Our investigations to date have concentrated on torsional and steric interactions involving nonpolar allylic groups. Studies are in progress to determine how electronic factors that may develop with polar allylic bonds may cause different types of substituents to prefer one or another of the three nonequivalent allylic conformations in addition transition structures.

Acknowledgment. We are grateful to Professor John A. Pople and Michael Frisch for assistance with the CMU version of GAUSSIAN80, the CMU Chemistry Department VAX 11/780, and to the National Science Foundation for financial support of this research. The drawings in Figure 3 were prepared on PROPHET, a computer resource sponsored by the Division of Research Resources of the National Institutes of Health, with the expert assistance of Nancy Woodring.

Registry No. BH_3, 13283-31-3; H^-, 12184-88-2; H·, 12385-13-6; propene, 115-07-1.

Noninterconverting Stereoisomeric Bicyclo[4.4.1] Bridgehead Alkenes

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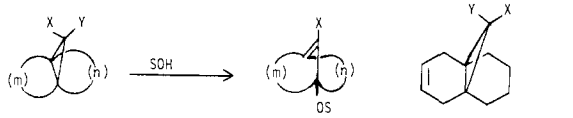
Abstract: The Ag^+-promoted hydrolysis products from epimeric bromochlorides **3a** and **3b** are reported. It is found that the bridgehead olefin-derived products fall into separate sets, depending upon the stereochemistry of their precursor. Importantly, participation of the Δ^3 double bond leading to one of the products derived from **3a** but not from **3b** provides evidence for rehybridization of the intermediate bridgehead olefins at both sp^2 carbon atoms of the bridgehead double bond. Also, hydrolysis of **3c** and **3d** is shown to be stereospecific, again implicating rehybridized bridgehead olefin intermediates.

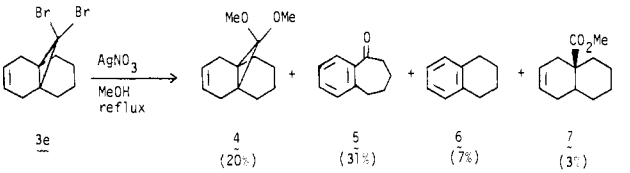
The generation of bridgehead alkenes of the bicyclo[*m.n.*1]alk-1 ($m + n + 3$)-ene (**2**) variety via solvolysis of ($m + n + 3$)-halo-[*m.n.*1] propellanes (**1**) is now a well-accepted reaction,[3] the first



1 2 3 a, X=Br, Y=Cl; b, X=Cl, Y=Br; c, X=Br, Y=H; d, X=H, Y=Br

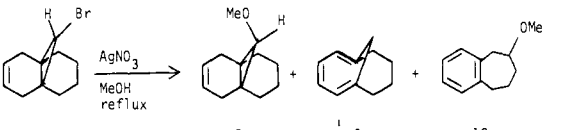
example having been reported less than a decade ago.[4] For some time we have been seeking chemical information regarding the structure of **2**, particularly with respect to the question of rehybridization.[5] Recently, we reported[6] that **2** ($m = n = 4$, X = Cl) maintains an unsymmetrical structure during its lifetime in aqueous solution; a rehybridized structure was deemed most reasonable. We now report on the generation and chemistry of stereoisomeric bridgehead olefins from the epimeric propellane pairs **3a** and **3b**, and **3c** and **3d**.

Previously, the methanolysis of **3e** (X = Y = Br) has been reported[7] to produce **4–7** in the yields shown. The stereochemistry

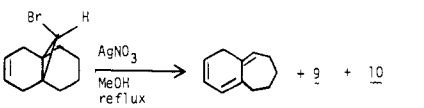


3e 4 (20%) 5 (31%) 6 (7%) 7 (3%)

of **7** (trans) is opposite to the major isomer we observe; we will address this point later. The methanolyses of **3c** and **3d** have also been studied;[8] the reported products are shown below.



3c 8 (12%) 9 (46%) 10 (19%)



3d 11 (12%) (73%) (2-3%)

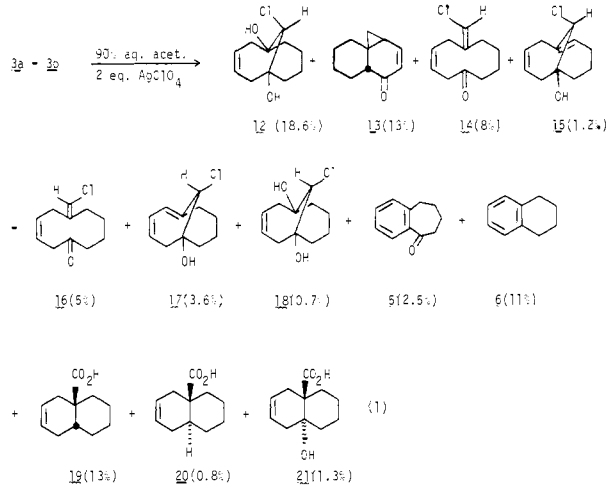
Results

Compounds **3a** and **3b** were simultaneously prepared via the addition of CBrCl to dihydrotetralin.[6] Because separation of these was extremely tedious (especially for **3a**, which required ca. 25

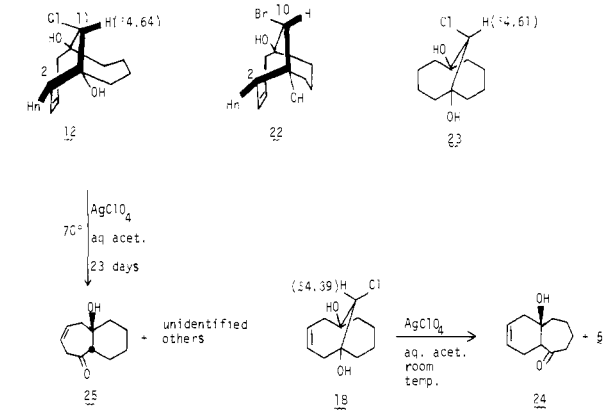
(1) Alfred P. Sloan Foundation Fellow, 1976–1980.
(2) NSF Trainee, 1974–1977.
(3) (a) For the latest review, see: Shea, K. J. *Tetrahedron* **1980**, *36*, 1683. See also: (b) Grice, P.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1980**, 424. (c) Grice, P.; Reese, C. B. *Tetrahedron Lett.* **1979**, 2563.
(4) Warner, P.; LaRose, R.; Lee, C.; Clardy, J. *J. Am. Chem. Soc.* **1972**, *94*, 7607.
(5) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1958**, *80*, 1953. (b) Dunitz, J. D. "Perspectives in Structural Chemistry"; Dunitz, J. D., Ibers, J. A., Eds.; Wiley: New York, 1968; Vol. 2, p 1. (c) Mock, W. L. *Tetrahedron Lett.* **1972**, 475. (d) Radom, L.; Pople, J. A.; Mock, W. L. *Ibid* **1972**, 479. (e) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.
(6) Warner, P.; Palmer, R. F. *J. Am. Chem. Soc.* **1981**, *103*, 1584.
(7) (a) Ledlie, D. B.; Knetzer, J. *Tetrahedron Lett.* **1973**, 5021. (b) Ledlie, D. B.; Knetzer, J.; Gitterman, A. *J. Org. Chem.* **1974**, *39*, 708.
(8) Ledlie, D. B.; Swan, T.; Pile, J.; Bowers, L. *J. Org. Chem.* **1976**, *41*, 419.
(9) Warner, P.; Lu, S.; Chang, S.-C. *Tetrahedron Lett.* **1978**, 1947.

0002-7863/82/1504-7166$01.25/0

recrystallizations from EtOH[6]), the hydrolysis (90% aqueous acetone/2 equiv $AgClO_4$) was initially conducted with a mixture of **3a** and **3b** (in a ca. 2:1 ratio); the products are shown in eq 1, with the absolute isolated yields in parenthesis (average of two runs).

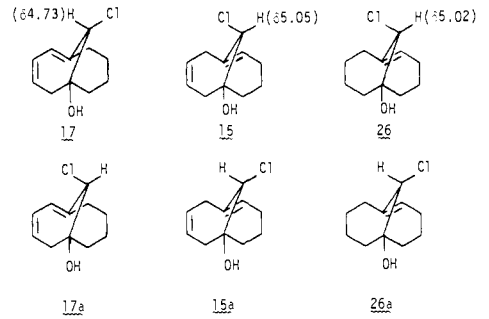


The products were purified by column chromatography (silica gel), sometimes followed by thin-layer chromatography (see Experimental Section). Tetralin (**6**) and benzocycloheptenone (**5**) were previously identified as products from the methanolysis of **3e**.[7] Diols **12** and **18** were each hydrogenated to the corresponding known saturated diol, **23**.[10] The stereochemistry of **12**



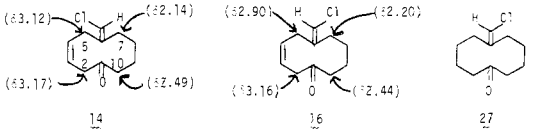
was assigned on the basis of the observed long-range coupling between H_{2n} and H_{11}, which was reminiscent of similar long-range coupling in **22**.[11] On the other hand, **18**, like **23**, showed no appreciable long-range coupling to H_{11}, presumably due to the greater flexibility (or different conformational preferences) of the saturated seven-membered ring. In accord with expectations, further treatment of **18** under the hydrolysis conditions gave **24** and **5**; similar rearrangement of **12** required forcing conditions (70 °C, sealed tube for 23 days), whereupon three products were produced, one of which was identified as **25**.

