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Halocyclopropanes

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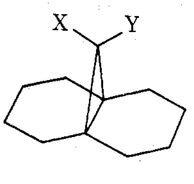
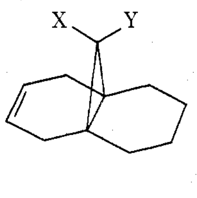
The chemistry of the tricyclic monobromides **4**, **5**, **6**, and **7** has been examined. Evidence is presented which implicates a partially opened cyclopropyl cation as a reaction intermediate.

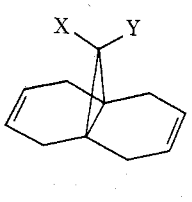
The chemical properties of various tricyclic cyclopropyl halides have been of interest to us and several others for some time now.[2] We recently reported on the silver ion assisted solvolysis of the *gem*-dibromides **1**, **2**, and **3**.[3] A continued interest in this area led us to examine the corresponding monobromo compounds **4**, **5**, **6**, and **7**. The chemistry of these monobromo derivatives differed significantly from that observed for the aforementioned dibromo systems. We now wish to report on these differences, and we attempt to offer reasonable explanations as to their origins.



1, X = Y = Br
4, X = H; Y = Br

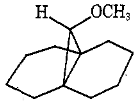
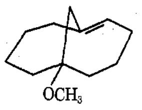
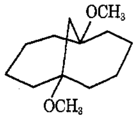
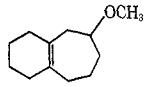
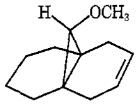
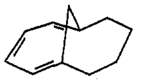
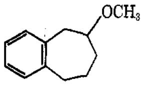
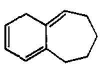
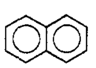
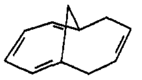
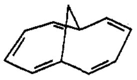


2, X = Y = Br
5, X = H; Y = Br
6, X = Br; Y = H



3, X = Y = Br
7, X = H; Y = Br

Table I
Products Obtained in the Silver Ion Assisted Solvolysis of 4, 5, 6, and 7

Compd	Products[a]			
4[b]	 8 (18, 18)	 9 (10, 24)	 10 (2, 20)	 11 (41, 8)
5	 12 (12)	 13 (46)	 14 (19)	
6	 15 (12)	13 (73)	14 (2–3)	
7[c]	 16 (3–4)	 17 (2–4)	 18 (2–3)	

[a] Absolute yields reprinted in parentheses. Reactions were carried out at reflux unless noted otherwise. [b] Yields reported are for reflux and room temperature runs, respectively. [c] Reaction carried out at 100°C. The remaining nonvolatile material consists of intractable substances.[2]

Results

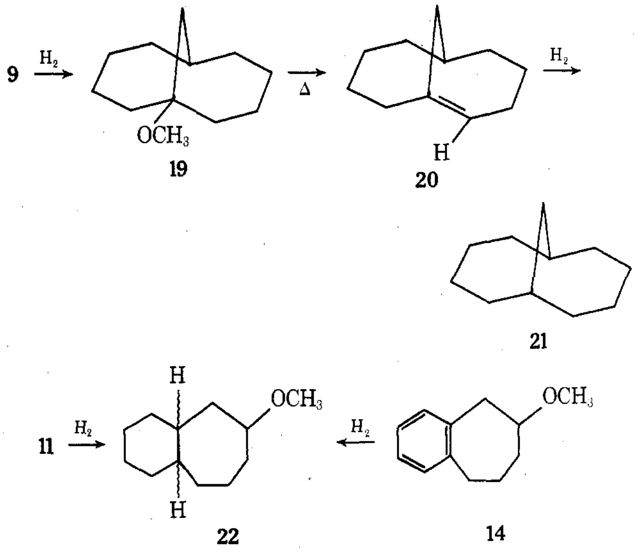
Synthesis of the requisite monobromides was readily accomplished by treating the corresponding dibromides with tri-*n*-butyltin hydride. Yields in all cases were between 50 and 60%. The structure of **4** was assigned based on a correct elemental analysis and an NMR spectrum which exhibits a sharp singlet at 2.94 ppm (1 proton). Monobromides **5, 6,** and **7** were identical in every respect with those reported by Paquette et al.[4] Isomers **5** and **6** were separated via column chromatography. Product studies were carried out using the same techniques reported previously.[3] Our results are contained in Table I.

