(16) The irreversibility of the hydrogen shift in the 2-brexyl-4-brexyl system[2a] compared with its known reversibility in the 2-norbornyl-2-norbornyl situation[13b] supports this conclusion.

(17) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, **89**, 880 (1967).

(18) See R. C. Weglein, Ph.D. Dissertation, Department of Chemistry, The Johns Hopkins University, 1973 [*Diss. Abstr. B*, **34**, 3717 (1974)], for a discussion of σ-route generated 2-brexyl cations.

(19) The ^{13}C NMR spectra were determined on a Varian XL-100-15 operating at 25 MHz and equipped with an 8 K (1 K = 1024 words) 620I computer; the final natural abundance spectra and the quantitative enriched spectra were run on a Varian CFT-20 NMR spectrometer equipped with 16 K of core and a Sykes 120 compu/Corder. The ^{13}C resonance frequency on the latter spectrometer was 20 MHz.

(20) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR", Academic Press, New York, N.Y., 1971, Chapter 2.

(21) R. Freeman, H. D. W. Hill, and R. Kaptein, *J. Magn. Reson.*, **7**, 327 (1972).

(22) Cf. (a) J. B. Stothers and A. N. Bourns, *Can. J. Chem.*, **38**, 923 (1960); (b) J. Bron and J. B. Stothers, *ibid.*, **46**, 1435, 1825 (1968); **47**, 2506 (1969); (c) K. R. Lynn and P. E. Yankwich, *J. Am. Chem. Soc.*, **83**, 53, 790 (1961).

(23) The brackets conventionally used to denote concentration have been omitted.

(24) Cf. J. B. Stothers, C. T. Tan, A. Nickon, F. Huang, R. Sridhar, and R. Weglein, *J. Am. Chem. Soc.*, **94**, 8481 (1972).

Synthesis and Thermal Rearrangements of 3-(2′-Methylprop-1′-enylidene)tricyclo[3.2.1.0^{2,4}]oct-6-ene

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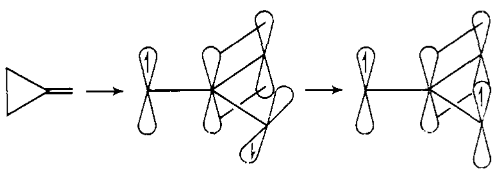
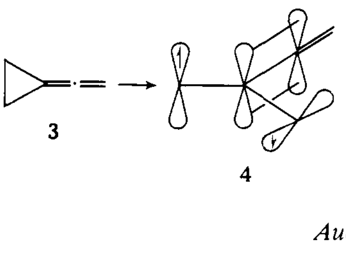
Abstract: The synthesis of the title compound **10** via a carbenoid route is reported. The thermal rearrangement of **10** in the gas phase has been studied and found to give three isomeric products, **11**, **12**, and **13**, which were characterized by ^{1}H and ^{13}C NMR spectroscopy. A kinetic study indicated that **11** and **12** are primary products and are formed in parallel first-order reactions which are not subject to catalysis. The third product, **13**, was found to be formed from **12**, in a process which is surface catalyzed. Formation of **11** is proposed to occur by a ten-electron ($\pi_s^2 + \sigma_a^2 + \pi_a^2 + \pi_s^2 + \sigma_s^2$) concerted mechanism to give a divinylcyclopropane **23** which then undergoes Cope rearrangement to **11**. Formation of **12** is interpreted in terms of C-2–C-4 cleavage of **10** to a substituted trimethylenemethane, **35**, followed by addition of this diradical to the proximate double bond to give **12**. The rate of rearrangement of the related methylenecyclopropane **8b** was determined and compared with rates for other methylenecyclopropanes and alkenylidenecyclopropanes. The rates are interpreted in terms of initial formation of orthogonal trimethylenemethane diradicals in the case of unconstrained systems. Formation of near planar diradicals from **10** and **8b** is only ca. 4 kcal/mol less favorable than for the orthogonal diradicals of comparable structure.

The geometry of trimethylenemethane diradicals has been the subject of considerable experimental and theoretical concern in recent years.[1-5] While calculations[3] and ESR experiments[1] both indicate that the ground state is a planar triplet **2**, the geometry of the singlet diradical is less clear. Some calculations indicate that the singlet prefers an orthogonal (or bisected) geometry **1** by 20–30 kcal/mol,[4] but more recent calculations indicate that the planar singlet may be only 3–6 kcal/mol less stable than the orthogonal singlet diradical **1**.[5] Gajewski's experiments on the racemization of optically active *trans*-2,3-dimethylmethylenecyclopropane indicate that the transition state leading to the planar singlet diradical is only 2 kcal/mol higher in energy than that leading to the chiral orthogonal form.[6a,7] Other rearrangements of methylenecyclopropanes and alkenylidenecyclopropanes (**3**) have usually been interpreted in terms of orthogonal diradicals **1** and **4**.



1 2



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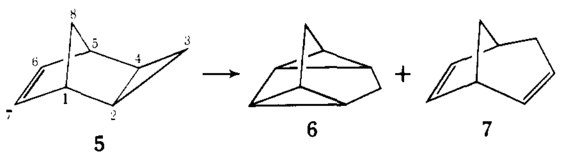
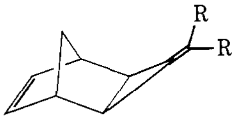
4

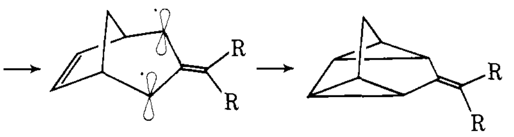
Cleavage of methylenecyclopropane or alkenylidenecyclopropane rings in the tricyclo[3.2.1.0^{2,4}]oct-6-ene system (**5**) cannot readily give rise to orthogonal diradical intermediates because the geometric constraints at the developing radical centers force the initial diradical to be planar, as from **8**. If the ring opening in a system such as **8** must proceed through a near-planar transition state,[9] then the activation energy for the process should indicate the stability of such a planar diradical. These activation energies could then be correlated with those of geometrically unconstrained methylenecyclopropanes and alkenylidenecyclopropanes to indicate whether the orthogonal



5 **6** **7**



8a, R = H
b, R = CH$_3$
c, R = (CH$_2$)$_5$



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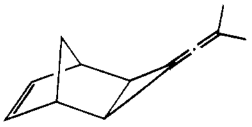
diradicals in the unconstrained systems are more readily formed than in systems forced to give near-planar diradicals.

It is known that the diradical formed by cleavage of the internal cyclopropane bond in **5** is trapped efficiently by the proximate double bond to give **6.**[10] It has also recently been shown that singlet[2] trimethylenediradicals from **8a**[11b] and **8b,c**[11a,c] can be intramolecularly trapped to give **9a,b,c.** Such intramolecular trapping reactions probably occur with a relatively small barrier, so that the rate of conversion of **8** to **9** should be a reasonable indication of the rate of formation of the trimethylenediradical from **8.** We report here the rate for **8b** → **9b**, a synthesis of the alkylidenecyclopropane **10**, and the rates and mechanisms of formation of its thermal rearrangement products. From an analysis of the rates of conversion of **8b** to **9b** and the analogous rearrangement of **10**, we then wish to suggest some limits on the energy difference between planar and orthogonal diradicals from methylenecyclopropanes and alkenylidenecyclopropanes.

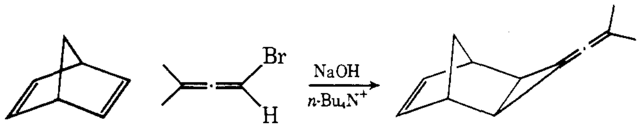


10

In addition, we were intrigued by the complex factors determining how cleavages of the C-2–C-4 bond (giving **6**) in systems like **5** compete with cleavage of the C-2–C-3 bond (giving **7**).[10] The C-2–C-4 cleavage process is observed in most of the substituted tricyclooctenes studied thus far.[12]

Derivatives of **5** with substituents in a position to promote C-2–C-3 diradical opening, however, give only C-2–C-3 cleavage thermally.[13,14] Heterocyclic derivatives of **5** also rearrange via C-2–C-3 cleavage; but whether these reactions are concerted, diradical, or acid catalyzed has not been demonstrated.[15]

The C-2–C-3 diradical cleavage of **10** could potentially be favored by allylic stabilization of the radical center at C-3. The rearrangement products of **10** have thus been investigated to determine the effect of the alkenylidene function on the balance between C-2–C-4 and C-2–C-3 cleavage as compared with compounds **5** and **8.**



10

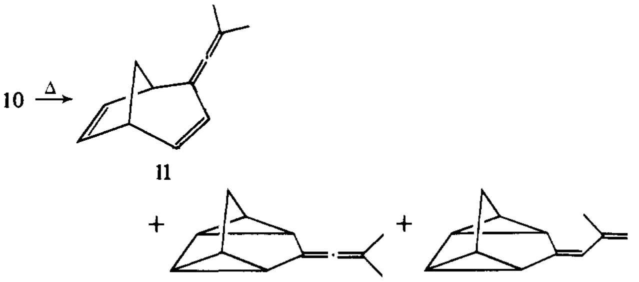
Results

Synthesis. Compound **10** was synthesized by addition of isobutenylidene carbene to norbornadiene. The best yields (ca. 20%) were obtained when the carbene was generated from 1-bromo-3-methyl-1,2-butadiene[16] and 50% aqueous sodium hydroxide at 50–60 °C in a two-phase system with a fourfold excess of norbornadiene using tetra-n-butylammonium iodide as a phase-transfer catalyst.[17]

