Propellanes. 16. Bridgehead Olefin Formation via 11,11-Dihalo[4.4.1]propellane Solvolysis[1]

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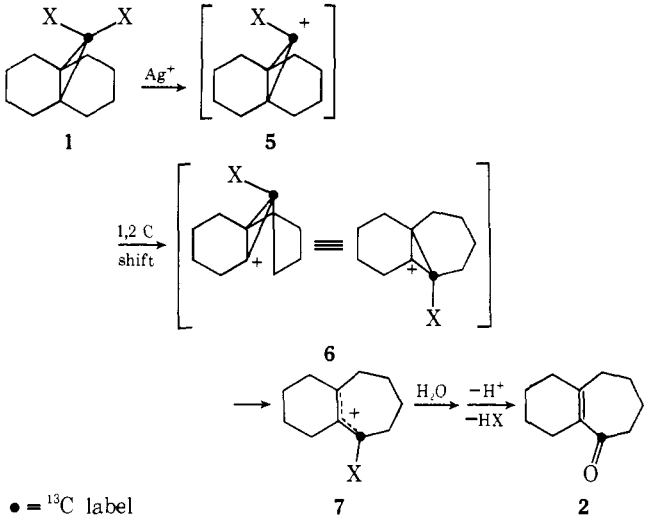
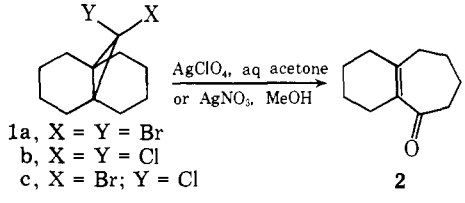
Abstract: 11,11-Dibromo- (**1a**), 11,11-dichloro- (**1b**), and 11-chloro-11-bromo[4.4.1]propellane (**1c**) have been hydrolyzed in various aqueous acetone mixtures. The products include the previously reported rearranged bicyclo[5.4.0]undec-1(7)-en-2-one (**2**), 6-halomethylenecyclodecanones (**3, 26**), 7-hydroxybicyclo[5.4.0]undecan-2-one (**25**), 11-chlorobicyclo[4.4.1]undecane-1,6-diol (**24**), and several decalyl carboxylic acids (**27, 28, 31**). Products **3, 26,** and **24** were particularly diagnostic for a bridgehead olefin intermediate. Hydrolysis of ^{13}C-labeled **1b** led to labeled **2,** where the excess ^{13}C was located at the α carbon of the enone system. This result, together with the isolation of **25** and the dependence of the **2:3** ratio upon water concentration, was consistent only with a bridgehead olefin mechanism (Scheme V). It was also shown that the carboxylic acids resulted from initial cyclopropyl–halogen bond heterolysis.

Paralleling our initial report[5] of bridgehead olefin formation via solvolysis of a [4.2.1]propellane system, Reese[6] and Ledlie[7] independently published that solvolysis of 11,11-dibromo[4.4.1]propellane (**1a**) led predominantly to a rearranged product, **2.** They both proposed a mechanism (Scheme I) involving an alkyl shift prior to cyclopropane ring opening

Scheme I



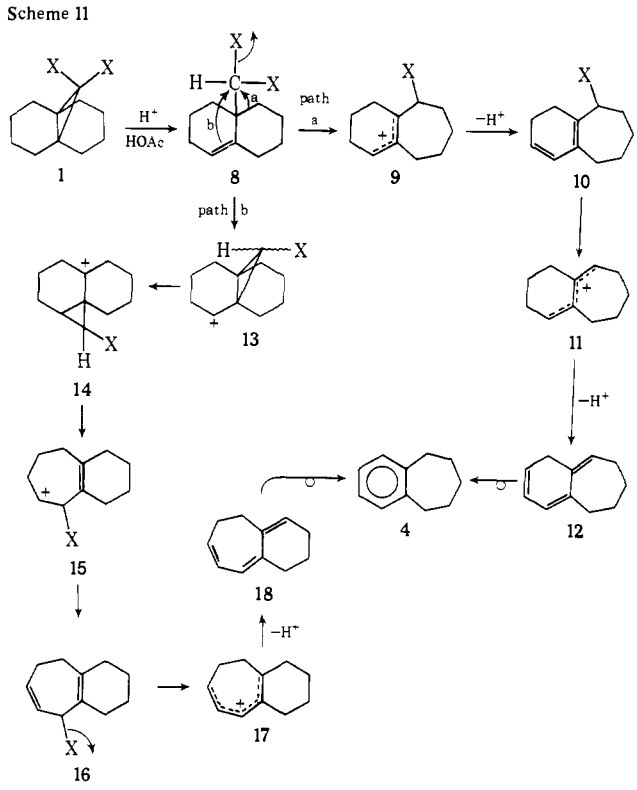
and excluding a bridgehead double bond. While initially accepted by us,[8] we soon became wary of this mechanism, in part due to Parham's[9] demonstration that such a rearrangement pathway could be ruled out in a related case. It rapidly became obvious that mechanisms including a bridgehead olefin intermediate could be written for the **1a** to **2** transformation, and these could be partially tested via labeling experiments.[10]



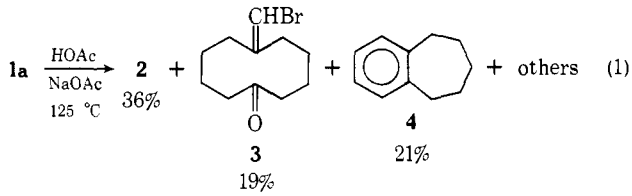
Results and Discussion

Our investigation of the chemistry of **1** began with an acetolysis experiment, where we hoped to compare the solvolysis rate of **1a** with results obtained in other propellane systems. Initial product studies were carried out in glacial acetic acid which was taken straight off the shelf without special drying.

