue. (b) Salinaro, R. F.; Berson, J. A. *Ibid.* **1979**, *101*, 7094. (c) Rule, M.; Berson, J. A. *Tetrahedron Lett.* **1978**, 3191. (d) Rule, M.; Salinaro, R. F.; Pratt, D. R.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2223.

[11] for reviews, see: (a) Gajewski, J. J. In "Mechanisms of Molecular Migrations", Thyagarajan, B., Ed.; Wiley-Interscience: New York, 1971; Vol. 4, p 1. (b) Berson, J. A. In "Rearrangements in Gound and Excited States", de Mayo, P., Ed.; Academic Press: New York, 1980; p 311.

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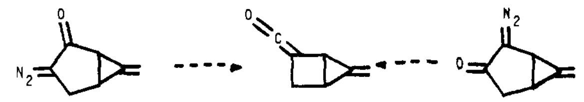
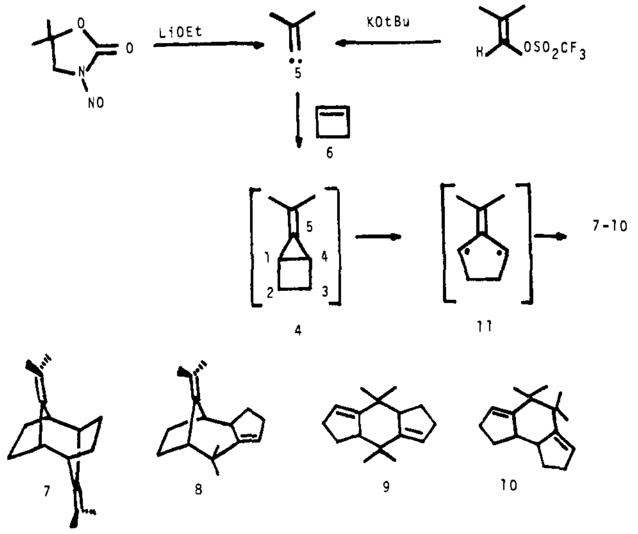
Method C



and are given merely in outline form here.

In Method D, 5-isopropylidenebicyclo[2.1.0]pentane (**4**) is generated by the addition of dimethylvinylidene (or a related carbenoid) (**5**) to cyclobutene (**6**). This was our first approach[13] to the synthesis of 5-alkylidenebicyclo[2.1.0]pentanes, and although the target compound was not isolated under the workup conditions (room temperature, followed by gas chromatography at elevated temperatures), small yields of the characteristic TMM dimers **7**–**10** (stereochemistry shown arbitrarily) were obtained. A large number of unidentified side products also were formed. The TMM dimers probably arose by cleavage of the C-1–C-4 bond of the intermediate bicyclic adduct, **4**, followed by dimerization of the TMM biradicals **11**. The early work[13] generated dimethylvinylidene by the base-induced decomposition of *N*-nitroso-5,5-dimethyloxazolidone, according to the method of Newman.[14] More recently, similar results have been obtained[15a] using isobutenyl trifluoromethanesulfonate as the source of dimethylvinylidene, according to the method of Stang.[15b]

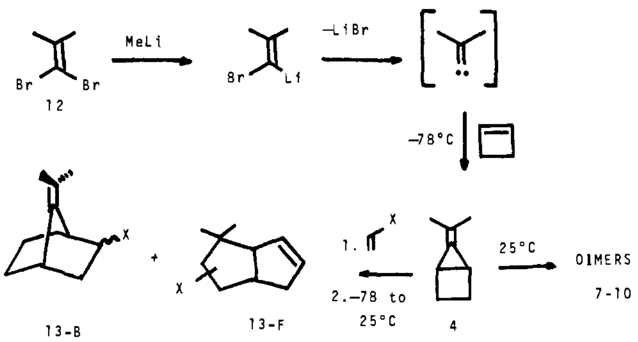
Method D



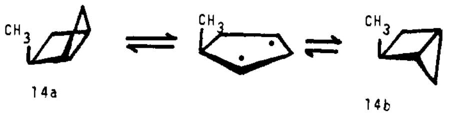
The chances of preserving monomeric **4** itself should be improved if the species could be generated at low temperature. For this purpose, the exceptionally facile transformation of 1,1-dibromo-2-methylpropane (**12**) to 1-lithio-1-bromo-2-methylpropene and the α-eliminative decomposition of the organometallic reagent to dimethylvinylidene (or its carbenoid) described by Hartzler[16] seem to offer substantial advantages. In fact, as Scheme I shows, when dibromide **12** and low-halide methyllithium in ether are successively added to a sample of excess cyclobutene maintained at −78 °C, quenched with methanol, and warmed to room temperature, the only volatile products observed are identified by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy as the TMM dimers **7**–**10**. None of the side products observed in Method D are obtained.

Apparently, the monomeric bicyclopentane **4** is cleanly formed at low temperature under the condition of Scheme I but suffers bond cleavage at some temperature above −78 °C. The TMM dimers **7**–**10** can be observed in the NMR spectrum of a reaction mixture whose temperature has not been allowed to rise above that of the ambiance of the NMR probe, so that about 30 °C represents an upper limit for the decomposition temperature of **4**. Is there a lower limit below which **4** is stable, or does it open to the biradical **11** at −78 °C or even below?

Scheme I (X = CO$_2$Me)



Either of two thermochemical-kinetic calculations serves as a rough guide to estimate the kinetic stability of **4**. In one, we note that the difference in Arrhenius activation energy (ΔE_a) between the thermal rearrangement of cyclopropane (65.1 kcal/mol[17a]) and a methyl-substituted methylenecyclopropane (40.4 kcal/mol[17b]) amounts to a facilitation of the cyclopropane cleavage by 24.7 kcal/mol. The thermal stereomutation of the 2-methylbicyclo[2.1.0]pentanes **14a** and **14b** occurs with E_a = 38.9 kcal/mol,[17c] presumably by way of a species with a broken bridge bond. If the cyclopropane cleavage in the transformation of **4** to the biradical **11** were facilitated by the same 24.7 kcal/mol ΔE_a as in the case of cyclopropane itself, the E_a for cleavage of the bridge bond of **4** would be 38.9 − 24.7 = 14.2 kcal/mol.



Alternatively, the strain energy of cyclopropane (27.0 kcal/mol[17d]) may be subtracted from that of bicyclopentane (54 kcal/mol[17e]) to obtain the incremental strain of fusing a four-membered ring onto a cyclopropane. If the same strain increment applied to fusion onto methylenecyclopropane, and if this strain were largely relieved in the reaction **4** → **11**, the E_a should be given by [E_a(methylenecyclopropane rearrangement) − 27] = 40.4 − 27 = 13.4 kcal/mol.

These estimates of E_a probably should be taken as upper limits, since the strain effects in the bicyclic systems of these rough models are here assumed to be simply additive.

If the thermal decomposition of **4** has a "normal" pre-exponential term ($A \sim 10^{13}$–10^{14} s^{-1}), the estimated activation energies would permit the substance a half-life of only about a second at −78 °C. Nevertheless, when **4** is generated as before at −78 °C, the reaction mixture quenched with methanol, *stored at -78 °C for 15 min*, treated with an excess of methyl acrylate, and then warmed to room temperature, the typical TMM adducts **13-B** and **13-F**[1,3-6,18] are obtained. One would not expect the biradical **11** to have survived storage. It should immediately have crossed over[1,4-7] to the more stable[1,3] triplet form, which then would have

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[12] Rule, M. Ph.D. Dissertation, Yale University, 1979.