Compound **17** was found to be a conjugated diene (UV: λ_{max} 241.7 nm (ϵ 5700); note the reduced extinction coefficient appropriate for a twisted diene), while **15** was unconjugated (UV: end absorption only). The stereochemistry (i.e., **17** vs. **17a**, **15** vs. **15a**) was assigned on the basis of ^1H NMR chemical shifts as follows. From the series of diols **12**, **18**, and **23**, it is apparent that the Δ^3 double bond shields the syn H at C_{11}. For **15** and **26**,[10] the shifts of H_{11} are virtually identical, indicating they are in very similar environments. This is consistent *only* with structures **15**



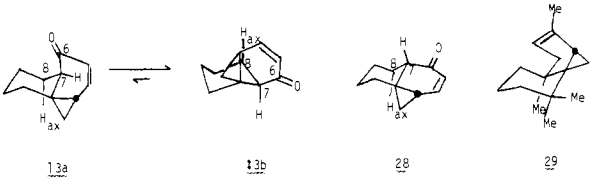
and **26** (not **15** and **26a**, **15a** and **26**, or **15a** and **26a**). Furthermore, the known[11] deshielding effect of the Δ^1 double bond on H_{11syn} (compare δ 5.05 for **15** with δ 4.64 for **12** and δ 5.02 for **26** with δ 4.61 for **23**) is operative and supportive of structures **15** and **26**. The observed shielding of H_{11} for **17** ($\Delta\delta = -0.29$ on going from **26** to **17**) is as expected (compare $\Delta\delta = -0.22$ on going from **23** to **18**) but is not consistent with structure **17a** (expected $\Delta\delta \approx -0.4$ to -0.6[11b]). Both **15** and **17** were stable under the hydrolysis conditions.

Monocyclic ketones **14** and **16**, isolated as a mixture, were spectroscopically similar to the previously obtained **27**.[10] Pure



16 was obtained from the hydrolysis of **3b** (vide infra). The assignment of stereochemistry is based on chemical shift differences and gives mechanistically consistent structures. Thus the four "doubly allylic" hydrogens (at C_2 and C_5) of **14** appear as two overlapping doublets at δ 3.17 and 3.12, whereas those of **16** are more widely spaced at δ 3.16 and 2.90. This can be explained by a syn deshielding effect of Cl in **14**. The "allylic" hydrogens appear as similarly placed triplets in both **14** and **16**.

The structure of the initially surprising cyclopropylketone **13** was assigned primarily from ^1H NMR spectra. Particularly instructive was the irradiation of a narrow band at δ 1.04, which resulted in the collapse of H_1 to a broad singlet. Of the two cis conformers (**13a** and **13b**) and the trans structure **28**, only **13b**



has a proton at C_8 (H_{8ax}) in the shielding cone of the double bond. The dihedral angle between H_{8ax} and H_7 in **13b** is 180°, wherefrom one predicts a coupling of ca. 10 Hz, which is very close to the observed J = 11 Hz. The calculated coupling between H_1 and either proton at C_8 for **13a** is ca. 4 Hz. The preference for **13b** may be understood by noting that the C_7–C_6 bond of **13b** is equatorial, whereas said bond in **13a** is axial. Similar conformational arguments have been used to explain the ^1H NMR spectrum of the structurally related thujopsene (**29**).[12] Mechanistic considerations (see Discussion) account for the absence of **28**.

Finally, separate chromatography of the basic extracts from the hydrolysate afforded three carboxylic acids, **19**, **20**, and **21**. Each was separately hydrogenated to the corresponding known *cis*-decalin-9-carboxylic acid,[13] *trans*-decalin-9-carboxylic acid,[13] and *trans*-10-hydroxydecalin-9-carboxylic acid.[10]

(10) Warner, P.; Palmer, R. F.; Lu, S.-L. *J. Am. Chem. Soc.* **1977**, *99*, 3773.

(11) (a) Warner, P.; Fayos, J.; Clardy, J. *Tetrahedron Lett.* **1973**, 4473. (b) Warner, P.; Lu, S.-L.; Myers, E.; DeHaven, P. W.; Jacobson, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 5102.

(12) (a) Ito, S.; Takeshita, H.; Muroi, T. *Tetrahedron Lett.* **1969**, 3091. (b) Enzell, C. *Acta Chem. Scand.* **1962**, *16*, 1553.

(13) (a) Pincock, R. E.; Grigat, E.; Bartlett, P. D. *J. Am. Chem. Soc.* **1959**, *81*, 6332. (b) Bartlett, P. D.; Pincock, R. E.; Rolston, J. H.; Schindel, W. G.; Singer, L. A. *Ibid.* **1965**, *87*, 2590.

Due to questions regarding the partitioning of some of the cationic intermediates, a mixture of **3a** and **3b** (somewhat different ratio from before) was hydrolyzed in 80% aqueous acetone, with the results shown in eq 2.

$$\mathbf{3a + 3b} \xrightarrow[2\text{ equiv of }AgClO_4]{80\%\text{ aqueous acetone}} \underset{18.9\%}{\mathbf{12}} + \underset{1.6\%}{\mathbf{13}} + \underset{4.5\%}{\mathbf{14}} + \underset{3\%}{\mathbf{15}} + \underset{5.4\%}{\mathbf{16}} + \underset{5.7\%}{\mathbf{17}} + \underset{1.6\%}{\mathbf{18}} + \underset{5.5\%}{\mathbf{5}} + \underset{9\%}{\mathbf{6}} + \underset{9\%}{\mathbf{19}} + \underset{1.9\%}{\mathbf{21}} \quad (2)$$

Repeated solvolysis of the **3a, 3b** mixture led to the recovery of starting material enriched in **3b**. Hydrolysis of a 95:5 mixture of **3b**:**3a** led to the products shown in eq 3.

$$\underset{5:95}{\mathbf{3a + 3b}} \xrightarrow[2\text{ equiv of }AgClO_4]{90\%\text{ aqueous acetone}} \underset{2\text{–}3\%}{\mathbf{12}} + \underset{16.3\%}{\mathbf{16}} + \underset{14.6\%}{\mathbf{17}} + \underset{4\%}{\mathbf{18}} + \underset{4.7\%}{\mathbf{5}} + \underset{12\%}{\mathbf{6}} + \underset{10.7\%}{\mathbf{19}} \quad (3)$$

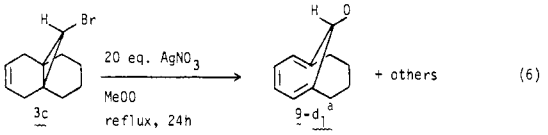
Compound **12** appears to be the only product clearly identifiable as coming from **3a**. The absence of **13** can be understood when one realizes that there should have been only ca. 2 mg of **13** produced, and this could have been missed. There is also some uncertainty about the amount of **12** produced (which seems high), as only 4–6 mg were isolated and a considerable weighing error could have been realized. From the amounts of the other six compounds isolated, one may calculate the expected yields of these from **3b** in eq 1: [**compd**, calculated (observed)] **16**, 5.7% (5%); **17**, 5.1% (3.6%); **18** + **5**,[14] 3.0% (3.2%); **6**, 4.2% (11%); **19**, 3.7% (13.2%). It is apparent that, within experimental error, **16**, **17**, **18**, and **5** arise from **3b** only, whereas **6** and **19** must come from both **3a** and **3b**. By subtraction, at least **12**–**15** must originate solely from **3a**; **20** and **21** may or may not come from **3b** as well as **3a**. These facts are summarized in eq 4 and 5.

$$\mathbf{3a} \xrightarrow[2\text{ equiv of }AgClO_4]{90\%\text{ aqueous acetone}} \mathbf{12 + 13 + 14 + 15 + 6 + 19 + 20 + 21} \quad (4)$$

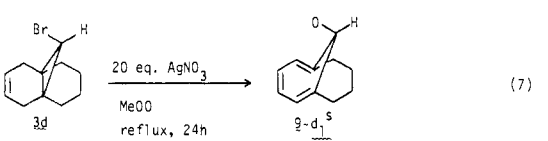
$$\mathbf{3b} \xrightarrow[2\text{ equiv of }AgClO_4]{90\%\text{ aqueous acetone}} \mathbf{16 + 17 + 18 + 5 + 6 + 19 + (20) + (21)} \quad (5)$$

Compounds **3c** and **3d** were methanolized together at room temperature by using a 20-fold excess of $AgClO_4$. Under these conditions, **3d** was twice as reactive as **3c**; Ledlie[8] found that **3d** was three times more reactive than **3c** using $AgNO_3$ under the same conditions (but the concentrations may have been different). With 5 equiv of $AgClO_4$ in 90% aqueous acetone, **3d** was only slightly more reactive than **3c**, while with 1 equiv of $AgClO_4$ in MeOH (room temperature), **3c** was more reactive than **3d**!