Scheme II

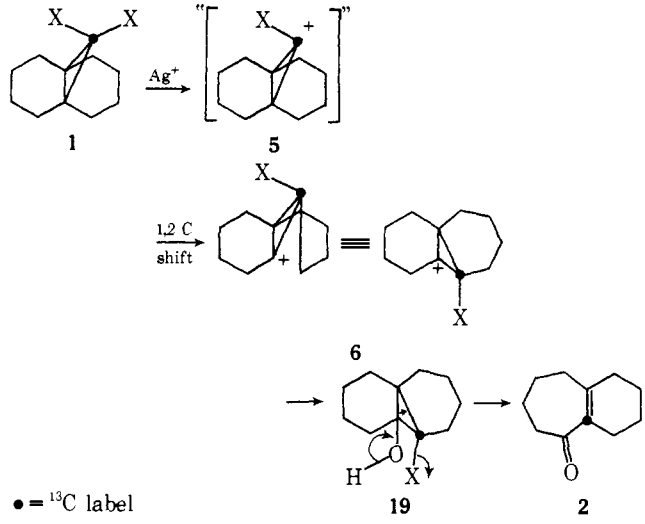


As will be seen, a small amount of water present was fortunate, and the products shown in eq 1 were identified. As expected,

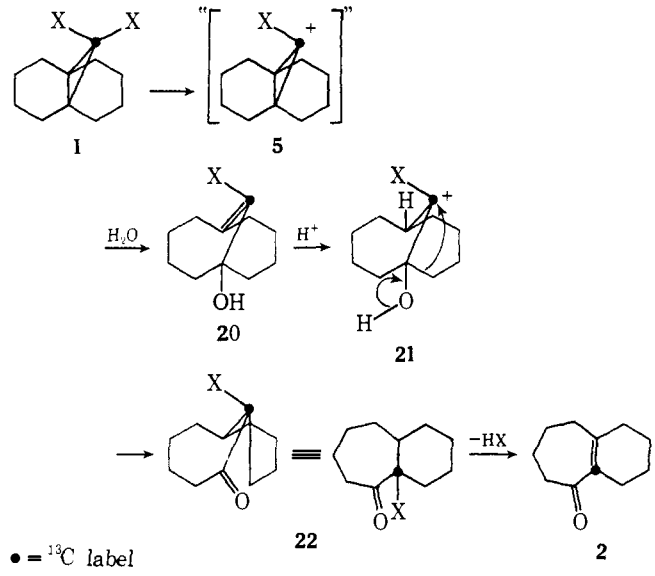


2 was the major product, but significant amounts of monocyclic ketone **3,** a product previously shown to be diagnostic for a bridgehead olefin intermediate,[8,11] were also found. Additionally, benzocycloheptene (**4**)[12] was a verifiable component of the product mixture. Of the various routes one could propose for producing **4,** we favor the addition–elimination–solvolysis paths shown in Scheme II. This preference is primarily dictated by the fact that the proportion of **4** increases sharply upon solvolysis in unbuffered acetic acid, a phenomenon which we attribute to HBr-catalyzed addition of acetic acid to **1a.**

Scheme III



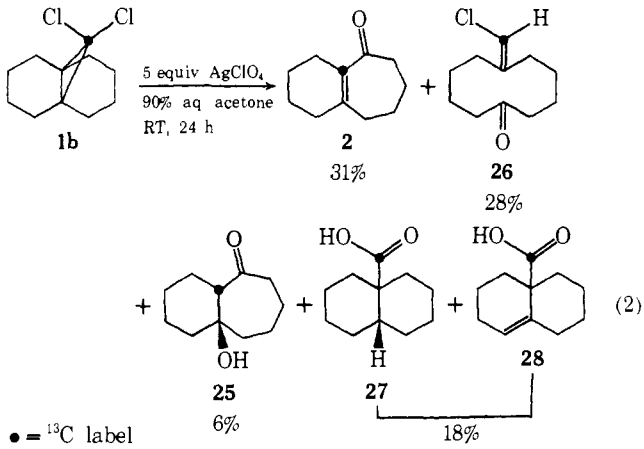
Scheme IV



Pathway b of Scheme II has analogy in the corresponding [4.3.1]propellane series[13,14] and in some steroid work.[15]

Buoyed by the isolation of **3**, we repeated the hydrolysis of **1a** in 90% aqueous acetone ($AgClO_4$). Not surprisingly, **3** was found to be a minor product (ca. 0.4% by GLC–mass spectrometry), thereby implicating a bridgehead olefin in the hydrolysis of **1a**. Nonetheless, the pathway to **2** remained obscure. We thus undertook a ^{13}C labeling experiment in order to distinguish between Scheme I and some other possibilities (Schemes III–V).

