Substituent Rate Effects on the Thermal Isomerizations of Bicyclo[3.2.0]hepta-2,6-diene

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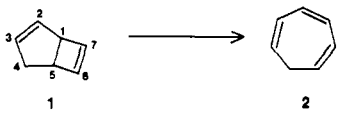
Abstract: Pyrolysis of 7-deuteriobicyclo[3.2.0]hepta-2,6-diene (**1**) gives its 1-deuterio isomer via a 3,3 shift $^1/_{20}$th as fast as the reported product, 1,3,5-cycloheptatriene. Pyrolysis of 4,4-dimethyl-2-deuteriobicyclo[3.2.0]hepta-2,6-diene gives the 3,3-shift product and ring-opened product in a 4:5 ratio with an overall rate factor of two higher than that of **1**. Substitution of a methyl group at C-1 of these materials or at C-5 of **1** has but a small effect on the rate of each reaction although 1,5-dimethyl substitution on **1** increases the rate of cycloheptatriene formation by a factor of 6.4 with no detectable 3,3-shift product being formed. This and other data suggest a preference for disrotatory ring opening to give cycloheptatriene and a small preference for conrotatory ring opening to give a *cis,trans,cis*-cycloheptatriene which gives the 3,3-shift product. However, consideration of energetics suggests little concert in either reaction, and molecular models suggest little difference between the two modes of ring opening due to the constraints of the molecular system.

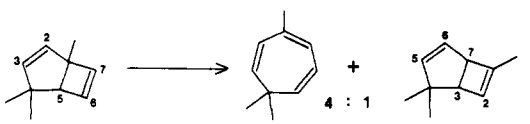
Among thermal isomerizations, the antara,antara-3,3-sigmatropic shift is both fascinating and elusive. Despite its congruence with the orbital symmetry conservation rules,[1] its demonstration is not without ambiguity. Most efforts in this area have focused on the rearrangements of substituted bicyclo[3.2.0]hepta-2,6-dienes where the well-known, concerted supra,supra-3,3 shift[2] is prohibited by the molecular framework.

Upon heating, bicyclo[3.2.0]hepta-2,6-diene (**1**) gives 1,3,5-



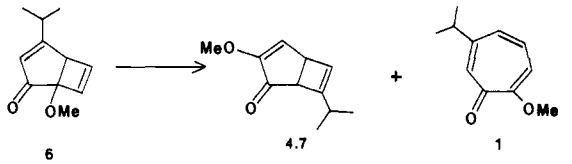
1 **2**

cycloheptadiene (**2**) with log k = 14.0 - 39 500/2.3RT.[3] Non-



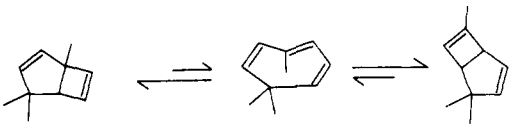
3 **4** 4 : 1 **5**

concerted disrotatory fission of the C-1,C-5 bond was proposed to account for the product although concerted conrotatory opening to a *cis,trans,cis*-1,3,5-cycloheptatriene followed by a 1,5-hydrogen shift or by trans double bond isomerization might also be involved. The possibility of the 1,5-hydrogen shift pathway is reduced by Baldwin's observation[4] that 1,4,4-trimethylbicyclo[3.2.0]hepta-2,6-diene (**3**) gives 3,7,7-trimethylcycloheptatriene (**4**) with a rate constant almost identical with that of the parent compound, **1** (vide infra). Also significant is Baldwin's observation that the apparent antara,antara 3,3-shift product **5** is also formed. This rearrangement was observed previously by Mukai with various phototropolones, e.g., **6** where the 3,3-shift product is formed 4.7 times



6 **4.7** **1**

faster than the tropolone.[5] Mukai argued that the 3,3 shift was concerted in a necessarily antara,antara mode since the ΔS^* was slightly negative and not positive as expected for a nonconcerted reaction.[5] Baldwin, however, pointed out that the 3,3 shift could be a two-step process involving a concerted conrotatory ring opening to the cis,trans,cis triene **7** (from **3**), followed by conrotatory recyclization in the opposite sense.

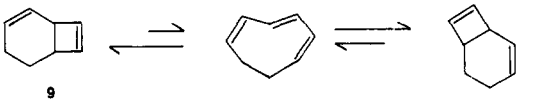


3 **7** **5**

The major arguments in favor of the Baldwin proposal are: (a) bicyclo[3.3.0]octa-2,6-diene (**8**), a material obviously lacking the

8

cyclobutene moiety, does not give a 3,3-shift product even at very high temperatures, and (b) the formal 3,3-shift product from bicyclo[4.2.0]octa-2,7-diene (**9**) appears to be formed from the



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cis,trans,cis triene (but the *c,t,c* triene does not give *cis,cis,cis*-1,3,5-cyclooctatriene under the reaction conditions).[6]

It can be argued that the lack of rearrangement of **8** does not preclude the 3,3 shift in **1**, **3**, or **6** where C-1,C-5 bond fission relieves roughly 20 kcal/mol more strain energy than in **8**. Further, the fact that the cis,trans,cis triene may be involved in the eight-carbon system may not be extrapolatable to the seven-carbon ring where substantially more strain energy accompanies the introduction of a trans double bond. Therefore, the question of how **1** is converted to **2** and to the 3,3-shift isomer is a matter of concern.