Separate methanolysis of **3c** and **3d** in MeOD was then effected. Only the major product (**9**) was investigated. The results are shown in eq 6 and 7. Importantly, only one deuterium was incorporated in **9** in each case.



(6)

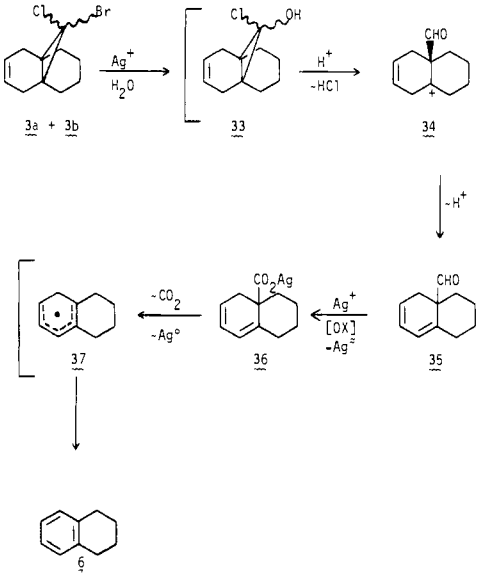


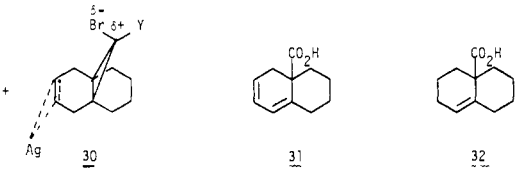
(7)

Discussion

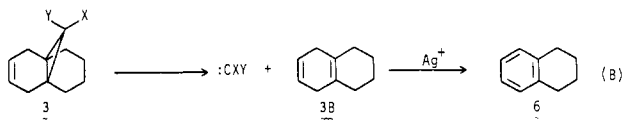
Kinetic Aspects. The fact that **3a**, with the leaving group anti to the double bond, reacted faster than its epimer (**3b**) was unexpected, since **5**, which results from initial ionization of the *syn*-bromine atom, was the major product from dibromide **3e**.[7] Consistent with greater reactivity of the syn leaving group was the greater relative rate of **3d** vs. **3c**. However, our results show that the relative reactivity of **3c** and **3d** is dependent upon $[Ag^+]$. While it may be attractive to think about double-bond complexation[11a] leading to a "field effect" favoring syn ionization (see **30**), it should be remembered that complex kinetic effects have been observed in systems without double bonds.[15] In any event, Ledlie's[8] thermodynamic arguments based on kinetic data for **3c** and **3d** must be viewed very cautiously.

Scheme I





Reaction Pathways. Dihalo[4.4.1]propellanes. (A) Acidic Products. The acidic products include not only the carboxylic acids **19**–**21** but also tetralin (**6**). These four compounds appear to arise from both **3a** and **3b** (**6** and **19** certainly do). Important to the understanding of the inclusion of tetralin (**6**) as an "acidic" product is the observation that **31** was not an observed product, whereas **32** was formed from the saturated 11,11-dihalo[4.4.1]-propellanes.[10] Routes to the saturated analogues of **19** and **21** have been published,[10] and identical schemes for **19** and **21** need not be repeated here. The very small amount of **20** may arise via epimerization of **19**. Although this is uncertain, it would nicely account for Ledlie's observation of (trans) **7**; the primary (cis) product may have epimerized under the refluxing MeOH conditions he employed. Scheme I shows our suggestion for the formation of tetralin (**6**). Thus the ring-opening of **33** (which also leads to **19** and **21**) may follow the path to diene **35**, oxidation of which produces silver carboxylate **36**.[16] This time, in analogy to a Hunsdiecker process,[17] decarboxylation to **37** occurs, aromatization of which produces **6**. The requisite finely divided silver was observed. This scheme seems more likely than the extrusion of dihalocarbene suggested by Ledlie[7] (eq 8), although Ledlie did demonstrate the conversion of **38** to **6** utilizing Ag^+. However,



(8)

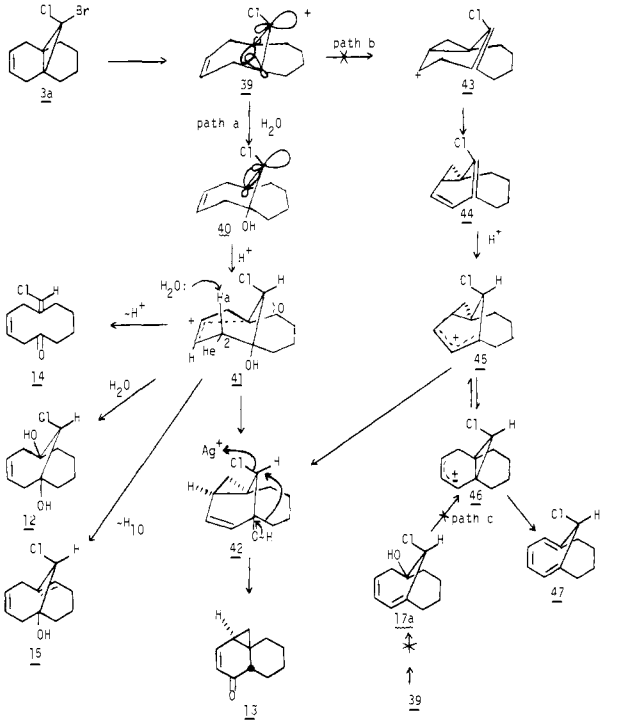
(14) These are added together since **18** gives **5** under the reaction conditions.

(15) Warner, P.; Palmer, R. F. *Tetrahedron Lett.* **1980**, 145 and references therein.

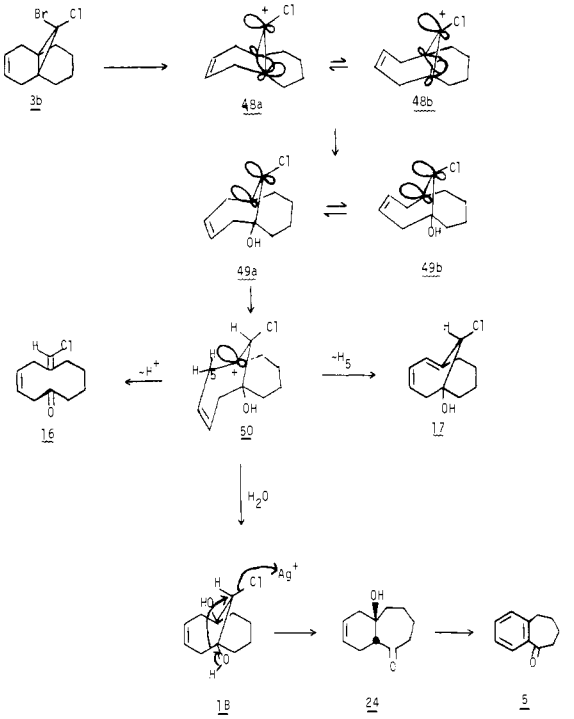
(16) Lepri, L.; Desideri, P. G. *J. Chromatogr.* **1973**, *84*, 155.

(17) Wilson, C. V. *Org. React.* **1957**, *93*, 32.

Scheme II



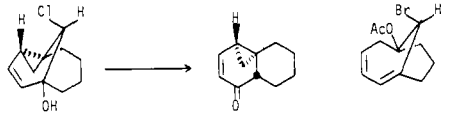
Scheme III



the known dihalocarbene extrusions,[18,19] all of which give *aromatic* products directly, nevertheless require higher temperatures than the hydrolysis reaction leading to **6**. Also, no decomposition was encountered during any of the distillations of **3** (75–90 °C).

(B) Neutral Products. The "neutral" products, **5** and **12–18**, fall into two sets of four—those from **3a** and those from **3b**. Schemes II and III illustrate the hydrolytic routes from **3a** and **3b**, respectively.

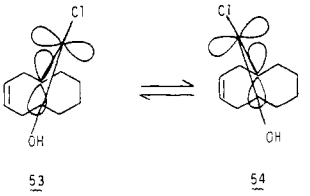
Ionization of the bromine of **3a** leads to ion **39**, which is expected to be conformationally stable with respect to conversion to **48**.[6] Collapse of **39** to **40** (again not expected to interconvert with **49**[6]), followed by protonation, affords **41**. Fragmentation of **41** to **14**, loss of H_{10} to **15**, and nucleophilic capture to give **18** are all precedented reaction channels.[10] The critically new aspect of the chemistry of **3a** is the formation of **13**, which we believe emanates from **42** in straightforward fashion. This postulate serves to explain the absence of trans enone **28**, which would have had to arise via the prohibitively strained inside–outside bicyclic molecule **51**.



