Propellanes. 17. Bridgehead Olefins via Solvolysis of 10,10-Dibromo[4.3.1]propellanes[1,2]

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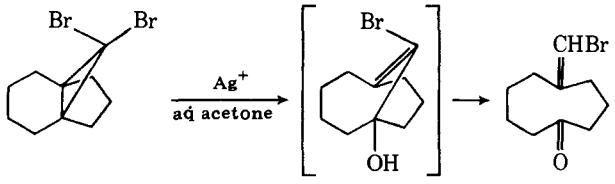
Abstract: This paper reports the results of the hydrolysis and acetolysis of 10,10-dibromo[4.3.1]propellane (**1**) and 10,10-dibromo[4.3.1]propell-3-ene (**4**). Hydrolytically (Ag^+ assisted, aqueous acetone), the former gave five products (**3**, **7**, **11**, **12**, and **13**), while the latter gave rise to only two (**6** and 9). The hydroazulenic products (**7** and **12**) were shown to arise via rearrangement of a bicyclo[4.3.1]decane nucleus (**11**); 9 rearranged to a hydroazulene under prolonged reaction conditions. The stereochemistry of **3** (and 6) was demonstrated via x-ray crystallographic studies of the derived 2,4-DNP (**19**); **3** and **6** were both found to undergo transannular cyclizations to bicyclo[4.3.1]decane ring systems. Acetolysis of **1** afforded **20** and **24**; the latter bridgehead olefin rearranged to cyclopropyl acetates **25** and **26**. The slower acetolysis of **4** gave **32**–**37**; cyclopropyl acetates **34** and **35** arose primarily from bridgehead olefin **33** and partially from **37**; **36** was the product of cyclopropyl ring and stereochemical retention. Acetolysis of tertiary mesylate **51** gave bridgehead olefin **50**, which was shown not to rearrange to bridgehead olefin **33**. Mechanistic explanations for the formation of these products are given.

The finding[4] that generation of cyclopropyl cations in constrained propellanic systems could lead to bridgehead olefin intermediates via ring opening is now well accepted.[5] The first report of such a process in [4.3.1]propellane systems[4b] was somewhat circumstantial, in that only **3** and **6** were identified



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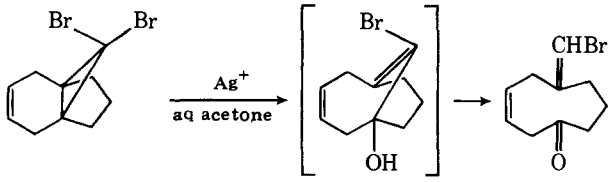
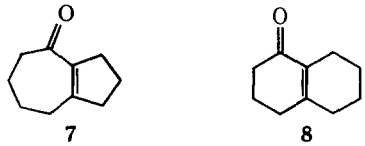


4 5 6

as bridgehead olefin products originating from **1** and **4**, respectively. Equally intriguing was the isolation of **7**, but *not* **8**, from **1**, via a process suggested to involve a 1,2-alkyl shift



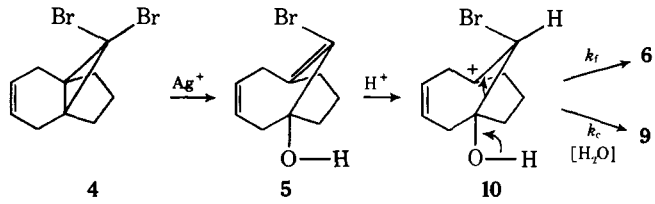
7 8

prior to cyclopropane ring opening. No analogous products were obtained from **4**.

Results and Discussion

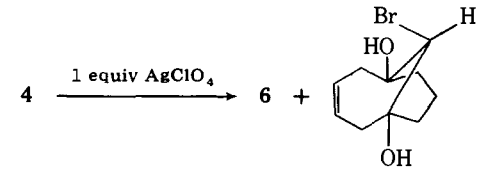
Our investigation of the solvolysis of [4.3.1]propellanes began with a hydrolytic study of **4**. Attempted dissolution of the crude solvolysate from **4** in 95% aqueous acetone led to a precipitate which proved to be bicyclic diol **9**, the stereochemistry of which was unequivocally proven via correlation with **32** (i.e., hydrolysis of **32** gave **9** and **22**). The other product found was the previously reported[4b] monocyclic ketone **6**. Since the mechanism shown in Scheme I was suspected, the silver assisted hydrolysis was repeated in 90% aqueous acetone. This

