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Chemistry of Bicyclo[3.1.0]hex-1-enes Contrasted with That of 2-Alkylidenecyclopentane-1,3-diyls[1,2]

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Abstract: Reaction of 1,1-dibromo-2,6-dimethylhepta-1,5-diene (**9**) with MeLi in Et_2O at −78 °C results in cyclization to 2,6,6-trimethylbicyclo[3.1.0]hex-1-ene (**3**), which undergoes [$\pi + \pi$] and [$\sigma + \pi$] dimerization to **6** and **11**, respectively (Scheme II). At 0 °C, this reaction gives in addition a set of trimethylenemethane dimers (including **7**), which result from ring opening of **3** at the C_5–C_6 bond. Metalation of 1,1-dibromo-2-methylhexa-1,5-diene (**21**) causes cyclization to 2-methylbicyclo-[3.1.0]hex-1-ene (**22**), which dimerizes to an ene product (**25**) in addition to [$\pi + \pi$] and [$\sigma + \pi$] dimers **24** (or **24a**) and **23** (or **23a**) (Scheme IV). These products are formed in the temperature-invariant proportions 5:2:5:1. The intermediate bicyclo[3.1.0]hex-1-ene (**22**) can be intercepted with 1,3-diphenylisobenzofuran (**26**) to give a low yield of the Diels–Alder adducts **27**. When **22** is generated by treatment of *N*-nitroso-5-methyl-5-(3-butenyl)oxazolidone (**28**) with NaOH under phase-transfer conditions in the presence of cyclopentadiene, both the intermediate carbenoid **30** and the bicyclic hydrocarbon **22** can be intercepted as characteristic adducts. The chemistry of bicyclo[3.1.0]hex-1-enes does not resemble that of the singlet trimethylenemethane species assigned the structures of 2-alkylidenecyclopentane-1,3-diyls.

One of the motivations for a study of bicyclo[3.1.0]hex-1-ene derivatives (**1**) is to determine whether such species can be the true active entities in the behavior nominally ascribed to 2-alkylidenecyclopentane-1,3-diyls (**2**).[4] The present work[1] shows that simple derivatives of **1** have chemical properties that differ in distinctive ways from those attributed to derivatives of **2**.

1

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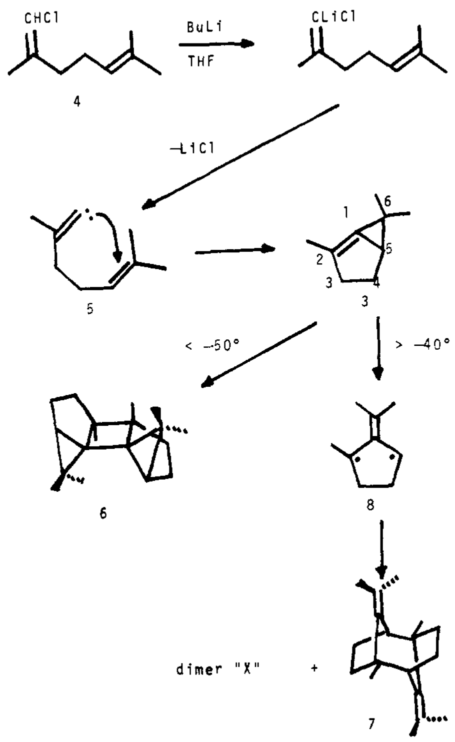
Prior knowledge of bicyclo[3.1.0]hex-1-enes rests on the pioneering work of Köbrich,[5,6] which was interrupted by his untimely death. Köbrich and Heinemann generated the 2,6,6-trimethyl derivatives **3** by treatment of 1-chloro-2,6-dimethylhepta-1,5-diene (**4**) with butyllithium in tetrahydrofuran (Scheme I). Initial metallation of the vinyl chloride followed by thermal α elimination of LiCl gave the unsaturated carbenoid **5**, which cyclized by intramolecular addition to the double bond. The bicyclic product was not directly detected but dimerized under the conditions of reaction or workup.

When the reaction was carried out at −50 °C or below, a crysalline product was obtained, which later was identified by an X-ray structure determination as the $_2\pi_s + {}_2\pi_s$ dimer **6**.[5,6] Significantly, the same reaction run at temperatures above −40 °C gave a minor amount of **6** but now gave two new products, **7** (or its regioisomer with vicinal bridgehead methyl groups) and a dimer ("X") characterized as being "of lower symmetry".[5] Compound **7** is a trimethylenemethane dimer, and its formation was rationalized by a mechanism in which cleavage of the weak cyclopropane ring bond in **3** was followed by dimerization of the biradical **8**.

The observed temperature dependence of the product composition is consistent with the presence of a finite barrier to thermal dissociation of the C-5–C-6 bond of the bicyclo[3.1.0]hex-1-ene **3**.[5,6] This offers hope that it might be possible to observe the substance directly by nuclear magnetic resonance (NMR) spectroscopy, or at least to put a lower limit on its lifetime, provided that a method for generating it at lower temperatures could be found. A potential solution to the problem is based on the assumption that the metallation and α-elimination steps should be more facile from the geminal dibromide **9** (Scheme II) than those from the chloride **4**. Note that in this and the related studies to be described, the alkyl group on the double bond in a position vicinal to the eventual carbenic center is needed. A hydrogen at that site, for example, would migrate and give a terminal alkyne.[6]

Scheme I



Formation and Dimerization of Bicyclo[3.1.0]hex-1-enes by Carbenoid Cyclization. The required compound 1,1-dibromo-2,6-dimethyl-hepta-1,5-diene (**9**), can be prepared by treatment of 6-methylhept-5-en-2-one (**10**), with 2 equiv of carbon tetrabromide and four of triphenylphosphine in boiling benzene, according to a general procedure of Posner,[7a] which is based upon earlier work by Ramirez and co-workers.[7b] Reaction of dibromide **9** with methyllithium in ether at −78 °C (Scheme II) leads to a

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[1] For a preliminary communication see: (a) Rule, M.; Berson, J. A. *Tetrahedron Lett.* **1978**, 3191. For relevant work, see: (b) Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7094. (c) Salinaro, R. F.; Berson, J. A. *Ibid.* **1982**, *104*, 2228.