But how does **42** arise? We can envision three pathways (Scheme II, path a, b, and c), of which we can reasonably exclude two. Path b seems unlikely for at least three reasons. First of all, the interaction shown as producing **43** amounts to a bis-homoantiaromatic interaction and would be avoided as much as possible. More importantly, ion **45** would be expected to readily rearrange to the rather stable[20] ion **46**, which should deprotonate to **47** (see later for an example of this); however, **47** is not a reaction product. Most significantly, ion **43** and diene **44** are extremely strained *trans*-cyclohexenoid bridgehead olefins and would thus require a large energy expenditure to generate from **39**. Path c, in which the unobserved diene **17a** is envisioned as the source of **46**, also suffers from the absence of **47** among the products. More significantly, **17a** would be expected to survive the reaction conditions on the basis of the isolation of **17** and the known stability of **52**.[11b] This leaves path a as the most viable mode for formation of **42**. The structural implications will be discussed in the next section.

When the syn bromine of **3b** ionizes (Scheme III), ion **48** results, nucleophilic collapse of which yields **49**. On the basis of force-field calculations,[21] conformations **48a** and **48b**, and **49a** and **49b** should be rather close in energy. For maximal similarity to **41**, we have drawn **50** in the "a" conformation. The various routes leading from **50** to **16**, **18**, **24**, and **5** are unexceptional.[10]

(C) Rehybridization. That bridgehead olefins **40** and **49** might be rehybridized at the carbon bearing chlorine (C_{11}) is no surprise[6] nor is the overall stereospecificity of the reactions of **40** and **49**.[22] What is significant is the fact that **40** leads to an ion (**41**) that strongly interacts with the $\Delta^{3,4}$ double bond, whereas ion **50**, descended from **49**, does not interact with the corresponding double bond. The only reasonable explanation for this is side-to-side dissymmetry at C_6 in **41** and **50**. Such dissymmetry must originate from the bridgehead olefins **40** and **49**, which means that they are rehybridized at C_6 as well as at C_{11}. (Note that "bridge leaning" does not induce side-to-side dissymmetry at C_6—cf., **53** and **54**. Actually, Dreiding models indicate that leaning, as in



53, favors interaction with the double bond, whereas in **54**, the

(18) Extrusion to form naphthalene: Vogel, E. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1968**, *12*, 215.
(19) Extrusion of :CBr_2 from 10,10-dibromo[4.3.1]propella-2,4-diene to form indane: Warner, P., unpublished.
(20) Warner, P.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2280.
(21) Maier, W. F.; Schleyer, P. *J. Am. Chem. Soc.* **1981**, *103*, 1891.
(22) (a) Lindner, H. J.; Kitschke, B.; Liesner, M.; Seebach, D. *Helv. Chim. Acta* **1977**, *60*, 1151. (b) Liesner, K. M. Ph.D. Dissertation, ETH, Zürich, 1980.
(23) Palmer, R. F. Ph.D. Dissertation, Iowa State University, Ames, IA, 1978.
(24) Vogel, E.; Wiedemann, W.; Roth, H.; Eimer, J.; Gunther, H. *Liebigs Ann. Chem.* **1972**, *759*, 1.
(25) (a) Pouchert, C. J.; Campbell, J. R. "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, WI, 1974; Vol. VI, p 13D. (b) Pouchert, C. J. "The Aldrich Library of Infrared Spectra", 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1975; p 750E.

Table I. Relative Yields of Various Ionic Pathways (90% Aqueous Acetone)

starting material	bridghead olefin-derived prod (B): fragmentation (*f*)[c]	nucleophilic capture (*n*)[d]	elimination (*e*)[e]	cyclopropane-derived prod[a] (*C*)
 55	31	25.5	9.5	25
 3b	16.3	8.7	14.6	22.7
 3a	8	31.6[f]	1.2	19.5
 56	42[g]	24[g]		
 57	27[g]	44[g]		

[a] E.g., carboxylic acids, see Scheme I. [b] Data taken from ref 23; these numbers supersede the corresponding (similar) ones given in ref 10. [c] Fragmentation affords the monocyclic ketones, e.g., **14**. [d] Nucleophilic capture affords the diols and their rearrangement products, e.g., **12**, **5**. [e] Elimination affords bicyclic bridgehead olefins, e.g., **15**. [f] This figure includes **13**. [g] Data from ref 11.

Table II. Ratios of Ionic Processes (See Table I)

starting material	90% aqueous acetone: *C*/*B*	*f*/*n*	*f*/(*n* + *e*)	80% aqueous acetone: *f*/*n*	*f*/(*n* + *e*)
55	0.38	1.2	0.89	0.86[a]	0.66[a]
3b	0.57	1.9	0.70	0.76[b]	0.42[b]
3a	0.48	0.25	0.24	0.15[b]	0.13[b]
56		1.8	1.8		
57		0.61	0.61		

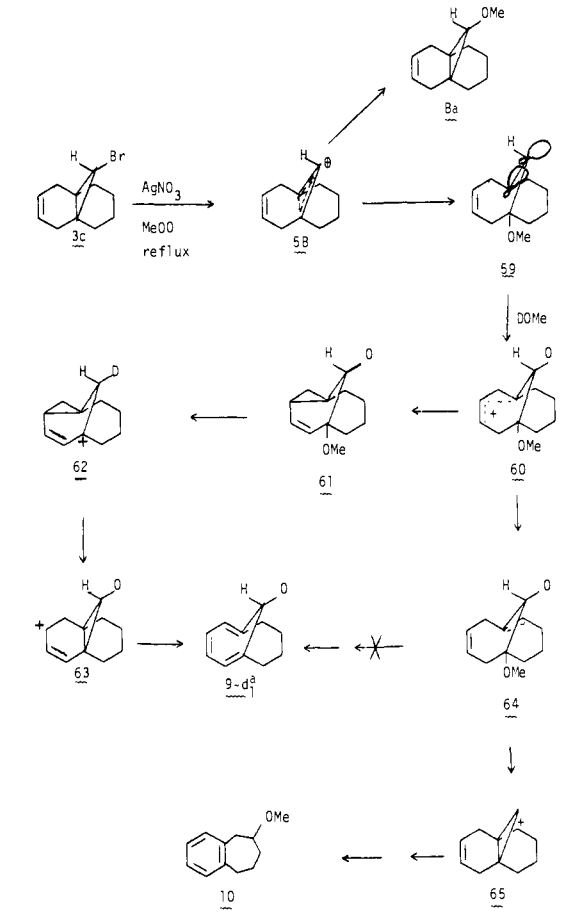
[a] From ref 23. [b] From eq 2.

opposite is the case. This leads to predictions of interactions *opposite* to what is observed.)

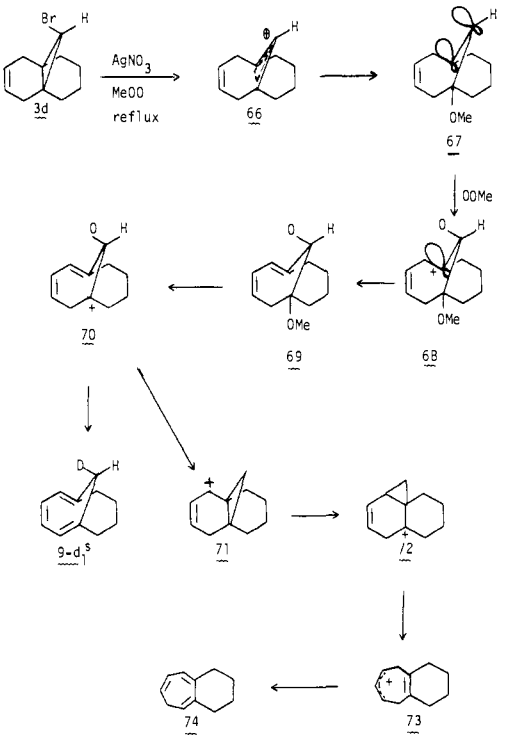
Apart from the product (**13**) derived from **42**, what other evidence is there for interaction of the $\Delta^{3,4}$ double bond with the cationic center in **41** but not in **49**? Tables I and II summarize some data in an instructive format. Upon comparing **3a** and **3b** to their saturated counterpart (**55**), it is seen that the amount of collapse of the initial ion at C_{11} (to form intermediate cyclopropanes) vs. that at C_1 (to form intermediate bridgehead olefins) does not vary very much. This also argues against the involvement of path b (Scheme II), which ought to cut down on the "C" products. On the other hand, the fate of **41** and **50** varies markedly. Thus the percent fragmentation seen for **50** (from **3b**) is very similar to that observed for the corresponding saturated ion (from **55**). Contrariwise, **41** shows the effects of double-bond stabilization—it fragments more slowly and is happier to wait for a nucleophile to either capture it or deprotonate it. The same stabilization effects are seen for **57** relative to **56**. In this case, rehybridization may well also occur at the bridgehead sp^2 carbon, but the product analogous to **42** does not form, perhaps due to strain effects. Lastly, it is noteworthy that **3a**, **3b**, and **55** all react normally to increased nucleophile concentration (80% aqueous acetone vs. 90% aqueous acetone—see Table II) but that **3b** remains similar to **55** in its reactivity pattern, while **3a** remains influenced by the stabilizing effect of the Δ^3 double bond.