[13] Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *J. Am. Chem. Soc.* **1971**, *93*, 1544.

[14] Newman, M. S.; Okarodudu, A. O. M. *J. Am. Chem. Soc.* **1968**, *90*, 4189, and subsequent papers.

[15] (a) Cichra, D. A., unpublished work at Yale University. (b) Stang, P. J.; Mangum, M. G.; Fox, D. P.; Haak, P. *J. Am. Chem. Soc.* **1974**, *96*, 4562.

[16] Hartzler, H. D. *J. Am. Chem. Soc.* **1964**, *86*, 526.

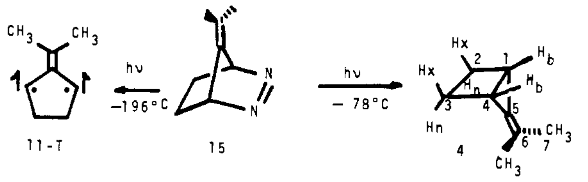
[17] (a) Schlag, E. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1960**, *82*, 5996. (b) Chesick, J. P. *Ibid.* **1963**, *85*, 2720. (c) Chesick, J. P. *Ibid.* **1962**, *84*, 3250. (d) Mortimer, C. T. "Reaction Heats and Bond Strengths"; Pergamon Press: New York, 1962; p 99. (e) Turner, R. B.; Goebel, P.; Mallore, B.; Doering, W. v. E.; Coburn, J. F., Jr.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315. (f) Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 768, 1471. (g) Newton, M. D.; Schulman, J. M.; Manus, M. M. *J. Am. Chem. Soc.* **1974**, *96*, 17. (h) Stothers, J. B. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1972. (i) Cf. also: Wehrli, F. W.; Withlin, T. "Interpretation of Carbon-13 NMR Spectra"; Hayden: Philadelphia, 1978.

[18] (a) Berson, J. A.; McDaniel, D. M.; Corwin, L. R.; Davis, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 5508. (b) Berson, J. A.; McDaniel, D. M.; Corwin, L. R. *Ibid.* **1972**, *94*, 5509.

formed the dimers **7**–**10**. The only reasonable hypothesis is that the persistent species which is the precursor of **13-B** and **13-F** is **4** and that its decomposition rate is orders of magnitude smaller than that calculated by the above assumptions. Either the bond additivity scheme is seriously in error, or the pre-exponential term is much smaller than "normal". As we shall see, the latter explanation is correct.

The Scheme I variant of Method D thus demonstrates the stability of the bicyclopentane **4** at −78 °C. However, the presence of the reagents and their transformation products in the reaction mixture is an unattractive feature of this approach if one hopes to make a direct spectroscopic identification of **4**.

Method E



Method E involves the minimum chemical change of all the syntheses considered. It consists merely of elimination of nitrogen from the diazene **15**. Since **15** is readily available and can be readily deazetated photochemically at low temperature,[1,4,13,19] it may be asked why this method was not tried earlier. The reason is that our previous relevant low-temperature photochemical studies had been carried out in matrices or glasses at 77 K, under which conditions we had concluded that the major product from diazene **25** could not be the ring-closed compound **4** but was instead the triplet ground state of the TMM biradical, **2**[4,20] (Method E). As we show later, this conclusion was correct, but out implicit assumption that triplet **2** would dominate the photolysis product at higher temperature was not.

In fact, the photolysis of **15** *at −78 °C* gives 5-isopropylidenebicyclo[2.1.0]pentane (**4**) in near-quantitative yield. This is implied first by a trapping experiment, in which the ethereal solution obtained after complete photolysis of **15** at −78 °C is treated with excess methyl acrylate and allowed to warm to room temperature. A high yield of cycloadducts **13-B** and **13-F** is obtained, together with a small amount of the TMM dimer mixture **7**–**10**. The cycloadduct mixture is essentially the same (by GC and NMR analysis) as that obtained[1,3–6,18] by pyrolysis of diazene **15** in the presence of a large excess of methyl acrylate.

Direct observation of **4** under circumstances in which it is indefinitely stable can be achieved by photolysis of a degassed 0.1 M solution of diazene **15** in CD_2Cl_2 at −78 °C in an NMR sample tube. After photolysis, the tube is quickly frozen in a liquid nitrogen bath (−196 °C) and then placed into the 270 MHz NMR spectrometer, the probe of which has been precooled to −80 °C. When the sample is allowed to warm to −80 °C, it melts, and the spectrum of the bicyclic hydrocarbon **4** can be recorded. It is stable for hours at −80 °C but rapidly disappears above −30 °C.

The results of photolyses of **15** in other solvent systems ($CDCl_3$–$CFCl_3$ or toluene-d_8) at −78 °C are similar. Bicyclic hydrocarbon **4** is formed as the sole product.

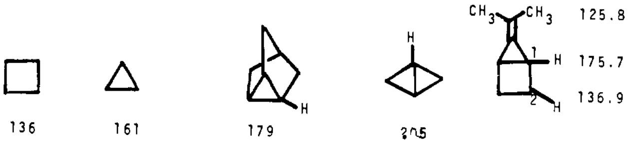
NMR Spectra of 5-Isopropylidenebicyclo[2.1.0]pentane. The proton spectrum (270 MHz) at −80 °C consists of only four resonances with the relative intensities 1:1:1:3. The most intense peak, a sharp singlet at δ 1.74, is assigned to the allylic methyl groups. The remaining resonances are assigned as follows: δ 2.17 (unresolved doublet, H_x or H_n), 1.99 (broad singlet, H_b), and 1.46 (doublet, H_n or H_x). The assignment of the δ 2.17 and 1.46 resonances to the protons of the ethano bridge (H_x and H_n) is based upon the deuteration experiment to be described.

The proton-decoupled ^{13}C spectrum (67.89 MHz) at −63 °C shows only five lines, which are assigned in Table I. The two quarternary olefinic carbons cannot be individually assigned on the basis of the present data. Table I includes two estimates of the s character (% s) of the carbon hybrid orbital participating in the C–H bond indicated. These values are calculated using either the empirical relationship[17f] $(\% s)_a = {}^1J_{CH}/(5\ Hz)$ or the improved relationship[17g] based on INDO-MO calculations of hybridization parameters $(\% s)_b = ({}^1J_{CH} + 18.4\ Hz)/(5.7\ Hz)$. As might be expected, $^1J_{CH}$ and % s for the bridge carbons (C-1–C-4) of **4** have the highest values. $^1J_{CH}$ for 5-isopropylidenebicyclo[2.1.0]pentane is comparable to the values found for similar structural units in several other strained systems in the literature:[17h,i]

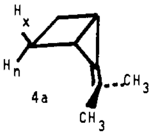
Table I. ^{13}C NMR Data for 5-Isopropylidenebicyclo[2.1.0]pentane (**4**)

chemical shift, δ^a	multiplicity^b	$^1J_{CH}$,^{b} Hz	assignment	$(\% s)_a$	$(\% s)_b$
126.50	s		C-5/C-6		
116.28	s		C-5/C-6		
22.13	q	125.77	C-7	25.2	25.3
21.56	t	136.87	C-2	27.4	27.2
21.42	d	175.71	C-1	35.1	34.0

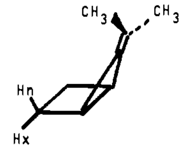
^{a} Obtained from a proton-decoupled spectrum. ^{b} Obtained from a proton-coupled spectrum. Solvent $CDCl_3$–$CFCl_3$.