Other phase-transfer catalysts such as cetyltrimethylammonium bromide and benzyltriethylammonium chloride gave no better yields than tetra-n-butylammonium iodide and caused difficulty in extraction due to the emulsions these agents produce. The reaction yield was quite time and temperature dependent. Below ca. 35 °C almost no adduct could be detected even after 3 days. At 50–60 °C, the yield of the desired allene reaches a maximum after 5–6 days of 21%. The spectral properties of **10** are consistent with the assigned structure and are not consistent with a product derived from 1,4 addition of the carbene to norbornadiene as found with some other carbenes.[18]

Other conditions for the synthesis of **10** were tried but gave lower yields. With potassium *tert*-butoxide and 3-chloro-3-methyl-1-butyne at −30 to 0 °C or with sodium hydroxide, phase-transfer catalyst, and 3-chloro-3-methyl-1-butyne at 25 to 60 °C, the yields were only 7–11%, and various unidentified side products were formed which were difficult to separate from **10.**

Pyrolysis of 10. Pyrolysis of **10** in the gas phase (static) at ca. 3 mm pressure at 140 °C gave three products, **11, 12,** and **13,** quantitatively in ratios which varied with the reaction time.

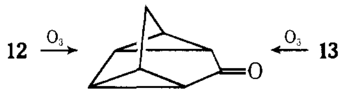


11

12

13

The structures of the products were determined from the spectral data of VPC collected samples. Both tetracyclooctanes **12** and **13** were ozonized to the known ketone **14.**



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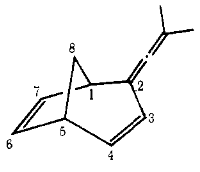
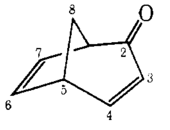
^{1}H and ^{13}C NMR Spectra. Comparison of the ^{1}H NMR spectrum of **11** with that of the known ketone **15** helped to confirm its structural assignment.[20] In addition, we have obtained ^{13}C NMR spectra for **8b, 10, 11, 12,** and **13.** The ^{13}C chemical shifts which were assignable are indicated in Figure 1 and in Table I.[21] The chemical shifts of the allene carbons in **10, 11,** and **12** correlate well with model compounds taking into account the usual α, β, and γ effects.[22a] Model compounds include methylenecyclopropane (**16**), vinylidenecyclopropane (**17**), and trimethyl-2′-methylprop-1′-enylidenecyclopropane (**18**). The terminal sp^2 carbon (C$_c$) shows an α effect of +10 ppm per methyl group in comparing 1,1-dimethylallene and **17** with tetramethylallene and **10, 11, 12,** and **18.** There is an upfield shift in C$_e$ induced by three-membered ring formation of 7 ppm from **12** to **10,** 18 ppm from 1,1-dimethylallene to **17,** and 10 ppm from isobutylene to methylenecyclopropane. This effect is analogous to that seen in the ^{13}C spectrum of cyclopropane.[22a] The sp hybridized allene carbon (C$_d$) in these



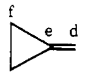
11

$J_{3,4}$ = 9.2 Hz
$J_{4,5}$ = 6.5 Hz
$J_{5,6}$ = 3.0 Hz
$J_{6,7}$ = 6.0 Hz
$J_{1,7}$ = 2.8 Hz

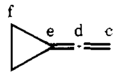


15

$J_{3,4}$ = 10.0 Hz
$J_{4,5}$ = 6.0 Hz
$J_{5,6}$ = 3.0 Hz
$J_{6,7}$ = 7.0 Hz
$J_{1,7}$ = 3.0 Hz



16a



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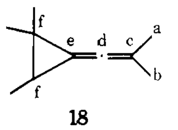

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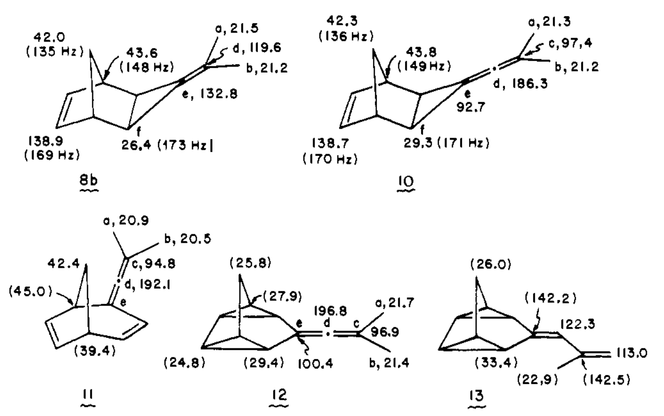


Figure 1. ^{13}C chemical shifts (ppm downfield from Me_4Si). Some $J_{^{13}C\text{-}H}$ values are shown for **8b** and **10.**

Table I. Chemical Shifts of Carbons in **10** and Corresponding Chemical Shifts in **11** and **12** and Related Compounds[a]

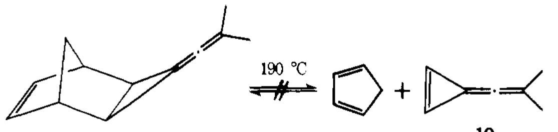
	C_a	C_b	C_c	C_d	C_e	C_f
10[d]	(21.3)	(21.2)	97.4	186.3	92.7	29.3
11[d]	(20.9)	(20.5)	94.8	192.1	99.5	
12[d]	(21.7)	(21.4)	96.9	196.8	100.4	
Vinylidenecyclopropane (**17**)[d]			76.3	194.1	75.3	7.7 (CH_2)
18[d]	(21.2)	(21.0)	96.4	184.7	92.0	25.9 (CHMe) 23.5 (CMe_2)
Tetramethylallene[b]	20.7	20.7	92.6	200.2	92.6	20.7 (CH_3)
1,1-Dimethylallene[b]			72.1	207.3	93.4	19.5 (CH_3)
Methylenecyclopropane (**16**)[d]				103.0	130.9	2.6 (CH_2)
Isobutylene[c]				109.8	141.2	
8b[d]	21.5	21.5		119.6	132.8	26.4

[a] All chemical shifts are in ppm downfield from tetramethylsilane. Chemical shifts in parentheses were not unambiguously assignable. [b] R. Steur, J. Van Dongen, M. DeBie, and W. Drenth, *Tetrahedron Lett.*, 3307 (1971). [c] Reference 22a, p 71. [d] This work.

systems also shows this effect. While β methyl substitution from 1,1-dimethylallene to tetramethylallene causes a small upfield shift of C_d by ca. 3.5 ppm per methyl group, closing a three-membered ring causes large upfield shifts. Comparison of the chemical shifts of C_d in **12** and **10** reveals a 10.5 ppm upfield shift in **10** as a result of ring closure, and a 13 ppm upfield shift is seen for C_d from 1,1-dimethylallene to **17.** A similar effect is noted between methylenecyclopropane and isobutylene; the chemical shift of the terminal sp ^{2}carbon (C_d) is 7 ppm further upfield in methylenecyclopropane.

The ^{13}C-H coupling constants for **8b** and **10** indicated on the structures in Figure 1 are quite similar to analogous coupling constants in norbornene[22b] and norbornadiene.[22a] Further $J_{^{13}C\text{-}H}$ and chemical shift data for these compounds are reported in the Experimental Section.

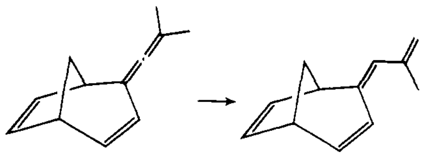
Kinetics. The rate of rearrangement of **10** to **11, 12,** and **13** at 140 °C and 2-10 mm pressure was measured by VPC analysis. The first-order rate constant for disappearance of **10** was found to be $(1.37 \pm 0.03) \times 10^{-5}\ s^{-1}$ at 140.0 °C. The rate constant for appearance of **11** is then $(8.1 \pm 0.3) \times 10^{-6}\ s^{-1}$ and that for **12** is $(5.6 \pm 0.3) \times 10^{-6}\ s^{-1}$. The rate of conversion of **12** to **13** was measured independently, and it varied from 0.7 to $6.4 \times 10^{-6}\ s^{-1}$, apparently because of surface effects. In control runs, thermolysis of **12** at 140 °C gave only **13,** with less than 0.5% of **10** or **11.** Both **11** and **13** were found to be stable at 140 °C for long periods; however, heating for ca. 5 days at 200 °C caused rearrangement of **13** to three unidentified products with shorter retention times. Similarly, compound **11** slowly gave two unidentified products at 200 °C, but with much longer retention times. These products appear to be the same as those obtained when **10** is heated at 300 °C.[23] The rate of conversion of **10** to **11** and **12** was measured over the temperature range 140-190 °C (see Experimental Section), giving $E_a = 34.8 \pm 0.5$ kcal/mol, $\log A = 13.6 \pm 0.3$ for **10** → **11** + **12.**