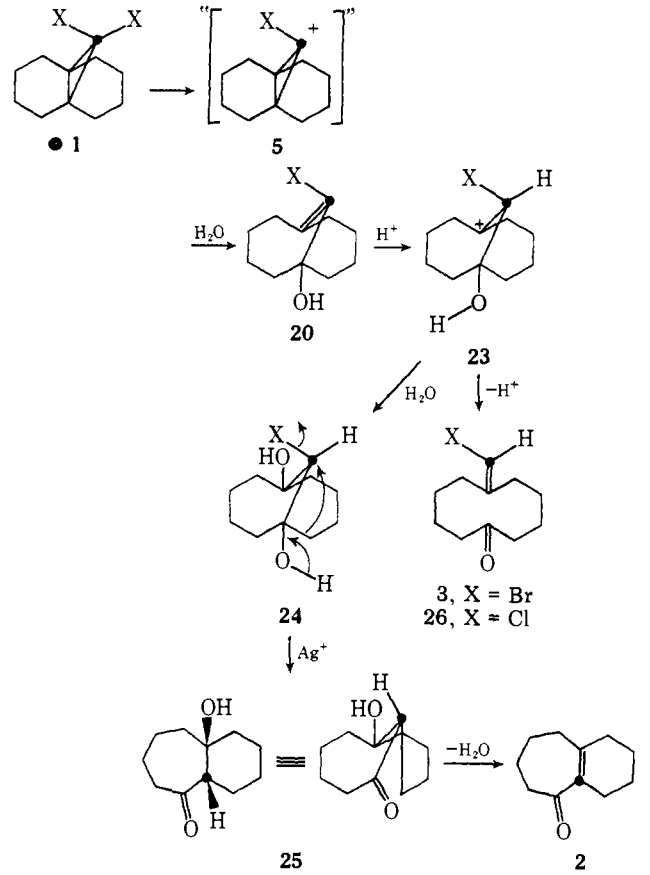
Availability considerations dictated the use of **1b**, labeled at C_{11}. The material we synthesized, using ^{13}C-enriched chloroform, had a total of 5.8% ^{13}C at C_{11} (note that this *includes* naturally occurring ^{13}C). Hydrolysis of labeled **1b** in 90% aqueous acetone (5 equiv of $AgClO_4$) was about 20 times slower than that of **1a**; the products isolated and identified are shown in eq 2. The key labeling result is that for **2**. From



(2)

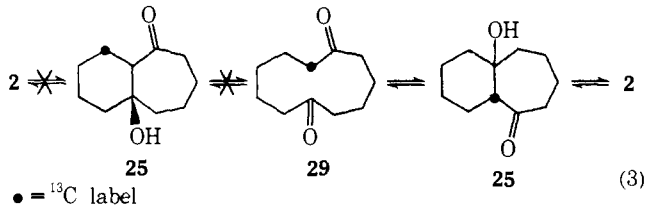
high-resolution mass spectral data, it was calculated that if all the excess (i.e., above natural abundance) ^{13}C remained at one position, then that position contained a total of 5.3% ^{13}C (the analogous carbon of **26** contained 5.8% ^{13}C). The mass spectral fragmentation pattern of **2** was useless for differentiating the carbonyl, α, and β carbons, as the chief losses involve retrocycloadditions. However, ^{13}C NMR proved fruitful. The data for the relevant carbon atoms are summarized in Table I. With the β carbon of the enone system as a standard, we calculated that the α carbon contained 5.6% ^{13}C (integration), in remarkable agreement with the mass spectral data. Further treatment of **2** (labeled) under the hydrolysis conditions for 48 h gave no scrambling and no **25**; this served to eliminate the process shown in eq 3, and showed that **25** was probably a

Scheme V



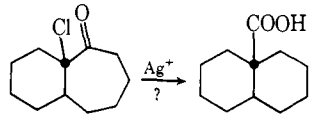
precursor to **2**. Conclusively, then, Scheme I is eliminated from consideration.

The isolation of **25**, which gave **2** upon treatment with concentrated HCl (room temperature) or exposure to the



(3)

solvolysis conditions, mitigated strongly against Scheme IV, and was consistent only with Scheme V. Nevertheless, an intermediate such as **22** could conceivably be a source of carboxylic acid **27,** via a Favorskii-type rearrangement (eq 4).[16] However, were this to occur the ^{13}C would have to be at the quaternary position of **27.** In fact, the label ends up at the carboxyl carbon, thereby excluding eq 4 (vide infra for mode of carboxylic acid production).



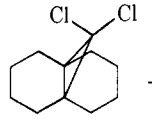
(4)

• = ^{13}C label

22 **27**

At this point the viability of Scheme III appeared quite low. Not only would **6** have to undergo exclusive trapping without ring opening, but there would have to be two pathways to **2,** as Scheme V seemed required by the isolation of **25.** Examination of Schemes III–V revealed that only Scheme V required reaction with water *twice,* and only Scheme V had a common intermediate (**23**) leading to both **2** and **3.** Furthermore, the fate of **23** (and thus the 2:3 ratio) was dependent upon water concentration. The prediction that small amounts of water would lead to more **3** was easily tested; Table II gives the results obtained utilizing **1a.** While the data do not fit a straight line (this would not be expected due to changes in solvent properties), the inescapable conclusion is that monocyclic ketone **3** increases at the expense of **2** and **25** as the amount of water decreases. This fact *supports only Scheme V,* and not Schemes III and IV.

As can be noted from eq 2, the amount of monocyclic ketone formed from **1b** (i.e., **26**) is much greater than that (**3**) from **1a.** The reason most likely is that ion **23** (X = Cl) is less stable (greater electron-withdrawing effect of Cl) than **23** (X = Br). In fact, synthetically useful amounts of **26** can be isolated from hydrolysis of **1b** in 99% aqueous acetone (eq 5).

