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).

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. We also acknowledge the award of a Dox Fellowship to one of us and the support provided by the National Science Foundation for the Northeast Regional NMR Facility at Yale University (CHE 7916210).

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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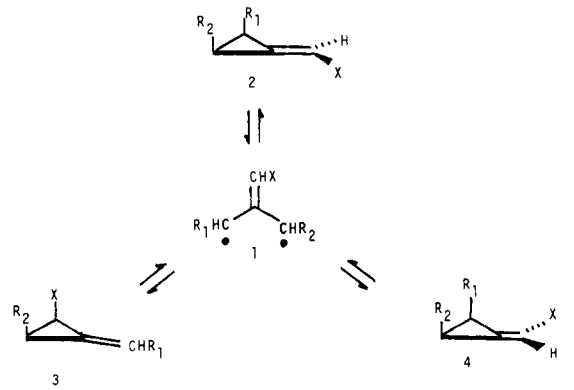
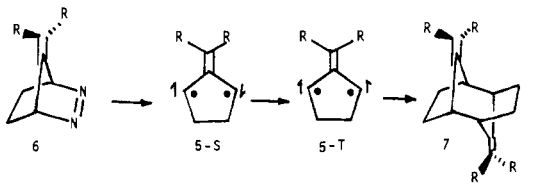
Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received July 7, 1981*

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

(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.

(4) For reviews and references to earlier work, see: (a) Reference 2b. (b) Gajewski, J. J. In "Mechanisms of Molecular Migrations", Thyagarajan, B., Ed.; Wiley-Interscience; New York, 1971; Vol. 4, p 1. (c) Berson, J. A. In "Rearrangements in Ground and Excited States", de Mayo, P., Ed., Academic: New York, 1980; Vol. 1, p 311.

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

(6) 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.

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

(8) (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.

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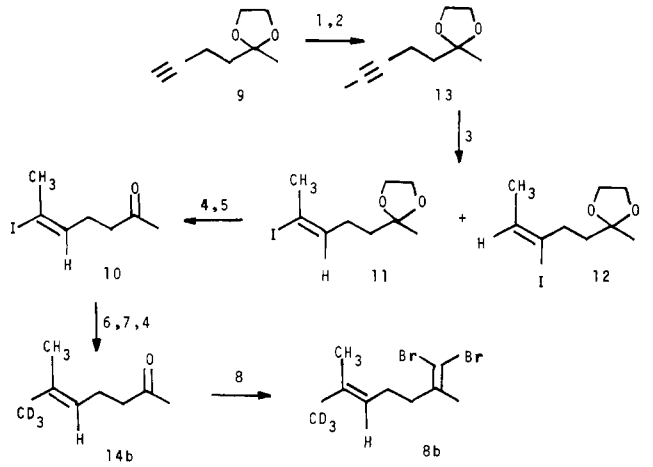
Scheme I[a]



[a] Methods: (1) $LiNH_2/NH_3$(l)THF, −78 °C; (2) MeI, THF, 0 °C; (3) Cp_2Zr-(H)Cl, PhH, 4 h, then I_2, following a general procedure of ref 12; (4) H_3O^+; (5) separation by GC; (6) $HOCH_2CH_2OH$, TsOH, PhH; (7) CD_3Li, 5% CuBr, following a general procedure of ref 13; (8) CBr_4, Ph_3P, $PhCH_3$, 12 h, 110 °C, following a modification of a general procedure of ref 14.

rearrangement and stereomutation could occur in a system that also exhibits TMM dimer formation would provide convincing evidence of a mechanistic continuity.[2b] We report such a demonstration here.