Scheme I



4 5 10

time the percent of diol (**9**) increased, as required; the yields are shown in eq 1. For each solvent, one may calculate k_f/k_c



(1)

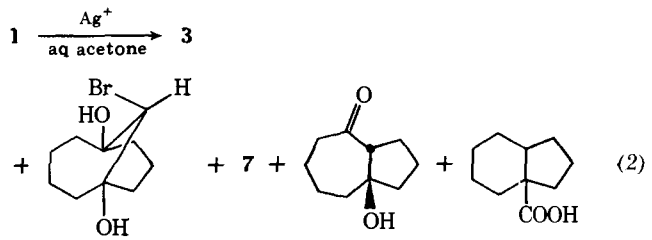
9

95% aq acetone 44% 18%
90% aq acetone 27% 44%

(the ratio of unimolecular fragmentation to bimolecular collapse rate constants). This ratio is 3.3 for 90% aqueous acetone and 6.7 for 95% aqueous acetone. Apparently the less polar solvent increases the lability of **10**, thereby hastening its fragmentation. (However, one should only take these numbers qualitatively, since we account for only 60–70% of the starting material.)

With the isolation of **9** to further support the intermediacy of **5**, several questions remained: (a) was an analogous product formed from **1**; (b) how was **7** formed; (c) what was the stereochemistry of **3** (**6**)?

Catalytic hydrogenation of **9** provided an authenic sample of the saturated diol (**11**), whereupon it was determined that **11** indeed was formed from the hydrolysis of **1**, albeit in smaller



(2)

11 12 13

Table I. Product Yields from Hydrolysis of 1

$[Ag^+]/[1]$	[1], M	% aq acetone	t, min	Yields, % 3	7	12	11	13	Ref
Excess	?	95	10	50	15				4b
2	0.02-0.06	90	20-30	43	13		15		This work
1.1	0.3	90	15	42	3	11	10	0.2	This work
3.6	0.2	90	300	52	16	4.4	0	0.2	This work

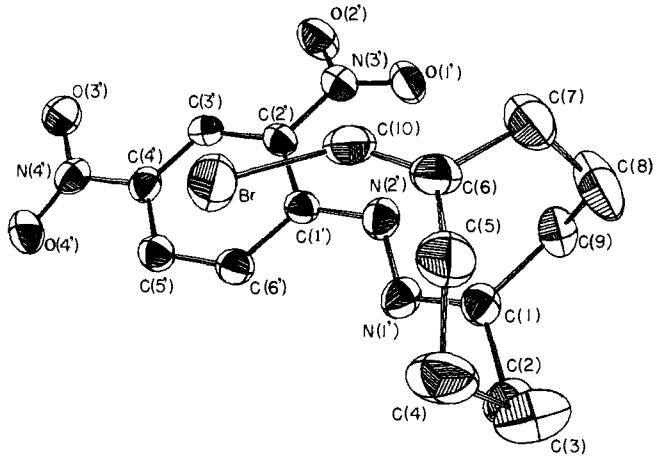


Figure 1. Computer generated drawing of the final x-ray model of 19.

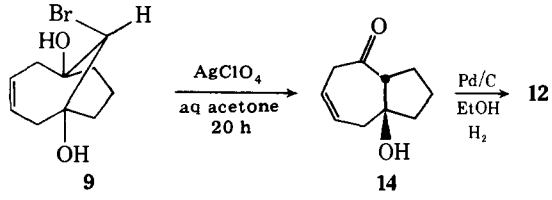
Table II. Atomic Displacements from the Least-Squares Plane[a] Describing the Benzene Ring in 19.

Atom	Deviation from planarity, Å
C(1')	0.008
C(2')	−0.007
C(3')	0.003
C(4')	−0.001
C(5')	0.003
C(6')	−0.007
N(1')	0.093
N(2')	−0.033
N(3')	0.052
N(4')	0.069
O(1')	−0.052
O(2')	0.176
C(1)	−0.086
C(2)	0.055

[a] Plane is defined by $c_1X + c_2Y + c_3Z - d = 0$, where X, Y, and Z are coordinates along the cartesian a, b, and c axes. Plane defined by atoms (C(1'), C(2'), C(3'), C(4'), C(5'), C(6')): $-0.91704X + 0.26185Y + 0.30076Z = 2.19264$.