The spectroscopic features leave no doubt of the bilateral symmetry of the photolysis product, but they require a C_s rather than a C_{2v} structure. On the NMR time scale, therefore, interconversion of two equivalent isomers of **4** (e.g., **4a** ⇌ **4b**) by double epimerization must be slow, since in the limit of fast isomerization H_x would become equivalent to H_n and the spectrum would appear as three lines with relative intensities 1:2:3.

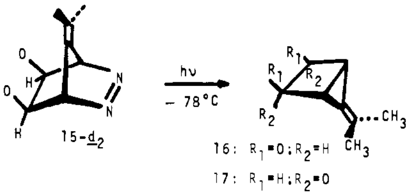


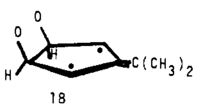
4a



4b

NMR examination at −80 °C of the solution obtained by photolysis of 7-isopropylidene-5,6-*exo,exo*-dideuterio-2,3-diazanorbornene (**15**-d_2),[18b] in CD_2Cl_2 at −78 °C shows the product to be a mixture of 50% each of the two double epimers **16** and **17**, as determined by the equal intensities of the *exo*- and *endo*-methylene ^1H NMR signals at δ 1.46 and 2.17. These resonances each have just one-sixth the intensity of the allylic methyl resonance at δ 1.74. The assignments are based on the assumption (see Experimental Section) that the protons being scrambled are the exo and endo pairs. There is no obvious pathway for scrambling an ethano and a bridgehead pair of protons or for conversion of the cis dideuterio configuration to trans. A plausible mechanism for the scrambling involves the formation of a nitrogen-free symmetrical intermediate, for example, a singlet TMM biradical, **18**.





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It is not immediately obvious whether endo–exo stereospecificity is lost during the photochemical deazetation-ring closure or

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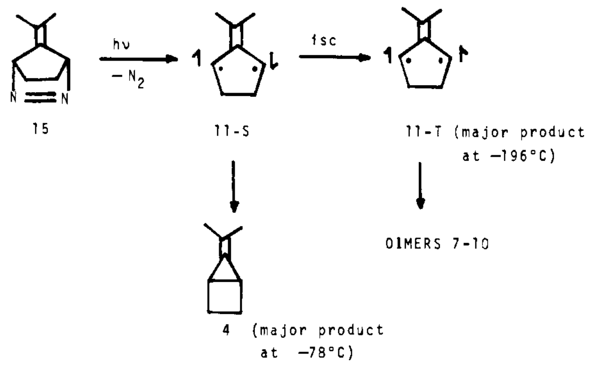
(19) Platz, M. S.; Kelsey, D. R.; Berson, J. A.; Turro, N. J.; Mirbach, M. *J. Am. Chem. Soc.* **1976**, *99*, 2009.

(20) Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5178.

subsequently by a double epimerization of the bicyclopentane product. The latter rearrangement, even though we know it to be slow on the NMR time scale, might still be fast enough on the time scale of ordinary laboratory manipulation to lead to stereoequilibration. However, the first explanation seems more plausible, since the double epimerization would have to be fast in the temperature range −78 to −196 °C, where the photochemistry, transfer, and spectroscopy are carried out. Since thermal dimerization of **4**, which occurs by rate-determining cleavage of the bridge bond (see below), takes place at a rate slow enough to be measured even at −33 °C, the hypothetical double epimerization, which would occur by cleavage of the same bond, might be expected to be very slow at the lower temperatures.

The "Thermal Window". It is now easy to confirm the previous conclusion[4,20] that the photochemistry of diazene **15** at *−196 °C* leads largely to the triplet TMM. Photolysis of a toluene-d_8 glass containing **15** at −196 °C gives a preparation which when transferred to an NMR spectrometer set at −80 °C, a temperature at which **4** is stable, is seen to consist of a mixture of 15–20% of **4** and 80–85% of the TMM dimers **7–10**. The observed switch in products from mainly dimers at −196 °C to mainly bicyclic hydrocarbon at −78 °C agrees with a corollary of the hypothesis that a singlet TMM biradical intermediate **11-S** is a common intermediate. The product distribution will depend on the competition in the rates with which **11-S** undergoes intersystem crossing (isc) and ring closure. If the activation energy for ring closure is slightly higher than that for isc, bicyclic compound **4** will be favored relatively at higher temperature. The triplets formed preferentially at −196 °C may be stored indefinitely in the matrix[1,7,13] but dimerize instantly[21] when the sample is warmed to −80 °C for NMR spectroscopy.

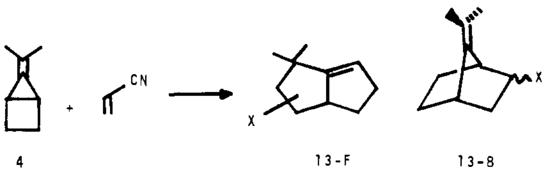
Efficient photochemical formation of **4** thus is the fortunate consequence of a "thermal window". It just happens that −78 °C is a high enough temperature to permit ring closure to dominate the competition in the two pathways from **11-S** but low enough to permit the survival of the thermally labile ring-closure product **4**.[22]



Kinetics of the Thermolysis of 5-Isopropylidenebicyclo[2.1.0]pentane. Solutions of the hydrocarbon **4** decompose at −53 °C with a half-life of about 3 h. The products are the TMM dimers **7–10**, formed in essentially the same proportions as those from the diazene **15**.[6,13] The kinetics of the disappearance of **4** can be monitored readily by NMR spectroscopy with the Bruker HX 270 instrument, using the intensity of the allylic methyl proton signal at δ 1.74. Although the product dimers also contain allylic methyl groups,[13] their proton resonances at 270 MHz are sufficiently well separated from that of **4** so that the reaction can be followed for 2–3 half-lives without interference. The Experimental Section reports kinetic measurements in two different solvent systems, 1:1 $CDCl_3$–CCl_4 and 1:1 $CDCl_3$–$CFCl_3$, at several temperatures in the range −53 to −33 °C. In all cases, the disappearance of **4** is *cleanly first order* as judged from the linearity of the plot of time vs. logarithm of the integrated intensity of the δ 1.74 signal.

The first-order kinetics do not permit the manipulation of the absolute rate by change of concentration. Therefore, we are restricted to a rather narrow temperature range by instrumental limitations. At the upper end, −33 °C, $t_{1/2}$ = 8 min, whereas at the lower end, −53 °C, $t_{1/2}$ = 3 h. The limiting factors thus are respectively the time required to record a single spectrum and the availability of the 270 MHz instrument. Nevertheless, Arrhenius activation parameters reliable to about ±1 kcal/mol and ±1 unit in log A can be obtained. For the $CDCl_3$–CCl_4 and $CDCl_3$–$CFCl_3$ runs respectively the values of E_a are 13.6 and 13.3 kcal/mol; the values of log A (A in s^{-1}) are 9.6 and 9.2.