Synthesis of a Stereospecifically Labeled Precursor of 2,6,6-Trimethylbicyclo[3.1.0]hex-1-ene. For investigation of the occurrence of stereomutation in the TMM intermediate, the present experiments require stereospecifically labeled 1,1-dibromo-2-methyl-6-*trans*-(trideuteriomethyl)hepta-1,5-diene (**8b**). Scheme I outlines the synthesis of this compound from the known[11] acetylenic ketal, **9**. The overall strategy is straightforward. Stereospecific introduction of the CD_3 group near the end of the synthesis is achieved when the (*E*)-iodoketal **11**, regenerated from ketone **10**, is treated with CD_3Li/CuBr. The key step in producing the desired iodoalkene configuration is the hydrozirconation–iodination sequence starting from the acetylenic ketal **13**. This reaction is not highly regiospecific, giving a 2:1 mixture of the desired compound **11** and the regioisomer **12** in overall 70% yield. However, it is highly stereospecific, since hydrolysis of the iodoketal mixture, gas chromatographic (GC) separation of the iodoketones, re-ketalization, methylation, hydrolysis of the ketal function, and dibromomethylenation give the 6-*trans*-(trideuteriomethyl) compound **8b** in >95% stereochemical purity, as judged by integration of the nuclear magnetic resonance (NMR) signals of the geminal allylic methyl groups. The only aesthetically objectionable feature of the synthesis is the hydrolysis–reketalization sequence, which is necessary to permit GC separation of the iodoketone **10** from its regioisomer. Attempted separation at the ketal stages (**11** and **12**) is inefficient.

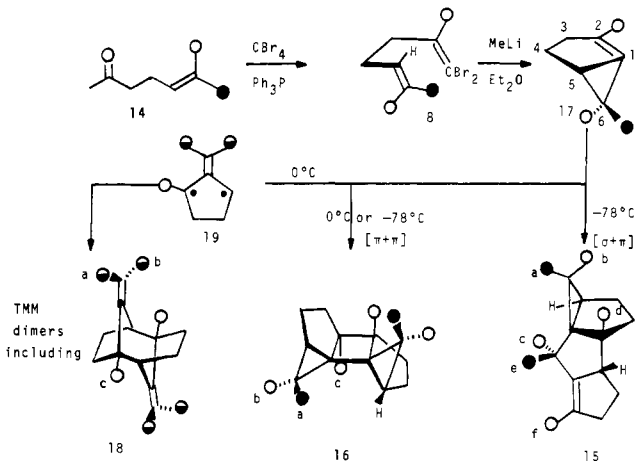
Stereomutation in the Trimethylenemethane Species Derived by Ring Opening of a Bicyclo[3.1.0]hex-1-ene. We previously have reported[2c] that 2-methylbicyclo[3.1.0]hex-1-ene (**17a**) generated from 1,1-dibromo-2,6-dimethylhepta-1,5-diene (**8a**) by the metalation–carbenoid cyclization technique of Köbrich and Heinemann[15] gives rise to two series of dimers (Scheme II): the [σ + π] and [π + π] dimers **15a** and **16a** respectively of the bicyclo[3.1.0]hex-1-ene system, and the characteristic dimers of the trimethylenemethane biradical **19a**, which results from ring opening of **17a**. The most easily identified and isolated of the

Table I. Chemical Shifts and Relative Intensities of Methyl Group Absorptions in Unlabeled and Labeled Dimers of Scheme II

compd	chemical shift, ppm	protons	rel intensity a	rel intensity b
15[a]	0.708		3	3
	0.776		3	3
	0.988		3	0
	1.194		3	3
	1.208		3	0
	1.680	f	3	3
16[a]	0.99	b	6	0
	1.03	a or c	6	6
	1.16	c or a	6	6
18	1.22	c	6	6
	1.69	a or b	6	3
	1.79	b or a	6	3

[a] In benzene-d_6.

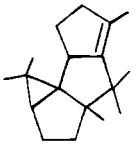
Scheme II[a]



[a] In structural formulas of Scheme II marked in the text a, ○ = ● = ⊖ = CH_3; for those marked b, ○ = CH_3, ● = CD_3; and for those marked c, ⊖ = $CD_3/2$.

TMM dimers is the symmetrical compound **18a** (or its regioisomer with vicinal bridgehead methyl groups).

Although the dimerizations leading to **15a** and **16a** appear to be highly regio- and stereospecific, the spectroscopic data do not distinguish structure **15a** from that of another regioisomer, **20**, in which the locations of a methyl and a cyclopropyl group have been interchanged.



20

Table I shows the ^1H NMR chemical shifts of the methyl groups of the three dimers, **15a**, **16a**, and **18a**, at 270 MHz observed on the substances with normal isotopic abundance (**a** series). Thanks to the resolving power of the spectrometer, each of the individual methyl resonances can be discerned. This provides the means to monitor the stereochemical integrity of the deuterium label.