amounts than the analogous diol **9**. However, a careful investigation of the hydrolysis of **1** showed that the product ratios were dependent upon reaction time and amounts of silver perchlorate used; the products isolated are illustrated in eq 2, while the quantities of each are given in Table I. The identification of β-hydroxy ketone **12** was based on its infrared spectrum (3600, 3450, 1707 cm^{-1}), the presence of a ^1H NMR triplet (J = 8 Hz, 1 H) at δ 3.03 for the tertiary hydrogen α to the carbonyl, and its dehydration to **7** with perchloric acid. The cis ring fusion was demonstrated by the fact that the aforementioned tertiary hydrogen was the most shifted one in the presence of $Eu(fod)_3$ (see Experimental Section for details), and the shifts were in good accord with those observed by Paquette[6] for a proton cis to a hydroxyl group in a triquinacene derivative. The carboxylic acid **13** was isolated in very minor amounts via base extraction; in addition to a typical infrared spectrum, the mass spectrum [168 (P), 151 (P − OH), 123 (P − CO_2H)] was observed. We cannot be sure that **13** was really a single substance.[7]

The implication of the data in Table I is that **7** arises from **12**, which in turn comes from **11**. Indeed treatment of **11** with excess silver perchlorate gave a 14:1 mixture of **12** and **7**. Additionally, exposure of unsaturated diol **9** to excess silver perchlorate for 20 h left a 97% yield of unsaturated β-hydroxy ketone **14**, the $Eu(fod)_3$ shifted ^1H NMR spectrum of which



again indicated the cis fusion. Hydrogenation of **14** produced **12** quantitatively.

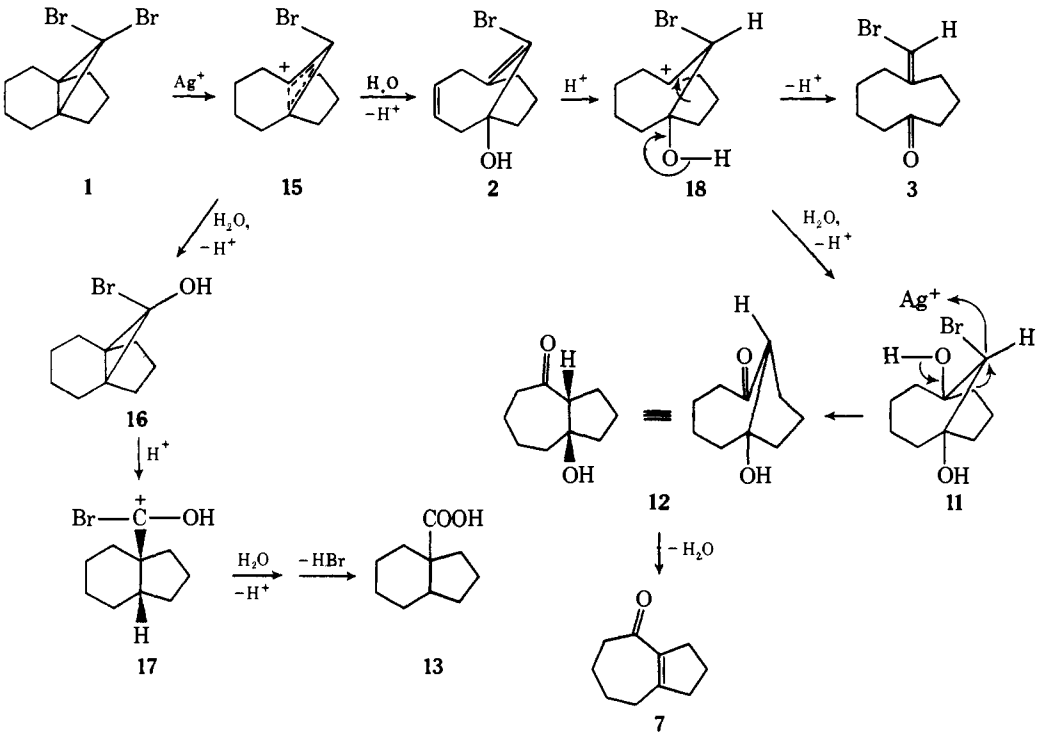
How does carboxylic acid **13** arise? As we have discussed in detail for the corresponding [4.4.1]propellane hydrolysis,[8] the most likely route is via protic cleavage of an intermediate α-bromohydrin (**16**). That protic cleavage of **1** did not occur was verified by a control experiment. Also, [4.3.1]propellane itself was not attacked by silver ion. The complete pathway for formation of all products is shown in Scheme II.[9] The formation of **7**, but not **8**, is seen to be a consequence of the stereochemistry of **11**.