Monohalo[4.4.1]propellanes. Ledlie[8] explained the formation of **10** from **3c** and tentatively assigned structure **8** to the cyclopropyl product from **3c**. Our results[9] strongly suggest that the product should be reassigned as **8a**. Ledlie also rationalized the absence of cyclopropyl product from **3d** on the basis of relative strain in the cyclopropyl cations (**58** and **66**) resulting from **3c** and **3d**. Very perplexing is his finding of 2–3% of **10** from **3d**.

Scheme IV



Scheme V



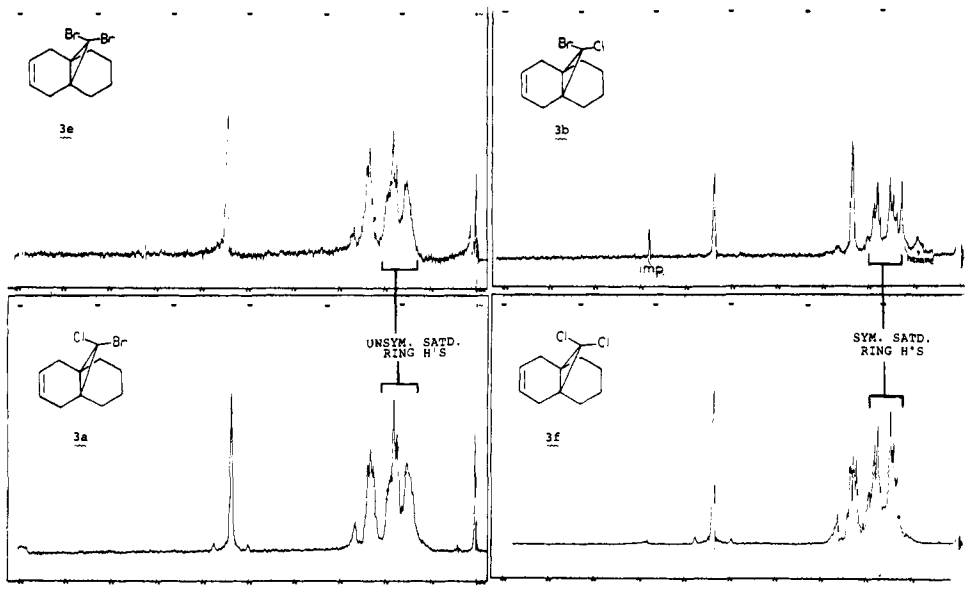


Figure 1. ^{1}H NMR spectra of **3a**, **3b**, **3e** and **3f** (60 MHz).

Unless this is just incorrect, it represents either conformational leakage of intermediate cation **68** to **60** or "wrong way" elimination of **68** to **64**. Lastly, as indicated to us by Ledlie,[26] structure **11** should be assigned as **74**, in accord with the spectral data and mechanistic considerations. Our mechanistic proposals are shown in Schemes IV and V.

Thus ionization of **3c** affords cation **58**, which is captured to give bridgehead olefin **59**. Protonation of **59** then occurs from the same side previously occupied by the bromine atom, resulting in cation **60**, where the double bond again participates. Elimination from **60** would lead to **61** and **64**. The former cannot rearrange a la **42**, so ionization produces **62**, which equilibrates with **63**, which subsequently eliminates to **9**-d_1^a. Cation **64**, which does not lead to **9**-d_1^a via a possible protonation–deprotonation sequence through **69** (**9**-d_1^a would have to contain two deuteriums for this pathway to be operative), rearranges to **10** straightforwardly.

Contrasting, **3d** yields bridgehead olefin **67**, syn protonation of which leads to ion **68**. Without the double-bond participation enjoyed by **60**, elimination affords only **69** (save a maximum of 2–3% that may give **64** and subsequently **10**). Derived ion **70** must then partition between elimination to **9**-d_1^s and the rearrangement pathway to **74**. It is not surprising to find relatively more **9**-d_1^s in this case, since the production of **9**-d_1^a requires the intermediacy of the rather more strained **61**.

Conclusion

It has been shown that epimeric [4.4.1]propell-3-ene halides afford diastereomeric bridgehead olefins that retain their configuration (i.e., they do not interconvert). Furthermore, the Δ^3 double bond participates only when it is oriented anti to the departing bromine. This fact serves as evidence for the rehybridization of the bridgehead sp^2 carbon atom. Thus the bicyclo[4.4.1]undec-1(11)-enes (and bicyclo[4.3.1]dec-1(10)-enes) contain bridgehead double bonds rehybridized at both ends.

Experimental Section

General Methods. IR spectra were recorded on Beckman IR-12, IR-18A, and IR-4250 spectrometers. UV spectra were recorded on a Cary Model 14 spectrometer. ^{1}H NMR spectra were measured on Varian HA-100 and Perkin-Elmer R-20B spectrometers, with CCl_4 as the solvent and Me_4Si as internal standard unless otherwise specified. ^{13}C NMR spectra were obtained on a Bruker HX-90 spectrometer equipped with a Nicolet Model 1089 data package. The mass spectral studies were conducted on a AEI High Resolution MS-902 spectrometer and a Perkin-Elmer 270 GLC-mass spectrometer. Melting points were measured on a Thomas-Hoover apparatus and are uncorrected. Spang Microanalytical Laboratory, Ann Arbor, MI, conducted the elemental analysis.

GLC analyses were conducted on a Varian Aerograph Model 90-P chromatograph. The following all-glass columns were utilized, with a glass insert in the inlet port to insure no contact with a metal surface: column A, 16 ft × 0.25 in. 10% diisodecyl phthalate on Chromosorb W A/W 60/80 mesh; column B, 16 ft × 0.25 in. 10% FFAP on Chromosorb W A/W 60/80 mesh; column C, 16 ft × 0.25 in. 14% Carbowax 20M on Chromosorb W A/W 60/80 mesh; column D, 26 ft × 0.25 in. 10% DEGS on Chromosorb W A/W 60/80 mesh; column E, 16 ft × 0.25 in. 14% DEGS on Chromosorb W A/W 60/80 mesh; column F, 16 ft × 0.25 in. 12% DC-550 (Dow Corning phenyl methyl silicone fluid) on Chromosorb W A/W 60/80 mesh.

11-Bromo-11-chloro[4.4.1]propell-3-enes (3a and 3b). Bromochlorocarbene, generated from dibromochloromethane, was added to dihydrotetralin according to Vogel's procedure.[24] Distillation of the crude product gave 7 g (78–80 °C, 0.18 torr) of a mixture of **3a**, **3b**, and end adduct, 4-bromo-4-chlorotricyclo[5.4.0.0^{3,5}]undec-1(7)-ene (**75**). GLC column F (142 °C) served to separate **3a** and **3b** (retention time = 170 min) from the stereoisomers of **75** (**3**:**75** = 77:23); ^{13}C NMR showed the **3a**:**3b** ratio was initially ca. 3:2. Separation of **3a** and **3b** from **75** was achieved via recrystallization from ethyl acetate (−78 °C).[24]

Separation of 3a and 3b. The solid mixture of **3a** and **3b** was recrystallized repeatedly from absolute EtOH; after 25–30 recrystallizations, pure **3a** (mp 45.8–46.2 °C) was obtained (purity was monitored by ^{13}C NMR): ^{1}H NMR δ 5.35 (s, 2 H), 2.7–2.2 (m, 4 H), 2.0–1.45 (m, 8 H); ^{13}C NMR, see Table III; IR (CCl_4) 2940 (s), 1670 (w) cm^{-1}. Anal. Calcd for $C_{11}H_{14}BrCl$: *m/e* 261.9942. Found, *m/e* 261.9961.

Epimer **3b** was not completely purified by preparative thin-layer chromatography (Silica gel), column chromatography (neutral Woelm alumina), high-pressure liquid chromatography [2 ft × 0.25 in. μ-porasil (normal phase) or 4 ft × 0.5 in. bondapak C_{18}-porasil (reverse phase) columns], gas chromatography (columns A–F), sublimation, or zone refining. Purification of **3b** via partial solvolysis was effected as follows.

