work and for graciously providing us with detailed experimental results of a portion of his own research.

Registry No. 1 (R = CO_2CH_3), 36914-92-8; **5**, 40028-33-9; **7**, 4604-65-3; **8**, 72207-02-4; **9**, 72207-03-5; **11**, 4231-35-0; **12**, 72207-04-6; **13**, 54494-80-3; **14**, 72207-05-7; **15**, 72207-06-8.

Flow System Pyrolysis of 7,7-Dimethylbicyclo[4.1.1]octa-2,4-diene

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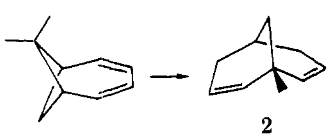
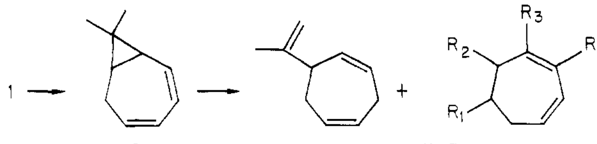
As part of our study of the chemistry of 7,7-dimethylbicyclo[4.1.1]octa-2,4-diene (**1**),[1] we have investigated its flow system pyrolysis. At temperatures of 350 °C and above we find the thermodynamically favored rearrangement product to be 1-methylbicyclo[3.3.1]nona-2,7-diene (**2**). We have isolated a number of the compounds formed


1 2

at lower temperatures and subjected them to repyrolysis. On the basis of the results of these studies, we propose a mechanism for the rather remarkable transformation of **1** to **2**.

Results

When the pyrolysis of **1** is carried out at 250 °C, although about 85% of **1** remains unreacted, the major rearrangement product is (Table I) 8,8-dimethylbicyclo[5.1.0]octa-2,4-diene (**3**).[2] This product of a 1,5 carbon



3 4

5, $R_1 = CH_3C{=}CH_2$
6, $R_2 = CH_3C{=}CH_2$
7, $R_3 = CH_3C{=}CH_2$
8, $R_4 = CH_3C{=}CH_2$

shift in **1** is the only isomer detected when **1** is irradiated through Pyrex or when the pyrolysis is conducted at 225 °C. When **3** is repyrolyzed at 250 °C, **3**–**8** are obtained in ratios similar to those measured when **1** is pyrolyzed; however, no **1** is detected. Thus, the equilibrium between **1** and **3** apparently favors the latter diene.

Repyrolysis of **4**–**8** at 250 °C shows that **5**–**8** are readily interconverted but that they do not equilibrate with **4** at this temperature. These results are consistent with the fact that the 1,5 hydrogen shifts that interconvert **5**–**8** are allowed by orbital symmetry whereas the 1,3 shifts necessary to transform **4** into any one of the latter four cycloheptadienes are forbidden.[3]

Table I. Composition of the Product Mixture Formed from 1 at 250 and 350 °C

	product distribution, %						
temp, °C	2	3	4	5	6	7	8
250[a]		41	24	3	7	19	6
350[b]	4		29			39	28

[a] At this temperature approximately 85% of **1** is recovered. [b] At this temperature several small peaks with relatively short retention times make up about 10% of the total product mixture.

Table II. Composition of the Mixture of 5–8 Formed from 1, 3, 5, and 6 at 250 °C

	product distribution, %			
reactant	5	6	7	8
1	9	20	54	17
3	11	22	52	15
5	44	11	34	11
6	11	19	55	15

The structures of **7** and **8** rule out both these molecules as the primary product of a sigmatropic rearrangment in either **1** or **3**. In order to determine whether **5** or **6** is the first-formed product in the pool of interconvertible cycloheptadienes, **5** and **6** were repyrolyzed at 250 °C so that the compositions of the resulting mixtures of **5**–**8** could be compared with those obtained by pyrolysis of **1** and **3**. Since **5** and **6** are formed as minor products in the pyrolysis of both **1** and **3**, it was necessary to synthesize **5** and **6** independently to obtain sufficient quantities for the repyrolysis studies.

