and extracted with three 25-ml portions of diethyl ether. The combined ethereal extracts were extracted with three portions of 25 ml of saturated $NaHCO_3$. The combined $NaHCO_3$ extracts were acidified at 0° with 6 *M* HCl, and the precipitate (0.154 g) was removed by filtration. The filtrate was saturated with NaCl and extracted twice with 25-ml portions of diethyl ether. Drying the combined ether extracts over anhydrous $MgSO_4$, and concentration on the rotary evaporator, gave an additional 0.037 g of product, making the total yield 0.191 g (30.7%). Recrystallization from benzene gave crystals, mp 117–118° (lit.[11] 117.5–118°).

***trans*-4-*tert*-Butylcyclohexanoic Acid (3).** Hydrolysis of 0.565 g (2.85 mmol) of the pure methyl ester of **3** by the procedure described for the methyl ester of **2** gave 0.202 g (35.4%) of **3**, mp 173–174° (lit.[11] 174–175°).

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

Registry No.—**1**, 53783-19-0; **2**, 943-28-2; **3**, 943-29-3; 4-*tert*-butylbenzoic acid, 98-73-7; 4-*tert*-butyl-1,5-cyclohexadien-1-oic acid, 31673-51-5; *cis*-1-carbomethoxy-4-*tert*-butylcyclohexanoic acid, 53783-20-3; *trans*-1-carbomethoxy-4-*tert*-butylcyclohexanoic acid, 53783-21-4.

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1,6-Methano[10]annulene *via* a Solvolytic Pathway

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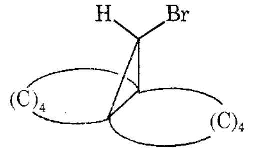
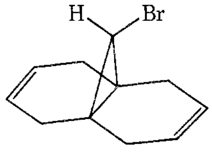
We and others have recently reported on the chemistry of various tricyclic dihalocyclopropanes.[1-8] Continued interest in this area has led us to study monohalo tricyclic systems of the general type **1**. We now wish to report on the chemistry of 11-bromotricyclo[4.4.1.0^{1,6}]undeca-3,8-diene (**2**). When **2** is treated with methanolic silver nitrate at 100°, three volatile products are obtained in a combined absolute yield of approximately 10% (Scheme I). The remaining, nonvolatile reaction product consists of apparently polymeric, intractable material from which we have not been able to isolate characterizable material by the usual separation techniques.

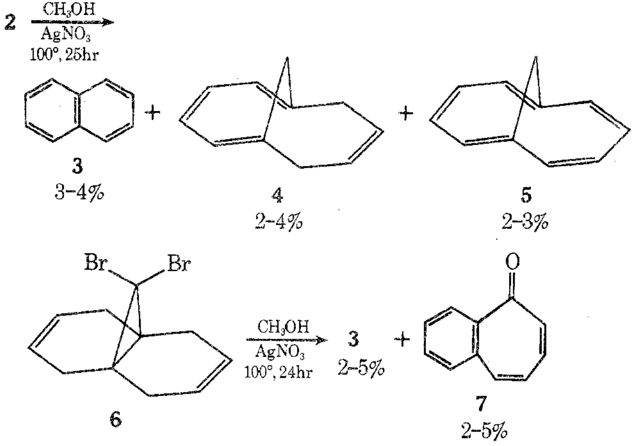


1



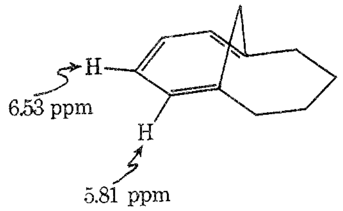
2

Scheme I



Compound **3** was readily identified as naphthalene by comparison of its nmr and infrared spectra with authentic material. The nmr spectrum of **5** was identical in all respects with that of the 1,6-methano[10]annulene published by Vogel.[9]

The structure of the tetraene **4** was assigned based on spectral data.[10a] The nmr of **4** exhibits absorption at 0.68 ppm (J = 9 Hz, 1 proton), 2.63 ppm (J = 9 Hz, 1 proton), 2.75–3.15 ppm (complex absorption, 4 protons), 5.32 ppm (broad singlet, 2 protons), 5.77 ppm (broad singlet, 2 protons), and 6.62 ppm (doublet of doublets, 2 protons). The low-field absorptions at 5.77 and 6.62 ppm are virtually identical in line shape and nearly identical in field position with the low-field absorptions reported by Vogel for the triene **8**.[10b,11]



8

While the volatile products obtained from **2** are quite different from those obtained from **6**, the rates of silver ion assisted solvolysis are similar (Table I).