The stereochemistry of **3**, as indicated in Scheme II, implies retention at C(10) in the conversion of **18** to **3**; the stereochemistry of **18** is known from the structure of **11**. Originally,[4b] **3** was thought to be one stereoisomer because of the sharpness of the ^1H NMR absorption of the bromomethylene proton. We could find only ten lines in the ^{13}C NMR spectrum of **3**, even after 21 000 scans (110-mg sample). Also, Professor Reese has examined the ^1H NMR of **3** in the presence of shift reagents, and could find no evidence for an epimer of **3**.[10] Finally, the stereochemistry of **3** (and via hydrogenative correlation, **6**) was determined by a single crystal x-ray analysis of the 2,4-dinitrophenylhydrazone derivative (**19**). The stereochemistry of **16** is presumed on the basis of the structure of **36**. Of course, the conversion of **16** to **13** could proceed via a cyclopropanone, formed from **16** via loss of HBr.[4h]

The x-ray structure (see Figure 1 for a drawing of the final model) shows that the conformation of the nine-membered ring of **19** closely resembles the "twisted chair boat" (TCB) conformation found for cyclononylamine hydrobromide[11] and cyclononanone.[12] The bond angles in all three structures generally agree; however, the average bond distances for the medium ring of **19** are significantly shorter (mean value 1.513 Å) than those for both cyclononylamine hydrobromide (mean value 1.532 Å) and cyclononanone (mean value 1.533 Å). This shortening is in accord with the presence of two sp^2 carbons in the nine-membered ring of **19**. As expected, the distances and angles in the dinitrobenzene ring of **19** agree well with those found in 2,6-dinitrophenol.[13]

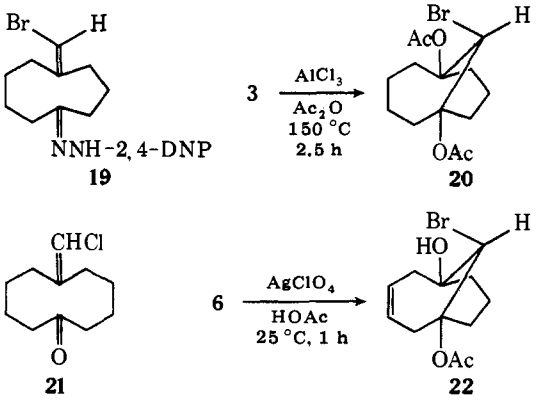
An interesting aspect of the structure of **19** is the orientation of the dinitrophenylhydrazone (DNP) moiety. This group shows an unusually high degree of planarity (see Table II) which, in addition to the observation that the C(1')-N(2')

Scheme II



distance of 1.356 (10) Å is midway between that of a conjugated system such as cyanuric chloride[14] (average C-N distance 1.33 Å) and a benzylic C-N single bond (e.g., the 1.39-Å value found for 4-bromo-2,3-dimethylphenyl-5-pyrazolone[15]), is consonant with increased π character of N(2′) due to withdrawal of electron density from the attached H(N). The consequent stabilization of the electron deficient hydrogen via intramolecular hydrogen bonding to an oxygen of the adjacent nitro group is evidenced by the short N(2′)-O(1′) distance of 2.610 (10) Å, as well as the high degree of planarity of the O(1′)-N(3′)-O(2′) group with respect to the benzene ring (the angle between the plane of the *o*-nitro group and that of the benzene ring is 6.2°, as opposed to 23.2° between the benzene ring plane and that of the *p*-nitro group).

An important conformational feature of **19** is the projection of the exocyclic carbon above the nine-membered ring ($r_{C(1)-C(6)}$ = 3.059 (10) Å, $r_{C(1)-C(10)}$ = 3.431 (11) Å), alerting one to possible transannular interaction in **3**. Thus, although **3** was stable to the hydrolysis conditions, treatment with aluminum trichloride in acetic anhydride caused its conversion to bicyclic diacetate, **20**. On the other hand, similar treatment of the ten-membered ketone **21**[4e] led to no bicyclic material,[16]



but rather to a mixture of enol acetates, wherefrom **21** was recovered (overall yield of 82%) upon hydrolysis.[17] Another example of bicyclization occurred when **4** was acetolyzed in the presence of silver perchlorate. If the reaction was allowed to stand (it was generally complete within 1 min), monocyclic ketone **6** was converted to hydroxy acetate **22**, the structure of which was proven by x-ray crystallography. Figure 2 is a drawing of the final model of **22**.