[2] Taken in part from the Senior Thesis of D. R. Pratt, Yale College, 1979.

[3] Dox Fellow, 1981.

[4] For a review, see: Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.

[5] Köbrich, G.; Heinemann, H. *Chem. Commun.* **1969**, 493.

[6] (a) Köbrich, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 41. (b) Köbrich, G. *Ibid.* **1972**, *11*, 473. (c) Köbrich, G. *Ibid.* **1973**, *12*, 464.

[7] (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.

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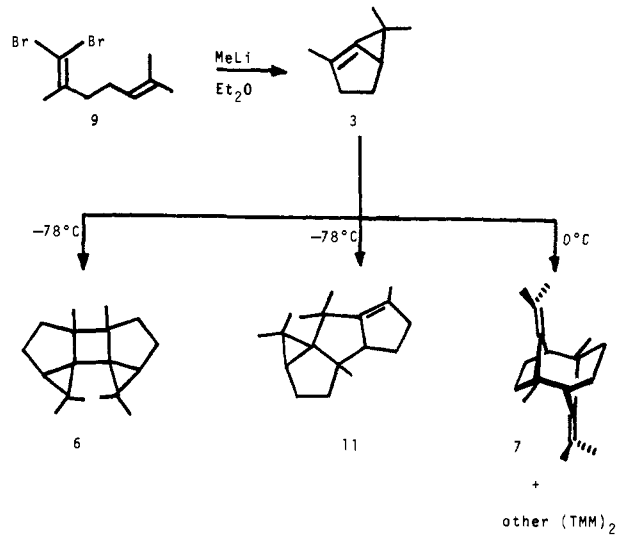
Scheme II



hydrocarbon product consisting mainly of the [$\pi + \pi$] dimer **6** together with about 5% of a new substance to which we tentatively assign the structure **11**, a [$\sigma + \pi$] dimer of the bicyclo[3.1.0]hex-1-ene (**3**), on the basis of its ^{1}H NMR spectrum. Although this product has only one bicyclo[3.1.0]hexane unit intact and therefore could be viewed formally as the cycloadduct of the TMM biradical **8** and the olefin **3**, evidence reported elsewhere[1b,c] strongly opposes this interpretation.

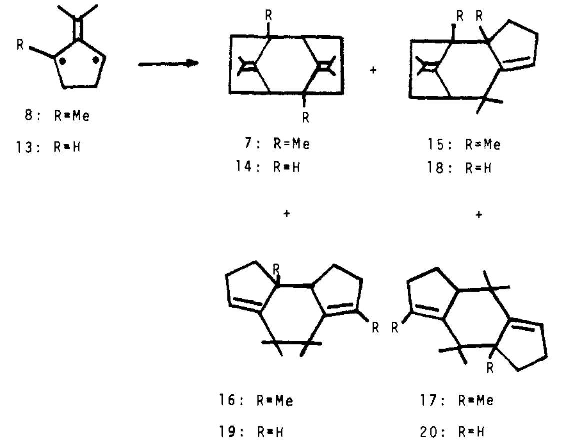
A side reaction, presumably involving attack of the 1-bromo-1-lithium compound on the methyl bromide formed in the metalation step, leads to the vinyl bromide **12**.

12

When the metalation of dibromide **9** is carried out at 0 °C, a small amount of the [$\pi + \pi$] dimer **6** again is observed, but the major hydrocarbon product now is a complex mixture, from which the symmetrical trimethylenemethane (TMM) dimer **7** can be isolated by gas chromatography (GC) and identified by its ^{1}H NMR spectrum (three sharp Me singlets). The remainder of the material consists of a mixture of dimers of C_9H_{14} which we believe to be also of the $(TMM)_2$ type. This assignment of structure is based in part on circumstantial and analogical evidence. These products occur only at higher temperatures, which suggests that a TMM intermediate (**8**) is involved. Thus, the homologously related TMM **13**, generated in a different manner, gives a dimer mixture containing not only product **14** (analogous to **7**) but also **18–20**.[8,9] This suggests that the analogous dimers **15–17** should be formed from **8** (Scheme III). Moreover, the NMR spectrum of the dimer mixture from **9** shows olefinic proton absorptions near δ 5.3, which are consistent with the presence of TMM dimers such as **15–17**, and the mass spectrum shows a base peak at *m/e* 122, which corresponds to the monomer cation. This symmetrical mass fragmentation pattern also is observed in the dimers **18–20**.[8,9] We assume, therefore, that the TMM dimers **15–17** represent the structures of Köbrich's dimer "of lower symmetry" ("X" of Scheme I).

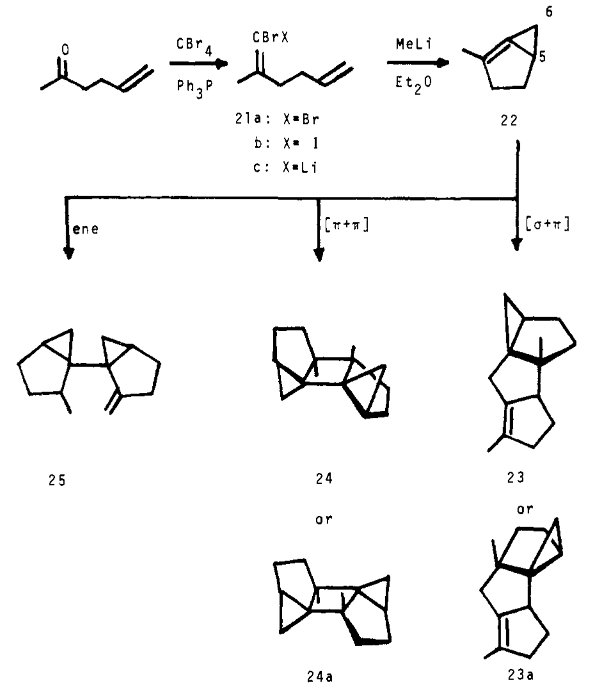
With reference to Schemes II and III, the behavior of 2,6,6-trimethylbicyclo[3.1.0]hex-1-ene (**3**) may be interpreted as the result of a competition between dimerization of the intact bicyclic system, leading to products **6** and **11**, and ring opening to a TMM, which gives the dimers **7**, **15**, **16**, and **17**. The observation that higher temperature favors the TMM products suggests that the activation energy for cleavage of the C-5–C-6 bond is greater than that for dimerization of **8**. We also find that relative to the TMM dimers, the yield of bicyclo[3.1.0]hex-1-ene dimers **6** and **11** increases as the initial concentration of reactant **9** is increased. This is again interpretable in terms of competition between a bimolecular dimerization and a unimolecular ring opening.