To a stirring solution of 0.748 g (2.98 mmol) of **3a** and **3b** in 42 mL of 90% aqueous acetone (by volume) was added dropwise a solution of 0.617 g (2.98 mmol) of $AgClO_4$ in 10 mL of 90% aqueous acetone. After the addition was complete, the mixture was stirred for 2 h, following which the acetone was removed on the rotary evaporator. Then 25 mL of ether and 25 mL of ice water were added and the layers separated. After extraction of the aqueous layer with 2 × 25 mL of ether, the combined organic layers were washed with 2 × 10 mL of saturated Na_2CO_3 solution and 10 mL of saturated NaCl solution prior to drying over $MgSO_4$. Removal of the solvent gave 0.70 g of product, which was relatively enriched in **3b**. Chromatography of this material on a 10% $AgNO_3$–silica gel column (hexane as eluting solvent) gave early fractions containing mainly **3a**, while later fractions were richer in **3b**. Repeated partial solvolysis and $AgNO_3$ chromatography of the later fractions provided ca. 0.1 g of pure **3b** after three such iterative processes: mp 30–31.5 °C (MeOH); ^{1}H NMR δ 5.36 (s, 2 H), 2.34 (br s, 4 H), 1.9–1.35 (m, 8 H); ^{13}C NMR, see Table III; IR (CCl_4) 2940 (s), 1670

(26) D. B. Ledlie, personal communication.

Table III. ^{13}C NMR Chemical Shifts[a] for **3**[b]

compd	C_1	C_2	C_3	C_7	C_8	C_{11}
3a	26.6	30.1	123.8	32.6	19.7	68.6
3f	26.3	30.6	123.7	29.2	20.2	76.5
3b	26.6	31.3	123.8	29.1	20.3	68.0
3e	26.7	31.3	124.0	32.2	19.7	58.1
3c	22.3	28.8	124.8	32.8	21.7	38.8
3d	22.2	31.9	124.2	32.3	21.2	41.0

[a] In ppm from Me_4Si in $CDCl_3$ solvent. Assignments from gated decoupling and reductive deuteration.[6] Key comparisons are bracketed. [b] **3a**; X = Br, Y = Cl; **3b**; X = Cl, Y = Br; **3c**; X = Br, Y = H; **3d**; X = H, Y = Br; **3e**; X = Br, Y = Br; **3f**; X = Cl, Y = Cl.

(w) cm^{-1}. Anal. Calcd for $C_{11}H_{14}BrCl$: *m/e* 259.9967. Found, *m/e* 259.9969.

The stereochemical assignments of **3a** and **3b** were based on ^{13}C NMR chemical shifts (see Table III) and, more importantly, on ^1H NMR *line shapes* (see Figure 1). The salient comparisons include the symmetry of the saturated ring protons when a chlorine atom lies syn to them vs. asymmetry in the band shape of the same protons when bromine lies syn, the extra splitting seen for the vinyl protons when chlorine is syn to them, and at the same time the broader splitting of the allylic protons.

Hydrolysis of 11-Bromo-11-chloro[4.4.1]propell-3-enes (3a and 3b) in 90% Aqueous Acetone with 2 Equiv of $AgClO_4$. To a stirring solution of 2.06 g (7.88 mmol) of **3a** and **3b** in 120 mL of 90% aqueous acetone was added dropwise a solution of 3.27 g (15.76 mmol) of $AgClO_4$ in 30 mL of 90% aqueous acetone. After the resulting mixture was stirred in the dark for 13 days, during which time a blackish precipitate appeared, 0.5 g of NaCl was added and the acetone evaporated. The residue was extracted with 4 × 25 mL of ether, and the combined ether extracts were washed with 25 mL of saturated Na_2CO_3 solution and 15 mL of saturated NaCl solution before drying over $MgSO_4$. Solvent evaporation gave 1.40 g of material, which was chromatographed on a silica gel column (1.3 × 120 cm). However, 115 mg of **12** failed to dissolve in the hexane used to start the column. It was recrystallized from CCl_4, and the mother liquor was added to the column with the rest of the crude product. Elution with hexane, then ether/hexane (1:99 for fraction 6–20; 2:98 for fractions 21–40; 4:96 for fractions 41–50; 8:92 for fractions 51–70; 16:84 for fractions 71–90; 20:80 for fractions 91–100), then acetone/hexane (15:85 for fractions 101–126), and finally methanol/hexane (15:85 for fractions 127–134) afforded the following products (50-mL fractions):

(1) Fractions 3–4. 3a, 3b, and tetralin (6), 835 mg. Analysis of the mixture by ^1H NMR (internal *p*-dibromobenzene standard) and distillative removal of **6** indicated that 75 mg (11.4%) of tetralin (**6**) was present.

(2) Fractions 33–35. Benzocycloheptenone (5),[7,25] 20 mg (2.5%).

(3) Fraction 36. *anti*-11-Chlorobicyclo[4.4.1]undeca-1,3-dien-6-ol (17): 12 mg (1.2%); mp 90–91.5 °C (hexane); ^1H NMR δ 6.15 (br, s, 2 H), 5.70 (br s, 1 H), 4.73 (s, 1 H), 2.88 (br, OH), 2.3–1.3 (m, 10 H); ^{13}C NMR ($CDCl_3$, rel area) δ 131.8 (1.73), 131.2 (1.38), 125.2 (small), 87.8 (small), 71.6 (small), 40.9 (1.0), 36.7 (1.07), 32.9 (1.35), 23.2 (1.88), 22.5 (1.98), C_1 not observed; IR (CCl_4) 3580 (s, OH), 2920, 1620, 1595, 1090 cm^{-1}; UV (95% EtOH) 241.7 nm (ε = 5700). Anal. Calcd for $C_{11}H_{15}OCl$: *m/e* 198.0812. Found, *m/e* 198.0804.

(4) Fractions 37–38. 17, (11*R*,6*S*)- and (11*S*,6*R*)-11-Chlorobicyclo[4.4.1]undeca-1(10),3-dien-6-ol (15), *syn*-6-Chloromethylenecyclodec-3-enone (14), and *anti*-6-Chloromethylenecyclodec-3-enone (16), 97 mg. A fraction (49 mg) of the mixture was placed on a preparative TLC (silica gel) plate and developed with 80:20 hexane/acetone. The first band (R_f 0.59) was **17** (12 mg, 2.4%). The second band (R_f 0.53) was **15** (6 mg, 1.2%): ^1H NMR δ 5.05 (s, 1 H), 5.65–5.35 (m, 3 H), 3.35–3.05 (m, 2 H), 2.85–1.35 (m, 9 H); IR (CCl_4) 3600 (s, OH), 2950, 1650, 1615, 1100 cm^{-1}. Anal. Calcd for $C_{11}H_{15}OCl$: *m/e* 198.0812. Found, *m/e* 198.0807.

The third band (br, R_f 0.47) was a mixture of **14** and **16** (31 mg, 6.3%). Pure **16** was obtained from pure **3b** (see below). The following spectra of **14** were obtained by subtraction. The ratio of **14**:**16** was from ^{13}C NMR. ^1H NMR: δ 5.87 (s, 1 H), 5.62 (m, 2 H), 3.17 (d, 2 H, *J* = 7 Hz), 3.12 (d, 2 H, *J* = 7 Hz), 2.49 (t, 2 H, *J* = 7 Hz), 2.14 (t, 2 H, *J* = 7 Hz), 1.9–1.45 (m, 4 H); ^{13}C NMR ($CDCl_3$, rel area) δ 212.6 (1.05, C_1), 140.0 (1.0, C_{11}), 130.0 (2.65), 124.9 (3.34), 113.7 (3.84), 42.4 (4.06), 40.3 (3.42), 31.8 (3.05), 28.5 (3.18), 26.2 (3.74), 24.7 (5.34); IR (CCl_4) 2940, 1707, 1650, 1630, 857 cm^{-1}. Anal. (**14** and **16**) Calcd for $C_{11}H_{15}OCl$: *m/e* 198.0812. Found, *m/e* 198.0804.

(5) Fractions 39–41. 14 and 16, 66 mg (6.7%).

(6) Fractions 43–47. *cis*-Tricyclo[5.4.0.0^{1,3}]undec-4-en-6-one (13): 106 mg (13%); ^1H NMR δ 7.04 (dd, H_4, *J* = 5, 9.5 Hz), 5.37 (d, H_5, *J* = 9.5 Hz), 2.48 (br d, H_7, *J* = 11 Hz), 2.0–1.0 (m, 9 H), 0.97 (br d, H_8, *J* = 11 Hz), 0.30 (dd, H_3, *J* = 3, 5 Hz); ^{13}C NMR ($CDCl_3$, rel area) δ 201.1 (1.0, C_6), 153.8 (4.34, C_4), 122.0 (4.18, C_5), 48.7 (4.09, C_7), 34.2 (4.48), 32.1 (5.02), 31.8 (4.01), 25.3 (4.47), 24.8 (4.51), 23.6 (1.93, C_1), 20.8 (4.26, C_2); IR (CCl_4) 2930, 2855, 1678, 1630, 1610, 1445, 1243 cm^{-1}. Anal. Calcd for $C_{11}H_{14}O$: *m/e* 162.1045. Found, *m/e* 162.1062.