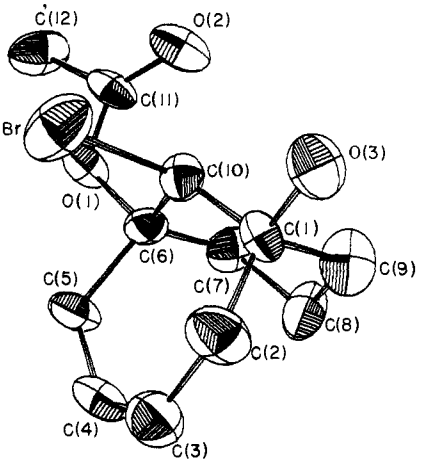
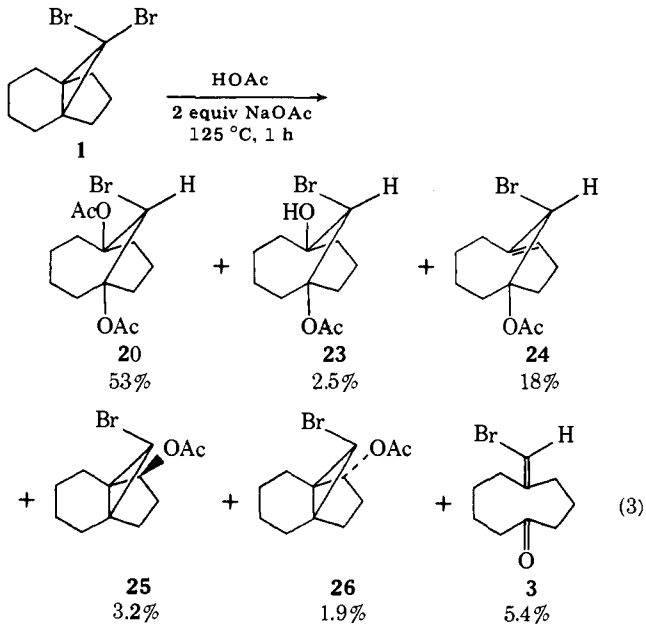


Figure 2. Computer generated drawing of the final x-ray model of **22**.

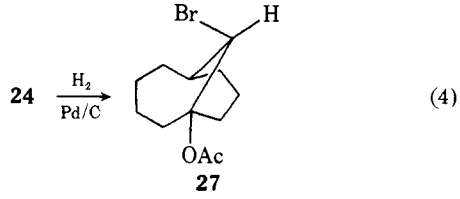
As mentioned previously, the hydrolyses under assisted circumstances were dependent upon silver concentration and time, both in terms of product makeup and rate. The rate effect was noticed for **4**,[4c] where a silver-olefin complex was apparently formed. In fact, a silver-olefin complex between [4.3.1]propell-3-ene and silver nitrate (acetonitrile) was observed. Conceivably, too, silver ion could have been influencing the reactivity of intermediate bridgehead olefins **2** and **5**. We thus decided to investigate the solvolysis of **1** and **4** under nonassisted conditions.

The acetolysis of **1** in glacial acetic acid, buffered with sodium acetate, proceeded smoothly at 125°C to give the products shown in eq 3. The epimeric cyclopropyl acetates (**25** and **26**), the structures of which were confirmed via hydrogenation of the corresponding unsaturated acetates (**34** and **35**, vide infra), became more plentiful with increasing reaction times.



(3)

As expected on the basis of Gassman's results,[19] **24** decreased correspondingly. Bridgehead olefin **24** was identified spectroscopically (^{1}H NMR gave $J_{C(9)-H}$ = 163 Hz, indicating the double bond had a normal olefinic hybridization) and via some chemical transformations (eq 4-6). First of all, hydrogenation



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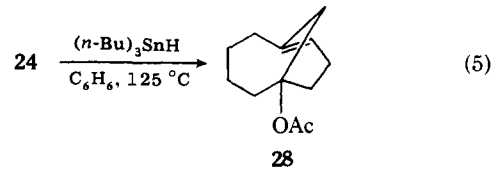

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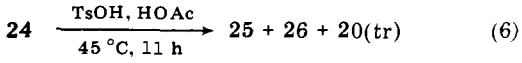
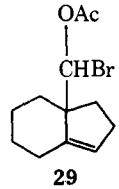