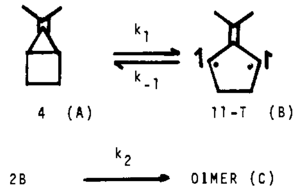
Cycloaddition of 4 and Acrylonitrile. When diazene **15** is photolyzed at −78 °C in $CDCl_3$–$CFCl_3$ solution containing 1 M acrylonitrile and the reaction mixture examined by NMR at −80 °C, the product is largely the bicyclopentane **4**, although small amounts of cycloadducts **13-B** and **13-F** are formed. This suggests that if the singlet TMM is an intermediate in the photolysis, acrylonitrile traps it only inefficiently under these conditions, and most of it ring closes. However, raising the temperature of the acrylonitrile–bicyclopentane mixture to −56.6 °C produces a mixture of adducts consisting largely of the fused isomers **13-F** (X = CN) and small amounts of bridged products **13-B** (X = CN). This is consistent with the formation of similar products (X = CO_2CH_3) from methyl acrylate when **4** is generated by Method D, Scheme I.



Discussion

The mechanism of dimer formation cannot consist of a simple combination of two molecules of the bicyclopentane **4**, since that would lead to second-order kinetics. The observed first-order kinetics seem to require unimolecular conversion of **4** to a reactive intermediate in the rate-determining step. Dimer then can be formed either by combination of two molecules of the intermediate (Mechanism I) or by attack of a molecule of the intermediate on a molecule of the bicyclopentane (Mechanism II). Two isomers of **4** might be considered for the role of the intermediate in question, but one of these, 6,6-dimethylbicyclo[3.1.0]hex-1-ene (**3**, R = Me) is highly unlikely, since closely related members of this class have an entirely different chemistry.[10] This leaves only a TMM biradical as a plausible candidate, and we formulate the intermediate as the triplet species **11-T** for reasons to be given.

Mechanism I



If B is assumed to be a steady-state intermediate,

$$-d[A]/dt = k_1[A]\left(1 - \frac{k_{-1}}{k_{-1} + k_2[B]}\right) \tag{1}$$

equation 1 reduces to eq 2 when formation of the intermediate (B) is rate determining ($k_2[B] >> k_{-1}$).

$$-d[A]/dt \simeq k_1[A] \qquad \text{(first order)} \tag{2}$$

Mechanism II

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$A + B \xrightarrow{k_3} C$$

Again from the steady-state assumption, we have

$$-d[A]/dt = (2k_1k_3[A]^2)/(k_3[A] + k_{-1}) \tag{3}$$

Two limiting variants may now be imagined:

(IIa) If the combination step is assumed to be rate determining, that is, A and B are in rapid equilibrium and $k_{-1} >> k_3[\mathrm{A}]$, eq 3 reduces to

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t \simeq (2k_1k_3/k_{-1})[\mathrm{A}]^2 \quad \text{(second order)} \qquad (4)$$

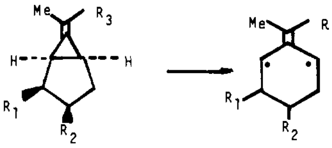
This does not correspond to the observed first-order behavior and can be excluded.

(IIb) If $k_3[\mathrm{A}] >> k_{-1}$, formation of **B** is rate determining, and eq 3 reduces to

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t \simeq 2k_1[\mathrm{A}] \quad \text{(first order)} \qquad (5)$$

The kinetic order alone does not permit a distinction between Mechanisms I and IIb, but a choice could be made if it were possible to measure the rate constant k_1 of the forward A → B reaction independently. Mechanisms I and IIb should have observed rate constants that are respectively equal to or twice as great as k_1.

It is a crucial point of both of the acceptable mechanisms that the rate-determining step involves unimolecular formation of a reactive intermediate. Since this is proposed to be a thermal homolysis of a cycloalkane to a biradical, one might have expected, by analogy to many other examples,[23] a pre-exponential term in the range 10^{13}–10^{14}, rather than the value observed here, which is about 10^9 (corresponding to $\Delta S^{\ddagger} \sim -16$ eu). Perhaps the closest models for our hypothetical unimolecular methylenecyclopropane pyrolysis are those provided by the ring-homologous 6-alkylidenbicyclo[3.1.0]hexanes **18a** and **18b**.[24,25] Stereomutations of these compounds, presumably[24,25] through TMM intermediates **19a** and **19b**, occur in the temperature range 160–200 °C and have log A values of 14.5 and 13.5, respectively.



18a R1,R3=Me; R2=H 19a,b

18b: R1,R3=H; R2=Me

We attribute the low A factor for the bicyclopentane **4** to the spin-forbidden nature of the rate-determining step. Because the reactant **4** is a singlet and the intermediate **11-T** a triplet, electron spin is not conserved, and the probability of reaction is diminished.[26] The necessary spin inversion might be imagined to occur in either (i) a direct bicyclopentane → triplet reaction, involving a crossing of energy surfaces, or (ii) the second, rate-determining step of a sequential mechanism bicyclopentane → singlet TMM (**11-S**) → triplet TMM (**11-T**). Presumably, in mechanism ii, the first step would have a "normal" pre-exponential term, but this would have no appreciable effect on the observed A factor if the second step is rate determining.

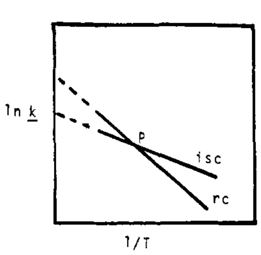


Figure 1. Schematic diagram of the Arrhenius form of the temperature effect on the competition between intersystem crossing (isc) and ring closure (rc) of a singlet TMM biradical. The intercepts on the ln k axis define the ln A values. The slopes are measures of E_a. At the crossing point (P), the two rates are equal.

Whether mechanism i or ii is correct, the 5-isopropylidenebicyclo[2.1.0]pentane molecule **4** 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 at −80 °C of ~1 s.

To our knowledge, there are no prior examples of the formation of TMM dimers in the extensive literature of thermal rearrangements and stereomutations of methylenecyclopropanes.[11] These rearrangements are most readily formulated with singlet TMM biradical intermediates. Since TMMs usually have triplet ground states,[3,27] it is a reasonable assumption that singlet → triplet conversion should have been thermodynamically feasible in the previous intermediates. By analogy to the behavior of 5-isopropylidenebicyclo[2.1.0]pentane (**4**), such conversion should have led to dimerization. Moreover, TMM triplet biradicals are inordinately sensitive to molecular oxygen, being selectively scavenged from reaction mixtures in its presence.[3-6] Yet at least one thermal rearrangement proceeding through TMM intermediates, that of 2,3-dicyanomethylenecyclopropane, has been found not to be affected by oxygen.[28] The conclusion seems inescapable that previous methylenecyclopropane rearrangements (which we call type A for ease of reference) do not involve triplet TMMs but stay entirely in the singlet manifold, in contrast to the behavior of **4** (type B), which readily goes over to the triplet.