Metalation of stereospecifically deuterated **8b** at 0 °C or −78 °C gives the [σ + π] and [π + π] dimers, **15b** and **16b**, respectively, of 2,6,6-trimethylbicyclo[3.1.0]hex-1-ene (**17b**). Dimer **16b**, whether formed at −78 °C or at 0 °C, shows two six-proton singlet absorptions at δ 1.16 and 1.03 but no absorption at δ 0.99. It is difficult to escape the conclusion that one of each pair of geminal methyl groups of **16b** is fully deuterated and the other is fully protonated. This suggests that cyclization of the carbenoid from **8b** (Scheme II) onto the isopropylidene group is stereospecific

(9) (a) Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7089. (b) Lazzara, M. G.; Harrison, J. J.; Rule, M.; Berson, J. A. *Ibid.* **1979**, *101*, 7092.

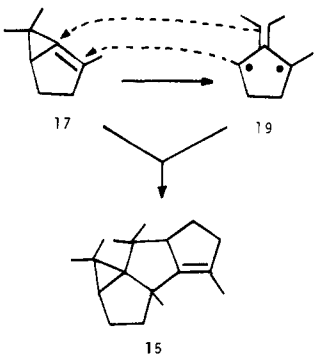
(10) Gajewski, J. J.; Yeshurun, A.; Bair, E. J. *J. Am. Chem. Soc.* **1972**, *94*, 2138.

(11) Heather, J. B.; Sood, R.; Price, P.; Peruzzotti, G. P.; Lee, S. S.; Lee, L. H.; Sih, C. J. *Tetrahedron Lett.* **1973**, 2313.

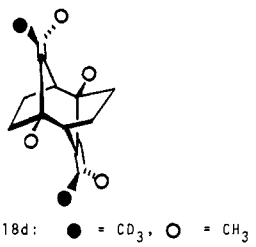
(presumably cis) and that the intermediate bicyclo[3.1.0]hex-1-ene (**17b**) dimerizes without perturbation of the configuration at C_6, even at the higher temperature.

As Table I shows, the unlabeled [$\sigma + \pi$] dimer **15a** gives rise to six three-proton singlet NMR resonances, corresponding to the six nonequivalent methyl groups a–f. In the spectrum of the labeled dimer **15b** obtained from **8b**, two of the six signals completely disappear. This is again consistent with stereospecific ring closure to **17b** and dimerization of the latter without loss of stereochemical integrity.

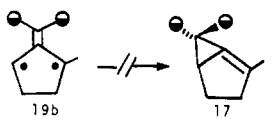
The mechanism of formation of compound **15** might be formulated with a trimethylenemethane intermediate **19**, derived by ring opening of the bicyclo[3.1.0]hex-1-ene **17**, which could react with a second mole of **17**, viz.,



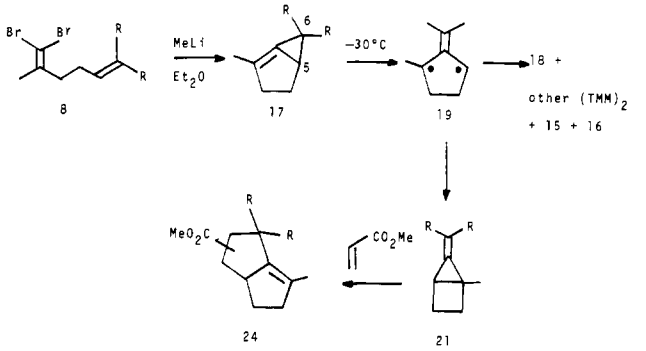
Although this hypothesis accounts for the obvious structural feature that the cyclopropane ring of one of the monomer units of **15** has been opened, it is difficult to reconcile with the complete retention of stereochemical integrity of the labeled methyl groups. A singlet trimethylenemethane biradical **19**, by analogy to closely related cases,[2b] would have been expected to suffer rapid torsion about the exocyclic double bond and hence randomization of the CD_3 and CH_3 groups. The stereospecificity observed in **15b** contrasts sharply with the randomization observed in the trimethylenemethane dimer **18b** which is formed at 0 °C but not at −78 °C. As Table I shows, the allylic methyl groups a and b of **18b** each are just half as intense as the six-proton singlet of the c methyl groups. Although the data themselves do not formally exclude a stereospecific dimer **18d**, formed by an even number of olefinic torsions of the exocyclic double bond in one partner and an odd number in the other, we consider this an unlikely alternative to the fully randomized structure **18b**.