(7) Fractions 84–92. *syn*-11-Chloro-1,6-dihydroxybicyclo[4.4.1]undec-3-ene (12): 86 mg (18.6%, including material recrystallized prior to chromatography); mp 165–166.5 °C (CCl_4, sealed tube); ^1H NMR ($CDCl_3$) δ 5.58 (m, 2 H), 4.64 (t, H_{11}, *J* = 2 Hz), 2.79 (apparent d, H_{2exo}, H_{5exo}, splitting = 15 Hz), 2.33 (s, 2 OH), 2.2–1.5 (m, 10 H); ^{13}C NMR ($CDCl_3$, rel area) δ 127.4 (2.35, $C_{3,4}$), 84.6 (1.0, $C_{1,6}$), 74.3 (1.16, C_{11}), 37.7 (2.02), 33.7 (2.01), 17.6 (1.99, $C_{8,9}$); IR (CCl_4) 3590 (OH), 2950, 1670, 1645, 1095, 1040 cm^{-1}. Anal. Calcd for $C_{11}H_{17}O_2Cl$: *m/e* 216.0917; C, 60.97; H, 7.91. Found, *m/e* 216.0908; C, 60.83; H, 8.03.

(8) Fractions 101–103. 7-Hydroxybicyclo[5.4.0]undec-9-en-2-one (24): 3–5 mg (slightly contaminated with **18**; ^1H NMR δ 5.65 (m, 2 H), 3.18 (m, 1 H), 2.75–1.4 (m, 13 H); IR (CCl_4) 3450 (OH), 2930, 1707, 1260 cm^{-1}. This material was converted to **5** under the reaction conditions.

(9) Fractions 104–106. *anti*-11-Chloro-1,6-dihydroxybicyclo[4.4.1]undec-3-ene (18): 7 mg (0.7%); ^1H NMR δ 5.87 (m, 2 H), 4.39 (s, H_{11}), 2.95 (br s, 2 OH), 2.6–1.3 (m, 12 H); IR (CCl_4) 3590 (OH), 2960, 1670, 1265, 1250 cm^{-1}. Anal. Calcd for $C_{11}H_{17}O_2Cl$: *m/e* 216.0917. Found, *m/e* 216.0918.

Acidification of the basic extracts followed by extraction with 4 × 10 mL of ether, drying ($MgSO_4$), and solvent evaporation left 188 mg of a brown semisolid. Chromatography on a 1.0 × 40 cm silica gel column (initial eluting solvent was 95% ethereal hexane, followed by a 45:50:5 mixture of $CHCl_3$/hexane/ether after fraction 16, followed by MeOH for fractions 32–36; 50-mL fractions) afforded the following.

(10) Fractions 4–7. *cis*-Bicyclo[4.4.0]dec-3-ene-1-carboxylic Acid (19): 119 mg (13.2%); mp 128–129 °C (CCl_4); ^1H NMR δ 11.55 (br, CO_2H), 5.51 (br s, 2 H), 2.8–1.1 (m, 13 H); IR (CCl_4) 3360–2500, 1707, 1460, 1255, 1230, 865 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_2$: *m/e* 180.1150. Found, *m/e* 180.1145.

(11) Fractions 11–12. *trans*-Bicyclo[4.4.0]dec-3-ene-1-carboxylic Acid (20): 7 mg (0.8%); ^1H NMR δ 11.6 (br s, CO_2H), 5.60 (br s, 2 H), 2.8–1.15 (m, 13 H); IR (CCl_4) 3500–2600, 1705, 1260, 1095, 1010 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_2$: *m/e* 180.1150. Found, *m/e* 180.1144.

(12) Fractions 22–25. *trans*-6-Hydroxybicyclo[4.4.0]dec-3-ene-1-carboxylic Acid (21): 13 mg (1.3%); ^1H NMR δ 11.6 (m, 1 H, CO_2H), 5.83–5.58 (m, 2 H), 3.15 (m, OH), 2.75–2.10 (m, 4 H), 1.9–1.2 (m, 8 H); IR (CCl_4) 3530 (OH), 3450–2500, 1712, 1270 cm^{-1}. Approximately one-third of the isolated **21** was hydrogenated (8 mL of ether, 2 mg of 5% Pt/C) in a Parr shaker apparatus under 30 psi H_2 for 30 min. Removal of catalyst and solvent gave a quantitative yield of the known *trans*-10-hydroxydecalin-9-carboxylic acid.[10]

Hydrogenation of 12. A solution of 60 mg of **12** in 14 mL of ether was placed in a Parr shaker bottle with 5 mg of 5% Pt/C and hydrogenated (30 psi H_2) for 45 min. Removal of the catalyst and solvent gave 59 mg (98%) of 11-chlorobicyclo[4.4.1]undecane-1,6-diol (**23**).[10]

Hydrogenation of 18. A solution of 10 mg of **18** in 4 mL of ether was placed in a Parr shaker bottle with 1 mg of 5% Pt/C and hydrogenated (30 psi H_2) for 20 min. Removal of the catalyst and solvent gave 10 mg (100%) of **23**.[10]

Treatment of 18 under the Hydrolysis Conditions. A solution of 9 mg (0.042 mmol) of **18** and 43 mg (0.21 mmol) of $AgClO_4$ in 2 mL of 90% aqueous acetone was stirred for 7 days. Sodium chloride was then added, the acetone evaporated, 3 mL of H_2O added, and the mixture extracted with 4 × 5 mL of ether. The combined ether extracts were washed with 5 mL of saturated NaCl solution, dried over $MgSO_4$, and freed of solvent to give 7 mg of yellow oil, which contained **18**, **24**, and **5**.

Treatment of 12 under the Hydrolysis Conditions. When **12** was stirred with $AgClO_4$, without or with perchloric acid (generated from $AgClO_4$ and 2-bromopropane), in 90% aqueous acetone for 22 days at room temperature, starting material was quantitatively recovered. Reaction was effected under more vigorous conditions:

A solution of 25 mg (0.21 mmol) of 2-bromopropane and 188 mg (0.91 mmol) of $AgClO_4$ in 1 mL of 90% aqueous acetone was allowed to stir for 30 min. Then 43 mg (0.21 mmol) of **12** dissolved in 6.5 mL of 90% aqueous acetone was added and the tube sealed. The reaction mixture was kept at 70 °C for 23 days, after which the tube was opened and the reaction worked up as for **18** (above); 48 mg of a black solid was obtained. Chromatography (1.0 × 37 cm silica gel column) of this material gave 12 mg of starting **12** and 20 mg of other products. These latter were separated on a preparative TLC plate (silica gel) with 80:20

hexane/$CHCl_3$. The first (R_f 0.35, 4 mg) and second (R_f 0.28, 5 mg) components were not identified; the third (R_f 0.19, 10 mg) proved to be ***cis*-7-hydroxybicyclo[5.4.0]undec-4-en-2-one (25)**: ^1H NMR δ 5.42 (s, 2 H), 2.8–1.25 (m, 14 H); IR (CCl_4) 3640–3200 (OH), 2940, 1710, 1270, 1100 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_2$: *m/e* 180.1150. Found, *m/e* 180.1157.

Treatment of 15 under the Hydrolysis Conditions. A solution of 5 mg (0.025 mmol) of **15** in 2 mL of aqueous acetone was stirred while 10 mg (0.050 mmol) of $AgClO_4$ was added. The resulting mixture was stirred for 13 days at room temperature. Workup as for **18** afforded 6 mg (120%) of starting material (**15**).

Treatment of 17 under the Hydrolysis Conditions. To a stirring solution of 44 mg (0.21 mmol) of $AgClO_4$ in 1 mL of 90% aqueous acetone was added 17 mg (0.14 mmol) of 2-bromopropane and the resulting mixture stirred for another 45 min. Then a solution of 7 mg (0.036 mmol) of **17** in 1.5 mL of 90% aqueous acetone was added and the resulting mixture stirred for 21 days. Workup as for **18** afforded 7 mg (100%) of starting **17**.