A mixture of **5** and **6** was prepared by reaction of isopropenyllithium with tropylium fluoroborate, followed by lithium in ammonia reduction of the resulting 7-isopropenylcycloheptatriene.[4] The mixture of **5** and **6** was separated by preparative GLC, and each compound was pyrolyzed at 250 °C. The results (Table II) show that the mixture of **5**–**8** obtained from **6** corresponds closely to those mixtures formed from **1** and **3** whereas the composition of the mixture obtained from **5** does not. These data provide strong evidence that **6**, rather than **5**, is formed first. Further proof comes from the pyrolysis of **3** at 225 °C. Although at this temperature conversion of **3** to rearrangement products is very low, the only two isomers of **3** detected are **4** and **6**.

When the temperature of the pyrolysis column is raised to 350 °C, only three of the isopropenylcycloheptadienes—**4**, **7**, and **8**—are present. A small amount of a new product (**2**) is also formed. Pyrolysis of **4**–**8** at this temperature shows that **2** is not formed from **4** but only from the equilibrating pool of cycloheptadienes (**5**–**8**). Raising the column temperature further[5] or recycling the pyrolysate leads to an increase in the amount of **2** present. Since **2** is recovered unchanged from pyrolysis at temperatures up to 450 °C, it appears to be the thermodynamically most stable isomer in the region of the potential surface that is accessible from **1** at temperatures up to 450 °C.

The structure of **2** was deduced from spectral data. The ^1H NMR spectrum shows the presence of a methyl group attached to a quaternary carbon, four protons on doubly bonded carbons, and a methylene group split by one proton with $J = 3$ Hz. The absence of UV absorption shows that

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(1) S. D. Young and W. T. Borden, *Tetrahedron Lett.*, 4019 (1976).

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(5) At temperatures of 400 °C 1,3 hydrogen shifts begin to occur, as evidenced by the partial conversion of **4** to **7** and **8**. In addition, 5- and 6-isopropylidenecyclohepta-1,3-diene are found among the pyrolysis products.

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the double bonds are not conjugated, and the appearance of only seven resonances in the ^{13}C NMR spectrum indicates the presence of an element of molecular symmetry. The spectral data are nicely accommodated by the 1-methylbicyclo[3.3.1]nona-2,7-diene structure that we assign to **2**.

Discussion

The first step in the rearrangement of **1** to **2** appears to be the equilibration of **1** with **3**. A similar equilibration of the parent bicyclo[4.1.1]octa-2,4-diene with bicyclo[5.1.0]octa-2,4-diene provides an alternative to the mechanism proposed by Grimme and Doering for the degenerate rearrangment of the latter molecule.[6] Since our results indicate that **1** is disfavored at equilibrium, it is likely that if bicyclo[4.1.1]octa-2,4-diene actually were an intermediate in the degenerate rearrangement discovered by Grimme and Doering, this molecule might be present in amounts small enough to escape detection.

The 1,5 sigmatropic shift that equilibrates **1** and **3** is analogous to the degenerate 1,5 carbon shift in norcaradiene,[7] of which **1** is a homologue. The stereochemistry of this rearrangement in norcaradiene has recently been probed,[8] and we are in the process of determining the stereochemistry of the thermal and photochemical reactions that transform **1** into **3**.

The fact that **3** is apparently favored over **1** at equilibrium does not necessarily imply that **3** is the immediate precursor of **4** and **6**. However, if **6** is formed in a concerted process, **3** must serve as its immediate precursor. The transformation of **3** to **6** is a ${}_{\sigma}2_{s} + {}_{\pi}2_{s} + {}_{\pi}2_{s} + {}_{\sigma}2_{a}$ reaction that is symmetry allowed,[3] since it involves a Möbius array of orbitals containing eight electrons. Models show that **3** can easily attain a conformation that would permit this reaction. A similar rearrangement of **1** would lead to **5** as the first formed molecule in the equilibrating pool of cycloheptadienes, a result not in conformity with the experimental finding that **6** is the progenitor of **5**, **7**, and **8**.