These observations may be explained by a mechanism (Scheme II) in which **18b** is formed by dimerization of a stereochemically randomized singlet trimethylenemethane, **19b**, which in turn results from cleavage of the C_5–C_6 bond of the stereospecifically labeled bicyclo[3.1.0]hex-1-ene **17a**. Apparently, recyclization of **19b** to a stereorandomized bicycle **17** does not occur on the time scale of dimerization of the latter, since no randomization is detected in the dimers **15a** and **16a**. Cyclization of singlet trimethylenemethanes of the 2-alkylidenecyclopentane-1,3-diyl class to 5-alkylidenebicyclo[2.1.0]pentanes is a facile process.[2] These relationships predict that thermal rearrangement of the bicyclo-

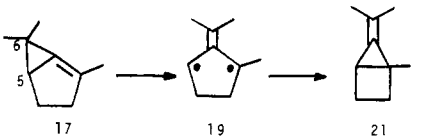


Scheme III[a]

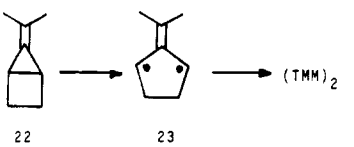


[a] a, R = CH_3; b, R = CD_3.

[3.1.0]hex-1-ene (**17**) to the 5-alkylidenebicyclo[2.1.0]pentane **21** via their common trimethylenemethane singlet **19** should occur essentially unidirectionally.



The experimental realization of this rearrangement requires a temperature high enough to make C_5–C_6 bond cleavage in **17** competitive with dimerization but low enough to permit observation of the unstable rearranged product **21**. With reference to Scheme II, one may estimate that an appropriate temperature to meet the first requirement would lie somewhere between −78 and 0 °C. As a guide for the second requirement, we use the rate of decomposition of the most closely related available model compound, 5-isopropylidenebicyclo[2.1.0]pentane (**22**), which undergoes thermal decomposition and ultimate dimerization via a triplet diyl **23** with a half-life of about 20 min at −40 °C.[2a,d,9a]



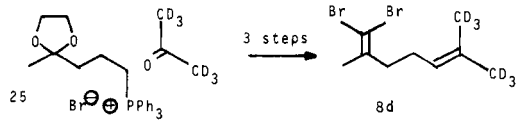
Metalation of the dibromide **8a** with methyllithium at −30 °C gives a reaction mixture which when cooled to −78 °C, treated with methanol, and stored in the cold for 8 min apparently contains some of the rearranged hydrocarbon **21a** (Scheme III). The latter can be detected by treatment of the cold reaction mixture with methyl acrylate and warming it to room temperature, whereupon one obtains not only the dimers **15**, **16**, and **18** and other $(TMM)_2$ species but also ~20% of a mixture of 1:1 cycloadducts of the familiar type **24a**.[2,7,16]

Apparently, there is a thermal barrier for the **17** → **21** rearrangement. Metalation of **8** *at −78 °C* followed by quenching and treatment with methyl acrylate gives **15** and **16** (the dimers of **17**), but no cycloadducts **24**.

Further evidence for the rearrangement **17** → **21** can be obtained by direct NMR observation. The mixtures from the metalation of dibromide **8a** contain too many resonances to permit the course of reaction to be monitored by proton spectroscopy, but the cyclization of the hexadeuterio compound **8d** can be followed by direct deuteron NMR. The synthesis of **8d** is achieved by the reaction of the Wittig reagent from the phosphonium salt

(12) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.
(13) Normant, J. F.; Villera, J.; Cahiez, G.; Commercon, A. *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1974**, *278*, 967.
(14) Posner, G. H.; Loomis, G. L.; Sawaya, H. S. *Tetrahedron Lett.* **1975**, 1373.
(15) Köbrich, G.; Heinemann, H. *Chem. Commun.* **1969**, 493.
(16) (a) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276. (b) Siemionko, R.; Berson, J. A. *Ibid.* **1980**, *102*, 3870.