10 **19**

To test the possibility that the alkenylidenecyclopropene **19** might form reversibly under these conditions, the pyrolysis was done at ca. 190 °C in the presence of ca. 1 equiv of perdeuteriocyclopentadiene. Analysis of the pyrolysis mixture after 30 min by mass spectrometry indicated that no deuterium had been incorporated into **11, 12,** or **13,** thus eliminating the intermediacy of **19.**

To check for surface effects, pyrolyses of **10** were done in a glass-packed reaction flask with a 12-fold surface area increase. Under these conditions, **12** rearranges nearly completely to **13** and is not isolable. The rate of decomposition of **10,** however, was not affected, nor was the ratio of (**12** + **13**) to **11** affected by more than ca. 3%. Thus, formation of **11** and **12** are both clearly first order and not subject to surface catalysis. Interestingly, there is an apparent metal catalysis of the conversion of **10** to **12,** even at temperatures below 100 °C on copper VPC columns. Copper powder caused increased rates for formation of **12** at 140 °C. Compound **12** also rearranges to **13** on VPC analysis in copper above ca. 120 °C. Stainless steel columns and fittings prevent these rearrangements. We have also observed a rearrangement of **12** to **13** on standing in carbon tetrachloride solution at room temperature. The analogous allene-butadiene rearrangement also occurs for **11,** but much more slowly than for **12.** In carbon tetrachloride solution, as well as during preparative VPC on copper columns above ca. 150 °C, **11** rearranges to **20.** This reaction



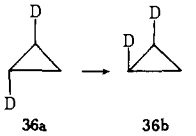
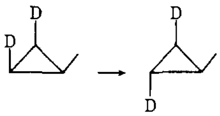
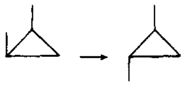
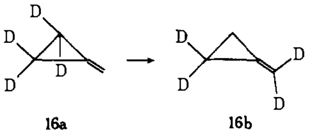
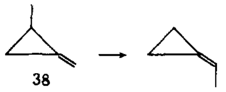
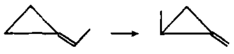
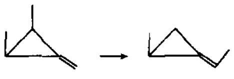
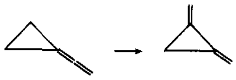
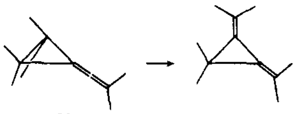
11 20

occurs irreproducibly and does not normally occur under the gas-phase reaction conditions. The rearrangements of **12** to **13** and **11** to **20** are forbidden 1,3-hydrogen shifts and are apparently catalyzed by glass surfaces, by surfaces in copper VPC columns, and in carbon tetrachloride solution.

The rate of rearrangement of **8b** to **9b** at 140 °C and at ca. 5 mm pressure (static) was measured by VPC analysis. The first-order rate constant for disappearance of **8b** was found to be $6.08 \times 10^{-5}\ s^{-1}$ at 140 °C. The yield of **9b** was quantitative by VPC analysis.[11a,c]

Of particular interest is the rate of formation of the unsubstituted trimethylenemethane diradical. We have measured the rate of isomerization of 2,2,3,3-tetradeuteriomethylenecyclopropane (**16b**) and found the rate constant for the formation of the trimethylenemethane diradical to be 2.6×10^{-5} s^{-1} at 210 °C.[24] We have also measured the rate of rearrangement of vinylidenecyclopropane **17** to 1,2-dimethylenecyclopropane at 210 °C and found the rate constant for this rearrangement to be $3.1 \times 10^{-6}\ s^{-1}$.[24]

Table II. Kinetic Parameters for Rearrangements of Various Cyclopropanes, Methylenecyclopropanes, and Alkenylidenecyclopropanes at 150 °C

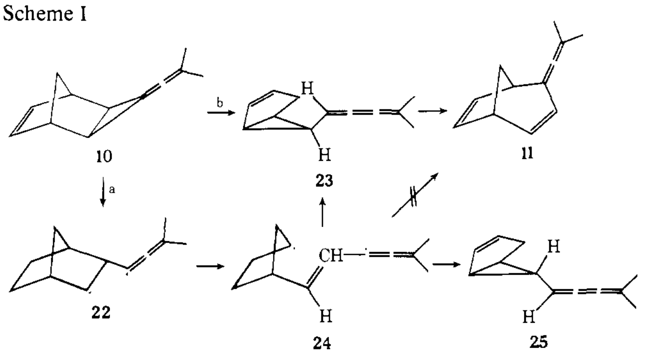
Reaction	k (150 °C), s^{-1}	$\Delta G^{\ddagger}_{150}$,[a] kcal/mol
 36a → 36b	3.4×10^{-18}[b]	58.9
 31a → 31b	1.2×10^{-16}[b]	55.9
 32a → 32b	6.6×10^{-16}[b]	54.5
 16a → 16b	~8.0×10^{-8}[c]	39[c]
 38	1.3×10^{-7}[b]	38.4
 37	8.7×10^{-8}[b]	38.7
	2.0×10^{-5}[e]	34.2[e]
 17	7.1×10^{-9}[d]	41[d]
 39	~7×10^{-7}[f]	~37[f]

[a] Rate constants were extrapolated to 150 °C using the Arrhenius parameters from footnote *b* or by using estimated parameters from analogous reactions. [b] "Kinetic Data on Gas Phase Unimolecular Reactions", S. W. Benson and H. E. O'Neal, NSRDS-NBS21, U.S. Government Printing Office, Washington, D.C., 1970. [c] Calculated from the rate constant at 209.5 °C assuming log A = 13 (ref 24). [d] J. M. Conia, R. Bloch, and P. LePerchec, *Angew. Chem., Int. Ed. Engl.*, 9, 798 (1970). We have measured the rate of this reaction at 210 °C and extrapolated the rate to 150 °C assuming log A = 13 (ref 24). [e] Reference 6a. [f] Reference 8a.

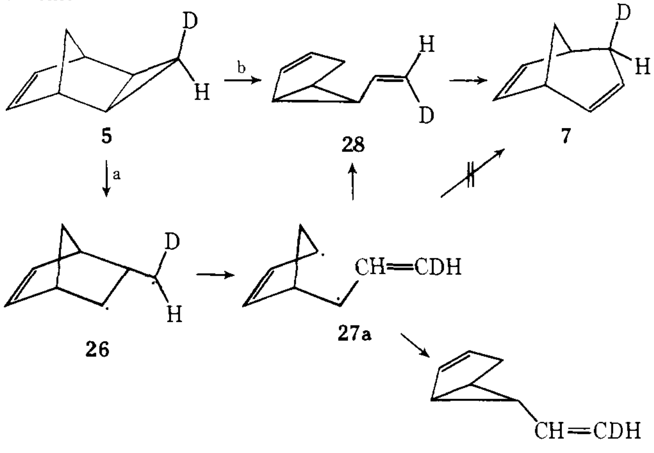
Discussion

C-2–C-3 Cleavage. The two primary reactions of **10** to give **11** and **12** are the result of competitive cleavage of the C-2–C-3 and C-2–C-4 bonds in **10**, analogous to the rearrangements observed in the parent hydrocarbon **5**. The C-2–C-3 cleavage product, **11**, can arise either (a) by a diradical mechanism involving homolytic C-2–C-3 cleavage to diradical **22**, or (b) by concerted rearrangement of **10** to the cumulene **23**, followed by a Cope rearrangement of **23** to **11** (Scheme I). The rearrangement of **5** to **7** offers an analogous choice of mechanistic alternatives (Scheme II). Freeman has concluded from the stereospecificity of the rearrangement of the deuterium labeled compounds (Scheme II) that this reaction occurs by way of path b. Path a might be expected to lead to loss of stereospecificity because C–C rotation is possible in diradical **26**. Such rotation could, however, be slower than the subsequent ring cleavage,[25] so that this evidence is not unambiguous. More convincing evidence that diradicals are not involved in the conversion of **5** to **7** comes from a comparison of the thermal products from **5** with the known products of diradical **27b** generated independently from pyrolysis of the pyrazoline **30**.[26] The *exo*-pyrazoline **30** gives both **7** and **29** on pyrolysis, but thermolysis of **5** gives none of the *exo*-vinylcyclopropane **29** that would be expected from a diradical **27**.[27,28] This evidence, then, strongly suggests that diradicals are not involved in the rearrangement of **5** to **7**. As with the deuterium labeling experiments, it is conceivable that the "endo" diradical **27a** from **26** might undergo C–C rotation to the "exo" diradical more slowly than bond closure to **28**.[28] Since the "exo" conformer **27b** must undergo such a C–C rotation, however, to give the "endo" diradical precursor to the *endo*-vinylcyclopropane **28** faster than simple closure to **29**, we expect that the C–C rotation of **27a** to **27b** should also be faster than ring closure to **28**. This argument then excludes diradical **27** as an intermediate in conversion of **5** to **7**.