The approach described below examines the rate effects of substituents on the two reaction paths and infers the nature of each of these paths by stereoelectronic considerations. The data

(1) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(2) (a) Hurd, C. D.; Pollack, M. A. *J. Org. Chem.* **1938**, *3*, 550. (b) Levy, H.; Cope, A. C. *J. Am. Chem. Soc.* **1944**, *66*. 1684. (c) Doering, W. von E.; Roth, W. R. *Tetrahedron, 1962*, **18**, 67. (d) Hill, R. K.; Gilman, N. W. *Chem. Commun.* **1967**, 619. (e) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 669.

(3) Willcott, M. R.; Goerland, E. *Tetrahedron Lett.*, **1966**, 6341.

(4) (a) Baldwin, J. E.; Kaplan, M. J. *J. Am. Chem. Soc.* **1972**. (b) *Ibid.* **1971**, *93*, 3969. (c) *Ibid.* **1972**, *94*, 1794.

(5) (a) Miyashi, J.; Nitta, M.; Mukai, T. *Tetrahedron Lett.* **1967**, 3433; *J. Am. Chem. Soc.* **1971**, *93*, 3441. (b) Miyamoto, R.; Mukai, T. *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, **1974**, 1619.

(6) Frey, H. M. *Trans. Faraday Soc.* **1964**, *60*, 83.

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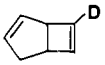
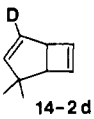
Table I. Rate Constants ($\times 10^5$ s) for Pyrolysis of 10–15 at 180.2 °C

	k_{CHT}	$k_{3,3}$
 10-7d	3.3	0.6
 11	4.1	<0.05
 12	6.3	0.22
 13	21.0	<0.05
 14-2d	4.4	3.6
 15	6.0	1.9

suggest that there is a reasonable indication of disrotatory ring opening to give the triene and a slight indication of conrotatory ring opening to give the 3,3-shift product. However, assessment of the energetics reveals but little evidence for concert in either reaction, and further, the rate effects of substitutents are relatively small compared with expectations based on model systems suggesting that little rotation accompanies the ring-opening event along either reaction coordinate. Indeed, molecular models reveal only a small difference between the con- and disrotatory ring-opening paths. This conclusion reinforces previous observations of Mukai which indirectly suggest that bulky substituents on *C-5* of bicyclo[3.2.0]hepta-3,6-dien-2-ones do not retard the rate of the 3,3 shift.[5b]

Results

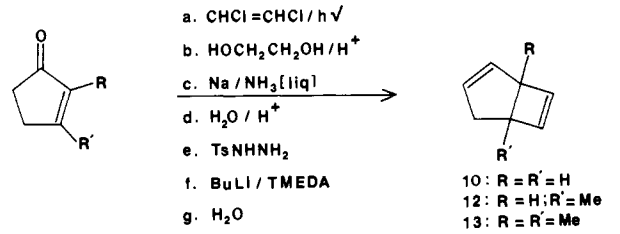
Pyrolyses. In order to examine substituent effects on the rates of isomerization of bicyclo[3.2.0]hepta-2,6-diene (**1**) to cycloheptatriene (**2**) and to its antara,antara [3,3] sigmatropomer, the 7-deuterio parent material (**10-7-*d***) and various mono-, di-, and trimethyl isomers, **11–15**, were synthesized (see below) and pyrolyzed at 180.2 °C. The pyrolyses were conducted in perchlorobutadiene solutions and analyzed by NMR at least five times over at least 3 half-lives.

In the cases of **11–13** the kinetic scheme could be analyzed as separate first-order reactions to the cycloheptatrienes and to the 3,3-shift product. In the cases of **10**, **14**, and **15**, where the 3,3-shift product subsequently rearranges to the cycloheptatrienes, the kinetic scheme was either integrated analytically (with **10** and **14**) or numerically (with **15**). The rate constants are given in Table I, the estimated error in each rate constant being ±5% with rate constants greater than 2×10^{-5}/s and ±30% with rate constants less than 0.3×10^{-5}/s.

In the pyrolyses of **10–13**, the cycloheptatrienes formed were mixtures of isomers due to interconversion via 1,5-hydrogen shifts, and these structures were assigned based on known chemical shifts.

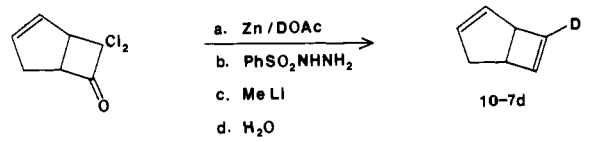
The structures of the 3,3-shift product in every case are based on the presence or absence of protons assignable from the parent structure where overlap of signals with starting material and cycloheptatriene product did not obscure resonances.

Syntheses. Compounds **10**, **12**, and **13** were prepared by photocycloaddition of 1,2-dichloroethene to the appropriate 2-



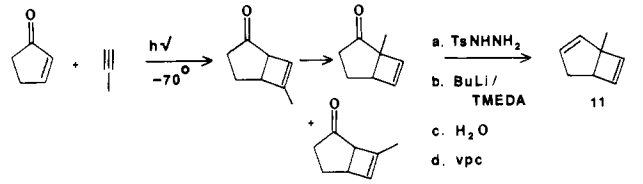
cyclopentenone followed by ketalization, reductive elimination, deketalization, and Shapiro elimination of the tosylhydrazones.