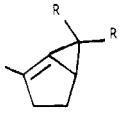
25 with acetone-d_6, followed by the usual steps: hydrolysis of the ketal and dibromomethylenation. Metalation of **8d** at −29 °C



followed by quenching of the reaction mixture with methanol gives a reaction mixture whose ^2H NMR spectrum at −80 °C shows resonances at δ 0.75, assigned to CD_3 groups attached to saturated carbons, and at δ 1.45 and 1.38, assigned to allylic CD_3 groups. The lower field resonance at δ 1.45 is at least partially due to the deuterated 5-isopropylidenebicyclo[2.1.0]pentane (**21d**). When the sample is warmed to room temperature, recooled to −80 °C, and examined in the ^2H NMR probe, the intensity of the δ 1.45 peak diminishes and that of the 1.38 peak increases. The upfield shift of the allylic methyl resonances upon dimerization of **21** parallels observations[2a,2d,9a] (made by proton rather than deuteron NMR) in the closely related case of 5-isopropylidenebicyclo-[2.1.0]pentane (**26**).

26

The rearrangement **17a** → **21a** (Scheme III) competes with the dimerizations of the bicyclo[3.1.0]hex-1-ene system, **17** → **15** + **16**. Thus, the latter reactions can serve as an internal "clock" by which to estimate the rearrangement rate and activation energy. Although the dimerization half-life for **17a** itself is not known accurately, it seems reasonable to use the upper limit of about 1 min at −90 °C observed[2c,17] for the analogue **17e**. On the assumptions that the concentration of **17a** is the same as that of the initial concentration of dibromide **8a** (2.9×10^{-2} M) and that the dimerizations **17a** → **15a** + **16a** are at least as fast at −29 °C as at −90 °C, we compute an upper limit for the activation energy of the competing rearrangement **17a** → **21a** as 16.8 kcal/mol.



17a: R = CH_3
e: R = H

Conclusions. The present work demonstrates both structural rearrangement (bicyclo[3.1.0]hex-1-ene → 5-alkylidenebicyclo-[2.1.0]pentane) and stereomutation (scrambling of CD_3 and CH_3 labels) by way of a 2-alkylidenecyclopentane-1,3-diyl singlet species, **19**. This biradical also crosses over to the triplet, which gives trimethylenemethane dimers. The results supplement the findings of competitive stereomutation and triplet dimerization observed in related cases[2b,9b] and support the idea that TMM species can serve as common intermediates in the various thermal reactions of methylenecyclopropanes.

Experimental Section

Solutions of methyllithium in diethyl ether and of butyllithium in hexane were commercial materials. NMR spectra at 90 MHz were recorded with the Varian EM-390 or Bruker FX-90 systems; spectra at 270 MHz (^1H) or 41.4 MHz (^2H) were recorded with the Bruker HX-270 instrument.

Synthesis of 1,1-Dibromo-2-methyl-6-*trans*-(trideuteriomethyl)hepta-1,5-diene (8b) (Scheme I). 5-Heptyn-2-one Ethylene Ketal (13). A 250-mL, three-neck flask equipped with a condenser cooled with solid CO_2, an addition funnel, and a magnetic stirring bar was flame dried, flushed with argon, and cooled to −78 °C. About 30 mL of liquid ammonia was condensed into the flask followed by addition of 20 mL of a 1.4 M MeLi (28 mmol) solution in hexane. After 15 min of stirring, 30 mL of dry tetrahydrofuran (THF) was added slowly. The addition funnel was charged with 23 mmol of 5-hexyn-2-one ethylene ketal[11] in 10 mL of dry THF, and this solution was added dropwise with stirring over a 10-min period. After 20 min at −78 °C 8 mL of methyl iodide was added dropwise and stirring was continued at −78 °C for 15 min, at 0 °C for 45 min, and at room temperature for 2 h. The solution was diluted with 100 mL of ether and poured into 100 mL of ice water. The layers were separated and the water layer was extracted with 50 mL of ether. The combined organic layers were washed successively with 50-mL portions of water and brine. The organic layer was then dried over $MgSO_4$ and concentrated at reduced pressure. The residue was distilled to yield 2.7 g (77%) of product **13**: bp 97 °C (13 mm Hg); NMR ($CDCl_3$) δ 3.77 (s, 4 H), 2.15 (m, 2 H), 1.95–1.55 (m, 5 H), 1.28 (s, 3 H).