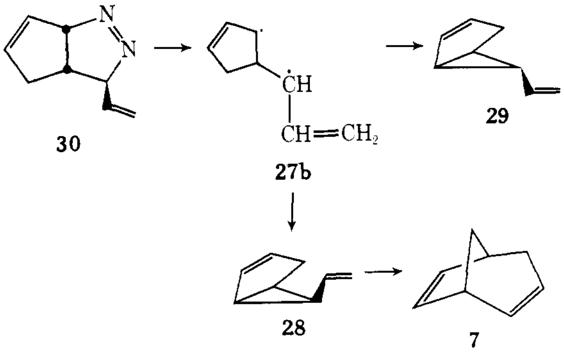
Scheme I



Scheme II

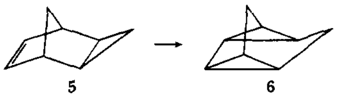
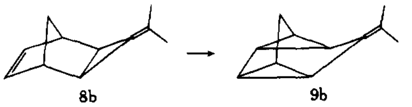
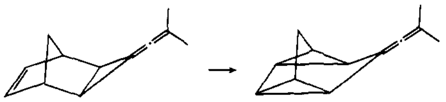
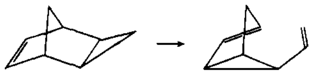
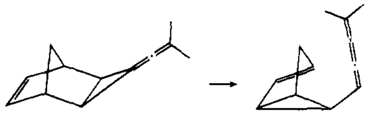
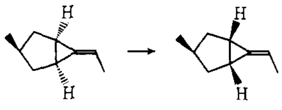


29



This conclusion is supported by thermochemical estimates of the activation energy required to form the diradical **26** from **5**. Using the free energy of activation at 150 °C of 56 kcal/mol for cis-trans isomerization of dideuteriomethylcyclopropane **31** (Table II) as a model for $\Delta G^{\ddagger}$ for the opening of **5** to **26**, we can conclude that **26** is not likely to be an intermediate in the

Table III. Kinetic Parameters and Estimated Heats of Reaction for Various Tricyclo[3.2.1.0]oct-6-ene Rearrangements

Reaction	$k(150\,^{\circ}\mathrm{C})$, s^{-1}	$\Delta G^{\ddagger}_{150}$,[a] kcal/mol	$\Delta G^{\ddagger}_{150^{\circ},\mathrm{est}}$,[b] kcal/mol	$\Delta H^{\circ}_{\mathrm{est}}$,[c] kcal/mol
 **5** → **6**	1×10^{-12}[d]	48	49[e]	−9[f]
 **8b** → **9b**	1.6×10^{-4}[g]	31.7	34[h]	−21[f]
 **10** → **12**	1.6×10^{-5}[g]	34.3	36[i]	−21[f]
 **5** → **28**	7×10^{-12}[d]	47	56[j]	+2[k]
 **10** → **23**	2.5×10^{-5}[g]	34.0	36[l]	−5[k]
 **36** → partially racemized	1.3×10^{-5}[n]	34.6[n]	34[m]	

[a] Free energies of activation were calculated from rate constants at 150 °C. [b] Estimates for $\Delta G^{\ddagger}$ were derived from the cleavage steps for diradical mechanisms from model compounds in Table II. [c] Estimated ΔH° for the overall reaction. [d] References 10. The rate constant at 150 °C was obtained by the extrapolation of the literature rate at 290 °C assuming $\log A \cong 14.5$, based on structural effects on $\log A$'s in 32, 37, and 10. [e] Estimated from $\Delta G^{\ddagger}$ for 32 (Table II) assuming a 5 kcal/mol strain difference in the norbornene and the bicyclo[3.2.1]octene diradical 33 (ref 37). [f] Estimated from strain energies for norbornene, bicyclo[3.2.1]octane, cyclopropane, and methylenecyclopropanes and from a bond energy difference of 22 kcal/mol between C–C π and σ bonds (ref 32, 37). [g] This work. The rate constant for **8**b was extrapolated from 140 °C using $\log A = 13$. [h] Estimated from $\Delta G^{\ddagger}$ for 37 (Table II) assuming 5 kcal/mol norbornane strain relief from 8b to diradical **34** (ref 37). [i] Estimated from $\Delta G^{\ddagger}$ for **17** (Table II) assuming 5 kcal/mol norbornane strain energy relief from 10 to diradical 35 (ref 37). [j] Estimated from $\Delta G^{\ddagger}$ for 31 (Table II). [k] Estimated for **5** → 28 and 10 → **23** from strain energies of norbornene, cyclopentene, and a 22 kcal/mol difference in C–C π and σ bond strengths (ref 32). The energy difference between the allene and cumulene strain and resonance energies in 10 and 23 was taken as 7 kcal/mol (ref 37). [l] Estimated from a $\Delta G^{\ddagger}$ of 54.5 kcal/mol for **32**, minus 12 kcal/mol allyl resonance energy (ref 33) minus 12 kcal/mol sp^2 strain relief (ref 32) plus 6 kcal/mol for extra strength of an sp^3–sp^2 bond (ref 34). [m] Estimated from $\Delta G^{\ddagger}$ for 37 (Table II) assuming 5 kcal/mol cyclopentane strain relief from 36 to the diradical. [n] Reference 6b.

conversion of **5** to **7**, since the experimental $\Delta G^{\ddagger}$ of 47 kcal/mol (Table III) for this conversion is 9 kcal/mol too low to give **26**. Thus, **5** appears to rearrange to **7** by path b in Scheme II. The intermediate **28** could be formed from **5** in a concerted $\pi_s^2 + \sigma_s^2 + \sigma_s^2$ mechanism (Figure 2), although the overlap between the σ bonds is not good, perhaps accounting for the rather high activation energy for this reaction. The subsequent Cope rearrangement of **28** to **7** in Scheme II should be very rapid by analogy to the known rapid rearrangement of *cis*-divinylcyclopropane to 1,4-cycloheptadiene at room temperature.[30,31]

The rearrangement of **10** to **11** takes place with a free energy of activation 13 kcal/mol lower than for the analogous conversion of **5** to **7**, suggesting significant electronic involvement of the alkenylidene functional group in the rearrangement mechanism. For the concerted mechanism (pathway a, Scheme I), a novel ten-electron ($\pi_s^2 + \sigma_a^2 + \pi_a^2 + \pi_s^2 + \sigma_s^2$) mechanism (Figure 2), with better orbital overlap than the six-electron pathway available for **5** → **7**, could explain the large rate difference. A thermochemical analysis of pathway a in Scheme I, however, suggests that the diradical **22** may be accessible under the reaction conditions. Thus, beginning with a $\Delta G^{\ddagger}_{150}$ of 54 kcal/mol for the cis–trans rearrangement of 1,2-dimethylcyclopropane **32**, a free energy of activation for C-2–C-3 cleavage of **10** to **22** can be estimated by subtracting 12 kcal/mol for the relief of the extra strain of the sp^2 cyclopropyl center in **10**,[32] by subtracting 12 kcal/mol for the allylic stabilization in **22**[33] and by adding ca. 6 kcal/mol for an anticipated increase in the $\mathrm{C_{sp^3}}$–$\mathrm{C_{sp^2}}$ bond strength in **10**.[34] This leads to a rough estimate of 36 kcal/mol for $\Delta G^{\ddagger}_{150}$, close to the experimental value of 34 kcal/mol.[35] Arguments analogous to those used to exclude such a pathway for **5** → **7** suggest, however, that a diradical pathway for **10** → **11** is unlikely. Should a diradical intermediate such as **24** participate in the rearrangement of **10** to **11**, we would anticipate the formation of **25** by analogy with the experiments on the pyrolysis of the pyrazoline **30**. Since we do not see any significant amount of **25** among the thermal rearrangement products of **10**, we conclude that the rearrangement of **10** to **11** is unlikely to have involved diradical intermediates. This then leaves pathway b

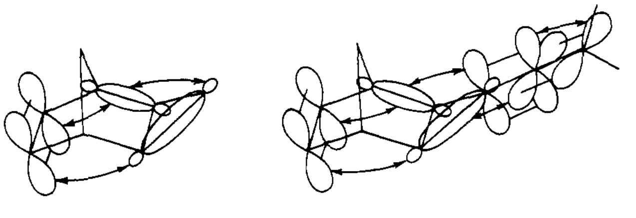
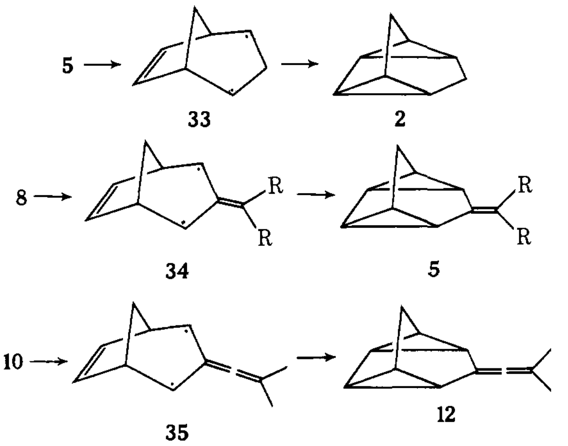


Figure 2. Orbital overlap configuration for rearrangement of **5** to **28** and **10** to **23**.

in Scheme I as the likely mechanism for rearrangement of **10** to **11.** This mechanism apparently involves in unusually intricate $\pi_s{}^2 + \sigma_a{}^2 + \pi_a{}^2 + \pi_s{}^2 + \sigma_s{}^2$ concerted ten-electron rearrangement of **10** to **23** in the first step (Figure 2), followed by a rapid Cope rearrangement[30] of **23** to **11.**

Such a concerted ten-electron mechanism involving all of the π electrons of the allene moiety can be compared with the rearrangement of cyclopropylallene.[36] In that case, the increased reactivity of the allene over vinylcyclopropane (by 8 kcal/mol) is attributed to a 13 kcal/mol increase in exothermicity,[36] but estimates of the $\Delta H°$'s for **5** → **7** and **10** → **23** (Table III) give a difference of ca. 7 kcal/mol,[37] which cannot account for the 13 kcal/mol higher reactivity of **10.** This then suggests some involvement of both sets of allene π electrons in the rearrangement of **10** and perhaps even cyclopropylallene. The cyclopropylallene energy surface, however, appears from MINDO/3 calculations to involve a biradicaloid transition state. A biradicaloid intermediate or transition state for **10** → **11** may also be possible, if it is sufficiently tight that rotation and closure to **25** is prohibited. In any event, the allene π electrons appear to facilitate the C-2–C-3 cleavage reaction in **10**[38] such that it competes with the rapid C-2–C-4 cleavage to a stabilized trimethylenemethane-type diradical. The methylenecyclopropane derivatives **8** do not give any C-2–C-3 cleavage in competition with C-2–C-4 cleavage, though, presumably because they lack the allene moiety.