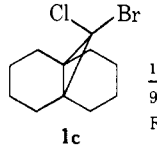


1b

99% aq acetone, 5 equiv $AgClO_4$, RT, 23 h → **2** + **25** + **26** + carboxylic acids (5)

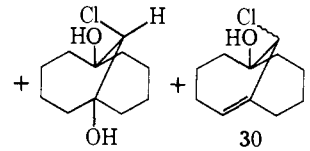
11% 12% 42% 20%

The "missing link" in Scheme V is diol **24.** We felt that it was probably more reactive than the dihalide from which it was derived. However, hydrolysis of **1c** held some promise, for **24** (X = Cl) should be less reactive than the starting bromochloride. In fact, the products isolated from hydrolysis of **1c** are shown in eq 6. Diol **24** was a major product, and the proportion



1c

1 equiv $AgClO_4$, 90% aq acetone, RT, 48 h → **2** + **25** (16% 6%)



24 12% + **30** 6% + **26** 30% + carboxylic acids ~16% (6)

of enone **2** decreased accordingly. Additionally, elimination product **30** (via deprotonation of **23**) was found for the first time.[17] It is significant that the partitioning of **23** (X = Cl) between **26** and **24** is essentially the same for starting halides **1b** and **1c,** as is the percent of carboxylic acids formed.

We now wish to focus on the carboxylic acids produced from

Table I. Fourier Transform ^{13}C NMR Data for **2**

Compd	Relative area: Carbonyl	C_α	C_β	No. of pulses[a]
Unenriched **2**	1.02	0.62	(1.00)	2000
^{13}C-Enriched **2**	0.84	5.06	(1.00)	1710

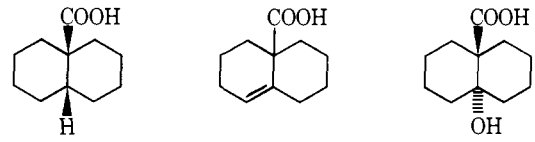
[a] Pulses were at 20-s intervals.

Table II. Product Ratios from Hydrolysis of **1a** in Various Aqueous Acetone Mixtures[a]

% water (by volume)	Product composition[b] **2**	**25**	**3**	(2 + 25)/3
1	93.5	1.5[c]	5.0	19
1	96.3	*d*	3.7	26
2	94.2	2.9[c]	2.9	34
2	97.3	*d*	2.7	36
5	90.3	7.4[c]	2.3	43
5	98.5	*d*	1.5	64
10	98.5	1.1[c]	0.4	246
10	99.4	*d*	0.6	170

[a] Analyses were via GLC, and corrections for thermal conductivity responses were made. [b] This excludes a mixture of carboxylic acids which were produced in ca. 35% yield in all cases. [c] Dilute sodium bicarbonate solution was used in the workup. [d] Sodium hydroxide solution was used in the workup, thereby converting any **25** present to **2,** as was verified separately.

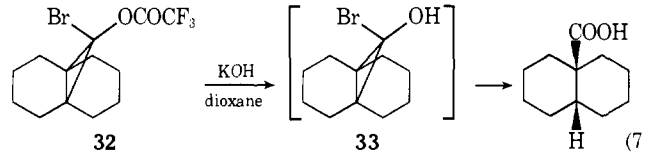
1. Careful examination of the acidic fraction formed from **1a** (and later **1b,** too) led to the identification of three different carboxylic acids: **27, 28,** and **31.** Hydroxy acid **31** was readily



27 3.6 : **28** 1.0 : **31** 1.2

isolated owing to its insolubility in chloroform, and was assigned the trans fusion on the basis of its broadly split ^1H NMR absorptions for the aliphatic hydrogens.[18] The ratio of **27:28:31** was determined by (a) GLC analysis of the corresponding methyl esters (3.6:1.0:1.2) and (b) ^1H NMR integration of the methyl groups of those esters (3.0:1.0:1.6).

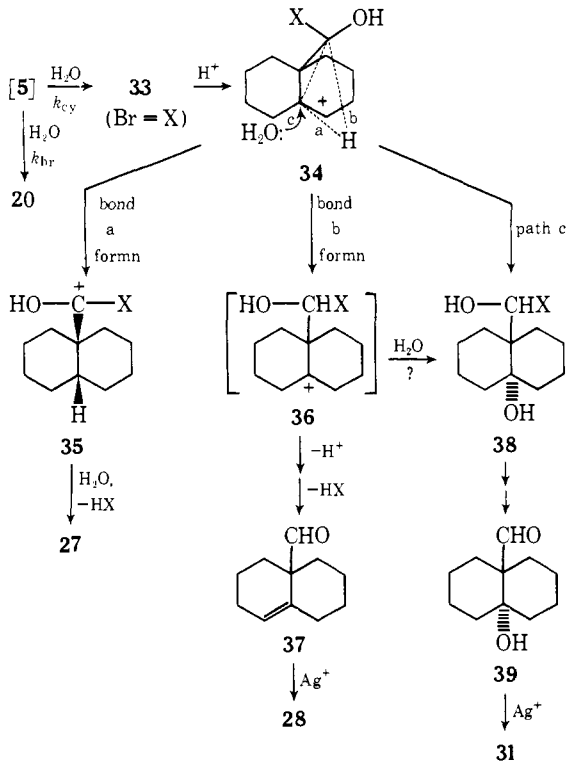
Clearly, the major acid (**27**) is the same one reportedly[19] formed quantitatively from **32** (eq 7). It is tempting to postu-



32 **33** (7)

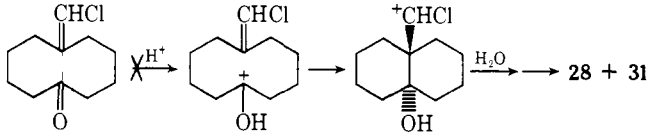
late **33** as the sole source of all three acids, as shown in Scheme VI. Thus edge protonation of **33** would yield **34.** subsequent formation of a tertiary C–H bond (a) would give stabilized ion **35,** and then **27.** Alternatively, formation of a primary C–H bond (b) would give tertiary ion **36; 36** could deprotonate and lose HBr to give aldehyde **37,** which, in the presence of excess silver ion, would be oxidized to **28.** The alternative nucleophilic hydroxylation of **36** to **38** appears less likely than direct attack of water on **34** (path c) with inversion,[20] for two reasons. First of all, the trans stereospecificity observed seems doubtful for the collapse of ion **36.** Secondly, the corresponding [3.3.1]-propellane system[21] gives no hydroxy acid. Presumably in that case invertive opening of the cyclopropane ring would provide