The structures of **8** and **10** were assigned on the basis of elemental analysis and spectral data (see Experimental Section). It should be noted that the ^{13}C NMR spectrum of **10** has five lines. This is consistent with the symmetry of the assigned structure and unambiguously rules out several mechanistically feasible isomers as possible structures.

The NMR spectrum of **9** exhibits absorption at 5.28 (triplet, $J = 6$ Hz, 1 proton), 3.03 (singlet, 3 protons), 2.66 (doublet, $J = 12$ Hz, 1 proton), and 0.80–2.35 ppm (complex, 15 protons). This is certainly consistent with the structure assigned; the doublet at 2.66 ppm is characteristic of bicyclic systems of this type and can be assigned to the proton on the methylene bridge which is anti to the olefinic linkage.[2,5a] Unambiguous proof of structure, however, was based on the synthetic sequence outlined in Scheme I.

A few comments concerning this sequence are perhaps necessary. The saturated bicyclic ether **19** had an NMR spectrum very similar to that of **10**. A sample of the material assumed to be **19** was collected via gas chromatography for elemental analysis. Surprisingly, it analyzed correctly for $C_{11}H_{18}$. The NMR absorption of the collected material shows absorption at 5.48 (triplet, $J = 6$ Hz, 1 proton), 2.73 (doublet, $J = 12$ Hz, 1 proton), and 2.53–1.06 ppm (complex, 16 protons). The triplet at 5.48 ppm and the doublet at 2.73 pm lend credence to the assigned structure **20**. Reduction of **20** afforded **21**, which was identical in every respect with authentic material. These facts we feel adequately support the structure assigned to **9**.

Scheme I



Scheme I also outlines the structure proof of **11**. Catalytic reduction of **11** afforded a mixture of four isomeric saturated ethers which were identical in every respect with those obtained from the reduction of **14**.[5b] Both structures **13** and **14** had infrared and NMR spectra identical with those of authentic material. The identity of **12** was confirmed by its reduction to **8**. The stereochemistry of the methoxyl group has been tentatively assigned. Comments as to this point will be made later.

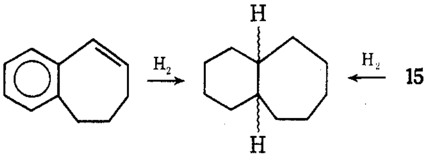
The nature of the bicyclic carbon skeleton of **15** was ascertained as outlined below.

Reduction of **23** afforded two isomeric hydrocarbons **24** which were identical in every respect with those obtained from the reduction of **15**.[7] The placement of the double

Table II
Rate Constants and Activation Parameters for the Silver Ion Assisted Solvolysis of 4, 5, 6, and 7

Compd	Temp, °C[a]	k, l. mol^{-1} sec^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, eu	k^{25}_{rel}
4	24.4	5.86×10^{-4} (±0.07)	21.6	−0.8	2×10^5
	39.6	3.63×10^{-3} (±0.03)			
	25.0	6.32×10^{-4} [b]			
	100.0	1.20 [b]			
5	76.0	5.41×10^{-4} (±0.08)	20.4	−15.3	1×10^3
	89.5	1.68×10^{-3} (±0.02)			
	25.0	3.01×10^{-6} [b]			
	100.0	3.83×10^{-3} [b]			
6	48.2	1.34×10^{-4} (±0.02)	21.4	−9.8	3×10^3
	65.4	7.76×10^{-4} (±0.12)			
	25.0	9.14×10^{-6} [b]			
	100.0	1.64×10^{-2} [b]			
7	124.8	5.03×10^{-4} (±0.06)	27.6	−4.7	1
	140.0	1.89×10^{-3} (±0.02)			
	25.0	3.12×10^{-9} [b]			
	100.0	4.62×10^{-5} [b]			

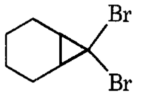
[a] At least two runs were made at each temperature. [b] This is an extrapolated value.