Scheme III[a]



[a] Dimers of the TMM biradicals **8** and **13**. In the series derived from **8**, only one relative orientation of the two methyl groups designated R is shown for each ring skeleton, although additional regioisomers probably are formed.

Scheme IV



This competition also is strongly dependent on the substitution pattern of the bicyclo[3.1.0]hex-1-ene system. A more complete study is underway,[10] but the result of replacing the *gem*-methyl groups of **3** with hydrogens provides information of special relevance here (Scheme IV).

The dibromomethylenation of 5-hexen-2-one gives 1,1-dibromo-2-methylhexa-1,5-diene (**21a**), which when treated with methyllithium in ether at −78 °C gives a 95% yield of a mixture of three hydrocarbons. Two of these, **23** and **24**, are dimers of the methylbicyclo[3.1.0]hex-1-ene **22** and have structures homologous with those of the [$\sigma + \pi$] (**11**) and [$\pi + \pi$] (**6**) dimers of the trimethylbicyclo[3.1.0]hex-1-ene (**3**). The third dimer (**25**) is the product of an ene reaction between two molecules of **22**:

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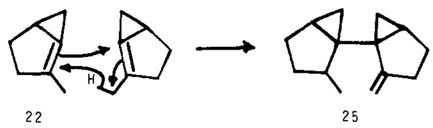
(8) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. *J. Am. Chem. Soc.* **1971**, *93*, 1544.

(9) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276.

(10) Salinaro, R. F. Ph.D. Thesis, Yale University, 1982.



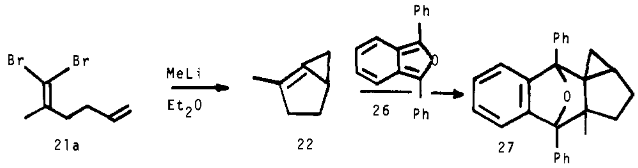
Although all three reactions appear to be highly regio- and stereospecific, the spectroscopic data do not distinguish the structures of **23** and **24**, respectively, from regioisomers **23a** and **24a**, which would result from addition to a monomer's π bond in the alternative orientation.

The carbenoid cyclization can be observed at even lower temperature. Metalation of the iodobromodiene **21b**, which is prepared by iodination of the α-bromolithium compound **21c**, can be effected at −110 °C, and cyclization occurs at −90 °C. Again, the same three products, **23**, **24**, and **25**, are formed. We also observe only these dimers when the reaction is carried out at 0 °C.

The proportions of the products **23**:**25**:**24** are 5:2.5:1 at all the temperatures investigated. Moreover, these ratios are invariant with the concentration of dihalide reactant from 0.1 to 3×10^{-4} M. The most straightforward interpretation of the insensitivity of the product proportions to temperature and concentration is that in the case of the less highly substituted bicyclo[3.1.0]hex-1-ene of Scheme IV (**22**), dimerization competes with ring opening to a TMM more effectively than in the case of the homologous bicyclo[3.1.0]hex-1-ene (**3**) of Scheme II. At the structural level, the reasons for this presumably include the bond-weakening effect of the gem-dimethyl substitution at C-6 of **3** and perhaps a steric retardation to dimerization of the more heavily substituted bicyclo[3.1.0]hex-1-ene (**3**). Apparently, this retardation is mode selective, since the dimerization of **3** (Scheme II) gives mainly the $[\pi + \pi]$ product **6** (corresponding to **24** of Scheme IV), but no ene product (corresponding to **25**) and <10% $[\sigma + \pi]$ dimer (corresponding to **23**).[1b,c]

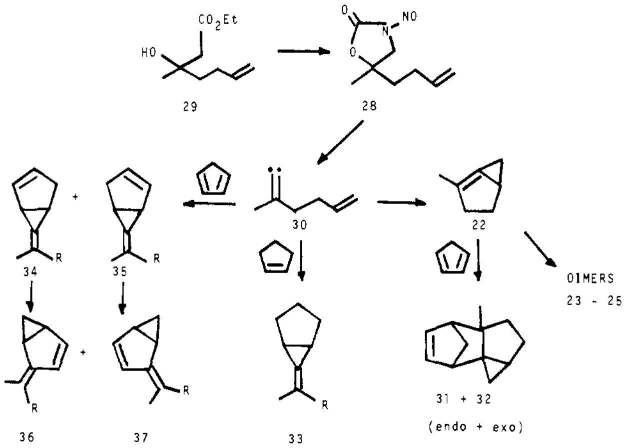
The course of the carbenoid reaction of Scheme IV can be followed at low temperature by effecting metal–halogen exchange between the iodobromo compound **21b** and CH_3Li in diethyl-d_{10} ether at −110 °C in the probe of the 270-MHz spectrometer. Formation of the intermediate bromolithium compound **21c** can be observed spectroscopically. This substance decomposes at −90 °C with the simultaneous appearance of the ^1H NMR absorptions characteristic of the dimers **23**, **24**, and **25**. No signals attributable to the monomeric bicyclo[3.1.0]hex-1-ene (**22**) are observed. With Fourier transform data acquisition, the time needed to accumulate detectable signals of the dimers is about 1 min. It may be concluded, therefore, that the lifetime of the monomer **22** at −90 °C is less than that.

Intermolecular Capture of Bicyclo[3.1.0]hex-1-enes. When the carbenoid cyclization of the dibromide **21a** is carried out at 0 °C in diethyl ether in the presence of an excess of 1,3-diphenylisobenzofuran (**26**), a small amount (~5% yield) of a 2:1 mixture of stereoisomeric Diels–Alder adducts **27** can be obtained. Attempts to prepare other adducts by this path comprise a history of frustration: Furan does not capture 2-methylbicyclo[3.1.0]hex-1-ene, even when used as solvent for the carbenoid cyclization, and other common dienes (butadiene, cyclopentadiene) are incompatible with the alkyllithium reagent needed to effect reaction.