The formation of **4** could occur by a concerted ${}_{\sigma}2_{s} + {}_{\pi}2_{s} + {}_{\sigma}2_{s}$ reaction from either **1** or **3**. There is, however, considerably more precedent for the occurrence of such a 1,5 hydrogen shift in molecules containing cyclopropane rather than cyclobutane rings.[3]

As noted above, **4** is not a precursor of **2**, except at temperatures in excess of 350 °C, where 1,3 hydrogen shifts begin to occur.[5] Instead, **2** must be formed from one of the equilibrating cycloheptadienes (**5**–**8**). Their equilibration is rapid relative to the process by which **2** is formed, as shown by the fact that all four of these cycloheptadienes are obtained at 250 °C whereas **2** is not detected at temperatures below 350 °C. Therefore, we have no experimental evidence as to which of these molecules is the immediate precursor of **2**. Nevertheless, we believe that it is **6** that lies on the direct pathway to **2**, since it is possible to devise a very plausible two-step sequence for the transformation of **6** into **2**.

An intramolecular Diels–Alder reaction in **6** leads to the methyl-substituted dihydrobarbaralane **9**. The reverse of this reaction has been postulated to occur in the pyrolysis of both barbaralane[9] and barbaralone.[10] Unlike these two more highly oxidized tricycles, **9** has available a hydrogen that is suitably situated to participate in a homodienyl 1,5 hydrogen shift. In fact, the parent dihydrobarbaralane, on heating to 200 °C, has been found to undergo precisely this sigmatropic rearrangement, yielding bicyclo[3.3.1]nona-2,7-diene.[11]

6 9 2

In summary, we believe that the transformation of **1** to **2** occurs by a four-step sequence involving the intermediacy of **3**, **6**, and **9**. Each of the reactions in this sequence is allowed by orbital symmetry and might, therefore, be concerted. We are now determining whether the 1,5 carbon shift that converts **1** into **3** actually does follow the stereochemistry predicted by the Woodward–Hoffmann rules and whether the formation of **4** and **6** proceeds by parallel concerted reactions or, instead, via a common diradical intermediate.

Experimental Section

Pyrolyses. The flow system pyrolysis apparatus used has been described previously.[12] Pentane solutions of the compound to be pyrolyzed were added dropwise from a syringe at 1 drop/s to the top of the column, through which nitrogen gas flowed at the rate of 40 mL/min. The pyrolysate was collected, the pentane evaporated, and the product mixture separated and collected by GLC on a 10 ft × $^3/_8$ in. column of 20% Carbowax 20 M on Chromosorb W. The column was operated at 100 °C with a helium flow rate of 180 mL/min in a Varian Model 920 instrument equipped with a thermal conductivity detector. The relative peak areas, given in Tables I and II, were not corrected for possible differences in detector response to compounds **1**–**8**. On the Carbowax column, **1** has a retention time of 23 min. The spectral data for this compound have already been published.[1] The retention times and spectral data for **2**–**8** follow. NMR spectra were obtained in $CDCl_3$, and UV spectra in hexane solutions.

1-Methylbicyclo[3.3.1]nona-2,7-diene (2): retention time 24 min; ^1H NMR δ 1.10 (s, 3 H), 1.60 (d, 2 H, J = 3 Hz), 1.67–2.80 (m, 5 H), 5.3–6.2 (m, 4 H); ^{13}C NMR 26.51, 27.49, 32.12, 34.61, 37.54, 125.82, 138.33.

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1010.

8,8-Dimethylbicyclo[5.1.0]octa-2,4-diene (3): retention time 31 min; ^1H NMR δ 1.00 (s, 3 H), 1.06 (s, 3 H), 0.90–1.37 (m, 2 H), 2.17–2.70 (m, 2 H), 5.37–6.27 (m, 4 H), identical with the spectrum of an authentic sample synthesized by Staley and Pearl;[2] ^{13}C NMR δ 19.03, 20.78, 28.91, 31.48, 32.11, 35.72, 129.76, 130.35, 136.41, 137.53; UV λ_{max} 258 nm (log ϵ 3.51).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1112.

6-Isopropenylcyclohepta-1,4-diene (4): retention time 37 min; ^1H NMR δ 1.77 (s, 3 H), 2.07–2.57 (m, 2 H), 2.77–3.40 (m, 3 H), 4.80 (s, 2 H), 5.63–6.23 (m, 4 H); ^{13}C NMR δ 20.75, 28.37, 31.98, 45.21, 110.14, 127.64, 128.95, 129.72, 134.41, 148.86.

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1096.