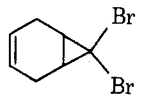
23 **24**

bonds within **15** was based on its NMR spectrum.[8] Complex absorption was observed between 1.40 and 1.75 (4 protons) and 1.75–2.50 ppm (6 protons). Absorption in the olefinic region (complex, 5.05–6.35 ppm) accounted for four protons. The structures of **16**, **17**, and **18** have been previously assigned.[2]

Rate studies were carried out as previously described.[3] Rate data as well as activation parameters for both mono- and dibromides are contained in Tables II and III. We have also solvolyzed the bicyclic dibromides **27** and **28** (see Table IV).



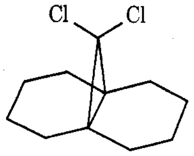
27



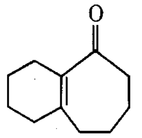
28

Discussion

We observe that the products of solvolyses of the monobromo derivatives **4**, **5**, **6**, and **7** are strikingly different from those obtained in the silver ion assisted solvolyses of **1**, **2**, and **3**. Warner has recently performed a labeling experiment with the *gem*-dihalide **29**.[9] His results indicate that the bicyclic enone **30** does not arise via the alkyl shift mechanism postulated initially by us and other workers.[2,3] Rather it is derived from the intermediate **31**, which after capture by solvent then undergoes an alkyl shift (Scheme II). This mechanistic scheme clearly explains the lack of bicyclic product of the general type **33** or **34** in the solvolysis of the monobromides **4–7**. According to our earlier mechanistic suggestions, products of this type would have been expected; however, they cannot form if a mechanism as outlined in Scheme II is in operation. One would thus expect "cyclopropyl" trapping products and bicyclic products derived directly from a bridgehead double bond species. This is exactly what we have observed.



29



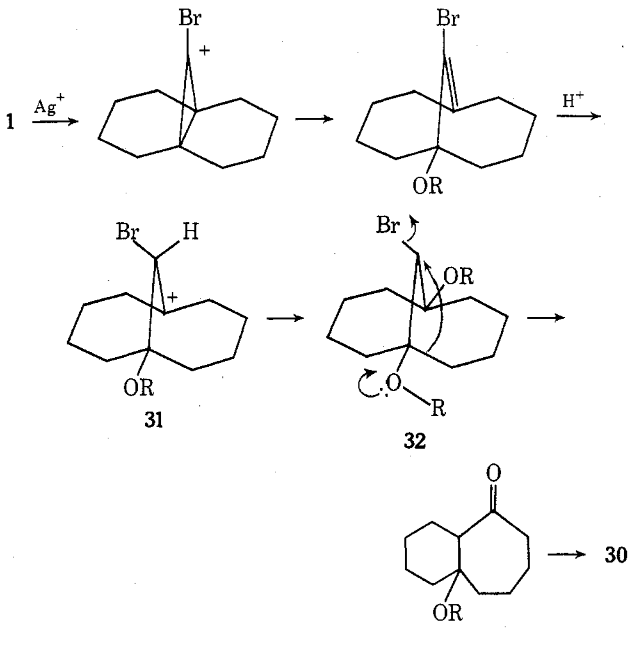
30

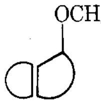
Table III
Rate Constants at 25° for the Silver Ion Assisted Solvolysis of 1, 2, and 3[a]

Compd	k, l. mol^{-1} sec^{-1}	k^{25}_{rel}
1	1.87×10^{-2}	3×10^6
2	4.83×10^{-4}	7×10^4
3	6.97×10^{-9}	1

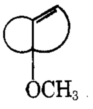
[a] These are extrapolated values.

Scheme II





33



34

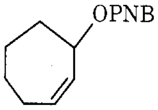
Whether or not a full-fledged cyclopropyl cation is an intermediate in the solvolysis of these tricyclic cyclopropyl systems has been briefly discussed.[3] We offer here evidence which seems to point toward a partially opened species.[10]

Table IV
Rate Constants and Activation Parameters for the Silver Ion Assisted Solvolysis of 27 and 28

Compd	Temp, °C[a]	k, l. mol^{-1} sec^{-1}	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, eu	k^{25}_{rel}
27	86.7	8.34×10^{-4} (±0.10)	24.3	−5.5	24
	100.5	3.04×10^{-3} (±0.12)			
	25.0	6.11×10^{-7} [b]			
	100.0	2.90×10^{-3} [b]			
28	120.0	3.12×10^{-4} (±0.15)	22.4	−18.26	1
	136.0	1.03×10^{-3} (±0.08)			
	25.0	2.55×10^{-8} [b]			
	100.0	6.29×10^{-5} [b]			

[a] At least two runs were made at each temperature.
[b] This is an extrapolated value.