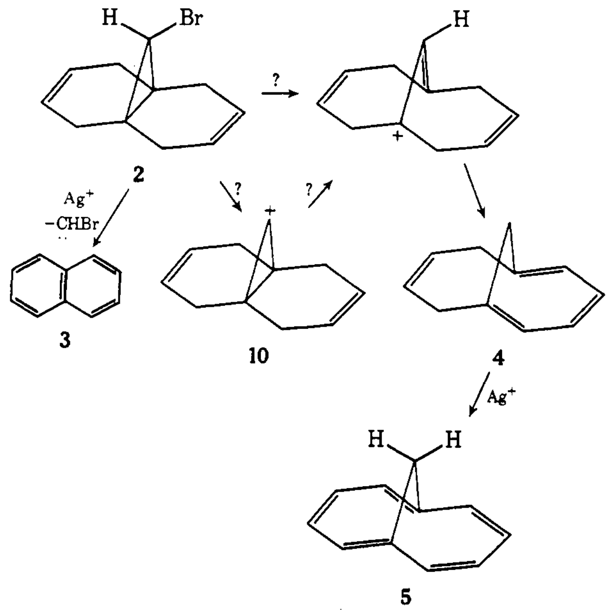
If one assumes that the rate-determining step in the solvolysis of each compound is the formation of a cyclopropyl cation, then any difference in rate between the two compounds should be a reflection of the difference in ground-state energy between the two. Implicit in this argument is the assumption that the cyclopropyl cation is planar and the further assumption that the effect of the α-bromo sub-

Table I[a]
Rate Constants and Activation Parameters of the Ag$^+$-Assisted Solvolysis of 2 and 6

Compd	Temp,[c] °C	k, l. mol^{-1} sec^{-1}	k_{rel} (25°)	ΔH^*, kcal/mol	ΔS^*, eu
2	140	1.89×10^{-3} (±0.02)	1	27.6	−4.7
	124	5.03×10^{-4} (±0.06)			
	25	3.12×10^{-9} [b]			
6[8]	25	6.97×10^{-9} [b]	2.2	30.3	5.7

[a] Silver perchlorate (~20-fold excess) in 95% methanol was employed in all solvolyses. [b] This is an extrapolated value. [c] At least two runs were made at each temperature.

Scheme II



stituent on the stability of the cyclopropyl cation formed from 6 will be negligible.[12,13]

One might thus expect to observe a larger difference in rate between 2 and 6 since the larger bromine substituent should increase the ground-state energy of 6 due to increased steric strain. In fact molecular mechanics indicate a difference in ground-state strain energy between 2 and 6 of 3.78 kcal/mol. This would correspond to a relative rate $k_6/k_2 = 600$.[14] However, it is risky to put too much faith in the absolute difference in strain energy between compounds of this type calculated in this manner.[15]

In addition, the low yields of isolable products preclude an unambiguous interpretation of the rate and product data. We offer a mechanistic scheme (Scheme II) as a suggested mode for the formation of 3–5. Whether or not a cyclopropyl cation (*e.g.*, 10) is in fact an intermediate in the solvolysis of 2 awaits further experimentation.[16]

Experimental Section[17]

11-Bromotricyclo[4.4.1.0^{1,6}]undeca-3,8-diene (2). To a refluxing solution of compound 6 (7.9 g, 0.026 mol) and a small amount of AIBN in 125 ml of absolute ether was added dropwise with stirring and under a nitrogen atmosphere 7.6 g (0.33 mol) of tri-*n*-butyltin hydride dissolved in 8 ml of absolute ether. After the addition was complete (2 hr) the reaction mixture was refluxed an additional 5 hr and then stirred at room temperature for 18 hr. The solvent was removed under reduced pressure and the resulting solution was then distilled. The fraction boiling between 90 and 100° (0.5 mm) was collected and then sublimed. Recrystallization of the sublimate from methanol afforded 3 g (56%) of material, mp 50–51° (lit.[18] mp 51°). The nmr spectrum of 2 was identical with that reported by Paquette.[19]