We offer a simple (even if not unique) resolution of this dichotomy as a temperature effect. Intersystem crossing to the triplet can be considered to be in competition with ring closure of the TMM singlet. If ring closure is opposed by a small barrier, as is suggested by the "thermal window" effect seen in the formation of **4**, the Arrhenius plots for intersystem crossing (low E_a and low A factor) and ring closure (higher E_a and higher A factor) may not be parallel (Figure 1). The type A rearrangements all were observed at high temperatures, typically 160–200 °C. Suppose that this corresponds to the region to the left of the crossing point (P) in Figure 1, where the rate of ring closure (rc) exceeds the rate of intersystem crossing (isc). The singlet TMM then could form and re-close repeatedly, rearrangement would occur, but population of the triplet state would be indetectably slow. However, thermal reaction of the bicyclopentane **4** occurs at much lower temperature, −50 °C. This region is further to the right in Figure 1 where the competition is relatively more favorable to intersystem crossing. It is not necessary that point P be traversed, that is, that the intersystem crossing rate constant actually exceed the ring-closure rate constant. As long as intersystem crossing competes appreciably, triplet behavior will become manifest as the TMM is irreversibly drained off to dimer.

If this explanation is correct, there is no point in trying to favor isc in the competition by raising the temperature. This should have an effect just opposite to that desired. Of course, higher temperature also would increase the *overall absolute rate* of both the rearrangement and dimerization reactions by increasing the rate of formation of the biradical intermediate. Thus, with

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(21) (a) Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 6743. (b) Platz, M. S.; Berson, J. A. *Ibid.* **1980**, *102*, 2358.

(22) The present finding of a small amount of **4** in the −196 °C photolysis of **15** necessitates a redetermination of the singlet–triplet energy gap[20] in the TMM **11**, because **4** gives the typical singlet products. For discussion, see ref 30b.

(23) (a) O'Neal, H. E.; Benson, S. W. *J. Phys. Chem.* **1968**, *72*, 1866. (b) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, No. 21.

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

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

(26) For discussions of spin-forbidden processes, see inter alia: (a) Glasstone, G.; Laidler, K.; Eyring, H. "The Theory of Rate Processes"; McGraw-Hill, New York, 1941; pp 306 and 325–329. (b) Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14. (c) McGlynn, S. P.; Azumi, T.; Kinoshita, M. "Molecular Spectroscopy of the Triplet State"; Prentice-Hall: Englewood Cliffs, N.J., 1969; p 183 ff. (d) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962. (e) Jortner, J.; Rice, S. A.; Hochstrasser, R. M. *Adv. Photochem.* **1969**, *9*, 144. (f) Duncan, C. D.; Halevi, E. A.; Trindle, C. *J. Am. Chem. Soc.* **1979**, *101*, 2269.

(27) Baseman, R.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726.

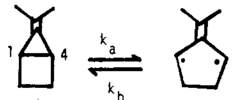
(28) Doering, W. v. E.; Buchwalter, S., unpublished observations cited by Borden: Borden, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 2096.

sufficient patience, one might hope ultimately to observe dimerization after prolonged runs at temperatures higher than the observable threshold of rearrangement, despite the unfavorable competition. Examples of this behavior are given in two accompanying papers.[9,10]

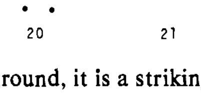
An alternative approach would be to find ways to generate the singlet TMM at temperatures lower than the threshold of rearrangement. This may fail if the barrier to ring closure is very small.

The mixture of cycloadducts obtained from the bicyclic hydrocarbon **4** and acrylonitrile consists mostly of the fused products **13-F**. This is typical of the regiospecificity of the singlet TMM rather than the triplet.[1,3-6] The regiospecificity is an orbital symmetry effect which is most economically explained in terms of the singlet TMM as the true reactive intermediate in cycloaddition.[29] Although the same regiospecificity would be expected from a direct reaction of the bicyclic hydrocarbon with the olefin, recent kinetic observations[30] leave little doubt that ring opening of the bicyclic hydrocarbon to the singlet biradical is a necessary step in the mechanism of the cycloaddition.

On the Question of a Negative Dissociation Energy of the Bridge Bond in 5-Isopropylidenebicyclo[2.1.0]pentane. The bicyclic hydrocarbon **4** suffers rapid ring opening to the triplet TMM **11-T** above −30 °C in fluid media. Clearly, if one could measure the rate of the reverse reaction by some means, one would obtain the equilibrium constant for the reaction **4** ⇌ **11-T** as the ratio of the two rate constants. The free-energy change, $\Delta G^\circ = \Delta\Delta G^\ddagger = -RT \ln (k_a/k_b)$ would serve as a measure of the dissociation energy of the bridge bond. This value should not differ greatly from the more properly defined bond dissociation energy, which is the different in heats of formation, $\Delta\Delta H_f^\circ$, between the hydrocarbon **4** and the biradical **11-T**. The vibrational entropies should differ only slightly. Two statistical corrections to the entropy, one of which tends to favor **4** by a factor of $R \ln 2$ in the rotational entropy because of the ratio of symmetry numbers, and the other of which tends to favor **11-T** by a factor of $R \ln 3$ because of the ratio of multiplicities, almost offset each other. Moreover, $\Delta\Delta G^\ddagger = \Delta\Delta H^\ddagger = \Delta E_a$(Arrhenius) $= \Delta\Delta H_f^\circ$, provided the Arrhenius pre-exponential terms (A) of the forward and reverse reactions are the same. We do not have a direct measure of A for the **11-T** → **4** reaction, but a closely related model reaction, **20** → **21**, has $\log A = 9.1$ (A in s^{-1}),[31,32] which does not differ significantly from the value we measure for **4** → **11-T**.



4 11-T



20 21

With this as background, it is a striking fact that when **11-T** is generated by partial photolysis of a crystalline sample of diazene **15**, the EPR signal intensity follows the Curie–Weiss law from 14 to 268 K, that is, up to temperatures as high as −5 °C.[3] Intensity measurements involve maintenance of the sample for times of the order of a few minutes at each temperature. Ring closure, **11-T** → **4**, would depopulate the triplet state, causing a decrease in the signal and a departure from the observed linear intensity vs. $1/T$ behavior.

At −5 °C, the ring-opening reaction **4** → **11-T** has a half-life of about 35 s in fluid media. Thus, ring closure of **11-T** under the crystalline matrix conditions is at least 1–2 orders of magnitude *slower* than ring opening of **4** in fluid medium. This would correspond to a difference in activation energy for the two processes of at least 1–2 kcal/mol. It does not seem likely that the crystalline environment would impose a large additional retarding barrier on the ring closure. Several examples in the literature,[34] especially the structurally very similar ring closure of cyclopentane-1,3-diyl,[35] suggest 1–2 kcal/mol as an upper limit of the incremental effect of the solid medium. If this is correct, the rate constant for ring closure (k_b), even in fluid medium, cannot be much faster than that for ring opening (k_a). Hence, biradical **11-T** cannot be much less stable than bicyclic hydrocarbon **4**. The triplet biradical may not only be the ground state of the 2-isopropylidenecyclopentane-1,3-diyl manifold, but also the global ground state of the system **4**, **11-S**, and **11-T**. In that case, the dissociation energy of the C-1–C-4 bond of **4** would be negative.