5- and 6-*trans*-Iodo-5-hepten-2-one Ethylene Ketals 11 and 12a. A flame-dried, 250 mL, three-necked flask equipped with a magnetic stirring bar and an addition funnel was flushed with argon. A sample of 16.2 mmol of **13** in 125 mL of dry, oxygen-free benzene was added to the flask followed by 16.3 mmol of bis(cyclopentadienyl)zirconiumhydrido chloride.[12] After the mixture had been stirred for 4 h, 4.2 g of iodine in 50 mL of benzene was added. The mixture was then stirred for 45 min and filtered and the solvent was removed at reduced pressure. The residue was dissolved in 150 mL of ether and vigorously stirred with 200 mL of saturated aqueous sodium thiosulfate solution. The resulting precipitate was filtered off and the layers were separated. The ether layer was dried over $MgSO_4$ and concentrated to yield 3.2 g of a 2:1 mixture of **11** and **12** (70%).

The components could not be separated on a preparative scale with GC columns OV-17, OV-101, Carbowax, or SE-30.

6-*trans*-Iodo-5-hepten-2-one (10). A sample of 3.2 g (11.3 mmol) of the mixture of **11** and **12** was dissolved in 30 mL of ether and stirred with 150 mL of 5% aqueous sulfuric acid for 2.5 h. The mixture was then diluted to 300 mL with ether and the layers were separated. The organic layer was then washed successively with 75-mL portions of water, saturated aqueous sodium bicarbonate, water, and brine. The ether layer was dried over $MgSO_4$ and concentrated to yield a yellow liquid. Compound **10**, retention time 17.5 min, was well separated from its isomer, which had retention time ~10 min, on a 3.5 ft × 0.25 in., 15% OV-17 column, column temperature 140 °C, carrier flow 78 mL/min. Compound **10** showed the following NMR (CCl_4, benzene-d_6): δ 6.03 (t, 1 H, J = 7.3 Hz), 2.4 (m, 5 H), 2.23 (pseudo q, 2 H, J = 7.3 and 7.3 Hz), 2.08 (s, 3 H).

6-*trans*-Iodo-5-hepten-2-one ethylene ketal was regenerated when 0.33 g of **10** (1.38 mmol), 0.5 mL of ethylene glycol, and a crystal of *p*-toluenesulfonic acid in 75 mL of benzene were heated at reflux under N_2 for 5 h with continuous removal of water. The solution was placed in a separating funnel and washed successively with 25-mL portions of saturated aqueous sodium bicarbonate, water, and brine. The organic layer was then dried over $MgSO_4$, concentrated, and distilled (kugelrohr) to give 0.38 g of ketal (97% yield). NMR (CCl_4, benzene-d_6) δ 5.95 (t, 1 H), 3.53 (s, 4 H), 1.98 (s, 3 H), 1.68 (m, 2 H), 1.31 (m, 2 H), 0.80 (s, 3 H).

6-*trans*-(Trideuteriomethyl)-5-hepten-2-one Ethylene Ketal. A 50-mL flask equipped with a magnetic stirring bar and serum cap was flame dried and flushed with argon. To the flask was added 0.38 g of the above ketal (1.34 mmol) in 18 mL of dry, oxygen-free THF and 20 mg (0.14 mmol) of anhydrous CuBr. The solution was cooled to −78 °C and 1.5 mL of 1.4 M CD_3Li (2.1 mmol) in ether was added dropwise with stirring. After 2 h at −78 °C, the solution was warmed to room temperature, 1 mL of saturated aqueous ammonium chloride was added, and the solution was diluted with 50 mL of ether and 50 mL of H_2O. The layers were separated and the organic phase was washed successively with 25 mL of water and 25 mL of brine. The organic layer was dried over $MgSO_4$ and concentrated by distillation through a vigreux column to give crude deuterated ketal. NMR (CCl_4) δ 5.07 (t, 1 H), 3.85 (s, 4 H) 2.01 (m, 2 H), 1.67 (m, 2 H), 1.65 (s, 3 H), 1.25 (s, 3 H).

***trans*-6-(Trideuteriomethyl)-5-hepten-2-one (14b).** The above crude ketal in 15 mL of ether was allowed to stir vigorously with 35 mL of 5% aqueous H_2SO_4 for 2.5 h at room temperature. Following the usual workup, the ether solution was concentrated by distillation through a vigreux column. The crude product was purified by GC (3.5 ft × 0.25 in., OV-17, 15%, column temperature 110 °C, carrier flow 78 mL/min) to give 110 mg of **14b** along with 30 mg of recovered ketal. NMR (CCl_4, benzene-d_6) δ 4.88 (t, 1 H), 2.10 (m, 4 H), 1.84 (s, 3 H), 1.48 (s, 3 H).