This problem can be circumvented by the generation of **22** by a different route. Newman's method[11] for preparation of dialkylvinylidenes involves the treatment of a 5,5-dialkyl-*N*-nitrosooxazolidone with an alkali metal alkoxide. The appropriate precursor of the vinylidene **30**, which can lead to **22**, is the oxazolidone **28** (Scheme V), which is readily prepared by standard methods from the known[12] ethyl 3-hydroxy-3-methyl-6-heptenoate (**29**). In the present work, the Newman conditions are modified. Treatment of **28** with aqueous sodium hydroxide under phase-transfer conditions (tetraheptyl ammonium bromide, 33% NaOH, ether–pentane, −6 °C) gives the same three dimers **23**–**25** in approximately the same proportions observed from the dibromide precursor (Scheme IV). When the reaction is carried out in the presence of cyclopentene, these dimers are accompanied by the hydrocarbon **33**, which results from capture of the carbene **30** before it cyclizes. In the presence of cyclopentadiene, a similar competition between intramolecular cyclization and intermolecular capture of the carbene can be observed. Dimers **23**–**25** are accompanied by compounds **36** and **37**, which are secondary products resulting from vinylcyclopropane rearrangement[11c,13] of the carbene–cyclopentadiene adducts, **34** and **35**. In addition, two other substances are formed which are tentatively identified by mass and NMR spectroscopy as the stereoisomeric cyclopentadiene Diels–Alder adducts **31** and **32**.

Scheme V



Comparison of the Chemistry of 2-Alkylidenecyclopenta-1,3-diyls and Bicyclo[3.1.0]hex-1-enes. The characteristic feature of the chemistry of the bicyclo[3.1.0]hex-1-enes is the presence of the intact bicyclic ring system in its dimers and cycloadducts. Compounds containing this structural unit are not observed in products from the trimethylenemethane species **13** or **38** when they are generated from the diazenes **39** and **40**, respectively,[8,9,14] and are found only as minor components in the cycloadduct mixture from **41**, generated from diazene **42**. In the case of the compounds derived from precursors having unsubstituted terminal methylene groups (**38** and **41**), it should be especially easy to detect the presence of the bicyclo[3.1.0]hexane unit in the NMR spectra of the dimers or cycloadducts. The endo cyclopropyl methylene proton in each of the dimers **23**–**25** (Scheme IV) and in the Diels–Alder adducts **27** and **31**–**32** (Scheme V) is strongly shielded and appears far upfield at δ 0.2–0.6, in a region that is not associated with any of the other protons in these compounds. A careful search of this region in the 270-MHz spectra of the dimers

39: R = Me, X = H
40: R = X = H
42: R = H, X = OMe

13: R = Me, X = H
38: R = X = H
41: R = H, X = OMe

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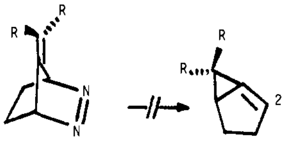
[11] (a) Newman, M. S.; Patrick, T. B. *J. Am. Chem. Soc.* **1970**, *92*, 4312. (b) Newman, M. S.; Okarodudu, A. O. M. *Ibid.*, **1968**, *90*, 4189. (c) Newman, M. S.; Zwan, M. C. V. *J. Org. Chem.* **1974**, *39*, 761.

[12] Rupert, J. F.; White, J. D. *J. Org. Chem.* **1974**, *39*, 270.

[13] Rey, M.; Huber, U. A.; Dreiding, A. S. *Tetrahedron Lett.* **1968**, 3583.

[14] (a) Siemionko, R.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3870. (b) Siemionko, R. Ph.D. Dissertation, Yale University, 1978.

obtained by deazetation of **40** and of the cyclopentadiene adducts of the derived biradical **38** shows these resonances to be absent.[14] Moreover, when the deazetation of **40** is carried out in the presence of 1,3-diphenylisobenzofuran under the same conditions used to trap 2-methylbicyclo[3.1.0]hex-1-ene (**22**) as the Diels–Alder adduct, no evidence of a corresponding adduct of the bicyclic hydrocarbon **43** is found. It is true that the present work does not generate this very compound in the carbenoid ring closures of Schemes II, IV, and V, but instead is restricted to analogues bearing a C-2 methyl group. Nevertheless, it seems unlikely that this structural difference could completely alter the chemistry of the bicyclic compound and thereby vitiate the use of the 2-methyl derivative **22** as a model for the parent system **43**. We infer, therefore, that the properties of the diyls generated from the diazenes **39** and **40** are not consistent with the chemistry expected of bicyclo[3.1.0]hex-1-enes.



43: R = H

Activation Energy for Ring Opening of Bicyclo[3.1.0]hex-1-enes. A crude lower limit for the strength of the strained C_5–C_6 bond of 2-methylbicyclo[3.1.0]hex-1-ene (**22**) can be calculated from the observation that when a 3×10^{-4} M solution of the dibromide **21a** is treated slowly with excess methyllithium at 0 °C, only the bicyclo[3.1.0]hex-1-ene dimers **23**–**25** are formed. The TMM triplet biradical that would result from C_5–C_6 bond cleavage should dimerize in the usual way (see Scheme III), but no such dimers are observed. The hypothetical triplet dimerization rate can serve as an internal "clock." If we assume that a 5% yield of TMM-derived dimers would be detectable (corresponding to 10% of ring-cleavage), that the rate-determining step of $(TMM)_2$ formation is ring cleavage to a triplet TMM, that the conversion of dibromide **21a** to hydrocarbon **22** is instantaneous and quantitiative, i.e., [**22**] is 3×10^{-4} M, and that the rate of dimerization of the bicyclo[3.1.0]hex-1-ene **22** cannot exceed the diffusion-controlled limit, k_d, we can write eq 1, where k_c is the unimolecular rate constant for bond cleavage. Substituting appropriate values

$$k_c \leq 0.1 k_d[\mathbf{22}] \qquad (1)$$

for k_d and [**22**], we obtain $k_c \leq 3 \times 10^4\ \mathrm{s}^{-1}$ at 0 °C. This corresponds to $\Delta G^{\ddagger} \geq 10$ kcal/mol. Since the Arrhenius pre-exponential term for this reaction is likely to be near $10^{9.5}\ \mathrm{s}^{-1}$ by analogy to the related spin-forbidden cleavage of 5-alkylidenebicyclo[2.1.0]pentanes,[15] a lower limit of 6.4 kcal/mol may be assigned to E_a for C_5–C_6 bond rupture in **22**.