If one compares the relative rates of solvolysis of the bicyclic dibromides **27** and **28** at 25° a rate ratio (k_{27}/k_{28}) of approximately 24 is observed, while the tricyclic dibromides **1** and **2** give a ratio (k_1/k_2) of 39. The difference in free energy of activation between the members of each pair is for all practical purposes identical. Now, the mechanism of solvolysis of the bicyclic system **27** is well documented, i.e., concerted ionization to a cis allyl cation and subsequent capture by solvent.[12] The mechanism of solvolysis of **28** is not well documented, however. It could be argued that rather than form an antiaromatic allyl cation, **28** would ionize to form a cyclopropyl cation.[13] However, Gassman has demonstrated that the allyl p-nitrobenzoates **35** and **36** solvolyze at essentially the same rates (k_{35}/k_{36} = 1.9 at 120°).[14] The additional double bond in **36** apparently does not interact sufficiently with the allyl ribbon to impart any degree of antiaromaticity. The effect observed is probably purely an inductive one (slightly destabilizing). It would seem reasonable then that both **27** and **28** solvolyze via similar mechanisms and that the difference in relative rates between the two pairs can be attributed for the most part to the electron-withdrawing effect of silver ion which can complex with the double bond in **28**.[3]



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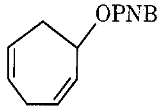

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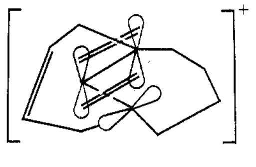
If one assumes that both **1** and **2** ionize initially to form a cyclopropyl cation, then one would expect that the difference in energy of activation between **1** and **2** would be less than the difference observed between **27** and **28** since the site of positive charge in the ion formed from **2** is further removed from the complexed silver ion than in the allyl ion formed from **28**.[15] The fact that the observed relative rates are nearly identical then implies that there is some degree of ring opening (i.e., some allyl character) at the transition state in the solvolysis of **1** and **2**. An increase in strain energy might well accompany this partial opening and be of a greater magnitude for **2** than **1**.

That a true cyclopropyl cation is probably not a viable intermediate in the solvolysis of the tricyclic monobromides is exemplified by the behavior of the unsaturated isomeric monobromides **5** and **6**. Molecular mechanics were carried out on the systems in question (see Table V).[16]

Table V
Calculated Strain Energies for Tricyclic Bromocyclopropanes

Compd	Strain, kcal mol^{-1}	Compd	Strain, kcal mol^{-1}
1	120.30	5	113.18
2	117.26	6	109.71
3	108.50	7	104.72
4	112.32		

These calculations indicate that there is a difference in ground state energy between **5** and **6** of about 3.5 kcal/mol (**6** being more stable than **5**). The method of calculation in all probability exaggerates this difference.[17] Our rate data (25°) put an upper limit on this value of approximately 2.5 kcal/mol (compare **1** vs. **2**, **4** vs. **6**, and **27** vs. **28**). This does not take into consideration the destabilization of the transition state afforded the unsaturated ions by the complexed silver ion. A more reasonable estimate (which takes the effect of the silver ion into consideration) of the difference in ground state strain between **5** and **6** would be on the order of 1.0–1.5 kcal/mol. Thus, one would expect that isomer **5** would solvolyze some ten times faster than **6** if the reaction proceeded via a common intermediate, namely, a cyclopropyl cation. In fact the observed reactivity is reversed, i.e., **6** solvolyzes approximately three times faster than **5**. The kinetic evidence thus seems to eliminate a common intermediate for the two reactions. The product data (Table I) are also consistent with this hypothesis. We would like to propose that both **5** and **6** begin to open in a disrotatory fashion, the direction of which depends on the stereochemistry of the leaving groups and thus should be different for each isomer. Thus, if taken to the limit, **5** would afford **37** while **6** should yield **38**. We stress that these are limiting cases and that ion **37** has a greater amount of inherent strain owing to the presence of the double bond in the same ring as the trans allyl ion. We suggest, then, that **5** on solvolysis yields an ion having less allyl character than either **37** or **38**, i.e., it has more cyclopropyl character and is represented by structure **39**. This would nicely explain the lack of any cyclopropyl trapping product observed in the solvolysis of **6**.