Hydrogenation of 19. A solution of 20 mg of **19** in 10 mL of ether was hydrogenated (3 mg of 5% Pt/C catalyst) on a Parr shaker (30 psi H_2) for 30 min. Removal of catalyst and solvent gave 20 mg (96%) of *cis*-decalin-9-carboxylic acid.[13]

Hydrogenation of 20. A solution of 7 mg of **20** in 7 mL of ether was hydrogenated (2 mg of 5% Pt/C catalyst) on a Parr shaker (30 psi H_2) for 30 min. Removal of catalyst and solvent gave 7 mg (100%) of *trans*-decalin-9-carboxylic acid.[13]

Hydrolysis of 3a and 3b in 80% Aqueous Acetone. To a stirring solution of 1.50 g (5.96 mmol) of **3a** and **3b** in 75 mL of 80% aqueous acetone was added dropwise a solution of 2.47 g (11.9 mmol) of $AgClO_4$ in 15 mL of aqueous acetone. The resulting solution was stirred for 8 days, following which the reaction was worked up as in the previous hydrolysis to yield 1.020 g of crude neutral product. This material was chromatographed on a 1.4 × 107 cm silica gel column; however, 84 mg of **12** failed to dissolve in the initial hexane eluent, whereupon it was recrystallized from CCl_4 and the mother liquor added to the column. Further elution, conducted with ether/hexane (1:99 for fractions 5–24; 2:98 for fractions 25–49, 4:96 for fractions 50–59; 8:92 for fractions 60–69; 16:84 for fractions 70–85; 50-ml fractions), gave the following products.

(1) Fractions 3–4. 3a, 3b, and 6, 559 mg. ^1H NMR (internal *p*-dibromobenzene) and distillative removal of **6** showed 45 mg (9%) of **6**. The ratio of recovered **3a**:**3b** was 1:9 (^{13}C NMR).

(2) Fractions 8–13. 5, 33 mg (5.5%).

(3) Fractions 19–21. 17, 27 mg (3.6%).

(4) Fractions 22–23. 17, 15, 14, and 16, 91 mg. The amounts of each were determined by ^1H NMR (internal *p*-dibromobenzene): **17,** 16 mg (2.1%); **15,** 25 mg (3%); **14,** 23 mg (3.1%); **16,** 27 mg (3.6%).

(5) Fractions 24–27. 14 and 16, 23 mg, consisting of **14,** 10 mg (1.4%), and **16,** 13 mg (1.8%).

(6) Fractions 28–32. 13, 71 mg (11.6%).

(7) Fractions 47–53. 12, 70 mg (8.6%). The total yield of **12** (including the initially recrystallized portion) was 18.9%.

(8) Fractions 57–60. 18, 13 mg (1.6%). (Acidification of the basic extracts and workup gave 83 mg of material, which was added to the column during collection of fraction 56.)

(9) Fractions 62–66. 19, 62 mg (9.0%).

(10) Fractions 72–74. 21, 15 mg (1.9%).

Hydrolysis of 3b in 90% Aqueous Acetone. To a stirring solution of 0.71 g (2.72 mmol) of a 19:1 mixture of **3b**:**3a** in 30 mL of 90% aqueous acetone was slowly added a solution of 1.13 g (5.44 mmol) of $AgClO_4$ in 24 mL of 90% aqueous acetone. The resulting mixture was stirred for 13 days at room temperature and then worked up as in previous hydrolyses to afford 601 mg of crude material. Subsequent chromatography on a 1.3 × 95 cm silica gel column with hexane as the initial eluting solvent, followed by ether/hexane (0.5:99.5 for fractions 25–33, 1:99 for fractions 34–43, 2:98 for fractions 44–53, 4:96 for fractions 54–63, 8:92 for fractions 64–73, 16:84 for fractions 74–89, 32:68 for fractions 90–100, and 60:40 for fractions 100–125; 50-mL fractions) gave the following:

(1) Fractions 2–3. 3b and 6, 485 mg. The amounts of each were **3b,** 470 mg, and **6,** 15 mg (12%), determined as before.

(2) Fractions 22–24. 5, 7 mg (4.7%).

(3) Fraction 31. 17, 17 mg (9.2%).

Table IV. Mass Spectral Data For Deuterated 9

	relative intensities		
m/e	9-d_0	9-d_1^a	9-d_1^s
144		0.87	2.02
145	31.27	6.72	7.71
146	(100)	38.92	38.49
147	10.46	(100)	(100)
148		11.39	13.08
149		1.48	1.00

(4) Fractions 32–33. 17 and 16, 21 mg. By ^1H NMR (internal *p*-dibromobenzene), the following amounts were established: **17,** 10 mg (5.4%); **16,** 11 mg (6.0%).

(5) Fractions 34–36. 16: 19 mg (10.3%); ^1H NMR δ 5.86 (s, 1 H), 5.66 (m, 2 H), 3.16 (d, 2 H), 2.90 (d, 2 H), 2.44 (t, 2 H), 2.20 (t, 2 H), 1.9–1.5 (m, 4 H); ^{13}C NMR ($CDCl_3$, rel area) δ 212.6 (1.02, C_1), 140.4 (1.0, C_{11}), 130.6 (2.39), 125.4 (2.05), 113.8 (2.36), 42.4 (1.77), 40.8 (1.49), 33.6 (1.27), 26.4 (1.98), 25.0 (1.63), 24.6 (2.37); IR (CCl_4) 2950, 1710, 1650, 1630, 1250, 860 cm^{-1}. Anal. Calcd for $C_{11}H_{15}OCl$: *m/e* 198.0812. Found, *m/e* 198.0801.

(5) Fractions 71–73. 12, 4–6 mg (2–3%).

(6) Fractions 78–81. 18, 8 mg (4.0%). The acidic products (21 mg), obtained from acidification and workup of the basic extracts, were added to the column during the collection of fraction 98.

(7) Fractions 121–123. 19, 18 mg (10.7%).

Relative Solvolysis Rates of 3c and 3d. General. Each solvolysis was followed by removing aliquots at measured time intervals, adding NaCl to quench the reaction, and injecting into the GLC (column F at 175 °C). The retention times were biphenyl (standard), 23 min; **3c,** 29 min; **3d,** 32 min. Both **3c** and **3d** respond nearly identically to the thermal conductivity detector (correction factors of 3.00 and 3.01, respectively).

(A) Methanolysis with 20 Equiv of $AgClO_4$. To a stirring solution of 31 mg (0.14 mmol) of **3c,** 23 mg (0.084 mmol) of **3d,** and 15 mg of biphenyl in 6 mL of MeOH was added a solution of 913 mg (4.4 mmol) of $AgClO_4$ in 16 mL of MeOH and the resulting solution stirred at room temperature. After intervals of from 3 to 122 h, 1-mL aliquots were withdrawn and analyzed. Treatment of the data as if the reaction were pseudo first order gave **3c,** $k = 1.58 \times 10^{-6}$ s^{-1} ($r = 0.97$), and **3d,** $k = 2.9 \times 10^{-6}$ s^{-1} ($r = 0.96$).

(B) Methanolysis with 1 Equiv of $AgClO_4$. To a stirring solution of 34 mg (0.15 mmol) of **3c,** 28 mg (0.12 mmol) of **3d,** and 17 mg of biphenyl in 4 mL of MeOH was added a solution of 57 mg (0.275 mmol) of $AgClO_4$ in 6 mL of MeOH and the resulting solution stirred at room temperature. Aliquots were taken and analyzed as in (A). The results were treated as if the reaction followed second-order kinetics, with the assumption that [Ag^+] was always equal to [**3c** + **3d**]. The derived "rates" were **3c,** $k = 6.4 \times 10^{-7}$ M^{-1} s^{-1} ($r = 0.97$), and **3d,** $k = 6.1 \times 10^{-7}$ M^{-1} s^{-1} ($r = 0.97$).

(C) Hydrolysis with 5 Equiv of $AgClO_4$ in 90% Aqueous Acetone. To a stirring solution of 28 mg (0.12 mmol) of **3c,** 19 mg (0.08 mmol) of **3d,** and 19 mg of biphenyl in 7 mL of 90% aqueous acetone was added a solution of 213 mg (1.03 mmol) of $AgClO_4$ in 8 mL of 90% aqueous acetone and the resulting mixture stirred at room temperature. Aliquots were taken and analyzed as in (A). The data were again treated as if the reaction were second order. The derived rates were **3c,** $k = 1.1 \times 10^{-6}$ M^{-1} s^{-1} ($r = 0.68$), and **3d,** $k = 1.9 \times 10^{-6}$ M^{-1} s^{-1} ($r = 0.87$). Essentially the same rate constants were obtained by treating the reactions as pseudo first order and then dividing by the [Ag^+].

Deuteriomethanolysis of 3c and 3d. Compounds **3c** (1g) and **3d** (0.5 g) were separately treated with 20 equiv of $AgNO_3$ in 25 mL of refluxing MeOD under N_2 for 24 h. The reaction was cooled, NaCl added, and worked up as for **3a** and **3b**. Compound **9** was, in each instance, isolated on column C. The ^1H NMR of the product from **3c** (9-d_1^a) showed a narrowly split multiplet (H–D and long-range coupling) at δ 0.7 for H_{11syn} and no detectable peaks centered at δ 3.1 for H_{11anti}. On the other hand, the product from **3d** (9-d_1^s) showed a narrow triplet (H–D coupling) at δ 3.1 for H_{11anti} and no detectable peaks centered at δ 0.7 for H_{11syn}. The mass spectral data in Table IV are in accord with the incorporation of 93% d_1 in each deuteration, with 7% d_0.