C-2–C-4 Cleavage. The C-2–C-4 cleavage reactions of **10** and **8** are very much accelerated by the alkenylidene or methylene functional groups compared with **5.** The free energies of activation for these reactions have been found to be 31.7 kcal/mol for **8b** → **9b** and 34.3 kcal/mol for **10** → **12** at 150 °C. The rearrangement of **10** to **12** has a $\Delta G^{\ddagger}$ 14 kcal/mol lower than for **5** → **6**, while the rearrangement of **8b** to **9b** has a $\Delta G^{\ddagger}$ 16 kcal/mol lower than for conversion of **5** → **6.** All three of these reactions are geometrically constrained to occur by a $\sigma_s{}^2 + \pi_s{}^2$ mechanism, which is a symmetry forbidden reaction. They have therefore been generally interpreted to occur by cleavage to a diradical followed by rapid intramolecular trapping of the diradical by the π bond.[10,11]



The 20–22 kcal/mol decrease in $\Delta G^{\ddagger}$ for the C-2–C-4 cleavage of **8b** and **10** relative to C–C cleavage of dimethylcyclopropane **32a** can be attributed to a stabilization of these diradicals by resonance interaction in the near-planar trimethylenemethane-type transition states and by a relief of the extra strain energy from the sp^2 center in the three-membered rings in **8** and **10** relative to **5.** The total maximum magnitude of these effects should be ca. 12 kcal/mol for the allylic resonance energy expected of an *orthogonal* trimethylenemethane diradical[33] and ca. 12 kcal/mol for the extra strain energy relief in methylenecyclopropanes.[32] Some strain energy relief in opening the norbornene ring could also be expected for compounds **5, 8,** and **10.** The difference in the strain energy of norbornane and bicyclo[3.2.1]octane of 5 kcal/mol gives an estimate of this effect.[39] This agrees well with the observed difference of 6 kcal/mol in the values of $\Delta G^{\ddagger}{}_{150}$ for cleavage of **1** to **33** (Table III) and for cis–trans isomerization of *cis*-1,2-dimethylcyclopropane (**32a**) (Table II). Work by Roth and Wegener on the thermal interconversion and racemization of *syn*- and *anti*-3-methyl-6-ethylidenebicyclo[3.1.0]hexane (**36**) (Table III) indicates that the $\Delta G^{\ddagger}$ for cleavage of this bicyclic methylenecyclopropane to a diradical is 34.6 kcal/mol (syn → anti).[7] This value is nearly identical with our measured values for $\Delta G^{\ddagger}$ for the rearrangement of **8b** to **9b** and **10** to **12.** This is not unexpected, since the relief of strain in these two systems should be the same.[32] The fact that **36** rearranges with a barrier very similar to that of **8b** and **10** further shows that any possible participation by the proximate double bond in **8b** or **10** in a $\pi_s{}^2 + \sigma_s{}^2$ fashion has little effect on the rate-determining transition state for rearrangement of **8b** to **9b**, suggesting that this reaction occurs in two steps via a diradical intermediate as assumed.

The 16 and 14 kcal/mol differences in $\Delta G^{\ddagger}{}_{150}$ between the model reaction **5** → **33** and the two C-2–C-4 cleavage reactions of **8b** and **10** then give an indication of the conjugative stabilization and sp^2 strain relief felt in the transition states leading to the near-planar diradicals **34** and **35.** These values can be compared with the corresponding differences in $\Delta G^{\ddagger}$ between unconstrained cyclopropanes and methylenecyclopropanes or alkenylidenecyclopropanes for a direct estimate of the difference in the conjugative stabilization felt in transition states leading to near-planar and orthogonal trimethylenemethane-type diradicals.

The $\Delta G^{\ddagger}{}_{150}$ for cis–trans isomerization of 1,2-dideuteriocyclopropane **36** is 58.9 kcal/mol and may be used as a model for cleavage of a cyclopropane ring to an unstabilized trimethylene diradical. We have found the $\Delta G^{\ddagger}{}_{150}$ for isomerization of the deuteriomethylenecyclopropane **16b** to be ca. 39 kcal/mol, which indicates that formation of the orthogonal trimethylene diradical is favored over the unstabilized trimethylene diradical by 20 kcal/mol. This value is only 4 kcal/mol larger than the corresponding 16 kcal/mol difference between $\Delta G^{\ddagger}{}_{150}$ for **8b** → **34** and $\Delta G^{\ddagger}{}_{150}$ for **5** → **33.** From this observation, we can conclude that the conjugative stabilization of the formation of these near-planar trimethylenemethane diradicals is only slightly larger (~4 kcal/mol) than would be expected for a corresponding trimethylenemethane diradical capable of adopting an orthogonal geometry.[9]

The $\Delta G^{\ddagger}{}_{150}$ for rearrangement of methylenecyclopropane **16b** (39 kcal/mol) can be compared with that for rearrangement of ethylidenecyclopropane **37** (38.7 kcal/mol, Table II) to show the two methyl groups in **34a** would not be expected to affect the $\Delta G^{\ddagger}$ for **8b** → **34.** Comparison of $\Delta G^{\ddagger}$ values for alkylcyclopropanes and alkylmethylenecyclopropanes (Table II) indicates that, for corresponding alkyl substitution, the difference in $\Delta G^{\ddagger}$ produced by the methylene group is 18 kcal/mol for one methyl and 20 kcal/mol for *cis*-1,2-dimethyl substitution.[38,40] The spread in these values suggests a ±2 kcal/mol ambiguity in our quantitative model comparisons could be expected.

An 18 kcal/mol effect of alkenylidene substitution on cyclopropane ring opening can be seen by comparing the $\Delta G^{\ddagger}{}_{150}$ value for isomerization of 1,2-dideuteriocyclopropane **36** (58.9 kcal/mol) with the $\Delta G^{\ddagger}{}_{150}$ we have found for vinylidenecyclopropane **17** (41 kcal/mol). A similar effect appears in comparing the approximate $\Delta G^{\ddagger}{}_{150}$ of 37 kcal/mol for 2,2,3,3-tetramethyl-2′-methylprop-1′-enylidenecyclopropane (**39**) rearrangement[41] with that for rearrangement of *cis*-1,2-dimethylcyclopropane (**32**).[42]

A comparison of the $\Delta\Delta G^{\ddagger}{}_{150}$ of 14 kcal/mol for **10** → **35** and **5** → **33** with the $\Delta\Delta G^{\ddagger}{}_{150}$ of 18 kcal/mol for the effect of the alkenylidene group in alkenylidenecyclopropanes capable of forming orthogonal diradicals (cf. **36a** and **17**, Table II) indicates again that formation of the near-planar diradical **35** is only ca. 4 kcal/mol less favorable than would be expected for an orthogonal diradical. Both this result and the 4 kcal/mol effect observed in the methylenecyclopropane system **8b** agree well with Gajewski's conclusion that the transition state for formation of the planar diradical from *trans*-2,3-dimethylmethylenecyclopropane is only 2 kcal/mol higher than that for formation of an orthogonal diradical.[6a] The most reliable recent ab initio molecular orbital calculations[5] on the energy difference between the planar and orthogonal singlet trimethylenemethane diradicals now indicate that the Jahn-Teller distorted C_{2v} planar diradical lies only 3–6 kcal/mol higher in energy than the orthogonal form in good agreement with the experimental results.