Scheme VI



the energetically unfavorable *trans*-bicyclo[3.3.0]octane skeleton; an ion analogous to **36** does not collapse with water, but always deprotonates. One might well question the intermediacy of **36** (i.e., **34** may give an olefin directly). Finally, **38** would proceed to **31** via hydroxy aldehyde **39**. We note that **34** is a reasonable intermediate, but the whole scheme could be written with **33** proceeding to the corresponding cyclopropanone, followed by protonation, etc. While we can offer no evidence on this point, the important thing is that ionization of the cyclopropyl halide precedes product formation.

Before Scheme VI can be accepted, one must exclude some other obvious possibilities. The ring closure shown in eq 8 was

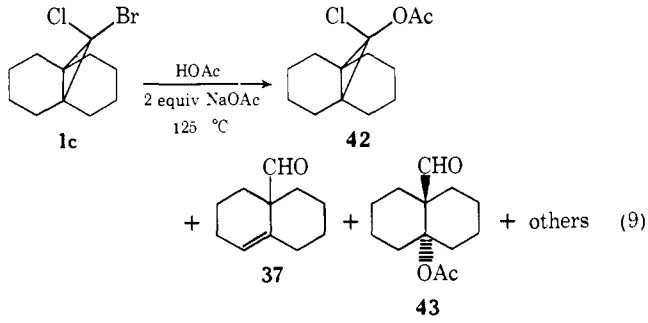


(8)

readily eliminated by the finding that **26** was stable under the hydrolysis conditions. More worrisome was the possibility that electrophilic attack, either by Ag^+ or H^+, was taking place on **1**, prior to any ionization. This would imply an intermediate analogous to **34**, but where OH was replaced by X. However, exposure of **1a** to the acidic solvolysis conditions (without Ag^+) led to its recovery unchanged. Additionally, [4.4.1]propellane itself (**1**, X = Y = H) was recovered unchanged after exposure to the acidic solvolysis conditions in the presence of $AgClO_4$. We thus feel that electrophilic attack upon **1** can be excluded.

Further support for Scheme VI came from the acetolysis of **1c**. While preliminary, the relevant products are shown in eq 9. While aldehydes **37** and **43** may come from hydrolysis of the α-chloroacetate precursors during workup, such hydrolysis may also occur under the reaction conditions due to the moisture in glacial acetic acid. Cyclopropyl acetate **42** is analogous to **33**.

As indicated in Scheme VI, an initially formed ion (**5**) partitions between bridgehead olefin product (**20**, k_{br}) and cyclopropyl product (**33**, k_{cy}). We view **5** as a partially opened



(9)

cyclopropyl ion,[22] although we have written only one resonance form for simplicity (Schemes IV and V). The ratio k_{br}/k_{cy} is 1.8 for X = Br and 3.6 for X = Cl. Apparently bromine is better at stabilizing an α positive charge than chlorine, at least in this system.

Conclusion

The solvolysis of 11,11-dihalo[4.4.1]propellanes (**1**) has been shown to proceed via bridgehead olefin intermediates (Scheme V) which lead to a number of products. Additionally, the partially opened cyclopropyl cation precursors to the bridgehead olefins may collapse at the cyclopropyl position, ultimately giving several carboxylic acid products. "Unusual" cyclopropyl cation processes have been excluded. We will soon report further studies aimed at elucidating the structure of the bridgehead olefins.[26]

Experimental Section

General. Infrared spectra were recorded on Beckman IR-12, IR-18A, and IR 4250 spectrophotometers. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. The proton magnetic resonance (^{1}H NMR) spectra were obtained on Varian A-60 and Hitachi Perkin-Elmer R20B spectrometers, using carbon tetrachloride as the solvent and tetramethylsilane as the internal standard, unless otherwise specified. The carbon magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker HX-90 spectrometer equipped with a Nicolet Model 1089 data package. The mass spectral studies were conducted using Atlas CH-4, High Resolution MS-9, and Perkin-Elmer 270 GLC–mass spectrometers. Melting points were taken on a Thomas-Hoover apparatus, and are uncorrected. GLC analyses were carried out on a Varian Aerograph Model 90-P gas chromatograph equipped with a thermal conductivity detector; intensities were corrected for differential detector response. The following GLC columns were utilized: A, 10 ft × 0.125 in., 3% DEGS on Chromosorb P; B, 6 ft × 0.25 in., 20% DEGS on Chromosorb P; C, 8 ft × 0.25 in., 20% SE-30 on Chromosorb P; D, 15 ft × 0.125 in., 12% DC-550 on Chromosorb W.

Synthesis. 11,11-Dibromo[4.4.1]propellane (1a). Propellane **1a** was synthesized according to the literature procedure[23] from isotetralin, mp 43–44 °C (lit.[23] 45–46 °C) after recrystallization from pentane.