7-Deuteriobicyclo[3.2.0]hepta-2,6-diene (**10-7-*d***) was prepared



by dichloroketene addition to cyclopentadiene followed by zinc reduction in acetic acid-*O-d*, and Shapiro elimination of the benzenesulfonylhydrazone.

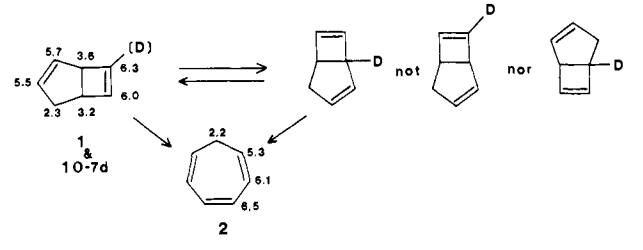
Diene **11** was prepared by −70 °C photocycloaddition of propyne to 2-cyclopentenone which was allowed to proceed to photoisomerize one of the adducts to 1-methylbicyclo[3.2.0]hept-6-en-2-one via the 1,3-acyl shift. Shapiro elimination of the mixture of tosylhydrazones and VPC separation gave the diene **11**.



Diene **14-2-*d*** was prepared in a manner similar to that of **10**, **12**, and **13** starting with 4,4-dimethyl-2-cyclopentenone with deuterium being incorporated in a D_2O quench of the Shapiro elimination product. Diene **15** has been reported by Baldwin.[4]

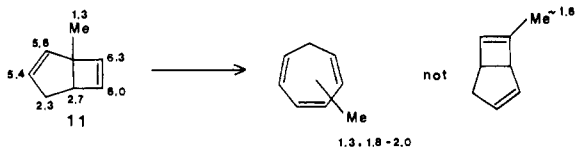
NMR Structural Assignments of Starting Materials and Products. 10-7-*d*. The structural assignments of the products of pyrolysis of **10–15** follow from NMR assignments of **10–15** and those of cycloheptatriene and its methylated derivatives. The ^{1}H NMR chemical shifts of **1** and **2** are given below. Those of CHT (**2**) are well known and those of **1** can be assigned easily on the basis of ^{1}H chemical shifts and multiplicities. However, the pair at C-2 and C-3 and the pair at C-6 and C-7 could not be assigned directly. The latter assignment was made on the basis of the NMR of **10-7-*d***, and the former was made on the basis of the ^{1}H NMR of **14** where the downfield proton of the two was removed by deuteration at C-2 in the form of **14-2-*d***. This comparison was possible since the downfield cyclopentene proton had virtually the same chemical shifts in both **1** and **14** while the upfield proton in **14** was shifted upfield relative to that in **1**.

The rearrangement of **10-7-*d*** gives all monodeuterio CHT's



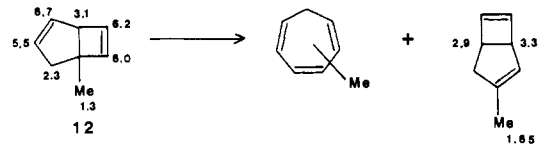
where all proton resonances of starting material and proton are separated in the 220-MHz spectra. However, the loss in intensity of the hydrogen at C-1 occurred faster than those at other positions of **10-7-*d*** indicating formation of some 3,3-shift products. Further, proton intensity grew at C-7. These observations rule out any degenerate [1,3] shift of either carbon of the three-carbon bridge.

11. Rearrangement of **11** gave all possible monomethyl CHT's whose Me proton resonances are at δ 1.3 and 1.8–2.0; however,



no Me resonance at δ 1.6 was observed and this is the expected position of methyl on a simple double bond as in the [3.3] shift products of **12** and **15** (see below).

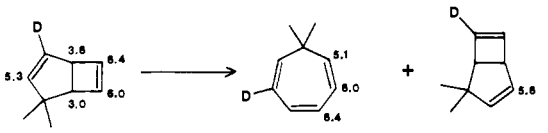
12. Rearrangement of **12** gave the same mixture of methyl



CHT's, but in addition a methyl resonance at δ 1.6 developed along with those of bicyclo[3.2.0]hepta-2,6-diene bridgehead protons. This structure was assigned to the [3,3] shift product. The ^{1}H NMR of this 3,3-shift product might also be due to one of the possible 1,3-shift products, but it was ruled out on the basis of energetics. The C-4,C-5 bond strength is of the order of 55 kcal/mol and no 1,3-shift in 1,5-hydrocarbon diene systems has ever been demonstrated to occur with an activation energy less than the bond dissociation energy of the σ bond being broken.

13. Rearrangement of **13** gave only dimethyl CHT's based on the chemical shifts of the methyls described above. No material with a methyl proton resonance between δ 1.3 and 1.8 was formed.

14-*2-d*. Rearrangement of **14**-*2-d* gave the 7,7-dimethyl CHT



and the proton intensity at C-2 grew during the reaction, then decreased. This indicates incursion of the 3,3 shift. No [1,3] process involving the three-carbon bridge could exchange hydrogens at C-2.