Silver Ion Assisted Methanolysis of 2. Compound 2 (3.0 g, 0.013 mol) and silver nitrate (22.5 g, 0.13 mol) were dissolved in 100 ml of methanol and heated for 25 hr at 100° in a glass pressure flask. After the usual work-up the crude reaction mixture was subjected to gas chromatographic analysis on an 8 ft × ¼ in. Hi-EFF (DEGS) 15% column. Three major components (3–5) were shown to be present. These were collected and identified (see text).[20] The absolute yields of 3–5 were determined using standard gas chromatographic techniques. α-Methylnaphthalene was employed as the internal standard.

Kinetic procedures as previously outlined[8] were employed. Eight points were taken for each run and 1,3-diphenylpropane was employed as an internal standard.

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

Registry No.—2, 4622-37-1; 4, 38795-15-2; 5, 2443-46-1; 6, 4578-96-5.

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(10) (a) All attempts to free the sample of naphthalene met with no success. The spectra reported contain ~10% naphthalene as an impurity. This precluded a correct elemental analysis for compound **4**. (b) E. Vogel, *et al., Justus Liebigs Ann. Chem.*, **759**, 1 (1972).
(11) The infrared spectrum of **4** exhibits absorption at 1630, 1597, and 1490 cm^{-1}, while **8** has absorption at 1494 and 1600 cm^{-1}.[10]
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(13) Hine has demonstrated that the S$_N$1 reactivities of benzal and benzyl bromides in aqueous acetone at 25° are essentially identical. See J. Hine and D. E. Lee, *J. Amer. Chem. Soc.*, **73**, 22 (1951).
(14) We thank Professor Paul Schleyer and Diane Khoury for performing the force field calculations mentioned above.
(15) For a critical review of molecular mechanics see E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8005 (1973), and references contained therein.
(16) In a typical run for 25 hr at 100° the ratio of **4:3** was 1. However, when the reaction was carried out at 90° for approximately 15 hr, the ratio of **4:3** was 5. Starting material was still present and no detectable amounts of **5** were observed. Vogel has studied the thermal behavior of **4** extensively.[9] He has demonstrated that **4** is stable at temperatures below 250°. At temperatures above 250° **4** rearranges exclusively to benzocycloheptatriene. It thus seems unlikely that **4** is converted to **3** at 100°.
(17) Infrared spectra were determined with a Perkin-Elmer 457 recording spectrophotometer. The nmr spectra were measured at 60 MHz with an Hitachi Perkin-Elmer R20 spectrometer using tetramethylsilane as the internal reference. All spectra were measured in CCl$_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.
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(20) It was found advantageous in subsequent experiments to separate the volatile materials from polymeric material by chromatographing the crude reaction mixture on a silica gel column eluted with ligroin before final isolation of the components *via* gas chromatography.

Steroids and Related Natural Products. 90. 15β-Hydroxydigitoxigenin[1]

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Biologically active steroids of the cardenolide type generally occur in plants[2] as glycosides and have also been isolated from butterflies[2] and toad venoms.[3] Isolation of the parent aglycone by acid hydrolysis of the corresponding glycoside is most useful with sugar attachments of the 2-deoxy type (*cf.* ref 1). If the aglycone is bound to a 2-hydroxy sugar such as D-glucose, acid hydrolysis is much less practical. In such cases enzymatic hydrolysis is considerably more useful.[4] One of the earliest procedures for acid-catalyzed cleavage of cardiac glycosides utilized a mixture of hydrochloric acid in aqueous acetic acid.[5] Another early procedure was based on alcoholysis with 2% hydrogen chloride in methanol.[6] The Reichstein[7] modification of these methods utilized an equal volume mixture of 0.1 *N* sulfuric acid–methyl alcohol to hydrolyze odoroside A and we have