There is no reason why this situation should not be observable in other strained systems. For example, a similar energetic relationship has been postulated on theoretical grounds for the system bicyclo[2.2.0]hexatriene ⇌ benzene-1,4-diyl.[36]

A corollary (whose significance may be psychological as well as chemical) is that for many biradicals, all of the unimolecular pathways for achieving the maximum Kekulé valence may be endothermic. Under these circumstances, the conventional classifications "molecule" and "reactive intermediate" lose their clarity. From the practical point of view, one may hope to construct and study some further members of the potentially large class of non-Kekulé molecules.

Experimental Section

Routine nuclear magnetic resonance (NMR) spectra (^{1}H) were taken on either a Varian EM-360A NMR spectrometer (60 MHz) or a Perkin-Elmer R-32 90 MHz NMR spectrometer, as indicated; high-resolution and variable-temperature spectra were taken on a Bruker Hx 270 MHz NMR spectrometer. ^{13}C spectra were taken with either a Varian CFT-20 NMR spectrometer or a Bruker HX 270 with a 67.19 MHz carbon probe. Deuteriochloroform was utilized as an NMR solvent, except where noted. Chemical shifts were recorded as follows: chemial shift δ (parts per million downfield from Me$_4$Si), multiplicity, number of protons, coupling constants (in Hertz), and assignment. ^{1}H 270-MHz coupling constants, although reported to three decimal points, are accurate to only ±0.18 Hz. Carbon multiplicities were established by off-resonance decoupling of the carbon spectra.

Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer, either as a neat film or as a KBr pellet. Ultraviolet spectra were recorded on a Shimadzu-Bausch and Lomb Spectronic 200. Mass spectra (MS) were recorded on a Hitachi Perkin-Elmer RMU-6 single-focusing instrument. The exact masses were obtained on a Hitachi Perkin-Elmer RMU-9 by Dr. Walter McMurray and Mr. Craig Whitehouse of the division of Health Physical Sciences of Yale University.

Preparative gas chromatography (GC) was performed on a Varian Aerograph Model 90-P with $^1/_4$ or $^3/_8$ in. aluminum columns; analytical GC was performed on a Perkin-Elmer 900 gas chromatograph on $^1/_8$ in. columns with a flame-ionization detector. Melting points were taken with a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were performed by Dr. R. C. Rittner of Olin Corporation, New Haven, CT.

Photolyses were carried out with either a 450-W medium-pressure Hanovia lamp or with a Rayonet Photochemical Reactor, using 16 tubes emitting 350-nm light. Photochemistry performed in the cavity of the ESR utilized a 200-W high-pressure mercury lamp.

Least-squares analysis of kinetic data was performed on a Texas Instruments SR 51-II, graciously loaned by Ms. Lan Shen.

Reagents. Chemicals used were generally reagent grade, except as spectral solvents, when they were spectrophotometric grade. Special purification procedures are noted where appropriate. Solvents were not dried or distilled unless indicated, except for tetrahydrofuran (THF),

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(29) (a) Siemionko, R.; Shaw, A.; O'Connell, G. C.; Little, R. D.; Carpenter, B. L.; Shen, L.; Berson, J. A. *Tetrahedron Lett.* **1978**, *3529*. (b) Siemionko, R.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3870.

(30) (a) Mazur, M.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 684. (b) Mazur, M.; Berson, J. A. *Ibid.*, accompanying paper in this issue.

(31) Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1977**, *99*, 6438.

(32) Some caution in choosing models for A factors of spin-forbidden reactions is advisable, since a wide range of values has been reported. For a summary, see ref 33.

(33) Platz, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1192.

(34) (a) Chezeau, J.-M.; Strange, J. H.; Brot, C. *J. Chem. Phys.* **1972**, *56*, 1380. (b) Fyfe, C. A.; Harold-Smith, D.; Ripmeester, J. *J. Chem. Soc., Faraday Trans. 2* **1976**, 2269.

(35) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857; **1979**, *101*, 4688.

(36) Noell, J. O.; Newton, M. D. *J. Am. Chem. Soc.* **1979**, *101*, 51.

which was always distilled over benzophenone sodium ketyl (under N_2) before use. All organolithium reagents used were low halide.

1,1-Dibromo-2-methyl-1-propene (12) (Scheme I). Following a general procedure of Posner et al.[37a] and Ramirez et al.,[37b] a mixture of 158 g (0.6 mol) of triphenylphosphine and 23 mL (18.1 g; 0.31 mol) of acetone in 150 mL of benzene was treated with 100 g of carbon tetrabromide in 500 mL of benzene, which was added by filtration through a short column of alumina. The contents of the flask were heated at reflux for 3 h and cooled. The reaction mixture was suction filtered to remove triphenylphosphine oxide, and the filter cake was rinsed several times with benzene. The combined filtrates were transferred to a 1-L round-bottom flask equipped with a magnetic stirring bar and a vacuum-jacketed distillation column. The solvent was distilled off at atmospheric pressure. The pot residue was then distilled at reduced pressure to give 30.0 g (140 mmol) of **12**,[37c] bp 65.6 °C (45 mmHg). The yield of **12** was 46%, based on CBr_4.

^1H NMR (90 MHz): δ 1.89 (s, 6 H).

Generation of 4 by Carbenoid Addition to Cyclobutene. In an oven-dried, 15-mL three-neck, round-bottom flask equipped with an addition funnel, magnetic stirring bar, N_2 inlet, and dry-ice condenser connected to the cyclobutene container was placed 150 μL (280 mg; 1.3 mmol) of 2-methyl-1,1-dibromopropene (**12**).[37] Dry ice and acetone were placed in the condenser, and 3 mL of cyclobutene[38] was distilled in, while the round-bottom flask was cooled to −78 °C with a dry ice–acetone bath. Two milliliters of 1.8 M methyllithium (3.6 mmol) was then added dropwise over several minutes. After the addition was complete, the solution was stirred at −78 °C for 30 min, then the reaction mixture was quenched by addition of 1 mL of methanol. Excess cyclobutene was distilled off at reduced pressure into a trap at −78 °C as the reaction mixture was allowed to warm to room temperature. The recovered cyclobutene was saved for future recycling. The pot residue was diluted with ethyl ether, transferred to a separatory funnel, and washed with H_2O and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was subjected to GC analysis (5% OV-101, column temperature 100 °C). Aside from a few volatile rapidly eluted fractions, the only material present had a GC retention time and peak shape identical with that of TMM dimers **7**–**10** prepared by pyrolysis of diazene **15**. NMR analysis of this fraction, collected by preparative GC (15% OV-17, column temperature 155 °C), showed it to be the TMM dimers **7**–**10**.

^1H NMR (90 MHz): δ 5.28 (bs), 1.71 (s), 1.69 (s), 1.4 (bs), 1.1 (s), 1.08 (s), 0.95 (s), 0.89 (s), 0.79 (s). ^1H NMR for authentic dimers, prepared by the photolysis of **15** (90 MHz): δ 5.28 (bs), 1.71 (s), 1.69 (s), 1.4 (bs), 1.1 (s), 1.08 (s), 0.95 (s), 0.89 (s), 0.79 (s).