6-Isopropenylcyclohepta-1,3-diene (5): retention time 43 min. This compound was identified by coinjection of an independently synthesized sample (vide infra) on the Carbowax column and also on 24 ft x $^1/_8$ in. analytical columns of Apiezon L and DEGS.

5-Isopropenylcyclohepta-1,3-diene (6): retention time 40 min. This compound was identified by coinjection of an independently synthesized sample (vide infra) on the preparative and two analytical GLC columns described above.

1-Isopropenylcyclohepta-1,3-diene (7): retention time 72 min; ^1H NMR δ 1.95 (s, 3 H), 1.63–2.73 (m, 6 H), 4.95 (s, 1 H), 5.13 (s, 1 H), 5.93 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 21.47, 26.94, 30.98,

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32.26, 111.64, 122.25, 125.47, 134.35, 144.66, 145.05; UV λ_{max} 283 nm (log ϵ 4.20).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1056.

2-Isopropenylcyclohepta-1,3-diene (8): retention time 50 min; ^{1}H NMR δ 1.93 (s, 3 H), 1.75–2.65 (m, 6 H), 4.75–5.10 (m, 2 H), 5.98–6.42 (m, 3 H); ^{13}C NMR δ 21.11, 28.09, 28.92, 32.58, 111.54, 127.85, 130.00, 133.75, 139.77, 144.40; UV λ_{max} 247 nm (log ϵ 3.94).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1094.

Synthesis of 7-Isopropenylcyclohepta-1,3,5-triene.[4] Isopropenyllithium was prepared by the dropwise addition of 4.5 mL (0.05 mol) of 2-bromopropene to a stirred suspension of 0.7 g (0.1 mol) of oil-free lithium dust (containing 2% sodium) in 60 mL of dry ether at 0 °C under nitrogen. After the mixture was stirred for 2 h, excess lithium was allowed to float to the top of the solution, which was transferred through a cannula, using positive nitrogen pressure, from the bottom of the flask to an addition funnel. This solution of isopropenyllithium was added dropwise to a rapidly stirred suspension of 8.5 g (48 mmol) of finely ground tropylium fluoroborate in 100 mL of dry ether at 0 °C. The reaction mixture was stirred vigorously for 4 h under nitrogen at 0 °C and then poured into water. The organic layer was separated, washed with 5% HCl, and dried over sodium sulfate. Evaporation under reduced pressure and elution with pentane through a short column of alumina yielded 5.0 g (79%) of the desired product: ^{1}H NMR δ 1.87 (s, 3 H), 2.17 (t, 1 H, J = 5 Hz), 4.92 (s, 2 H), 5.10–5.47 (d of d, 2 H, J = 5 and 9 Hz), 6.00–6.37 (m, 2 H), 6.53–6.73 (t, 2 H, J = 3 Hz).

Exact mass: Calcd for $C_{10}H_{12}$, 132.0939. Found, 132.0862.

Synthesis of 5- and 6-Isopropenylcyclohepta-1,6-dienes (6 and 5). Lithium metal (80 mg, 11.5 mmol) was cut into small pieces and added to a solution of 7-isopropenylcyclohepta-1,3,5-triene (1.0 g, 7.6 mmol) in 100 mL of dry, distilled ammonia at −78 °C. The solution initially turned red and then purple. After the solution was stirred for 1 h, the ammonia was allowed to evaporate at room temperature, and the volatile products were distilled under vacuum into a trap at −78 °C. Preparative GLC on the Carbowax column allowed the separation of **5** and **6**, which were identified by their spectra. The data for **5** were the following: ^{1}H NMR δ 1.60–1.87 (br s, 3 H), 2.43 (s, 5 H), 4.60–4.83 (br s, 2 H), 6.87 (s, 4 H); ^{13}C NMR δ 20.45, 36.76, 44.85, 108.82, 125.48, 132.17, 150.19; UV λ_{max} 253 nm (log ϵ 3.95).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1112.

The spectral data obtained for **6** were the following: ^{1}H NMR δ 1.75 (s, 3 H), 1.50–2.00 (m, 2 H), 2.00–2.50 (m, 2 H), 2.87–3.25 (m, 1 H), 4.63 (s, 1 H), 4.82 (s, 1 H), 5.78 (s, 4 H); ^{13}C NMR δ 20.80, 28.95, 30.14, 49.65, 111.81, 125.12, 132.22, 134.32, 135.99, 148.48; UV λ_{max} 248–9 nm (log ϵ 3.94).