A similar number was derived by Roth and Wegener for this energy difference using a kinetic scheme in which the planar and orthogonal radicals are formed independently from the ethylidenecyclopropane **36** (Table III).[7] Like the ring fused methylenecyclopropane **8b**,[9] **36** might, however, have difficulty opening to an orthogonal diradical. Such a rotation about the external double bond in **36** or **8b** is likely to be severely hindered by the double bond character there, at least until the ring opening has progressed very far toward a planar diradical form so that loss of overlap in the rotating group can be effectively compensated by the developing allylic radical conjugation within the ring (see structure i, ref 9). In this case, even if the orthogonal diradical were formed directly, the transition state for its formation should closely resemble a planar diradical. We think it more likely, however, in view of the small energy difference between the planar and orthogonal forms,[6a] that the planar diradical is formed first from **36** and **8b**, since there may not be enough benefit energetically from rotation to the orthogonal form to compensate for the rotation required about the partial double bond in the transition state. In this event, an initially formed planar diradical could rotate rapidly to an orthogonal form, causing nearly complete racemization of **36** in its rearrangement.[44] The observation of only partial racemization of **36**, however, nicely shows that a planar diradical or transition state must play some role in the rearrangement of **36** (and presumably **8b** and **10**) independent of the orthogonal diradical.

The question of whether these diradicals are at energy minima or are transition states is an interesting one theoretically.[45] The heat of formation (78 kcal/mol) of the noninteracting orthogonal trimethylenemethane diradical can be estimated from the heat of formation of isobutylene,[46] the bond dissociation energy (88 kcal/mol) of its allylic hydrogen,[33] and a bond dissociation energy of 98 kcal/mol at the noninteracting orthogonal radical site.[34] This value is 30 kcal/mol higher than $\Delta H_f°$ for methylenecyclopropane, whose activation energy is 39 kcal/mol (log A assumed to be 13.0, Table II). The barrier to reclosure of the orthogonal trimethylenemethane diradical is thus indicated to be about 9 kcal/mol. If the theoretical calculations are correct with regard to the energy of the planar diradical,[5] then it too could have a comparable barrier to closure. The barrier to closure of the orthogonal diradical has also been found to be 9 kcal/mol from MO calculations, reflecting a loss of allylic stabilization in the transition state.[8b] Further calculations on the barrier to closure of the orthogonal and planar singlet diradicals would be of interest in this connection.

Experimental Section

All boiling points and melting points are uncorrected. VPC analyses were performed with a Varian Aerograph A-90-P3 gas chromatograph equipped with a thermal conductivity detector. Columns used were stainless steel ⅛ in. × 12 ft of 12% SE-30 on 30/60 Chromosorb W/NAW (column A), copper ¼ in. × 12 ft of 15% Carbowax 20M on 60/80 Chromosorb W/NAW (column B), and stainless steel ¼ in. × 12 ft of 11% Carbowax 20M on 80/100 Chromosorb W/AW (column C). Proton NMR spectra were taken on a Varian T-60 spectrometer. Where indicated, 100 MHz spectra were taken on a Varian HA-100 spectrometer. Carbon NMR spectra were taken on a Varian CFT-20 spectrometer and are referenced to Me_4Si.

IR spectra were recorded on a Perkin-Elmer 337 grating infrared spectrophotometer as solutions with a matched reference cell. UV spectra were recorded on a Cary-15 spectrophotometer. Mass spectra were obtained on an AEI MS-902 spectrometer.

3-(2′-Methylprop-1′-enylidene)tricyclo[3.2.1.0^{2,4}]oct-6-ene (10). To a 500-ml three-neck flask was added under nitrogen 100 ml (1.04 mol) of freshly distilled norbornadiene, 7.5 g of tetra-*n*-butylammonium iodide (0.02 mol), and 40.0 g (0.27 mol) of freshly distilled 1-bromo-3-methyl-1,2-butadiene.[16] While heating at 50 °C, with vigorous stirring, 100 ml of 50% sodium hydroxide solution was added over 10 min. The contents were vigorously stirred under nitrogen at 60 °C for 1 week. After cooling in ice, the mixture was diluted with ether and water and then neutralized with 20% sulfuric acid. The ether solution was washed successively with water, saturated sodium bicarbonate, and saturated sodium chloride. The ether solution was dried over potassium carbonate and the solvent removed. The crude product was distilled through a short Vigreux column giving 9.0 g (21%) (>97% pure by VPC): bp 50–60 °C (0.3 mm); ^{1}H NMR (100 MHz) (CCl_4) δ 0.97 and 1.31 (AB, J = 8.0 Hz, 2 H, H_8), 1.72 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 1.77 (d, J = 1.0 Hz, 2 H, H_2, H_4), 2.97 (m, 2 H, H_1, H_5), 6.23 (t, J = 2.5 Hz, 2 H, H_6, H_7); ^{13}C NMR ($CDCl_3$) δ_{Me_4Si} 21.2 (q, $J_{C\text{-}H}$ = 128 Hz, CH_3), 21.3 (q, $J_{C\text{-}H}$ = 128 Hz, CH_3), 29.3 (d, $J_{C_2\text{-}H_2}$ = 173 Hz, C_2, C_4), 42.3 (t, t, $J_{C_8\text{-}H_8}$ = 136 Hz, $J_{C_8\text{-}H_{1,5}}$ = 4 Hz, C_8), 43.8 (d, q, $J_{C_1\text{-}H_1}$ = 149 Hz, $J_{C_1\text{-}H}$ = 7.0 Hz, C_1, C_5), 92.7 (s, C_3), 97.4 (sept, $J_{C\text{-}H}$ = 6.5 Hz, $=CMe_2$), 138.7 (d, m, $J_{C_6\text{-}H_6}$ = 170 Hz, $J_{C_6\text{-}H}$ = 3 Hz, C_6, C_7), 186.3 (sept, $J_{C\text{-}H}$ = 5 Hz, $=C=$); IR (CCl_4) 3100, 3050, 3010, 2975, 2945, 2010, 2000, 1450, 1425, 1375, 1360, 1320, 1285, 1245, 1100, 695, 650 cm^{-1}; mass spectrum (70 eV) *m/e* 158.1099 (calcd for $C_{12}H_{14}$: 158.1095), *m/e* (rel intensity) 159 (M + 1, 1), 158 (M$^+$, 7), 143 (11), 128 (16), 115 (9), 91 (8), 80 (7), 79 (8), 77 (7), 72 (7), 71 (7), 57 (20), 56 (8), 55 (6), 51 (6), 43 (100), 42 (56), 41 (41), 39 (21), 29 (21), 28 (8), 27 (27).

When 56.5 g of commercial potassium *tert*-butoxide and 250 ml of freshly distilled norborandiene at −10 °C was treated with 50.5 g of 3-chloro-3-methyl-1-butyne over 1 h and left to stir for 1 h at 0 °C, workup gave 5.75 g (7%) of impure **10**, bp 40–62 °C (0.3 mm), which was ca. 80% pure by VPC.

Pyrolysis of 10. To a 2200-ml flask filled with nitrogen was added 200 mg of freshly distilled **10**. The flask was evacuated and sealed after freeze–pump–thaw degassing cycles. The flask was placed in an oven maintained at 140.0 ± 0.2 °C for 600 min. After cooling in liquid nitrogen to condense the products, the flask was warmed to room temperature and opened under a nitrogen flow. Analysis of the products by VPC on column A showed three compounds in addition to recovered starting material: $T_R{}^{125°}$ 26.5 min (**11**), 39.5 min (**6**), 44 min (**12**), 49 min (**13**). The structures were determined on the basis of the NMR, IR, UV, and mass spectral data for VPC collected samples shown below.

2-(2′-Methylprop-1′-enylidene)bicyclo[3.2.1]octa-3,6-diene (11). ^{1}H NMR (100 MHz) (CCl_4) δ 1.72 (s, 3 H, CH_3), 1.74 (s, 3 H, CH_3), 1.99 (m, 2 H, H_8), 2.80 (broad m, 1 H, H_1), 5.50)m, $J_{3,4}$ = 9.2 Hz, 1 H, H_3), 5.72 (dd, $J_{5,6}$ = 3.0 Hz, $J_{6,7}$ = 6.0 Hz, 1 H, H_6), 5.90 (dd, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 6.5 Hz, 1 H, H_4), 6.09 (dd, $J_{6,7}$ = 6.0 Hz, $J_{1,7}$ = 2.8 Hz, 1 H, H_7); ^{13}C NMR ($CDCl_3$) δ_{Me_4Si} 20.5 (q, $J_{C\text{-}H}$ = 128 Hz, CH_3), 20.9 (q, $J_{C\text{-}H}$ = 128 Hz, CH_3), 39.4 (d, $J_{C_5\text{-}H_5}$ = 148 Hz, C_5), 42.4 (t, $J_{C_8\text{-}H_8}$ = 133, C_8), 45.0 (d, $J_{C_1\text{-}H_1}$ = 143 Hz, C_1), 94.8 (sept, $J_{C\text{-}H}$ = 7 Hz, $=CMe_2$), 99.5 (m, $J_{C\text{-}H}$ = 6 Hz, C_2), 122.5 (d, $J_{C\text{-}H}$ = 163 Hz, vinyl C), 129.0 (d, $J_{C\text{-}H}$ = 167 Hz, vinyl C), 130.8 (d, $J_{C\text{-}H}$ = 167.5 Hz, vinyl C), 137.2 (d, $J_{C\text{-}H}$ = 168 Hz, vinyl C), 192.1)m, $J_{C\text{-}H}$ = 5 Hz, $=C=$); IR (CCl_4) 3050, 3025, 2940, 2890, 2800, 1935, 1435, 1390, 1365, 1355, 1315, 1100, 1050, 940, 920, 905, 875, 855 cm^{-1}; UV (95% ethanol) λ_{max} 252 nm, ϵ 10 400; mass spectrum (70 eV) *m/e* 158.1095 (calcd for $C_{12}H_{14}$: 158.1095), *m/e* (rel intensity) 159 (M + 1, 14), 158 (M$^+$, 73), 157 (5), 147 (7), 144 (68), 143 (64), 142 (23), 141 (21), 129 (27), 128 (100), 127 (16), 117 (14), 116 (23), 115 (50), 91 (36), 80 (18), 79 (27), 78 (14), 77 (32), 66 (9), 65 (23), 64 (7), 63 (16), 58 (12), 53 (14), 52 (9), 51 (27), 50

(7), 43 (18), 41 (18), 40 (7), 39 (41), 38 (5), 28 (64), 27 (21).