In the preparation of TMM adducts **13-B** and **13-F** (X = CO_2Me) the above reaction was repeated, except that after being stirred for 15 min at −78 °C, the reaction mixture was quenched with 1 mL of methanol and stirred at −78 °C for an additional 15 min. Freshly distilled methyl acrylate (2 mL) was then added in one portion, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was worked up as before. GC analysis (5% OV-101, column temperature 80 °C) shows the presence of four TMM adducts (**13-B** and **13-F**, X = CO_2Me) identical in retention times and relative intensities with the TMM adducts formed[6] in the pyrolysis of **15** in the presence of methyl acrylate.

^1H NMR of adducts from cyclobutene after preparative GC (15% OV-17, column temperature 120 °C) (90 MHz): δ 3.65 (s), 1.3 (s), 1.25 (s), 1.21 (s), 1.05 (s), 0.99 (s), 0.93 (s). ^1H NMR of TMM adducts from pyrolysis of **15** in the presence of methyl acrylate (90 MHz): δ 3.65 (bs), 1.22 (s), 1.04 (s), 0.99 (s), 0.95 (s).

5-Isopropylidenebicyclo[2.1.0]pentane (4) from 2,3-Diaza-7-isopropylidenebicyclo[2.2.1]hept-2-ene (15). Method E. Adducts with Methyl Acrylate. In a Pyrex test tube were placed 5 mL of ethyl ether and 5 mg of **15**.[6] This solution was photolyzed at −78 °C (dry ice–methanol) with a 450-W Hanovia lamp for 1 h. After photolysis was stopped, 1 mL of freshly distilled methyl acrylate was added to the cold solution and the mixture was allowed to warm to room temperature. The solvent was removed under reduced pressure at room temperature, and the residue was dissolved in deuteriochloroform. NMR analysis showed complete photochemical decomposition of **15**, as evidenced by the lack of the bridgehead absorption at δ 5.3. The analysis also showed the presence of a carbomethoxy peak at δ 3.65, but no absorptions for the vinyl region of methyl acrylate. Therefore, it can be concluded that the excess methyl acrylate (bp 80 °C) had been removed and some methyl acrylate had reacted to form adducts. The upfield region of the NMR spectrum (δ 2–0.8) contained a variety of methyl absorptions. The chemical shifts for these absorptions were identical with those obtained from the pyrolysis of **15** in the presence of methyl acrylate. GC analysis (5% OV-101, column temperature 80 °C) revealed four adducts with identical retention times and similar relative ratios to those obtained from the aforementioned pyrolysis.

Table II. Rate Data for the Decomposition of 4 at 229.71 K ($CDCl_3$–$CFCl_3$)[a]

time, min	(CH_3) integral intensity, cm	ln (intensity)
0	3.65	1.2947
10	2.85	1.0473
20	2.25	0.8109
30	1.70	0.5306
40	1.35	0.3001
50	1.10	0.0953

[a] The rate constant calculated from these data by least-squares analysis is 4.057×10^{-4} s^{-1} ($t_{1/2}$ = 28.47 min). The correlation coefficient for these data is 0.991.

Table III. Rate Constants for Thermal Decomposition of Hydrocarbon 4 at Various Temperatures in $CDCl_3$–CCl_4

temp, K	$k \times 10^4$, s^{-1}	correl coeff	no. of $t_{1/2}$[a]
229.96	4.440	0.9909	1.76
224.96	2.673	0.9994	0.56
220.96	1.293	0.9942	0.20
214.96	0.519	0.9957	0.12
204.96	0.117	0.9486	0.03

[a] Number of half-lives over which data were collected. From these data least-squares analysis shows E_a = 13.57 kcal/mol, log A = 9.57 (A in s^{-1}); correlation coefficient = 0.9986.

Thermal Decomposition of 5-Isopropylidenebicyclo[2.1.0]pentane (4). In each of four clean, dry 5-mm NMR tubes, joined to 6 in., 6-mm glass tubes was placed 250 L of a 0.07 M stock solution of diazene **15** in 1:1 (v:v) $CDCl_3$–$CFCl_3$ (containing a small amount of benzene as an internal standard) or CD_2Cl_2. The solutions were thoroughly degassed by 4 freeze–thaw cycles and then sealed off under vacuum with an oxygen–methane flame. ^1H NMR of diazene **15** (90 MHz): δ 5.35 (s, 2 H, bridgeheads), 1.69 (s, 6 H), 1.8–1.5 (m, 2 H), 1.2–1.0 (m, 2 H). These tubes were then suspended in a dry ice–methanol bath at −78 °C and were photolyzed either with a 450-W Hanovia lamp or 350-nm light from the Rayonet. After 1 h (~95% conversion), photolysis was stopped, and the tubes were transferred to a dry ice–acetone bath. The transfer to the precooled probe (−80 °C) of the 270-MHz NMR spectrometer was accomplished as follows: the spinner was inserted onto the tube from the top, then this assembly was wiped with a tissue as the tube was removed from the bath and was briefly inserted into a liquid N_2 filled dewar. This procedure was accomplished in one motion. When the solvent had partially frozen, the tube was inserted in the depth gauge and the depth was adjusted. The tube was then reinserted in the dry ice–acetone bath to thaw the solution. After thawing, the tube was removed, wiped, cooled in liquid N_2 for ~2 s, and transferred to the precooled probe. It is important that the solvent not be completely frozen when the tube is inserted into the probe, as there is a high incidence of broken tubes under these conditions. Apparently the mechanical stress the NMR tube undergoes is great enough to break the more fragile frozen tubes. The ^1H NMR spectrum of hydrocarbon **4** at −80 °C is as follows (270 MHz): δ 2.17 (m, 2 H, ethano bridge hydrogens), 1.99 (bs, 2 H, bridgehead methines), 1.74 (s, 6 H, allylic methyls), 1.47 (d, 2 H, ethano bridge hydrogens). The ^{13}C spectrum is given in Table I. When the above procedure is repeated on the dideuteriodiazene (**15**-d_2),[18b] the spectrum obtained at −80 °C is as follows: ^1H NMR (270 MHz): δ 2.17 (bs, 1 H, –C*H*D–), 1.99 (bs, 2 H, bridgehead methines), 1.74 (s, 6 H, allylic methyls), 1.46 (bs, 1 H, –C*H*D–).

The decomposition of **4** with time was followed by monitoring the decrease in the integrated intensity of the methyl absorption. It had previously been established that no product resonances grew in under the methyl absorption. Each spectrum at a given temperature was obtained in the same fashion, using identical pulse angle (~90°), spectrum amplitude, sweep width (3000 Hz), and number of data points (8000). Four scans in the Fourier-transform mode were sufficient to obtain high-quality spectra (~1.359 s pulse delay between scans). Between data collections, spectra were either stored as their FID for later retrieval, or

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(37) (a) Posner, G. H.; Loomis, G. L.; Sawaya, H. S. *Tetrahedron Lett.* **1975**, *1373*. (b) Ramirez, F.; Desai, N. B.; McKelvie, N. *J. Am. Chem. Soc.* **1962**, *84*, 1745. (c) This compound had been prepared by a different method in the earlier literature: Farrell, J. K.; Bachman, G. B. *J. Am. Chem. Soc.* **1935**, *57*, 1281.