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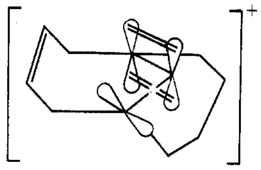

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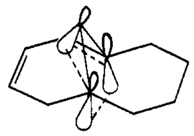

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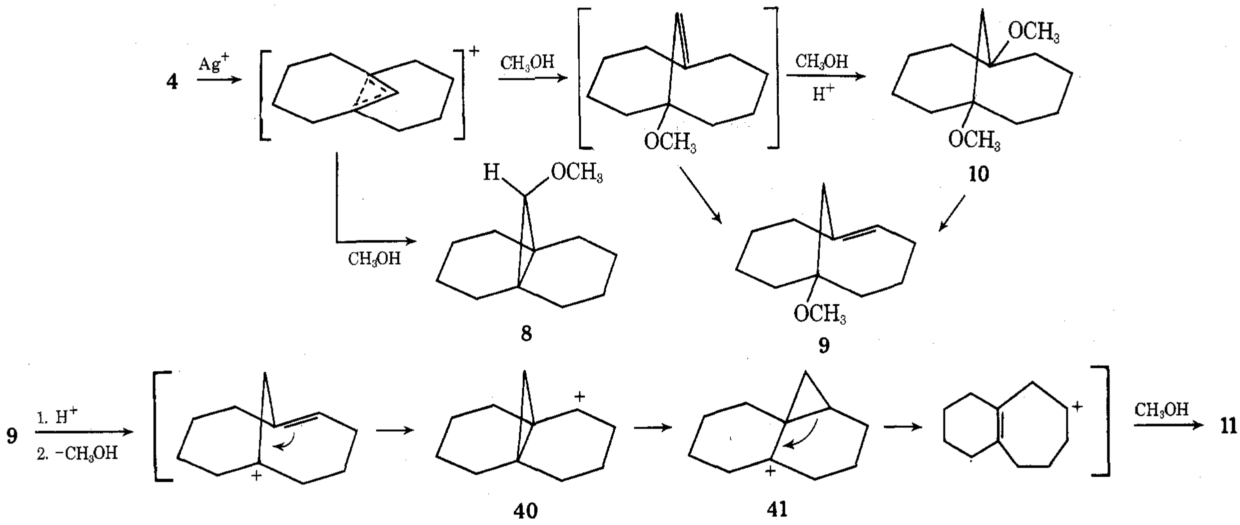
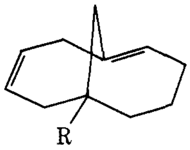
The product ratios obtained in the solvolysis of **4** are temperature dependent (see Table I). While the absolute yield of **8** remains unchanged, at the higher temperature **11** is formed at the expense of both **9** and **10**. We have demonstrated that both **9** and **10** are converted quantitatively into **11** when refluxed in methanol containing a trace of nitric acid. It is postulated, then, that **9** and **10** are initially formed from a partially opened ion and then rearrange to **11** under the condition of the reaction (see Scheme III).[18]

The major product obtained in the solvolysis of both **5** and **6** is the bicyclic conjugated triene **13**. However, the yield of the material obtained from **6** is almost 30% higher than that obtained from **5** (Table I). We have stated previously that the ion formed from **6**, namely **38**, in all probability has a greater degree of allyl character than the ion (**39**) formed from **5**. It would seem that the conformation of **38** is well suited such that either elimination of a proton or rearrangement of the bridgehead double bond will prefer-

Scheme III

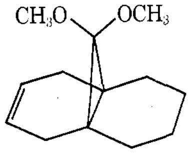


entially place a double bond in the ring already containing unsaturation. We emphasize that we are not sure as to the timing of these steps. Monobromide **5** tends to open in the opposite sense and not to as great an extent. The conformation of **39** would favor the formation of **42** which would account for the higher yield of **14** obtained from **5**, for **42** is an intermediate in the formation of **14**.[20]