Discussion

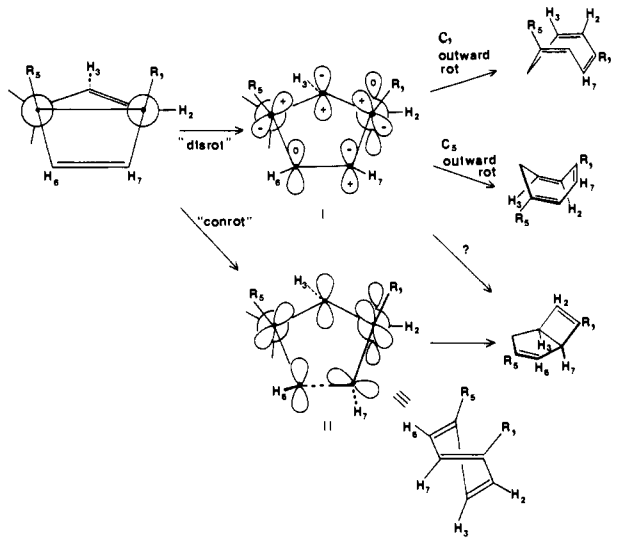
The data of Table I make it clear that the formal 3,3 shift in the parent bicyclo[3.2.0]heptadiene occurs only $^1/_{20}$th as fast as ring opening to cycloheptatriene. Further, methyl substitution at C-1 or C-5 increases the rate of ring opening by 24 and 91%, respectively, but methyl substitution on C-1 decreases the rate of 3,3 shift although it could only be a factor of 3 since a rate constant of 0.05×10^{-5}/s or less would not be observed. Methyl substitution on C-5 increases the rate of the 3,3 shift by 38%. Finally, 1,5-dimethyl substitution results in exclusive cycloheptatriene formation with a rate constant 6.4 times that of the parent.

While 4,4-dimethylbicyclo[3.2.0]hepta-2,6-diene (**14**) gives the cycloheptatriene only 1.3 times faster than the parent hydrocarbon, **1**, it gives the 3,3-shift product substantially faster than the parent so that the relative rates of the two processes is nearly the same in **14**. Methyl substitution on C-1 of **14** has virtually the same effect on cycloheptatriene formation as C-1 methyl substitution on the parent hydrocarbon, that is, a 36% rate increase. However, the decrease in rate of formation of the 3,3-shift product is only 50%. The dramatic effect of 4,4-dimethyl substitution on increasing the relative rate of the 3,3 shift in both **14** and **15** relative to **10** and **11** is not at all clear although a number of factors present themselves, the discussion of which is best deferred until some of the other effects can be pursued.

If ring opening were conrotatory to a cis,trans,cis triene, then alkyl substitution on C-1 should retard the opening since this methyl must rotate inward into the carbon framework. The extent of retardation would appear to be a function of the extent of inward rotation balanced against the usual rate of acceleration attending alkyl substitution on C-3 or C-4 of a cyclobutene.[6-9] The facts indicate that methyl substitution on C-5 accelerates both cycloheptatriene formation and 3,3 shift by factors of 1.9 and 1.4, respectively (in **12** and **15**), suggesting a slight preference for outward rotation of the group at C-5.

The facts also indicate a slight rate acceleration in the formation of cycloheptatriene upon C-1 or C-5 methyl substitution and a relatively larger rate factor with C-1 and C-5 dimethyl substitution suggesting a preference for disrotatory ring opening to the cycloheptatriene. However, the formation of 3,3-shift product is retarded by roughly a factor of 2 in the case where it is measurable, namely, in **14** and **15**, suggesting a weak preference for a conrotatory process to the 3,3-shift product.

All of the data suggest little rotation of C-1 in either the cycloheptatriene formation or in the 3,3 shift. Remarkably, inspection of molecular models suggests behavior similar to that observed. From models it would appear that two different species i and ii can be formed upon dis- and conrotatory opening of the



C-1,C-5 bond in **1**, respectively. Because of the constraints of the ring, species i has a near 90° dihedral angle between the p orbitals in C-1 and C-7 while species ii has a smaller dihedral angle in the sense of a trans double bond. If it is not clear from the figures, molecular models indicate that both con- and disrotatory ring opening motions give virtually the same relative positions of all atoms except C-7 where in species ii it is closer to C-3 than it is in species i. Thus the terms conrotatory and disrotatory may be inappropriate descriptors of ring-opening motions in this case.

Species i can give the cycloheptatriene by continued outward rotation of either C-1 or C-5, but both of these are orbital symmetry "forbidden" reactions which in this case are probably nonconcerted judging by the energetics of the reaction (see below). Species i can also give rise to the 3,3-shift product by bonding between C-3 and C-7, and this appears to be orbital symmetry "allowed" (the HOMO's are shown in the figure). Whether C-3,C-7 bonding occurs in concert with C-1,C-5 fission or subsequent to it is difficult to tell—if i is indeed involved in 3,3-shift product formation. But again the energetics suggest little concert in the reaction.

Species ii is the *cis,trans,cis*-cycloheptatriene formed by an orbital symmetry conserving pathway, and it can form the 3,3-shift product by orbital symmetry conserving C-3,C-7 bonding. This reaction can only occur to give the same stereoisomer as that formed from species i unless the entire trans double bond rotates 180°. This is a racemization process, and it must be viewed as unlikely considering the high barrier to racemization of *trans*-cyclooctene[10] and its high barrier compared with that of *trans*-

(7) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. Carr, R. W.; Walters, W. D. *J. Phys. Chem.* **1965**, *69*, 1073.
(8) Criegee, R.; Seebach, P.; Winter, R. E.; Borretzen, B.; Brune, H. A. *Chem. Ber.*, **1965**, *98*, 2339.
(9) Frey, H. M. *Trans. Faraday Soc.* **1963**, *59*, 1619.