Exact mass: Calcd for $C_{10}H_{14}$, 134.1096. Found, 134.1094.

Acknowledgment. We thank the National Science Foundation and the Alfred P. Sloan Foundation for support of this work.

Registry No. **1**, 62235-10-3; **2**, 72269-00-2; **3**, 57354-42-4; **4**, 72269-01-3; **5**, 72269-02-4; **6**, 72269-03-5; **7**, 72269-04-6; **8**, 72269-05-7; 7-isopropenylcyclohepta-1,3,5-triene, 72269-06-8; tropylium fluoroborate, 27081-10-3; 2-bromopropane, 75-26-3.

Sodium Bismuthate Oxidation of Olefins

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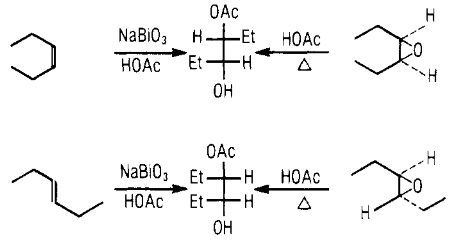
In 1950 Rigby first discovered the synthetic potential of sodium bismuthate in organic oxidations when he demonstrated the cleavage of vicinal diols and the conversion of acyloins to α-diketones in high yield.[2] In spite of Rigby's work and more recent studies by a number of groups on the oxidation of phenols[3-5] with sodium bismuthate, bismuth reagents are seldom used in organic synthesis. Considering the high oxidation potential of bismuth(V) compounds,[6] we decided to explore the oxidation of olefins with sodium bismuthate.[7]

We have found that sodium bismuthate in acetic acid oxidizes olefins to vicinal hydroxy acetates in moderate to low yield (Table I). The yields are highest when a tertiary center is present in the olefin as in trisubstituted and geminally disubstituted olefins. Mono- and 1,2-disubstituted olefins react sluggishly and only afford low yields of hydroxy acetates.[8] The reactions were typically run by mixing equimolar amounts of sodium bismuthate and olefin in glacial acetic acid and stirring the heterogenous mixture in a stoppered flask until the orange color of the sodium bismuthate had dissipated. Filtration and extractive workup afforded the crude products which were further purified by chromatography or distillation to obtain a yield. Under these conditions between half and one-third of the starting olefin was usually recovered. However, the addition of more than 1 molar equiv of oxidant does not improve the yields since the products are unstable to the reaction conditions.

In order to determine whether the olefin maintained its integrity during its exposure to the sodium bismuthate, we examined the three products of oxidation of α-trideuteriomethylstyrene by both GC/MS and NMR. Deuterium scrambling was not observed in either of the products or in the recovered starting material. Furthermore, the olefins react specifically since both (E)-3-hexene and (Z)-3-hexene are converted cleanly to distinguishable hydroxy acetates. The hydroxy acetate obtained from (Z)-3-hexene is identical with that obtained from opening the cis epoxide of 3-hexene and has thus been assigned the threo structure. (E)-3-Hexene similarly affords the erythro hydroxy acetate. The unreacted olefin recovered from these oxidations maintained its stereochemical integrity.



Two mechanistic pathways seemed possible for the production of the hydroxy acetates. They could be generated either by a sodium bismuthate mediated epoxidation of the olefin[9] followed by solvolysis in the acetic acid or via an oxymetalation sequence.[10] To distinguish

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[7] Since the completion of our work, a report on the use of an organobismuth(V) compound to oxidize alcohols has appeared. See, D. H. R. Barton, J. P. Kitchin, and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, 1099–100 (1978). For a similar reagent, see F. Challenger and O. V. Richards, *J. Chem. Soc.*, 405–11 (1934).

[8] The hydroxy group is presumably derived from water in the reagent. The commercial sodium bismuthate we used (Ventron) contained 84% sodium bismuthate, 4% bismuth(III) oxide, and 13% water.

[9] Sodium bismuthate does not oxidize the solvent to peracetic acid.

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