42

The stereochemistry of the tricyclic ether **12** has been tentatively assigned. The location of the methoxyl absorption in its NMR spectrum indicates that the methoxyl is syn to the double bond. The methoxyl absorbtions in **44** occur at 3.17 and 3.24 ppm, while in **8** and **12** methoxyl absorbs at 3.15 and 3.25 ppm, respectively. If the stereochemical assignment is correct, the behavior of ion **39** is quite different from that of the bicyclic ion reported by Schleyer, Schollkopf, et al.[11]



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The products **17** and **18** isolated in the solvolysis of **7** can also be rationalized in terms of a partially opened species similar to **39**. The origin of the naphthalene has been discussed previously.[3]

Experimental Section[22]

11-Bromotricyclo[4.4.1.0^{1,6}]undecane (4). To a refluxing solution of 4.7 g (0.015 mol) of 11,11-dibromotricyclo[4.4.1.0^{1,6}]undecane and a trace of AIBN was added with stirring and under a nitrogen atmosphere 4.4 g (0.015 mol) of tri-*n*-butyltin hydride dissolved in an equal volume of ether. After addition of the hydride the reaction mixture was refluxed for 5 hr and then stirred at room temperature for 18 hr. Distillation of the crude reaction mixture followed by elution chromatography and redistillation afforded 1.7 g (50%) of the desired material. The NMR of **4** exhibited absorption at 2.97 (singlet, 1 proton) and 0.97–2.18 ppm (complex absorption, 16 protons).

Anal. Calcd for $C_{11}H_{17}Br$: C, 57.65; H, 7.48; Br, 34.87. Found: C, 57.78; H, 7.54; Br, 34.67.

***anti-* and *syn*-11-Bromotricyclo[4.4.1.0^{1,6}]undec-3-ene (5 and 6).** The procedure described for the synthesis of **4** was employed. A mixture of the two isomers was obtained which was separated via elution chromatography (silica gel eluted with ligroin). A yield of 3.24 g (20%) of the anti isomer **5** [bp 74–75° (0.6 mm)] and 1.69 g (10%) of the syn isomer **6** [bp 77–78° (0.5 mm)] was obtained. Spectral properties of the above isomers were in complete agreement with those reported by Paquette et al.[4]

11-Bromotricyclo[4.4.1.0^{1,6}]undeca-3-diene (7). The material was prepared according to the procedure previously reported.[2]

Silver Ion Assisted Solvolysis of 4. A. At Reflux. Silver nitrate (0.738 g, 4.36 mmol) and **4** (0.060 g, 0.218 mmol) dissolved in 25 ml of methanol were refluxed for 20 hr. After the usual work-up the crude reaction mixture was subjected to gas chromatographic analysis on a 3 ft × 0.25 in. 10% Carbowax 20M column.[3] Four major components were shown to be present and all were collected. The NMR spectrum of **8** exhibited absorption at 3.15 (singlet, 3 protons), 2.50 (singlet, 1 proton), and 2.05–0.68 ppm (complex absorption, 16 protons).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.11; H, 11.28.

Compound **11** exhibited absorption in the NMR at 0.95–2.47 (complex absorption, 16 protons), 2.70 ppm (complex multiplet, 1 proton), and 3.12 ppm (singlet, 3 protons).

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.75; H, 11.02.

The third component **10** absorbs in the NMR at 1.55 (broad singlet, 16 protons), 1.90 (singlet, 2 protons), and 2.97 ppm (singlet, 6 protons).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.27; H, 11.18.

In addition a ^{13}C NMR spectrum of **10** exhibits the expected five-line spectrum: 41.5, 52.3, 61.6, 61.9, and 88.2 ppm relative to Me_4Si.

The NMR of the fourth component (**9**) is reported in the text.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.77; H, 11.27.

In runs in which yields were determined an internal standard (β-methylnaphthalene) was added directly to the reaction mixture after all starting material had been consumed. The reaction mixture was then analyzed via VPC without further work-up. For a tabulation of yields see text.

B. At Room Temperature. The same procedures were followed as described in A. The reaction mixture was stirred for 20 hr at room temperature and then analyzed.

Reduction of 9. A mixture of 50 mg of **9** and approximately 0.1 g of 5% Rh on alumina in ethanol was stirred under a hydrogen atmosphere until thin layer chromatography indicated that all the starting material had been consumed. The reaction mixture was analyzed via gas chromatography on a 3 ft × 0.25 in. 10% Carbowax 20M column. Only one volatile component was shown to be present. The material was collected and its NMR measured. The compound absorbed at 0.28–2.22 (complex absorption with a broad singlet at 1.53 ppm and a smaller one at 1.88 ppm, 19 protons) and 3.02 ppm (singlet, 3 protons).