cyclononene.[11] Species ii can form all *cis*-cycloheptatriene by isomerization of the trans double bond, a reaction that occurs with *trans*-cycloheptene at 135 °C but must occur much faster in ii owing to conjugation of the developing radical sites at C-1 and -7 with two double bonds. Indeed, there should be some concern as to whether species ii exists long enough to undergo C-3,C-7 bond formation rather than giving cycloheptatriene. Nonetheless, both species i or ii can rationalize the data of Table I in terms of reasonable steric and electronic effects. For instance, the effect of 4,4-dimethyl substitution may be compression of the C-3,C-4,C-5 bond angle in either species,[12] thus favoring 3,3-shift product formation. The preference for 3,3-shift product from phototropolone may be due to retardation of pathways to tropolone that involve eclipsing of the C-5 methoxy with the C-4 carbonyl due to dipole–dipole repulsion.[13] Thus there would appear to be little difference between the pathways suggested with the possible exception that strong bonding between C-3 and C-7 in the rate-determining step might be revealed by an isotope effect. However, this would require concert in the 3,3 shift, and there is little evidence for bond breaking being assisted by bond making. Indeed, even the formation of a *cis,trans,cis*-tropilidene would appear to have little energetic benefit over simple C-1,C-5 bond cleavage (see below).

Energetics. If a thermally induced rearrangement has an activation energy substantially less than the bond dissociation energy (BDE) of the bond being broken, then it is reasonable to conclude that the reaction is concerted where bond making is assisting bond breaking. This assumes that bond making is not a low-energy process. If the E_a is substantially higher than the BDE, then the reaction is nonconcerted provided that the BDE can be reasonably estimated.

In the case of bicyclo[3.2.0]hepta-2,6-diene, the estimate of the BDE of the C-1,C-5 bond should be compared to the E_{act}. If a strain-free biradical were generated in the pyrolysis of **1**, the BDE of the C-1,C-5 bond is about 23 kcal/mol. The estimate for this BDE comes from the BDE of a tertiary C–C bond of 78 kcal/mol minus the strain energy of a bicyclo[3.2.0]heptane (30.5 kcal/mol)[14] minus the resonance energy of two allyl radicals (25 kcal/mol).[15] Willcott's E_a for reaction of **1** would normally indicate a highly nonconcerted reaction, but there are other considerations. Despite estimates that the BDE of the C-1,C-5 bond of bicyclo[3.2.0]hept-6-ene should be 36 kcal/mol, the actual E_a for its isomerization to *cis,cis*-1,3-cycloheptadiene is 45 500 (log A = 14.3).[16] Here it must be recognized that the strain energy in the product, which is roughly 7 kcal/mol,[17] may effect a diradical transition state for ring opening. By comparison, the $\Delta G^{\ddagger}$ for conversion of *cis*-3,4-dimethylcyclobutene is 10 kcal/mol higher than that for conrotatory opening[18] and corresponds almost directly with that expected if E_a were the BDE and the A factor were normal. So confinement of the cyclobutene moiety in the [3.2.0] ring system dramatically raises the observed E_a relative to the estimated BDE, possibly by the strain energy in the biradical. Addition of a second double bond in the form of **1** might be expected to lower the E_a by ~12 kcal/mol to about 33 kcal/mol assuming no more added strain. Thus Willcott's E_a is still reasonably consistent with a nonconcerted reaction or, at best, one which is but weakly concerted.

Table II. Relative Concentrations during Pyrolysis of **10**-*7-d* at 180.2 °C

time, h	X-**10**-*7-d*	X-**10**-d_1	d_1-CHT
0	1.000	0	0
1.01	0.790	0	0.210
2.00	0.661	0.049	0.290
3.00	0.597	0.037	0.366
4.00	0.526	0.033	0.441
6.00	0.418	0.027	0.555
8.50	0.289	0.041	0.670
11.50	0.177	0.071	0.752
15.00	0.132	0.052	0.816
21.09	0.065	0.041	0.894
40.00	0.033	0.018	0.949

Table III. Relative Concentrations during Pyrolysis of **14**-*2-d* at 180.2 °C

time, h	X-**14**-*2-d*	X-**14**-d_1	Me_2-CHT-*2-d*
0	1.000	0	0
0.75	0.82	0.131	0.048
1.50	0.754	0.156	0.090
2.25	0.719	0.197	0.084
3.75	0.508	0.225	0.267
5.25	0.414	0.230	0.356
8.25	0.253	0.225	0.523
11.25	0.164	0.154	0.682
17.25	0.075	0.081	0.844

Experimental Section

General. NMR spectra (60 MHz with tetramethylsilane, Me_4Si, as internal standard unless indicated otherwise) were recorded on Varian T-60, XL-100, and/or HR-220 spectrometers. Chemical shifts are reported in ppm downfield of Me_4Si. Infrared spectra were recorded on Perkin-Elmer Model 137 or 467 spectrometers. Mass spectra were obtained on Varian CH-7, Hewlett-Packard 5992A GC-MS, or Varian MS-9 spectrometers. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Gas chromatography (GC) utilized the Varian Aerograph Model 90-P with helium as the carrier gas. All columns were packed in copper tubes. Column A is 10 ft × $^1/_4$ in. 25% SE-30 on 60/80 Chromosorb W. Column B is 5 ft × $^1/_4$ in. 15% DBTCP on 60/80 Chromosorb P. Column C is 11 ft × $^3/_8$ in. 30% FFAP on 60/80 Chromosorb P. Column D is 10 ft × $^1/_4$ in. 30% UCON HB-2000 on 60/80 Chromosorb W. Column E is 5 ft × $^1/_4$ in. 30% XF-1150 on 60/80 Chromosorb WAW. Column F is 6 ft × $^1/_4$ in. 15% $AgNO_3$ (saturated in triethylene glycol) on Chromosorb P.