11,11-Dichloro[4.4.1]propellane (1b). Ordinary, known propellane **1b** was prepared according to the literature procedure[23] from isotetralin, mp 37–38 °C after recrystallization from acetone/methanol. ^{13}C-labeled **1b** was similarly prepared, except that enriched chloroform (obtained from Merck as 60% ^{13}C, and diluted to ca. 12% enrichment with ordinary chloroform) was used in the dichlorocarbene addition to isotetralin. Enriched **1b** showed the following spectral properties: high-resolution mass spectrum (70 eV) *m/e* (rel intensity) 217 (4.2, P − 1), 218 (100, P), 219 (20.5, P + 1), 220 (62.8, P + 2), 222 (10.9, P + 4). The enrichment at C_{11} was calculated as follows. After the P + 1 peak was corrected for the contribution from P + 2 (see P − 1 peak), the percentage due to the natural abundance of deuterium was subtracted. The resultant total ^{13}C contribution to P + 1 was then divided by the sum of itself and the parent ion to give the total percent ^{13}C in the molecule. Lastly, subtraction of the natural ^{13}C abundance of 10 carbons gave the total ^{13}C content at C_{11} (5.8%). ^{13}C NMR ($CDCl_3$, rel area per carbon) δ 78.9 (4.9; C_{11}), 29.9 (1.4; C_2, C_5, C_7, C_{10}), 27.5 (1.2; C_1, C_6), 20.8 (1.0; C_3, C_4, C_8, C_9).

11-Chloro-11-bromo[4.4.1]propellane (1c). The preparation of previously unreported **1c** was carried out using dibromochloromethane

as the bromochlorocarbene precursor; the carbene was added to dihydrotetralin according to Vogel's procedure.[23] A ca. 1:1 mixture of central and end adducts was obtained, as observed by Vogel[23] for the dibromo- and dichlorocarbene additions. Separation via recrystallization from ethyl acetate (−78 °C) and then methanol followed by catalytic hydrogenation (Pt/C, ether) afforded **1c:** mp 38–39.5 °C; ^{1}H NMR δ 1.80 (m, 8 H), 1.45 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 71.5 (C_{11}), 32.1, 29.7, 28.0 (C_1, C_6), 20.9, 20.4.

Anal. Calcd for $C_{11}H_{16}ClBr$: *m/e* 262.0124. Found: *m/e* 262.0116.

Solvolysis. Acetolysis of 11,11-Dibromo[4.4.1]propellane (1a). A solution of 1.10 g (3.58 mmol) of **1a** and 0.60 g (7.32 mmol) of anhydrous sodium acetate in 6 mL of glacial acetic acid was heated in a sealed tube at 125 °C for 32 h. After cooling, the mixture was poured into ice–water and neutralized with solid sodium carbonate. Ether extraction, drying of the combined ethereal extracts, and solvent evaporation left 0.71 g of brown oil, which was chromatographed over silica gel. Elution with hexane afforded 330 mg (30% recovery) of **1a,** followed by 70 mg of **4;** elution with 2% ether in hexane gave **2, 3,** a new acetate tentatively identified as **44,** and an unidentified acetate. GLC analysis of a saved sample of crude product on column C indicated the yields shown in eq 1. Product identification was made on the basis of the following.

Bicyclo[5.4.0]undec-1(7)-en-2-one (2): identical with material produced upon hydrolysis of **1** (vide infra).

6-Bromomethylenecyclodecanone (3): ^{1}H NMR δ 5.95 (s, 1 H), 1.5–2.5 (m, 16 H); IR (film) 1710 cm^{-1}.

Anal. Calcd for $C_{11}H_{17}OBr$: *m/e* 244.0463. Found: *m/e* 244.0473.

Benzocycloheptene (4): ^{1}H NMR δ 6.95 (br s, 4 H), 2.70 (m, 4 H), 1.7 (m, 6 H); IR (film) 3040, 1500, 1460, 750 cm^{-1}; UV (95% EtOH) 271 nm (ϵ 380) [lit.[12b] 271 (292)].

Bicyclo[5.4.0]undecan-2-one 7-Acetate (44): ^{1}H NMR δ 2.2–1.2 (m, with a sharp singlet at 2.0); IR (CCl_4) 1740, 1710, 1240 cm^{-1}.

Hydrolysis of 11,11-Dichloro[4.4.1]propellane (1b) in 90% Aqueous Acetone. To 1.62 g (7.42 mmol) of **1b** in 15 mL of 90% aqueous acetone was added 7.70 g (37.2 mmol) of silver perchlorate in 10 mL of 90% aqueous acetone. After stirring at room temperature for 22 h, the mixture was diluted with ether. The ether solution was then washed with water and thrice with 5% sodium hydroxide solution. The combined basic extracts were acidified with concentrated hydrochloric acid solution to yield a white precipitate which was extracted into ether, dried (sodium sulfate), and concentrated to afford 239 mg (17%, based on ratios of acids, vide infra) of acids **27, 28,** and **31.** The ether solution which remained after base extraction was washed with water and saturated NaCl solution and dried over sodium sulfate. Solvent removal left 960 mg of oil which was chromatographed to give **2, 25,** and **26.**

^{13}C-enriched **1b** was hydrolyzed as follows. To a solution of 0.92 g (4.2 mmol) of enriched **1b** in 90% aqueous acetone was added 4.35 g (21.0 mmol) of anhydrous silver perchlorate in 4 mL of 90% aqueous acetone. The resulting milky mixture was allowed to stir for 23 h at room temperature. Workup and chromatography was as above. The following data are for the ^{13}C-enriched products, although some of the information was obtained from ordinary samples, too (e.g., ^{13}C NMR shifts).

Bicyclo[5.4.0]undec-1(7)-en-2-one (2): IR 1662, 1632 cm^{-1} (lit.[7] 1660, 1630 cm^{-1}); mass spectrum (70 eV) *m/e* (rel intensity) 163 (4.5, P − 1), 164 (100, P), 165 (19.2, P + 1), 166 (1.7, P + 2); ^{13}C NMR ($CDCl_3$, rel area) δ 205.4 (0.84), 153.2 (1.00), 135.3 (5.06), 41.7 (1.24), 34.1 and 33.9 (1.94), 24.8 (1.08), 24.4 (1.36), 22.7 (1.21), 22.1 (1.23), 21.4 (1.26).