Treatment of 9 with Acid. Compound **9** (40 mg, 0.22 mmol) and 2 drops of concentrated nitric acid in 25 ml of methanol were refluxed for 12 hr. After the usual work-up the crude product was analyzed via VPC. One volatile product was in evidence. It was collected and its infrared spectrum was measured. It was identical with that of 11.

Treatment of 10 with Acid. Compound 10 (60 mg, 0.33 mmol) and 2 drops of concentrated nitric acid in 25 ml of methanol were refluxed for 12 hr. After the usual work-up the crude product was analyzed via VPC. A single volatile product was shown to be present. Its infrared spectrum was identical with that of 11.

Reduction of 11. Compound 11 (50 mg, 0.27 mmol) was reduced in a manner identical with that described for the reduction of 9. Gas chromatographic analysis of the crude product showed four major components. These were collected and their infrared spectra were measured. These were identical with the products obtained in the reduction of 14. An NMR of the mixture showed no olefinic absorption.

Synthesis of Benzocyclohepten-2-ol. The compound was synthesized according to the method of Huisgen et al.[7] It was identical in all respects with the reported material.

Synthesis of 14. 1,2-Benzocyclohepten-4-ol (0.1 g, 0.617 mmol) in 5 ml of anhydrous ether was added dropwise with stirring and under a nitrogen atmosphere to a suspension of 0.044 g (1.8 mmol) of sodium hydride. The resulting mixture was stirred at room temperature for 1.5 hr. Methyl iodide (2.5 g, 6.0 mmol) was then added and the reaction mixture was stirred for 48 hr. After the usual work-up the product was subjected to VPC analysis. One major component was in evidence. It was collected and its NMR spectrum exhibited absorption at 1.07–1.90 (complex absorption with a broad multiplet centered at 1.70 ppm and complex absorption between 2.47 and 3.17 ppm, 9 protons), 3.23 (singlet, 3 protons), and 6.93 ppm (singlet, 4 protons).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.02. Found: C, 81.54; H, 9.02.

Silver Ion Assisted Solvolysis of 5. The reaction was carried out in exactly the same manner as described for the solvolysis of 4. Three major volatile products were isolated: 12, 13, and 14. The NMR spectrum of 12 exhibited absorption at 1.08–2.42 (complex, 12 protons), 2.83 (singlet, 1 proton), 3.25 (singlet, 3 protons), and 5.40 ppm (broad singlet, 2 protons). The infrared and NMR spectra of 13 were identical with those of authentic material.[5] The infrared spectrum of 14 was identical with that of authentic material. Yields were determined as described previously. Biphenyl was employed as the internal standard. See text for yield tabulations.

Silver Ion Assisted Solvolysis of 6. The reaction was carried out in the same manner as reported for the solvolysis of 5. Yields were determined via gas chromatography and are listed in the text. The proof of structure for 15 is discussed in the text.

Reduction of 15. Compound 15 was reduced at atmospheric pressure (H_2, PtO_2, EtOH). The usual work-up yielded 24 which was identical with material obtained in the catalytic reduction of 23.

Silver Ion Assisted Solvolysis of 7. Details concerning the solvolysis of 7 are contained in a previous publication.[2]

Kinetic Procedures. Rate constants and activation parameters were determined as previously described.[2]

Catalytic Hydrogenation of 12. Compound 12 was reduced at atmospheric pressure (H_2, 5% Rh/alumina, EtOH). The usual work-up afforded material whose infrared spectrum was identical with that of 8.

Synthesis of 27 and 28. Both 27 and 28 were synthesized in a manner analogous to that employed for 1, 2, and 3.[3] The properties of the materials obtained were identical with those reported earlier.[23,24]

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Registry No.—**1**, 20564-71-0; **2**, 38760-88-2; **3**, 4578-96-5; **4**, 57379-33-6; **5**, 52910-32-4; **6**, 52949-67-4; **7**, 4622-37-1; **8**, 57346-27-7; **9**, 57346-28-8; **10**, 57346-29-9; **11**, 57346-30-2; **12**, 57346-31-3; **14**, 57346-32-4; **15**, 57346-33-5; **27**, 2415-79-4; **28**, 6802-78-4; tri-*n*-butyltin hydride, 688-73-3; silver nitrate, 7761-88-8; 1,2-benzocyclohepten-4-ol, 13249-77-9.