1,1-Dibromo-6-*trans*-(trideuteriomethyl)hepta-1,5-diene (8b) (Scheme II). A three-neck, 500-mL flask equipped with a magnetic stirring bar, an addition funnel, and a condenser was flame dried and flushed with argon. The flask was charged with 110 mg (0.85 mmol) of **14b**, 5 g of triphenylphosphine (1.9 mmol, recrystallized from hexanes), and 150 mL of dry toluene. The addition funnel was packed with a short pad of

(17) Rule, M.; Berson, J. A. *Tetrahedron Lett.* **1978**, 3191.

activated neutral alumina, and 3.5 g of CBr_4 (0.9 mmol) was chromatographed into the reaction mixture with toluene. The mixture was refluxed for 12 h before being cooled to room temperature and filtered. The precipitate was triturated with hexanes and the combined hexanes and toluene extracts were concentrated at reduced pressure. The residue was taken up in hexanes and passed through a column containing 5 g of florisil. The first 100 mL of hexanes contained the desired product **8b** along with some triphenylphosphine. The product was further purified by distillation (kugelrohr) to give 100 mg of pure **8b** (41% yield). NMR (CCl_4, benzene-d_6) δ 4.94 (t, 1 H, J = 7.3 Hz), 2.11 (t, 2 H, J = 7.0 Hz), 1.97 (pseudo q, 2 H, J = 7.3 and 7.0 Hz), 1.72 (s, 3 H), 1.49 (s, 3 H).

Reaction of 8b with Methyllithium at 0 °C. A sample of 60 mg (0.21 mmol) of **8b** in 8 mL of ether was placed in a flame-dried, 25-mL flask with a magnetic stirring bar under an atmosphere of nitrogen. The solution was cooled to 0 °C and 0.4 mL of 1.4 M MeLi (0.56 mmol) was added dropwise. After 15 min the mixture was quenched with 1 mL of saturated ammonium chloride. The solution was then diluted with 10 mL of water and allowed to stir for 5 min before further dilution with 15 mL of ether. The layers were separated and the ether layer was washed with brine before being dried over $MgSO_4$ and concentrated. The reaction products were isolated by preparative GC (3.5 ft × 0.25 in., OV-17, 15%, column temperature 145 °C, carrier flow 78 mL/min) to give **16** and **18**.

16: retention time 22.5 min; NMR (CCl_4, benzene-d_6) δ 1.14 (s, 3 H), 1.00 (s, 3 H); mp 80–82 °C (lit.[15] mp 82 °C).

18: NMR (CCl_4, benzene-d_6) δ 1.79 (s, 3 H), 1.69 (s, 3 H), 1.22 (s, 6 H); mp 162–164 °C (lit.[15] mp 164 °C).

Reaction of 8b with Methyllithium at −78 °C. A sample of 30 mg (0.11 mmol) of **8b** was treated with 0.2 mL of 1.4 M methyllithium (0.28 mmol) by the same procedure as the reaction at 0 °C. After the usual workup the products were isolated by preparative GC as before.

16: retention time 22.5 min; mp 81–83.5 °C; 90% of the volatile fraction.

15: retention time 30 min; NMR (CCl_4, benzene-d_6) δ 2.58 (m, 3 H), 2.14 (m, 2 H), 1.92–1.44 (m, 5 H), 1.63, 1.17, 1.12, and 0.67 (all s, 3 H). When the same reaction was carried out in the undeuterated series, **15** showed all the above NMR peaks in addition to peaks at δ 0.94 and 0.78 (both s, 3 H).

Rearrangement of 2,6,6-Trimethylbicyclo[3.1.0]hex-1-ene (17) to 5-Isopropylidenebicyclo[2.1.0]pentane 21 (Scheme III). To a flame-dried, 25-mL flask containing a magnetic stirring bar flushed with argon was added 120 mg of 1,1-dibromo-2,6-dimethylhepta-1,5-diene (**8**) in 10 mL of ether. The flask was cooled to −29 °C. Then 0.8 mL of 1.4 M MeLi was added in a stream by allowing it to run down the inside of the flask. After 1 min at this temperature, 2 mL of methanol (previously cooled to −78 °C) was added rapidly. The flask was then cooled to −78 °C and after 8 min 5 mL of methyl acrylate was added. Stirring was continued at −78 °C for 5 min and then at −29 °C for 10 min. Finally, the solution was warmed to room temperature. The reaction was worked up as usual and the products were isolated by preparative GC (3 × 0.25 in., OV-17, column temperature 130 °C, flow rate 78 mL/min). In addition to dimeric materials (**18**, **15**, **16**), a group of adducts with retention times 12.5–15 min was collected. The adduct mixture was identified by exact mass spectrometry and NMR.