7-Hydroxybicyclo[5.4.0]undecan-2-one (25): ^{1}H NMR δ 3.7 (br, OH), 2.7–1.0 (m, 17 H); IR (CCl_4) 3450, 1705 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 215.1 ($C_{C=O}$), 72.9 (C_{OH}), 62.3 (C_1, enriched).

6-Chloromethylenecyclodecanone (26): mp 45.5–46 °C (aqueous methanol); ^{1}H NMR δ 5.87 (s, 1 olefinic H), 2.6–1.5 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 214.3 ($C_{C=O}$), 141.4 (quaternary olefinic C), 113.1 (olefinic C, enriched), 43.1, 37.8, 31.2, 30.9, 24.5, 23.2, 22.9, 22.5; IR (CCl_4) 1710, 1620 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 200 (5, P), 184 (22, P − 16), 183 (14, P − 17), 182 (72, P − 18), 164 (100, P − 36) (^{13}C content of 5.8% at C_{11} calculated from *m/e* 183, 182 peaks).

Anal. Calcd for $C_{11}H_{17}OCl$: *m/e* 200.0968. Found: *m/e* 200.0975.

Carboxylic Acids 27, 28, and 31. Upon attempted dissolution in CCl_4 or $CDCl_3$, hydroxy acid **31** precipitated.

***trans*-6-Hydroxybicyclo[4.4.0]decane-1-carboxylic Acid (31):** mp 191–194 °C (CCl_4); ^{1}H NMR (acetone-d_6, Me_4Si) δ 9.5 (s, 1 H), 2.5–0.9 (m, 17 H); IR (KBr) 3400–2400, 1705, 1182 cm^{-1}; ^{13}C NMR (acetone-d_6, unenriched, rel intensity) δ 174.3 (0.11, carboxyl C), 80.3 (0.24, C_6), 50.3 (0.25, C_1), 27.3 (1.55), 25.3 (1.22), 21.9 (1.04), 19.8 (1.00).

Anal. Calcd for $C_{11}H_{18}O_3$: *m/e* 198.1256. Found: *m/e* 198.1255.

The remaining solution of acids in carbon tetrachloride was concentrated to provide a mixture of **27** and **28.**

***cis*-Bicyclo[4.4.0]decane-1-carboxylic Acid (27) and Bicyclo-[4.4.0]dec-5-ene-1-carboxylic Acid (28):** mp 168–175 °C; ^{1}H NMR δ 10.8 (br s), 5.5 (m, **28**), 2.4–1.1 (m); IR (CCl_4) 3600–2400, 1695 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 184.6 (enriched), 181.7 (enriched), 137.7 (**28**), 123.1 (**28**), 65.9, 48.3, 36.4, 35.7, 34.3, 31.7, 30.7, 29.4, 28.2, 28.0, 25.4, 22.9, 21.1, 15.2. A mixture of **27** and **28** (55 mg) was dissolved in 20 mL of ethanol and subjected to room pressure catalytic (10% Pd/C) hydrogenation. The resulting product (57 mg) was primarily **27,** mp 120–122 °C (acetone, lit.[24] 121.8–123 °C), IR spectrum[25] essentially identical with that reported.

In order to determine the relative amounts of **27, 28,** and **31,** an ethereal solution of the acid mixture was titrated with diazomethane to yield the corresponding methyl esters (**27a, 28a, 31a**): ^{1}H NMR ($CDCl_3$, rel intensity) δ 3.70 (s, 1.0, $-CO_2Me$ of **28a**), 3.66 (s, 3.0, $-CO_2Me$ of **27a**), 3.62 (s, 1.6, $-CO_2Me$ of **31a**); GLC analysis (column D, 140 °C) **27a** (33 min), **28a** (60 min), **31a** (66 min), relative ratio of 3.6:1.0:1.2. The retention time assignments were based on work with pure **31a** and **27a.**

Hydrolysis of 1b in 99% Aqueous Acetone. To 2.40 g (11.6 mmol) of anhydrous silver perchlorate in 10 mL of 99% aqueous acetone was added dropwise 0.50 g (2.3 mmol) of **1b** in 10 mL of 99% aqueous acetone. After stirring at room temperature for 23 h, the mixture was diluted with ether. The ether solution was washed with water, dried, and concentrated to afford 0.45 g of oil which was chromatographed on silica gel. Elution afforded 230 mg of **1b** (46% recovery, hexane), 103 mg of **26** (42%, 1% ether/hexane), 23 mg of **2** (11%, 2% ether/hexane), 28 mg of **25** (12%, 10% ether/hexane), and 45 mg of **27, 28,** and **31** (20%, 40% ether/hexane), respectively.

Hydrolysis of 11,11-Dibromo[4.4.1]propellane (1a) in 90% Aqueous Acetone. To 1.00 g (3.24 mmol) of **1a** in 10 mL of 90% aqueous acetone was added dropwise a solution of **4**.5 g (21.8 mmol) of silver perchlorate in 5 mL of 90% aqueous acetone. After stirring at room temperature for 1 h, workup as described for **1b** gave 0.50 g of yellow oil. The crude ^{1}H NMR showed a singlet at δ 5.95 for **3,** while the IR had an absorption at 1710 cm^{-1} (**3**). GLC–mass spectral analysis (column A at 50–180 °C) showed a peak with the same retention time and mass spectrum as those of an authentic sample obtained from acetolysis.