Experimental Section

Routine nuclear magnetic resonance (NMR) spectra (^{1}H) were taken on either a Varian E-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 67.9 MHz carbon probe. Deuteriochloroform was used as an NMR solvent, except where noted. Chemical shifts were recorded as follows: chemical shift δ (parts per million downfield from Me_4Si), 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 spectrometer, 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.

Metalation of 1,1-Dibromo-2,6-dimethylhepta-1,5-diene (9) is described in the accompanying paper.[1b]

1,1-Dibromo-2-methyl-1,5-hexadiene (21a). In a 1-L, three-neck round-bottom flask fitted with reflux condenser, positive N_2 pressure, mechanical stirrer, and a short alumina column were placed 157.2 g (0.6 mol) of triphenylphosphine, 15 g (0.15 mol) of 5-hexen-2-one, and ~150 mL of benzene. Next, 99.5 g (0.3 mol) of carbon tetrabromide was dissolved in a minimal amount of benzene and was flushed through the alumina column with 500 mL of benzene. The alumina column was removed, that neck of the flask was stoppered, and the reaction mixture was heated to reflux for 24 h. The material was cooled to room temperature and suction filtered to remove triphenylphosphine oxide; the filter cake was washed repeatedly with benzene. The filtrate was then concentrated under reduced pressure until solidification occurred. This residue was triturated with hexane and the hexane washings were concentrated under reduced pressure. The resulting residue was distilled by bulb-to-bulb distillation at room temperature and 50 μm vacuum into a trap at −78 °C to remove unreacted ketone. The pot residue was then flash distilled in the same apparatus at 50 μm with a heat gun. The product obtained by this procedure was typically >90% pure, as determined by NMR and GC analysis. High-purity material could be obtained by preparative GC (25% Carbowax 20 M, column temperature 150 °C). The yield of **21a** was 39% (15.0 g, 59 mmol).

Mass spectra parent *m/e* 252, 254, 256 (1:2:1); ^{1}H NMR (90 MHz) δ 5.5–6.0 (m, 1 H), 4.9–5.2 (pseudo t, 2 H), 2.6–2.0 (m, 4 H), 1.85 (s, 3 H). The density is ≃1.75 g/mL.

Metalation of 21a. 4,8-Dimethyltetracyclo[6.4.0.0^{3,7}.1^{1,11}]dodec-1-ene (23), (2-Methylbicyclo[3.1.0]hexyl)-2-methylenebicyclo[3.1.0]hexane (25), and 1,2-Dimethyl[6.4.0.0^{2,7}.1^{5,7}.1^{8,10}]dodecane (24). Into an oven-dried, 100 mL, three-neck flask fitted with a rubber septum, glass stopper, magnetic stirring bar, and N_2 inlet were placed 250 μL (437 mg; 1.72 mmol) of **21a** and 50 mL of anydrous ethyl ether. The solution was cooled to −78 °C with a dry ice–acetone bath, and 4 mL of 1.2 M methyllithium (5 mmol) was added in one portion. After the solution was stirred for 15 min, solid ammonium chloride was added and the solution was warmed to room temperature. The material was poured into a separatory funnel, washed with H_2O and brine, then dried over $MgSO_4$. The solution was concentrated under reduced pressure, and the residue was purified by preparative GC (25% Carbowax 20 M, column temperature 150 °C, or 25% γ-methyl-γ-nitropimelonitrile, column temperature 90 °C).

Spectral data for **23**: ^{1}H NMR (270 MHz) δ 1.638 (s, 3 H, allylic CH_3), 1.255 (m, 1 H, J = 5.148 and 8.089, endo cyclopropyl),[16] 0.902 (s, 3 H, quaternary CH_3), 0.592 (pseudo t, 1 H, J = 5.148 and 4.412, exo cyclopropyl); ^{13}C NMR (67.9 MHz) δ 143.252 (1 C, quaternary olefinic C), 125.672 (1 C, quaternary olefinic C), 52.219–11.664 (12 C, aliphatic C); mass spectra parent *m/e* 188.15509, calcd for $C_{14}H_{20}$, 188.15660.

Spectral data for **25**: ^{1}H NMR (270 MHz) δ 4.967 (s, 1 H), 4.816 (s, 1 H, terminal CH_2), 1.327 (m, 1 H), 1.022 (m, 1 H, J = 4.412 and 8.098, cyclopropylmethines), 0.976 (d, 3 H, J = 6.619, tertiary CH_3), 0.760 (m, 3 H, J = 4.412 and 8.098, cyclopropyl CH_2), 0.447 (pseudo t, 1 H, J = 4.412, endo cyclopropyl), 0.207 (q, 1 H, J = 5.148 and 8.089, exo cyclopropyl); ^{13}C NMR (67.9 MHz) δ 154.555 (1 C, quaternary olefinic C), 103.275 (1 C, secondary olefinic C), 37.936–9.572 (12 C, aliphatic C); mass spectra parent *m/e* 188.15509, calcd for $C_{14}H_{20}$, 188.15660.

Spectral data for **24**: ^{1}H NMR (270 MHz) 1.109 (s, 6 H, quaternary CH_3), 0.499 (q, 2 H, J = 5.148 and 8.089, exo cyclopropyl), 0.237 (pseudo t, 2 H, J = 4.413 and 5.147, endo cyclopropyl); ^{13}C NMR (67.9 MHz) 53.739 (2 C), 42.877 (2 C), 36.032 (2 C), 30.866 (2 C), 23.117 (2 C), 18.726 (2 C), 11.60 (2 C); mass spectra parent *m/e* 188.15563, calcd for $C_{14}H_{20}$, 188.155660.