7-Deuteriobicyclo[3.2.0]hepta-2,6-diene (10-*7-d*). 7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one was reduced by acetic acid-*O-d* to 7,7-dideuteriobicyclo[3.2.0]hept-2-en-6-one in 67% yield (93% D incorporation) according to literature procedures for the nondeuterated material.[19] NMR (CCl_4, 220 MHz): the 1 H signal at 3.19–3.25 ppm and half of the 2 H signal at 2.58–2.73 were absent and the multiplets at 3.75–3.89 (1 H) and 3.28–3.50 (1 H) were simplified. The benzenesulfonylhydrazone was prepared in 100% yield by reaction of the ketone with an equivalent amount of benzenesulfonylhydrazide in a minimum volume of refluxing methanol for 10 min followed by cooling and evaporation of the methanol: NMR ($CDCl_3$, 220 MHz) 7.88–8.01 (m, 2 H), 7.45–7.65 (m, 3 H), 5.63 (broad s, 2 H), 3.63 (m, 1 H), 3.27 (m, 1 H), 2.81–3.06 (m, 1 H), and 2.34–2.59 (m 2 H). The Shapiro elimination was conducted as described below for preparation of **14** starting with 1.14 g (4.32 mmol) of the benzenesulfonylhydrazone giving 14 mg (3.5% yield) of **10**-*7-d*: NMR (CCl_4, 220 MHz) 6.28 (d, 0.06 H), 6.00 (s, 1 H), 5.70 (m, 1 H), 5.51 (m, 1 H), 3.60 (broad s, 1 H), 3.23 (m, 1 H), 2.06–2.42 (m, 2 H).

1-Methylbicyclo[3.2.0]hepta-2,6-diene (11). A solution of 2-cyclopentenone (5.83 g, 71 mmol) and propyne (72 mL, 1.27 mmol) in 705 mL of CH_2Cl_2 was irradiated through Pyrex at −70 °C (dry ice/acetone bath) with a 450-W Hanovia medium-pressure lamp with nitrogen ebullition for mixing. After 13.9 h (100% conversion by NMR), the clear, light yellow solution was rotovapped and distilled under reduced

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pressure. The distillate (3.58 g, bp 78–119 °C/(17 mmHg)) contained 5.1% 1-methylbicyclo[3.2.0]hept-6-en-2-one (0.18 g, 2.1% yield): NMR (CCl_4, 220 MHz) 6.24 (d, J = 3 Hz, 1 H), 6.06 (d, J = 3 Hz, 1 H), 3.03 (bd, 1 H), 2.77–2.99 (m, 1 H), 1.99–2.13 (m, 1 H), 1.74–1.88 (m, 2 H), 1.20 (s, 3 H); MS 122 (27, M), 107 (5, M – Me), 94 (13, M – CO), 79 (100, M – CO – Me). To a hot solution of the mixture of ketones (3.47 g, 28.4 mmol, 5.1% pure, obtained from photocycloaddition of propyne to 2-cyclopentenone) in 3.5 mL of methanol was added a hot solution of *p*-toluenesulfonylhydrazide (5.29 g, 28.4 mmol) in 9.2 mL of methanol. The solution was refluxed 10 min, cooled to room temperature, and left in the freezer overnight. The clear yellow supernatant was removed with a pipet. The crystals were washed once with cold ether and dried at 0.05 mmHg for 1.5 h (4.16 g, 50%). The supernatant was combined with the ether wash, rotovapped, and dried at 0.05 mmHg for 2 h (3.80 g, 46%). Since NMR analysis of both the crystals and the residue from the supernatant showed that cyclobutene vinyl hydrogens were present, the samples were combined.

Addition of the impure material (7.96 g, 27.4 mmol) to 137 mL of dry TMEDA under nitrogen gave a yellow suspension which was cooled in a chloroform slush bath. With stirring, *n*-butyllithium 27.4 mL, 65.8 mmol, 2.4 M in hexane) was added over 7 min. The reaction mixture was stirred 10 min at −68 °C (during which nitrogen evolution began), warmed to room temperature (30 min), and stirred 50 min (during which nitrogen evolution stopped). The dark, red-black solution was cooled in an ice bath and quenched by the dropwise addition of H_2O (4.94 mL, 274 mmol). The orange suspension was stirred 1 h at room temperature, diluted with 3–4 vol of CH_2Cl_2, washed 9× 5% HCl solution (until wash had pH 1 twice in succession), 1× 5% $NaHCO_3$ solution, 1× saturated NaCl solution, dried (Na_2SO_4), concentrated by distillation (≤41 °C), and vacuum transferred (0.05 mmHg). The clear, colorless distillate was purified by preparative gas chromatography on column A. 11 (133 mg, 1.8% overall yield from 2-cyclopentenone) was obtained as a clear, colorless liquid: NMR (hexachlorobutadiene, 220 MHz) 6.31 (d, J = 3 Hz, 1 H), 5.95 (d, J = 3 Hz, 1 H), 5.54 (m, 1 H), 5.39 (m, 1 H), 2.70 (dd, J = 3, 10 Hz, 1 H), 2.33–2.49 (m, 1 H), 2.04–2.17 (m, 1 H), 1.25 (s, 3 H).