References and Notes

(1) Address correspondence to Department of Chemistry, University of Vermont, Burlington, Vt. 05401.

(2) D. B. Ledlie and L. Bowers, *J. Org. Chem.*, **40**, 792 (1975), and references cited therein.

(3) D. B. Ledlie, J. Knetzer, and A. Gitterman, *J. Org. Chem.*, **39**, 708 (1974).

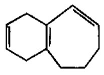
(4) L. A. Paquette, W. E. Heyd, and G. L. Thompson, *J. Am. Chem. Soc.*, **96**, 3177 (1974).

(5) (a) E. Vogel, W. Wiedemann, H. D. Roth, J. Eimer, and H. Gunther, *Justus Liebigs Ann. Chem.*, **759**, 1 (1972). (b) Compound **14** was synthesized via a modified Williamson ether synthesis from the corresponding alcohol.[6] The alcohol was synthesized according to the procedure of Hulsgen et al.[7]

(6) W. G. Dauben and G. H. Berzin, *J. Am. Chem. Soc.*, **85**, 468 (1963).

(7) R. Huisgen, E. Ravenbusch, G. Seidl, and I. Wimmer, *Justus Liebigs Ann. Chem.*, **671**, 41 (1964).

(8) Another reasonable structure would be the isomeric triene **26**; however,



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the ratio of allylic to nonallylic protons would be 4:1. We feel that structure **15** is the only one which fits the data at hand. It is, however, puzzling as to why **15** does not aromatize under the conditions of the reaction.

(9) P. Warner and S. Lu, *J. Am. Chem. Soc.*, **97**, 2536 (1975).

(10) A partially opened cyclopropyl cation has been postulated by Schöllkopf and Schleyer for a bicyclic cyclopropyl tosylate.[11]

(11) U. Schöllkopf, P. V. R. Schleyer, K. Fellenberger, M. Patsch, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967).

(12) See D. B. Ledlie, *J. Org. Chem.*, **37**, 1439 (1972), and references cited therein.

(13) R. Hoffmann and M. J. Goldstein, *J. Am. Chem. Soc.*, **93**, 6193 (1972).

(14) P. G. Gassman and X. Creary, *J. Am. Chem. Soc.*, **95**, 6852 (1973).

(15) We assume here that the differences in ground state energy between the members of the two pairs are essentially the same.

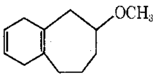
(16) We are deeply indebted to Diane Khoury of Professor Schleyer's group for performing these calculations for us.

(17) For a critical review of molecular mechanics see P. v. R. Schleyer, J. D. Andose, and E. M. Engler, *J. Am. Chem. Soc.*, **95**, 8005 (1973).

(18) Formation of **41** from **40** may occur either as shown or through a cyclobutyl cation.[19]

(19) For a discussion of cyclopropylcarbinyl and cyclobutyl cations see K. B. Wiberg et al. in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1972.

(20) We envision that **14** arises via a mechanism similar to that postulated for **11** (Scheme III). Oxidation of the diene **43** by silver ion yields **14**.[3]



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(21) We are rather perplexed as to the origin of **15**. The NMR data are certainly consistent with the assigned structure, and we are certain that the carbon skeleton is correct. However, if **15** arose from the immediate precursor to **43** (and this would negate our arguments above), then **26** would be a likely structural candidate. As pointed out earlier the NMR is not in agreement with this structure.

(22) Infrared spectra were determined with a Perkin-Elmer 457 recording spectrohotometer. The NMR spectra were measured at 60 MHz with an Hitachi Perkin-Elmer R20 spectrometer using tetramethylsilane as the internal reference. All spectra were measured in CCl_4 unless otherwise stated. A Hewlett-Packard 5750B gas chromatograph was used for all VPC analyses. All peak areas were integrated with a planimeter. Magnesium sulfate was employed as the drying agent. All reactions involving air- or moisture-sensitive compounds were carried out under a nitrogen atmosphere.

(23) W. V. E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

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