1-Bromo-1-iodo-2-methyl-1,5-hexadiene (21b). In a flame-dried, 250-mL, three-neck, round-bottom flask (one neck fitted with a two-neck adaptor) equipped with a mechanical stirrer, addition funnel, thermocouple, and N_2 inlet were placed 90 mL of dry THF–ethyl ether (1:1) and 4 mL (4 mmol) of 1 M methyllithium. The solution was cooled to −100 °C with an ethanol–liquid nitrogen bath, and 0.3 mL (2 mmol) of dibromide **21a** in 10 mL of ethyl ether was added dropwise over 5 min, while the solution temperature was kept below −95 °C. After addition

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[15] (a) Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7088. (b) Rule, M.; Mondo, J. A.; Berson, J. A. *Ibid.* **1982**, 104, 2209.

[16] (a) Dauben, W. G.; Wipke, W. T. *J. Org. Chem.* **1967**, *32*, 2976. (b) Wiberg, K. B.; Barth, D. E.; Schertler, P. H. *Ibid.* **1973**, *38*, 378.

was complete, the solution was stirred an additional 20 min. Excess iodine dissolved in a minimum amount of THF was added slowly, again maintaining the solution temperature below −95 °C. when addition was complete (the iodine color of the solution did not fade), the mixture was slowly warmed to 0 °C. The solution was poured into a separatory funnel and washed with aqueous sodium thiosulfate until clear. The organic layer was then washed with brine and dried over $MgSO_4$ and the solvent evaporated to give a greenish residue. Preprative GC of this material gave pure **21b**, uncontaminated with **21a**. The dimers **23–25** were not formed under these reaction conditions.

Mass spectra parent *m*/*e* 300, 302 (1:1); ^1H NMR (90 MHz) δ 5.5–6.0 (m, 1 H), 4.9–5.2 (pseudo t, 2 H), 2.6–2.0 (m, 4 H), 1.85 (s, 3 H).

NMR Study of the Thermal Decomposition of 1-Bromo-1-lithio-2-methyl-1,5-hexadiene (21c). An NMR tube was sealed to a small manifold equipped with two stopcocks and a rubber septum. One stopcock was used for N_2 inlet, and the other was connected to a vacuum. A 100-μL sample of 1.2 M CH_3Li in ether was syringed into the tube. The ether was evaporated under vacuum, the system filled with N_2, and the long finger immersed in an ethanol–liquid N_2 bath at −110 °C. A solution of 10 μL of the bromoiododiene **21b** in 300 μL of ethyl-d_{10} ether was added in one portion. Then the solution was frozen in a liquid N_2 bath and placed under a high vacuum and the NMR tube-finger was sealed off with an oxygen–methane flame. The NMR tube was then replaced in the ethanol–liquid N_2 bath (at −110 °C) for 30 min to allow halogen–metal exchange to proceed to completion. Following this, the tube was placed in a liquid N_2 bath and transferred to the probe of the 270-MHz NMR, precooled to −100 °C. On melting of the ether solution, a spectrum of **21c** was observed (essentially identical with the NMR spectrum of dibromodiene **21b**) superimposed on the residual protons in the solvent (δ 3.413 and 1.196) and methyl iodide (2.178). (The internal chemical shift reference was excess methyllithium δ −1.3[17]). On warming to −90 °C decomposition set in, as evidenced by the change in the vinyl region; two singlets (δ 4.956 and 4.804) appeared and increased in intensity with time, while the remainder of the vinyl region decreased in intensity. Also cyclopropyl protons (δ 0.225, 0.462, 0.612, 0.811) and methyl absorptions (δ 0.939 and 0.997) appeared concurrently. Decomposition was complete on warming to −70 °C. (The chemical shifts of these absorptions are slightly different from those reported for **23–25** due to the different internal reference and solvent, but the spectra are virtually superimposable.) No further changes were observed on warming to 0 °C, and no transient absorptions that could be assigned to **22** were observed.

3,4-Benzo-6-methyl-11-oxatetracyclo[4.4.0.$1^{2,5}$.$1^{1,7}$]undecene (27). In an oven-dried, three-neck, 100-mL flask fitted with a magnetic stirring bar, addition funnel, and N_2 inlet were placed 1.0 g (3.7 mmol) of 1.3-diphenylisobenzofuran, 25 mL of anhydrous ethyl ether, and 2 mL of 1.2 M methyllithium (2.4 mmol). The solution was cooled to 0 °C with an ice-water bath, and 200 μL (350 mg; 1.38 mmol) of **21b** in 25 mL of anhydrous ethyl ether was added dropwise over 30 min. After addition was complete, the solution was stirred at 0 °C for 30 min, then 20 mL of H_2O and additional ether were added. The solution was transferred to a separatory funnel and the layers were separated. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was percolated through a neutral alumina column with benzene. The eluant was evaporated under reduced pressure, and the residue was subjected to a high vacuum (50 μm) for 13 h. NMR analysis of the aliphatic region of this product showed two isomers in a ratio of 1:2, presumably an exo:endo mixture. This residue consisted of small amounts of **27** mixed with 1,3-diphenylisobenzofuran. The estimated yield of **27** was ~5%.

Major isomer of **27**: ^1H NMR (270 MHz) δ 1.037 (m, 1 H, exo cyclopropyl), 0.977 (s, 3 H, quaternary CH_3), 0.710 (q, 1 H, J = 5.148 and 4.412, endo cyclopropyl); parent *m*/*e* 364.18135, calcd for $C_{27}H_{24}O_4$, 364.18283. Minor isomer of **27**: ^1H NMR (270 MHz) δ 1.143 (q, 1 H, J = 5.883 and 8.059, exo cyclopropyl), 0.830 (s, 3 H, quaternary CH_3), 0.569 (q, 1 H, J = 5.883), 3.677 (endo cyclopropyl).

5-(1-Butenyl)-5-methyl-*N*-nitroso-2-oxazolidone (28). A crude sample of 3-hydroxy-3-methyl-6-heptenoic acid hydrazide was prepared by treatment of 1 equiv of ethyl 3-hydroxy-3-methyl-6-heptenoate[17] with 1.2 equiv of hydrazine hydrate. Ethanol and water were then exhaustively distilled from this mixture between 80 and 95 °C. The hydrazide was obtained in essentially 100% yield as an orange-red oil which forms a wet, crystalline solid in a few days. NMR ($CDCl_3$) δ 1.2 (s, 3 H), 1.4–1.75 (m, 2 H), 1.9–2.3 (m, 2 H), 2.29 (s, 2 H), 4.85–5.1 (m, 3 lobes, 2 H), 5.5–6.0 (m, 1 H).