3-(2′-Methylprop-1′-enylidene)tetracyclo[3.3.0.0.^{4,6}0^{2,8}]octane (12). ^{1}H NMR ($CHCl_3$) δ 1.85 (s, 6 H, CH_3), 1.35–2.30 (m, 8 H); ^{1}H NMR (C_6H_6) δ 1.33–1.77 (m, 2 H), 1.93 (s, 6 H, CH_3), 1.95–2.30 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ_{Me_4Si} 21.4 (CH_3), 21.7 (CH_3), 24.8 (C_8), 25.8, 27.9, 29.4, 96.9 (=CMe_2), 100.4 (C_3), 196.8 (=C=); IR (CCl_4) 3050, 3020, 2975, 2900, 2850, 2700, 2040, 2000, 1450, 1365, 1290, 1275, 1180, 1050, 1035, 975, 960, 900, 870 cm^{-1}; mass spectrum (70 eV) *m/e* 158.1096 (calcd for $C_{12}H_{14}$: 158.1095), *m/e* (rel intensity) 159 (M + 1, 4), 158 (M^+, 31), 157 (3), 143 (32), 142 (15), 141 (12), 129 (15), 128 (60), 127 (10), 116 (7), 115 (13), 114 (29), 92 (5), 91 (28), 81 (6), 80 (100), 79 (60), 78 (13), 77 (29), 65 (16), 64 (5), 63 (11), 53 (9), 52 (8), 51 (19), 50 (7), 43 (5), 41 (11), 39 (25), 28 (5), 27 (14).

3-(2′-Methylprop-2′-enylidene)tetracyclo[3.3.0.0^{4,6}0^{2,8}]octane (13). ^{1}H NMR (CCl_4) 1.93 (d, J = 1.0 Hz, 3 H, CH_3), 1.10–2.40 (m, 8 H), 4.70 (m, 2 H, vinyl), 5.76 (s, 1 H, vinyl); NMR (100 MHz) (C_6H_6) δ 1.50 (m, 2 H), 1.82 (m, 2 H), 1.97 (m, 2 H), 2.06 (broad s, 3 H, CH_3), 2.27 (m, 2 H), 5.00 (m, 1 H, vinyl), 5.10 (m, 1 H vinyl), 6.15 (broad s, 1 H, vinyl); ^{13}C NMR ($CDCl_3$) δ_{Me_4Si} 22.9 (CH_3), 23.8, 26.0 (C_8), 27.1, 28.7, 29.0, 33.4, 113.0 (=CH_2), 122.3 (=CH–), 142.2 (=C–), 142.5 (=C–); IR (CCl_4) 3075, 3050, 3025, 2960, 2915, 2850, 1650, 1620, 1600, 1455, 1380, 1300, 1280, 1100, 970, 900, 885 cm^{-1}; UV (95% ethanol) λ_{max} 254 nm (ϵ 13 100); mass spectrum (70 eV) *m/e* 158.1090 (calcd for $C_{12}H_{14}$: 158.1095), *m/e* (rel intensity) 159 (M + 1, 4) 148 (M^+, 34), 157 (11), 144 (8), 143 (79), 142 (12), 141 (13), 131 (12), 130 (12), 129 (34), 128 (61), 127 (13), 117 (16), 116 (13), 115 (42), 103 (7), 93 (8), 92 (11), 91 (34), 89 (5), 80 (42), 79 (100), 78 (16), 77 (42), 66 (11), 65 (16), 64 (5), 63 (13), 53 (9), 52 (8), 51 (24), 50 (8), 41 (12), 39 (34), 28 (26), 27 (18).

Ozonolysis of 12. To a 25-ml flask equipped with a Claisen adaptor was added under nitrogen 25 mg of VPC collected **12** in 5 ml of ethyl acetate. While sweeping with nitrogen the flask was cooled to −78 °C and ca. 2% ozone bubbled through the solution at a rate of 25 ml/min. After 30 min, a faint blue-gray color was visible and the bubbling was stopped. Excess dimethyl sulfide was added (ca. 1.5 ml) and the reaction left at −78 °C for 2 h. The flask was allowed to warm to room temperature while the excess dimethyl sulfide evaporated. After 8 h the solvent was removed on a rotory evaporator giving 47 mg of a crude oil which was shown to contain the ketone **14**, in addition to dimethylsulfoxide. The yield, as determined by NMR, was quantitative. NMR (CCl_4) δ 1.2–2.5 (m); IR (CCl_4) 1725 cm^{-1}.[19]

A 2,4-dinitrophenylhydrazone prepared in the usual way gave mp 226–227 °C dec [lit. 225–226 °C dec[19]] after two recrystallizations from ethanol-ethyl acetate.

Ozonolysis of 13. In a procedure similar to that above, 72 mg of VPC collected **13** in 15 ml of 2:1:1 ethylacetate:dichloromethane:methanol was converted to **14** in ca. 100% yield by NMR analysis.

Kinetic Procedure. All glassware was washed with methanolic sodium hydroxide, or a basic solution of ethylenediaminetetraacetic acid, and rinsed well with water and oven dried. Pyrolyses were carried out in a Blue M Electric Power-o-matic 60 saturable reactor proportioning control oven. Temperature control was ±0.2 °C. Temperatures were obtained from a Leeds and Northrup temperature potentiometer and a calibrated total immersion thermometer. Vessels used for kinetic runs were 500 ml and filled with ca. 10–25 mg of hydrocarbon (pressure: 3–8 mm). No polymerization occurred in this pressure range. Above ca. 25 mm polymerization occurred in pyrolyses after ca. 1 half-life. Samples were analyzed by VPC at 120–130 °C on a stainless steel column with stainless steel fittings. Copper and brass apparently catalyze the rearrangements of **10** to **12** and **12** to **13**. All samples were stored neat or as benzene solutions in a nitrogen atmosphere.

Rate of Rearrangement of 10. Dry 500-ml bulbs, each containing 10–15 mg of **10**, were evacuated, degassed, and sealed. Each was heated in an oven regulated to ±0.2 °C for intervals ranging from 2 to 72 h (>5 half-lives). The bulbs were withdrawn from the oven and cooled in liquid nitrogen to condense the material. The bulbs were opened in a nitrogen atmosphere and analyzed by VPC. Concentrations were determined as percentages of the total area for all material. Various runs throughout the entire reaction time were checked for complete material balance using mesitylene (corrected for measured response factors) as a VPC standard. All checks indicated that the material balance was 98 ± 2%. The rate constant for disappearance of **10** at 140.0 °C was determined to be $1.37 \pm 0.03 \times 10^{-5}$ s^{-1} (17 points, correlation coefficient = 0.9995). Product ratios were measured by VPC and checked by NMR integration. The ratio of products **11:12 + 13** was found after 1 half-life to be 59 to 41 ± 1% at 140.0 °C. Rate constants at other temperatures were measured with one kinetic point at each temperature as follows, k (temp, ratio of **11:12 + 13**): $4.1 \pm 0.3 \times 10^{-5}$ s^{-1} (150 °C, 60:40); $9.7 \pm 0.5 \times 10^{-5}$ s^{-1} (160 °C, 61:39); $2.6 \pm 0.2 \times 10^{-4}$ s^{-1} (170 °C, 62:28); $5.9 \pm 0.3 \times 10^{-4}$ s^{-1} (180 °C, 63:37); $1.4 \pm 0.1 \times 10^{-3}$ s^{-1} (190 °C, 60:40). An Arrhenius plot gives $E_a = 34.8 \pm 0.5$ kcal/mol, log $A = 13.6 \pm 0.3$ for **11** → **12** + **13**, correlation coefficient = 0.9998.

Control Experiments. The vessel used for these pyrolyses was a 500-ml flask filled with short lengths of uniform bore Pyrex glass tubing to give a 12-fold increase in surface area and a 19-fold surface-to-volume increase. Pyrolysis of **10** in three runs at less than 2 half-lives gave no increase in the rate of decomposition of **10**. Less than 1% of **12** was formed in these pyrolyses, but the percentage of **13** was equal to the sum of **12** and **13** for runs in unpacked vessels. The percentage of **11** was unaffected.

Pyrolysis of **10** with copper powder at 140 °C gave a fourfold increase in the rate of formation of **12** after 100 min.

Pyrolysis of **12** at 140 °C gave **13** with rate constants in the range of 0.6 to 7.0×10^{-7} s^{-1} in five runs of 10–94 h in identical vessels. When **12** was heated for ca. 5 days at 200 °C it was converted to **13** (55%) and three other unidentified compounds (45%) with shorter retention times than **13**.