5-Methylbicyclo[3.2.0]hepta-2,6-diene (12). A solution of 3-methyl-2-cyclopentenone (5.38 g, 0.056 mol, 1.0 equiv) and 1,2-dichloroethene (108.5 g, 1.12 mol) in 460 mL of CH_2Cl_2 was irradiated using a water-cooled 450-W Hanovia medium-pressure lamp through Pyrex. After 18 h (100% conversion by NMR), the solution was rotovapped to yield 23.0 g of crude adduct. This material (assumed: 56.0 mmol), ethylene glycol (3.44 mL, 61.6 mmol), 90 mL of benzene, and a few milligrams of *p*-toluenesulfonic acid were refluxed with H_2O separation for 19 h. The reaction mixture was rotovapped and then dried at 0.05 mmHg for 15 min to give 16.1 g of crude ketal. This material (assumed: 56.0 mmol) in 108 mL of anhydrous ether was cooled in a dry ice/acetone bath into which 250 mL of ammonia was condensed. The cooling bath was removed and the brown solution allowed to reflux. Sodium (3.1 g, 134 mmol) was added in four pieces over 25 min. After stirring 45 min, excess sodium present in the black reaction mixture was destroyed by the addition of solid ammonium chloride (7.2 g, 134 mmol). After evaporation of the ammonia, 360 mL of H_2O was added. The aqueous solution was extracted four times with ether. To the ether solution of the crude ketal (assumed: 56.0 mmol) was added 485 mL of 3 M aqueous hydrochloric acid. The mixture was stirred overnight (13 h). Solid $NaHCO_3$ was added in portions to neutralize the acid. Sufficient H_2O to dissolve the salts was added. The organic layer was washed once with H_2O and the combined aqueous phases were extracted three times with ether. The combined ether extracts were dried (Na_2SO_4), rotovapped, and distilled under reduced pressure to give 2.21 g, 34% yield of 5-methylbicyclo[3.2.0]hept-6-en-2-one: bp 69–77 °C (19 mmHg); NMR (CCl_4, 220 MHz) 6.28 (d, J. = 3 Hz, 1 H), 6.13 (d, J. = 3 Hz, 1 H), 2.73–2.94 (m, 1 H), 2.64 (s, 1 H), 1.98–2.16 (m, 1 H), 1.82–1.98 (m, 1 H), 1.52–1.70 (m, 1 H), 1.40 (s, 3 H); MS 122 (16, M), 107 (37, M – Me), 94 (25, M – CO), 79 (100, M – CO – Me).

To a solution of the ketone (0.885 g, 7.24 mmol) in 0.88 mL of methanol was added a hot solution of *p*-toluenesulfonylhydrazide (1.35 g, 7.24 mmol) in 2.3 mL of methanol. The solution was refluxed 10 min, cooled to room temperature, and left in the freezer overnight. The clear, yellow supernatant was removed with a pipet. The solid mass was rinsed once with cold ether and dried at 0.05 mmHg for 1 h. The tosylhydrazone (1.67 g, 79%) was obtained as a white solid. The 220-MHz NMR showed it to be a mixture of *E* and *Z* isomers, mp 141–50 °C. Isomer A: NMR ($CDCl_3$, 220 MHz) 7.85 (d, J = 8 Hz, 2 H), 7.72 (bs, 1 H), 7.30 (d J = 8 Hz, 2 H), 6.11 (d, J = 2 Hz, 1 H), 5.90 (d, J = 2 Hz, 1 H), 3.12 (s, 1 H), 2.41 (s, 3 H), 2.25–2.84 (m, 2 H), 1.61–1.84 (m, 1 H), 1.27–1.50 (m, 1 H), 1.29 (s, 3 H). Isomer B: NMR ($CDCl_3$, 220 MHz) 7.85 (d, J = 8 Hz, 2 H), 7.59 (bs, 1 H), 7.30 (d, J = 8 Hz, 2 H), 6.05 (d, J = 2 Hz, 1 H), 5.92 (d, J = 2 Hz, 1 H), 3.09 (s, 1 H), 2.41 (s, 3 H), 2.25–2.84 (m, 2 H), 1.61–1.84 (m, 1 H), 1.27–1.50 (m, 1 H), 1.29 (s, 3 H).

The Shapiro elimination used for preparation of **17** was followed except that the reaction was quenched after only 11 min at room temperature. **12** (132 mg, 22%) was obtained as a clear, colorless liquid after purification by preparative gas chromatography on column A: NMR (CCl_4, 220 MHz) 6.20 (d, J = 2 Hz, 1 H), 6.04 (d, J = 2 Hz, 1 H), 5.68 (narrow m, 1 H), 5.50 (m, 1 H), 3.05 (m, 1 H), 2.21–2.35 (m, 1 H), 1.97–2.11 (m, 1 H), 1.29 (s, 3 H); MS 106 (8, M), 105 (14, M – H), 91 (100, M – Me).