A 16-g (0.1 mol) sample of the hydrazide was placed in a 250-mL, round-bottom flask with 100 mL of tetrahydrofuran and cooled to 5 °C in an ice bath. To this was added 50 mL of 6 M H_2SO_4 (0.3 mol). The mixture was stirred while 28 g (0.4 mol) of $NaNO_2$ was slowly added over 30 min. Gas evolution was observed. When the addition was complete, the ice bath was replaced with an oil bath and the reaction mixture was allowed to stir at 60 °C for 2 h. The mixture was diluted with water, the organic layer was sepd., and the aqueous layer was extracted twice with ether. The extracts were combined with the organic layer which was then washed twice with aqueous $NaHCO_3$ and twice with brine. The organic layer was then dried with $MgSO_4$ and the solvent was removed on a Rotovap. The 2-oxazolidone was obtained in approximately 50% yield, including a sizable fraction (about 60% of the 50% yield) which had undergone a second nitrosation to form the *N*-nitroso-2-oxazolidone (**28**). It seems possible that this reaction could provide the *N*-nitroso-2-oxazolidone without the need for an additional step if the molar excess of the nitrosating agents were increased. This has not yet been explored formally. NMR ($CDCl_3$, 40 °C) δ 1.4 (s, 3 H), 1.6–1.9 (m, 2 H), 2.0–2.3 (m, 2 H), 3.2–3.4 (q, 2 H), 4.9–5.1 (m, 3 lobes, 2 H), 5.5–6.0 (m, 1 H), 6.4 (s, broad, 1 H).

The crude product from the previous step was cooled to 0 °C in a 250-mL, round-bottom flask with a fourfold excess of 12 M H_2SO_4 and 15 mL of tetrahydrofuran per mL of H_2SO_4. To this was added 6 M Na NO_2 in small portions, with stirring, over 30 min. The reaction mixture was worked up as in the previous step, except that ice, rather than water, was used to initially dilute it. The *N*-nitroso-2-oxazolidone (**28**) was obtained with 90% or better purity and in a 90% or better yield. NMR ($CDCl_3$) δ 1.5 (s, 3 H), 1.7–1.9 (m, 2 H), 2.0–2.3 (m, 2 H), 3.6–3.8 (m, 2 H), 4.9–5.1 (m, 3 lobed, 2 H), 5.5–6.0 (m, 1 H).

Generation of 2-Methylbicyclo[3.1.0]hex-1-ene (22). A mixture of 2 g (0.0116 mol) of *N*-nitroso-2-oxazolidone (**28**), 0.6 g of tetraheptylammonium bromide, and 10 mL of 30% ethyl ether/70% pentane was placed in a 50 mL, round-bottom flask maintained at −6 °C, with stirring, under nitrogen. Then 5 mL of 33% NaOH was slowly added over 2 h. Gas evolution was observed. The reaction mixture was allowed to stir at −6 °C for 30 min after the addition was complete and then diluted with pentane and water. The organic layer was separated and the aqueous layer was extracted twice with pentane. The extracts were combined with the organic layer which was then washed with brine and dried with $MgSO_4$. The filtration involved in the drying step is important because of a black, acetone-soluble oil which forms during the reaction. The pentane and ether were removed by fractional distillation. The remainder was separated via preparative GC with a 3-ft column packed with 15% OV-17 at 90–110 °C. In addition to the solvents, three compounds were collected and analyzed by high-resolution NMR and GC/MS. These proved to be identical with dimers **23–25** described above.

Peak 1, **24**: NMR δ 0.24 (m, 2 H), 0.50 (m, 2 H), 1.11 (s, 6 H), 0.7–1.2 (broad mass), 1.7 (m, 2 H), 2.0–2.1 (m, roughly 4 H); GC/MS parent *m*/*e* 188.

Peak 2, **23**: NMR δ 0.6 (m, 1 H), 0.90 (s, 3 H), 1.64 (s, 3 H), plus a series of multiplets from about 0.8 to 2.5; GC/MS parent *m*/*e* 188.

Peak 3, **25**: NMR δ 0.20 (m, 1 H), 0.45 (m, 1 H), 0.7 (m, 3 H), 0.98 (s, 3 H), 1.3 (m, 1 H), 1.6 (m, about 4 H), 2.1 (m, about 2 H), 4.8 (s, 1 H), 4.95 (s, 1 H), 4.65–5.0 (m, 1 H); GC/MS parent *m*/*e* 188.

The product ratio **23**:**25**:**24** was 5:2.5:1, in good agreement with the values found when **22** was generated by the α-halolithium route.

Trapping Experiments. A. Cyclopentene. The experiment previously described was repeated, except that the reaction was run in 30% ether/70% cyclopentene. In addition to the dimers of the [3.1.0] system **23–25**, a fourth compound was isolated with a shorter retention time than the dimers. On the basis of the NMR spectrum, it was assigned structure **33**.

NMR ($CDCl_3$) δ 0.83 (t, 1 H, cyclopropylmethine), 1.04 (m, 1 H, cyclopropylmethine), 1.69 (s, 3 H), allylic methyl), 1.3–1.8 (m, 7 H, ring methylenes and 1 equiv of a chain methylene), 1.8–2.3 (m, 3 H, chain methylenes), 4.87–5.02 (m, 2 H), 5.67–5.88 (m, 1 H) (the last two peaks have appeared in the spectra of all of the precursors and are indicative of the butenyl group).

B. Cyclopentadiene. The reaction was run as before but in a solvent of 30% ethyl ether/70% cyclopentadiene. GC/MS (OV-101 column, 111 °C) of the product mixture (after removal of solvent by preparative GC) showed three peaks of mass 160, corresponding empirically to adducts of the bicyclo[3.1.0]hex-1-ene **22** with cyclopentadiene, constituting about 30% of the mixture and three peaks of retention time, ratio (1:5:2.5), and mass (188) corresponding to the dimers of **22**, constituting about 60% of the mixture. In addition, five unidentified peaks of short retention times and different masses totaled about 10% of the mixture.