Pyrolysis of **11** at 140 °C for 144 h gave only **11** and ca. 10% polymer.

Pyrolysis of **13** at 140 °C for 188 h or 200 °C for 15.5 h gave only recovered **13**. After 5 days at 200 °C **13** gave two unidentified products with shorter retention times in ca. 30% conversion.

Pyrolysis of 10 with Perdeuteriocyclopentadiene. To a 500-ml bulb was vacuum transferred 56 mg of cyclopentadiene-d_6 (96% D).[42] The diene was purified by VPC at room temperature before use, and a 220-mg sample of VPC collected **10** was then transferred to the bulb and sealed. The bulb was placed in an oven for ca. 30 min at ca. 190 °C. VPC collection and mass spectral analysis showed no deuterium incorporation in any of the three products, **11**, **12**, and **13**.

3-Isopropylidenetricyclo[3.2.1.0^{2,4}]oct-6-ene (8b). To a dry 500-ml, three-neck flask was added under nitrogen 44 g (0.39 mol) of commercial potassium *tert*-butoxide, 50 ml (0.52 mol) of norbornadiene, and 50 ml of pentane. While stirring under nitrogen, the flask was cooled to 0 °C and 25 ml (0.25 mol) of 1-chloro-2-methylpropene was added dropwise over 1 h. After 3 h at 0 °C the pot was allowed to come to room temperature and left to stir for 3 days. Water was added to dissolve all precipitates, and the mixture was transferred to a separatory funnel and diluted with ether. The organic layer was separated, washed once with water, and dried over $MgSO_4$. After solvent removal, the residue was distilled to give, after a large forerun of unidentified material, 3.8 g (10%): bp 70–78 °C (35 mm);[11a] ^{1}H NMR ($CDCl_3$) 0.93 and 1.10 (AB, J = 9 Hz, 2 H, H_8), 1.43 (broad s, 2 H, H_2, H_4), 1.68 (t, J = 2.0 Hz, 6 H, CH_3), 2.87 (broad s, 2 H, H_1, H_5), 6.23 (t, J = 2.5 Hz, 2 H, H_6, H_7); ^{13}C NMR ($CDCl_3$) δ_{Me_4Si} 21.5 (q, q, $J_{C\text{-}H}$ = 126 Hz, $J_{C\text{-}H_{2,4}}$ = 4 Hz, CH_3), 26.4 (d, $J_{C_2\text{-}H_2}$ = 173 Hz, C_2, C_4), 42.0 (t, $J_{C_8\text{-}H_8}$ = 135 Hz, C_8), 43.6 (d, q, $J_{C_1\text{-}H_1}$ = 148 Hz, $J_{C_1\text{-}H}$ = 8 Hz, C_1, C_5), 119.6 (sept, $J_{C_9\text{-}H_{10,11}}$ = 6 Hz, =CMe_2), 132.8 (m, $J_{C_3\text{-}H_{2,4}}$ = 6 Hz, C_3), 138.9 (d, d, $J_{C_6\text{-}H_6}$ = 169 Hz, $J_{C_6\text{-}H_5}$ = 3 Hz, C_6, C_7).

Rate of Rearrangement of 8b. Dry 100-ml bulbs, each containing ca. 3 mg of **8b** were evacuated and sealed. Each was heated in the oven at 140 °C for intervals ranging from 15 min to 15 h (ca. 5 half-lives). The bulbs were cooled in liquid nitrogen to condense the contents, opened under a nitrogen flow, and diluted with benzene. Analysis was performed on a stainless steel ⅛ × 10 ft column of 10% Carbowax 4 M on 60/80 Chromosorb P, $T_R{}^{70°}$ 6 min (**8b**), 41 min (**9b**). The rate constant was determined to be 6.08×10^{-5} s^{-1} (5 half-lives, 6 points, correction coefficient = 0.9994) at 140 °C. The NMR spectrum of the product in benzene displayed a singlet at δ 1.8 and multiplets at δ 1.0–1.5 and δ 1.7–2.0 in accord with the literature data.[11a,c]

Rate of Rearrangement of 17. To a dry 500-ml bulb was added 25 mg of VPC collected **17** via vacuum transfer. The bulb was sealed under vacuum after freeze-degassing. The bulb was heated in the oven for an interval estimated to give ca. 50% reaction at each temperature. The bulbs were cooled in liquid nitrogen to condense the material and opened under a nitrogen atmosphere. The material was analyzed by VPC at room temperature on column A and analyzed by NMR. Both analyses indicated dimethylenecyclopropane was the sole product.

The rate constants determined were as follows: k (temp): $3.1 \pm 0.4 \times 10^{-5}\ s^{-1}$ (210 °C), $6.1 \pm 0.6 \times 10^{-5}\ s^{-1}$ (246 °C).

Rate of Isomerization of 2,2,3,3-Polydeuteriomethylenecyclopropane (16b). The rate of deuterium scrambling of **16b** was measured by heating samples containing 65% deuterium (1.5% d_0, 10% d_1, 30.5 d_2, 38% d_3, 20% d_4) in a 200-ml flask sealed with a threaded Teflon stopcock in a regulated brass oven at 209.5 ± 0.5 °C. The olefin was vacuum transferred into the heated vessel at a pressure of 400–500 mm. At intervals, aliquots ($^1\!/_{20}$ of sample volume) were withdrawn by vacuum transfer to an NMR tube and analyzed by NMR. A plot of $\ln [C_t - C_{eq}]$ vs. time gave the rate of equilibration as $5.1 \times 10^{-5}\ s^{-1}$ (two runs, 8 points and 10 points, correlation coefficients: 0.988 and 0.998). In both runs points were taken at equilibrium and the equilibrium constant found to be 1.0 for the isomerization. From this equilibrium constant, the individual rate constants for isomerization are one-half the rate of equilibration or $2.6 \times 10^{-5}\ s^{-1}$.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research.

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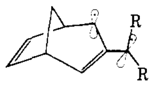
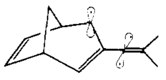
(9) The trimethylene diradical from **8** (or **10**) could eventually become orthogonal by rotation about the external C═CR$_2$ bond, as in i and ii. Because



i


ii

this rotation would require the cleavage of the external π bond, it seems unlikely that such rotation should have progressed very far in a transition state where rotation of the ring C–H's into the plane is incomplete (see surface in ref 4b), especially if the orthogonal diradical is not much more stable than the planar one (ref 6a, 7).

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(36) M. J. S. Dewar, G. J. Fonken, S. Kirschner, and D. E. Minter, *J. Am. Chem. Soc.*, **97**, 6750 (1975).

(37) The rearrangement of **10** to **23** should be more exothermic than that of **5** to **28** as a result of the relief of 12 kcal/mol of strain from the sp^2 cyclopropyl center (ref 32), but this exothermicity should be reduced considerably because of the extra strain involved in creating the cummulene in **23** from the allene in **10.** A strain energy difference of ca. 7 kcal/mol between an allene and 1,2,3-triene can be roughly estimated from related compounds [J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970; R. Kuhn and H. Fischer, *Ber. Dtsch. Chem. Ges.*, **94**, 3060 (1961)].

(38) For examples of reactions which appear to occur by concerted processes involving participation of both allene π bonds, see: D. J. Pasto and J. K. Borchardt, *J. Am. Chem. Soc.*, **96**, 6944 (1974); D. J. Pasto, A. F. T. Chen, and G. Binsch, *ibid.*, **95**, 1553 (1973). For examples of reactions which appear to occur by stepwise diradical processes without involving the second allene π bond, see: S.-H. Dai and W. R. Dolbier, *ibid.*, **94**, 3946 (1972); W. R. Dolbier and S.-H. Dai, *ibid.*, **92**, 1775 (1970); E. F. Kiefer and M. Y. Okamura, *ibid.*, **90**, 4187 (1968); W. R. Dolbier and Sheng-Hong Dai, *ibid.*, **90**, 5028 (1968).

(39) E. M. Engler, J. D. Androse, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).

(40) Curiously, the *cis*- and *trans*-dimethylmethylenecyclopropanes show about the same $\Delta G^{\ddagger}$, which is lower than expected from the small methyl effect in **38.**

(41) Estimated from data in ref 8a.

(42) S. McClean, C. J. Webster, and R. J. D. Rutherford, *Can. J. Chem.*, **47**, 1555 (1969).

(43) Interestingly, the alkenylidenecyclopropanes seem to generally have higher barriers to rearrangement than corresponding methylenecyclopropanes by ca. 2 kcal/mol. While the origin of this effect is not clear, it could result from some conjugative stabilization of the neutral alkenylidenecyclopropane. Our photoelectron spectrum of vinylidenecyclopropane shows evidence of such conjugative interaction, cf. D. J. Pasto, T. P. Fehlner, M. E. Schwartz, and H. F. Baney, *J. Am. Chem. Soc.*, **98**, 530 (1976).

(44) The racemization kinetics of **36** (ref 7) may then reflect the rate of rearrangement of the planar diradical to the orthogonal form vs. the rate of reclosure and would not give any indication of the magnitude or even the sign of the energy separation between the planar and orthogonal forms.

(45) L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Am. Chem. Soc.*, **95**, 2849 (1973).

(46) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.