NMR (CCl_4, benzene-d_6) δ 3.47, 3.42 (s, OCH_3), 1.59, 1.56, 1.54 (s, allylic CH_3), 1.26, 1.18, 0.88, 0.86 (s, CH_3); mol wt calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1459.

In a control experiment, metalation of **8** at −78 °C followed by quenching and addition of methyl acrylate as before gave no adducts. The products were the dimers **15** and **16**.

Phosphonium Bromide (25). A sample of 13 g (62 mmol) of 5-bromopentan-2-one ethylene ketal and 16.2 g (61.8 mmol) of triphenylphosphine (recrystallized from hexanes) was stirred under N_2 in a dry, 50-mL flask. The suspension was heated in an oil bath. The temperature was raised slowly to 130 °C over a 1-h period, at which point the clear solution began to boil before turning into a brown solid. The solid was collected and washed with ether before being dissolved in a minimal amount of methylene chloride. This solution was stirred while the solvent was slowly removed by blowing dry nitrogen over the surface until the solid precipitated out. At this point it was filtered and washed with ether to give 26.6 g (91%) of a pale yellow, electrostatically active solid.

1,1-Dibromo-2,6-dimethylhepta-1,5-diene-d_6 (8d). To a flame-dried, 1000-mL flask flushed with nitrogen was added 26.6 g (60.7 mmol) of **25** in 500 mL of ether. The suspension was cooled to 0 °C and 28 mL of 2.4 M *n*-BuLi (66.8 mmol) was added over a 15-min period. After 30 min, a twofold molar excess of acetone-d_6 was added to the red solution and stirring was continued at room temperature for 12 h. The solution was diluted with 200 mL of water and the layers were separated. The ether layer was washed with 100 mL of brine and dried over $MgSO_4$. The ether was distilled away with the use of a vigreux column; short-path distillation of the product gave 2.13 g of labeled material (21.3% yield): NMR (CCl_4) δ 5.08 (t, 1 H), 3.90 (s, 4 H), 2.02 (m, 2 H), 1.55 (m, 2 H), 1.30 (s, 3 H).

The ketal was converted to the ketone and the bis(bromomethylene) compound **8d** by the same procedures described in the d_3 series.

Metalation of the Bis(trideuteriomethyl) Compound 8d. The apparatus was flame dried, evacuated, and filled with argon. Then 11 μL of **8d** and 0.50 mL of Et_2O (containing 10 μL of benzene-d_6) was added. The solution was cooled to −29 °C (*o*-xylene/N_2 bath) and 0.25 mL of 1.6 M MeLi was added rapidly. After 1 min, the mixture was cooled to −78 °C and 0.25 mL of methanol was added. The NMR tube was broken off, capped, and placed in the deuterium probe (41.4 MHz) of a Bruker HX-270 spectrometer at −80 °C. The deuterium spectrum was recorded and the sample was removed from the probe and allowed to warm to room temperature. After 5 min the sample was placed in the probe at −80 °C and the deuterium spectrum was again recorded. The resonances observed are described in the Discussion section.

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Registry No. 8, 60014-82-6; **8b**, 72447-95-1; **8d**, 80963-81-1; **8d** ethylene ketal, 23303-12-0; **9**, 42541-87-7; **10**, 72448-00-1; **11**, 72448-01-2; **12**, 72448-02-3; **13**, 22592-16-1; **14b**, 41494-98-8; **15a**, 80963-82-2; **15b**, 80963-83-3; **16a**, 80963-84-4; **16b**, 72447-97-3; **17**, 69442-64-4; **18a**, 22935-22-4; **18c**, 80963-85-5; **21**, 72447-99-5; **25**, 5944-33-2; 6-*trans*-(trideuteriomethyl)-5-hepten-2-one ethylene ketal, 41495-03-8; 5-bromopentan-2-one ethylene ketal, 24400-75-7; acetone-d_6, 666-52-4.