1,5-Dimethylbicyclo[3.2.0]hepta-2,6-diene (13). A solution of 2,3-dimethyl-2-cyclopentenone (1.15 g, 10.4 mmol) and 1,2-dichloroethene (16.0 mL, 209 mmol) in 125 mL of CH_2Cl_2 was irradiated with a 450-W Hanovia medium-pressure lamp through Pyrex. After 16.5 h (100% conversion by NMR), the solution was rotovapped to give 4.09 g of crude adduct. Ketalization, reductive elimination, and deketalization were conducted as described in the preparation of **12** to 0.607 g (43% yield overall) of liquid 1,5-dimethylbicyclo[3.2.0]hept-6-en-2-one: bp 90–135 °C (33 mmHg); NMR (CCl_4, 220 MHz) 6.21 (d, J = 3 Hz, 1 H), 6.01 (d, J = 3 Hz, 1 H), 2.70–2.91 (m, 1 H), 1.95–2.11 (m, 1 H), 1.79–1.91 (m, 1 H), 1.39–1.59 (m, 1 H), 1.23 (s, 3 H), 1.02 (s, 3 H).

Conversion of this ketone to the tosylhydrazone and Shapiro elimination following the procedure for preparation of **12** (the reaction was quenched after 42 min at room temperature) gave 98 mg (25% yield) of **13** after VPC purification on column B: NMR (hexachlorobutadiene, 220 MHz) 6.25 (d, J = 3 Hz, 1 H), 5.96 (d, J = 3 Hz, 1 H), 5.57–5.64 (m, 1 H), 5.38–5.45 (m, 1 H), 2.31 (d of t, J = 18 and 3 Hz, 1 H), 2.10 (d of t, J = 18 and 3 Hz, 1 H), 1.10 (s, 3 H), 1.07 (s, 3 H).

2-Deuterio-4,4-dimethylbicyclo[3.2.0]hepta-2,6-diene (14-*2-d*). 4,4-Dimethyl-2-cyclopentene was converted to 4,4-dimethylbicyclo[3.2.0]-hept-6-en-2-one benzenesulfonylhydrazone in the same manner as that described above for the preparation of **12**. The Shapiro elimination was conducted with 1.47 g (5.07 mmol) of this material in 25 mL of dry TMEDA which was cooled in a chloroform slush bath under nitrogen. With stirring, *n*-butyllithium (8.45 mL, 20.3 mmol, 2.4 M in hexane) was added over 7 min. The orange suspension was stirred 10 min at −68 °C, warmed to room temperature over 20 min, and stirred 1 h. The clear, red-black solution was cooled in an ice bath and quenched by the dropwise addition of D_2O (0.92 mL, 51 mmol). The orange suspension was stirred 30 min at room temperature, diluted with 3–4 vol of CH_2Cl_2, washed 5× 5% HCl solution (until wash had pH = 1 twice in succession), 1× 5% $NaHCO_3$ solution, and 1× saturated NaCl solution, dried (Na_2SO_4), concentrated by distillation (≤42 °C), and vacuum transferred (0.05 mmHg). The clear, colorless distillate was purified by preparative gas chromatography on column B. **14-*2-d*** (44 mg, 7%) was obtained as a clear, colorless liquid. The residue from the vacuum transfer was starting hydrazone (1.23 g, 84% recovery) with deuterium incorporation at C-1: NMR of **14-*2-d*** (CCl_4, 220 MHz) 6.38 (d, J = 2 Hz, 1 H), 5.98 (d, J = 2 Hz, 1 H), 5.60 (m, 0.13 H), 5.25 (s, 1 H), 3.59 (broad s, 1 H), 2.95 (d, J = 3 Hz, 1 H), 1.05 (s, 3 H), 1.00 (s, 3 H); MS (**14**) 120 (2, M), 119 (4, M – H), 105 (100, M – Me).

General Pyrolysis Procedure. About 15–20 mg of the bicyclo-[3.2.0]hepta-2,6-diene, about 0.003 mL of tetramethylsilane, and 0.5 mL of hexachlorobutadiene were placed in an NMR tube attached to a vacuum line. After three freeze–pump–thaw degassing cycles, the tube was refrozen, sealed at 0.05 mmHg, and slowly thawed. The NMR tubes were stored in a freezer until used for a pyrolysis.

The pyrolysis bath consisted of a well-stirred 10:7 (w/w) KNO_3:$NaNO_2$ molten eutectic heated with a 500-W Vycor base heater. Fine temperature control (±0.2 °C) utilized a 125-W knife heater powered by a Bayley Model 124 precision temperature controller.

The mole fractions of starting material, cycloheptatriene, and 3,3-shift product were determined by multiple integration of the prominent ^1H NMR resonances. Typical data sets and method of determining rate constants are listed in Tables II and III for pyrolysis of **10-*7-d*** and **14-*2-d***. The rate constants in Table I for the two reactions were determined from the integrated rate equations: $\ln [(X\text{-}\mathbf{10}\text{-}7\text{-}d) + (X\text{-}\mathbf{10}\text{-}1\text{-}d)] = -k_{CHT}t$ and $\ln [X\text{-}\mathbf{10}\text{-}7\text{-}d] = -(k_{CHT} + 2k_{3,3})t$, where $k_{CHT} = 3.28 \times 10^{-5}$/s ($r^2 = 1.000$) and $k_{CHT} + 2k_{3,3} = 3.61 \times 10^{-5}$/s ($r^2 = 0.996$).

The kinetic data for pyrolysis of the other bicyclo[3.2.0]hepta-2,6-dienes listed in Table I and many others are given in E. W.O.'s Ph.D. Thesis, Indiana University, 1980. Copies of the data were made available to the referees.

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