The first mass 160 peak was collected by preparative GC on an OV-17 column, 90–100 °C, which did not separate it completely from the small amounts of unidentified material. The major mass spectra fragment

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(17) Fraenkel, G.; Adams, D. G.; Williams, J. *Tetrahedron Lett.* **1963**, 767.

(18) Rupert, J. F.; White, J. D. *J. Org. Chem.* **1974**, *39*, 270.

showed m/e 94, corresponding formally to a retro-Diels-Alder reaction of adduct **31** and/or **32**. The partial NMR (270 MHz) indicated an unequal mixture of **31** and **32**: δ 0.605 (t, 1 cyclopropyl proton of minor isomer (min.)); 0.85, 1.00 (2 m, cyclopropyls of major isomer (maj.)), 1.162 (s, methyl of maj.), 1.365 (s, methyl of min.), 2.26 (m, bridgehead proton of min.), 2.67 (m, bridgehead protons of maj.), 6.32, 6.39 (pair of multiplets, vinyl protons of both isomers).

The second mass 160 peak contained **36** and **37**, as indicated by the NMR: δ 0.21 (q, 1 H, endocyclopropyl methylene), 0.97 (m, 1 H, exocyclopropyl methylene), 1.779 (s, 2 H, methyl of **36**, 1.874 (s, 1 H, methyl of **37**, 2.1-2.3 (m, 6 H, methylenes and cyclopropyl methines), 4.93-5.09 (m, 2 H), 5.8 (m, broad, 1 H, characteristic of butenyl), 5.977 (d, 1 H, vinyl proton on ring), 5.999 (m, 1 H, vinyl proton on ring).

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Registry No. **21a**, 69442-58-6; **21b**, 67442-59-7; **21c**, 80954-25-2; **22**, 80954-26-3; **23**, 67442-61-1; **23a**, 80954-27-4; **24**, 67442-63-3; **24a**, 80954-28-5; **25**, 69442-62-2; *26*, 5471-63-6; **27**, isomer 1, 80954-29-6; **27**, isomer 2, 80996-34-5; **28**, 80954-30-9; **28**, denitrosylated, 80954-31-0; **29** hydrazide, 80954-32-1; **31**, 80954-33-2; **33**, 80954-34-3; **36**, 80954-35-4; **37**, 80954-36-5; 5-hexene-2-one, 109-49-9; cyclopentadiene, 542-92-7.

Implication of a Common Trimethylenemethane Intermediate in Dimer Formation and Structural Methylenecyclopropane Rearrangement of a Bicyclo[3.1.0]hex-1-ene to a 5-Alkylidenebicyclo[2.1.0]pentane[1,2]

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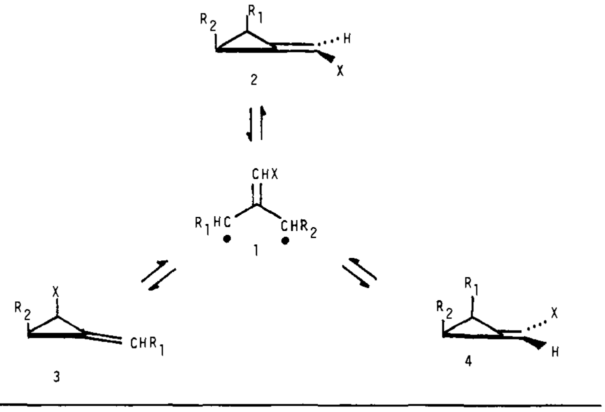
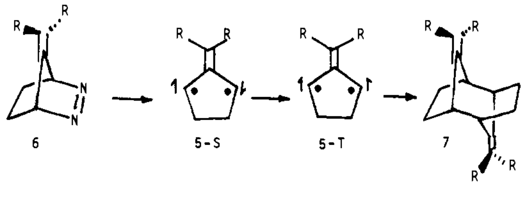
Abstract: Stereospecifically labeled 2,6,6-trimethylbicyclo[3.1.0]hex-1-ene (**17b**), generated by α-elimination from 1,1-dibromo-6-*trans*-trideuteriomethylhepta-1,5-diene (**8b**), dimerizes to stereospecifically labeled [$\sigma + \pi$] and [$\pi + \pi$] products, **15b** and **16b**, and to stereorandomized trimethylenemethane dimer **18**. In competition with these processes, **17b** rearranges to 1-methyl-5-isopropylidenebicyclo[2.1.0]pentane (**21**). Skeletal rearrangement thus is added to stereomutation as a reaction involving a singlet trimethylenemethane which is also capable of intersystem crossing to the triplet species.

The mechanism of the thermal reaction of methylenecyclopropane usually is formulated with a singlet trimethylenemethane (TMM) intermediate (**1**). In appropriately labeled cases, two characteristic processes are observed: structural rearrangement (e.g., **2** → **3**) and stereomutation (e.g., **2** → **4**).[4] Although the singlet TMM species postulated in these reactions serve well to explain many of the known facts, the failure of the alleged biradicals to cross over to the triplet form has introduced an element of inconsistency in the interpretation, because this behavior contrasts sharply with that observed in apparently closely related cases. Thus, for a number of TMM derivatives, there is direct electron spin resonance spectroscopic data that establishes the triplet TMM as the ground state of the biradical.[5,6] Moreover, the singlet TMM species in the 2-alkylidenecyclopentane-1,3-diyl series (**5-S**), which can be generated by deazetation of an appropriate diazene (**6**), readily crosses over to triplet biradicals (**5-T**). These then combine pairwise to give the characteristic TMM dimers (e.g., **7**).[7]





A major purpose of the present paper is to elucidate the apparent discrepancy. Since dimerization is a characteristic reaction of triplet TMM species,[2a,7-10] the demonstration that structural

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[1] For a preliminary communication, see: Salinaro, R. F.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7094.

[2] For related work, see the accompanying papers: (a) Rule, M.; Mondo, J. A.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2209. (b) Lazzara, M. G.; Harrison, J. J.; Rule, M.; Hilinski, E. F.; Berson, J. A. *Ibid.* **1982**, *104*, 2233. (c) Rule, M.; Salinaro, R. F.; Pratt, D. R.; Berson, J. A. *Ibid.* **1982**, *104*, 2223. (d) Mazur, M. R.; Berson, J. A. *Ibid.* **1982**, *104*, 2217.

[3] Dox Fellow, 1981.

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