Table IV. Rate Constants for Thermal Decomposition of Hydrocarbon **4** at Various Temperatures in $CDCl_3$-$CFCl_3$

temp, K	$k \times 10^4$, s^{-1}	correl coeff	no. of $t_{1/2}$[a]
239.71	13.775	0.9956	2.5[b]
234.71	7.331	0.9955	2.0[b]
229.71	4.057	0.9991	1.75[b]
224.71	1.659	0.9913	0.5[c]
219.71	1.078	0.9959	0.6[b]
214.71	0.746	0.9938	0.5[c]

[a] Number of half-lives over which data were collected. [b] From these data least-squares analysis shows E_a = 13.26 kcal/mol, log A = 9.23 (A in s^{-1}); correlation coefficient = 0.9998. [c] The data at these temperatures were not used in calculating E_a, due to the low correlation coefficients and small $t_{1/2}$ covered. If these data are included, the activation parameters are E_a = 12.3 kcal/mol, log A = 8.4 (A in s^{-1}); but correlation coefficient is only 0.989.

were immediately subjected to Fourier transform, plotted out, and integrated. The number of data points contained in the methyl absorption is ~40. The integrations were measured by determining the portion of the spectrum to be measured (which was then held constant over that temperature run) and measuring the integral with a ruler marked in millimeters. The values obtained are therefore good to 0.5 mm. The reaction time was measured with a Precision-Scientific Time-it. A sample of this raw data is presented in Table II. After each kinetic run, the temperature of that run was determined by inserting a methanol sample, allowing this sample to reach thermal equilibrium, and then determining the chemical shift difference (in hertz) between the methyl and hydroxyl protons. The absolute temperature was then obtained from a table relating this shift difference to temperature. The precision of the value obtained was limited to ~±0.5 °C, as the measured shift differences were precise to only ±0.2 Hz. The error limits on the activation parameters were determined by applying the equations of Benson and O'Neal.[39]

For assessment of whether metals present in the reaction mixture were affecting the rate (and hence potentially the reproducibility), the preparation and decomposition of hydrocarbon **4** were carried out as described above, except that the NMR tube was rinsed with solutions of Na_2EDTA and deionized H_2O and finally dried at 100 °C. The solution of **15** in $CDCl_3$–$CFCl_3$ was stirred over Na_2EDTA in D_2O for 1 h, then the organic layer was pipetted into the NMR tube and sealed in vacuum after 4 freeze–thaw cycles. The rate constant for decomposition obtained at −41.6 °C was $4.51 \times 10^{-4}\ s^{-1}$. The calculated rate at this temperature is $5.14 \times 10^{-4}\ s^{-1}$, or 12% faster than the observed rate. These values are indistinguishable within the error limits and rule out any drastic effect of adventitious heavy metals on the rate of decomposition.

Photolysis of 15 at −196 °C. A 0.1 M solution of **15** in toluene-d_8 was prepared by the above procedure and was photolyzed for 5 h at −196 °C with 350-nm light in a Pyrex dewar with a cold finger. Toluene-d_8 was employed as a solvent as it formed a transparent glass on rapid cooling. Several times during the photolysis, the material was warmed to −78 °C for ~5 min and then recooled to −196 °C and the photolysis was continued. On warming to −78 °C and transfer to the probe of the 270-MHz NMR spectrometer, a spectrum of TMM dimers was obtained, superimposed on a spectrum of **4**. The amount of **4** present is difficult to determine quantitatively, but it is about 20% of the total reaction mixture. When the above photolysis in toluene-d_8 is repeated at −78 °C, **4** is obtained essentially pure and free of dimers, ruling out any triplet sensitization by the solvent.

Acknowledgment. The support of this work by the National Science Foundation (CHE 8011399) and the National Institute of General Medical Sciences (GM 23375) is gratefully acknowledged, as is the support provided by the National Science Foundation for the Northeast Regional NMR Facility at Yale University (CHE 7916210).

Appendix

We have shown earlier[21] that photolysis of diazene **15** in moderately viscous medium generates the triplet **11-T**, whose dimerization can be followed kinetically by electron paramagnetic resonance (EPR) spectroscopy. It may be instructive to compare the kinetic situation in that experiment with the one discussed above, in which **11-T** is generated from the hydrocarbon **4**.

In the EPR experiment, the disappearance of the signal of the triplet **11-T** is a cleanly second-order reaction.[21] This immediately eliminates any substantial contribution of a reaction in which **11-T** is captured by any of hydrocarbon **4** that might be formed directly in the photolysis of diazene **15**. Compound **4** is EPR inactive, and the reaction **11-T** + **4** → dimer would only be first order in the EPR signal.

However, **4** might also be formed reversibly from **11-T**. This is just the reverse of the situation encountered in the pyrolysis of hydrocarbon **4**, but now **4** need not be present in more than microscopic concentration. The following mechanism and the assumption of a steady state in the intermediate A lead to eq 6, in which the designation of the rate constants is the same as those of the corresponding steps in Mechanism II.

$$\mathrm{B}\ (\mathbf{11\text{-}T}) \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{A}\ (\mathbf{4})$$

$$\mathrm{B} + \mathrm{A} \xrightarrow{k_3} \mathrm{C}\ (\text{dimers } \mathbf{7\text{–}10})$$

$$-\mathrm{d[B]}/\mathrm{d}t = 2k_{-1}k_3[\mathrm{B}]^2/(k_3[\mathrm{B}] + k_1) \qquad (6)$$

If the formation of A is the rate-determining step, $k_3[\mathrm{B}] >> k_1$, whereupon eq 6 reduces to

$$-\mathrm{d[B]}/\mathrm{d}t \simeq 2k_{-1}[\mathrm{B}] \quad \text{(first order)} \qquad (7)$$

This does not correspond to the experimental facts and can be excluded.

If B and A are in rapid equilibrium, $k_1 >> k_3[\mathrm{B}]$, eq 6 reduces to

$$-\mathrm{d[B]}/\mathrm{d}t \simeq (2k_{-1}k_3/k_1)[\mathrm{B}]^2 \quad \text{(second order)} \qquad (8)$$

This mechanism corresponds to the observed kinetic order, but the observed absolute rate[21] argues against it and in favor of the triplet + triplet mechanism. As was the case with a hypothetical **11-T** + **11-S** mechanism for dimerization in the EPR experiment,[21] the upper limit of the concentration of **4** permitted by the singlet–triplet energy gap does not provide enough **4** to produce the observed rate constant in an **11-T** + **4** reaction unless the mechanistic rate constant is assumed to exceed the bimolecular encounter frequency.

Registry No. 4, 72447-89-3; **7**, 22935-21-3; **8**, 31689-34-6; **9**, 31689-36-8; **10**, 31689-35-7; **12**, 13353-06-5; **13-B**, 80963-68-4; **13-F**, 80964-03-0; **15**, 31689-32-4; cyclobutene, 822-35-5; methyl acrylate, 96-33-3.

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(38) (a) Cope, A. C.; Haven, A. C., Jr.; Ramp, F. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1953**, *74*, 4867. (b) Ashe, A. J., III, Ph.D. Thesis (with K. B. Wiberg), Yale University, 1967.

(39) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, No. 21, p 8.