Hydrolysis of 1a in Various Aqueous Acetone Mixtures. Aqueous acetone mixtures were prepared, by volume, by adding the appropriate amount of distilled water (utilizing a graduated syringe or pipet) to a volumetric flask, and then filling the flask with reagent grade acetone (Fisher Scientific Co.). The acetone supposedly contained 0.5% water, and this was taken into account when preparing the aqueous solutions. The actual hydrolysis was performed as described for **1b** (with separation of the acids via basic extraction). Nitrobenzene was added to the neutral product mixture as an internal standard for GLC analysis (column B, see Table II).

Hydrolysis of 11-Chloro-11-bromo[4.4.1]propellane (1c). To a stirred solution of 595 mg (2.26 mmol) of **1c** in 38 mL of 90% aqueous acetone was added dropwise 470 mg (2.26 mmol) of silver perchlorate in 12 mL of 90% aqueous acetone. After stirring for 48 h, the acetone was evaporated; 25 mL of water and 25 mL of chloroform were then added to the reaction mixture. The aqueous layer was washed twice with 20 mL of chloroform. The combined chloroform layers were washed twice with 20 mL of saturated sodium carbonate solution, then 20 mL of saturated sodium chloride solution, dried over magnesium sulfate, and concentrated. Chromatography over silica gel (397 mg of oil on a 1.2 × 50 cm column, 1% ether/hexane) gave 260 mg of **1c,** followed by **26, 30, 2, 25,** and **24.**

11-Chlorobicyclo[4.4.1]undecane-1-en-6-ol (30): ^{1}H NMR δ 5.25 (m, 1 olefinic H), 4.91 (s, 1 H); IR 3600 (sharp), 3600–3450 cm^{-1} (broad). This compound has not been fully purified and its identification must be regarded as tentative.

11-Chlorobicyclo[4.4.1]undecane-1,6-diol (24): mp 93–94 °C; ^{1}H NMR δ 4.4 (s, 1 H), 2.2 (br s, OH), 1.7 (m, 16 H); IR 3600 (sharp),

3480 cm^{-1} (br).

Anal. Calcd for $C_{11}H_{19}O_2Cl$: C, 60.40; H, 8.76. Found: C, 60.54; H, 8.62.

Treatment of Enone 2 under Hydrolysis Conditions. To a mixture of 770 mg (37 mmol) of anhydrous silver perchlorate and 78 mg (0.73 mmol) of ethyl bromide in 1 mL of 90% aqueous acetone was added 120 mg (0.73 mmol) of **2** (enriched at C_1 from the hydrolysis of enriched **1b**). The mixture was allowed to stir for 2 days at room temperature. Workup, as described for the hydrolysis of **1b,** led to the recovery of 110 mg (92%) of **2.** Mass spectral analysis indicated a ^{13}C enrichment of 4.92% (as against 5.06% in the starting material), and ^{13}C NMR ($CDCl_3$) showed that the label had not scrambled: δ 205.4 (0.81), 153.1 (1.00), 135.3 (5.10)—compare with Table I.

Treatment of Chloro Ketone 26 under Hydrolysis Conditions. To 37 mg (0.34 mmol) of ethyl bromide in 1 mL of 90% aqueous acetone was added 350 mg (1.7 mmol) of silver perchlorate in 2 mL of 90% aqueous acetone. After stirring at room temperature for 30 min, 68 mg (0.34 mmol) of **26** in 1 mL of 90% aqueous acetone was added. After an additional 24 h at room temperature, the reaction mixture was worked up as described for **1b** to yield 60 mg (88%) of **26;** none of the other hydrolysis products was detected.

Dehydration of Hydroxy Ketone 25. A. Acid Conditions. To 40 mg of **25** was added 1 mL of concentrated hydrochloric acid and the resulting reddish solution was stirred for 5 h at room temperature. Ether extraction, followed by washing with dilute sodium bicarbonate solution and water, drying (magnesium sulfate), and evaporation of solvent gave a yellow oil which proved to be **2** (IR).

B. Base Conditions. An ethereal solution of **25** was shaken with a 5% sodium hydroxide solution. Drying of the ether layer, followed by solvent evaporation, gave a quantitative yield of **2** (IR, GLC).

Treatment of 1a with Acid. To 49 mg (0.455 mmol) of ethyl bromide in 1 mL of 90% aqueous acetone was added 85 mg (0.415 mmol) of anhydrous silver perchlorate in 1 mL of 90% aqueous acetone. After stirring at room temperature for 30 min, 140 mg (0.455 mmol) of **1a,** dissolved in 5 mL of 90% aqueous acetone, was added to the reaction mixture. The resulting mixture was allowed to stand at room temperature for 4 h. Workup, as described for the hydrolysis of **1a,** afforded 136 mg (97%) of **1a.**

Treatment of [4.4.1]Propellane (1, X = Y = H) under Hydrolysis Conditions. To 30 mg (0.27 mmol) of ethyl bromide in 1 mL of 90% aqueous acetone was added 112 mg (0.548 mmol) of anhydrous silver perchlorate in 1 mL of 90% aqueous acetone. After stirring at room temperature for 30 min, 41 mg (0.274 mmol) of **1** (X = Y = H)[23] in 1 mL of 90% aqueous acetone was added, and the resulting mixture allowed to stir for 2 h at room temperature. Workup, as described for the hydrolysis of **1a,** gave 28 mg (70%) of starting [4.4.1]propellane.

References and Notes

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(26) NOTE ADDED IN PROOF. Further support for the mechanism shown in Scheme V has recently appeared: C. B. Reese and A. C. Risius, *Tetrahedron Lett.*, 4847 (1976).