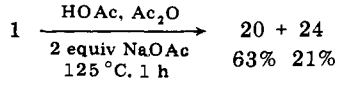
(6)

gave a saturated material which showed a ^{1}H NMR doublet (J = 5 Hz) for the proton α to the bromine atom. This vicinal coupling served to exclude **29** as a structural alternative to **24**, since hydrogenation of **29** could not yield a product with a vicinally coupled low field proton absorption. Secondly, removal



of the bromine atom led to a product (**28**) with only one proton absorption below ca. 3δ (**29** would give a product with three such absorptions). The very small upfield shift observed for this proton (0.15 ppm) as compared to that of **24**, indicated the bromine stereochemistry shown. Nevertheless, this was more conclusively demonstrated in the doubly unsaturated series (vide infra). Lastly, rearrangement of **24** to a mixture of **25** and **26** served to demonstrate the regiopositioning of the double bond.

Which products are kinetic ones, and how are they formed? As mentioned, **25** and **26** are secondary products of homoallyl to cyclopropylcarbinyl rearrangement; **23** was slowly formed from **20** under the reaction conditions, either via hydrolysis with adventitious water, or by further reaction with acetic acid (in which case acetic anhydride would be formed). Monocycle **3** is a kinetic product, and it does not give any bicyclic material under the reaction conditions. The suspicion that water could be involved led to an acetolysis experiment in acetic acid which contained 10% acetic anhydride; the results are summarized in the equation



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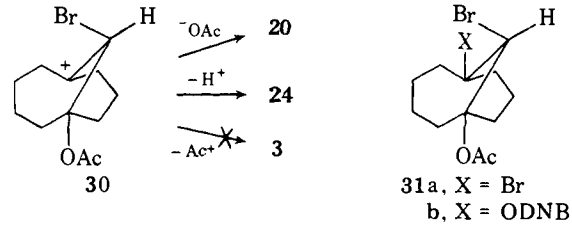
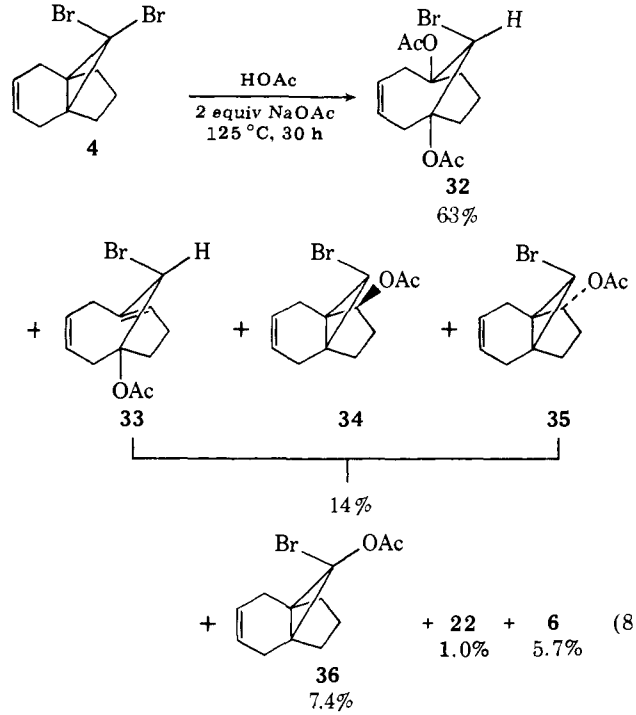
Most importantly, the fact that no **3** was formed, together with the stability of **20** and **23** to the reaction conditions, means that ion **30**, which presumably gives **20** and **24**, cannot fragment to **3** with the loss of the acetyl cation. This observation supports[4b] the concerted nature of the deprotofragmentation of **10** and **18**.

Since ion **30** is separated from initially formed ion **15** by a covalent bridgehead olefin (**2-OAc**), we wondered whether it



could be trapped by external nucleophilic attack, or even if internal return product **31a** could be a reaction intermediate. However, solvolysis of **1** in acetic acid/acetic anhydride (buffered), to which had been added 1 equiv of tetraethylammonium bromide, produced the same products as in the absence of bromide ion. Furthermore, acetolysis of **31b** (obtained from **23**) was much slower (still incomplete after 100 h at 125 °C) than that of **1**, inferring that **31a** was not formed as an intermediate; the products from **31b** were primarily **20**, **24**, **25**, and **26** (vide infra for a more detailed study of the corresponding unsaturated system).

The buffered acetolysis of **4** afforded the products shown in eq 8; in the presence of acetic anhydride (10%), the products



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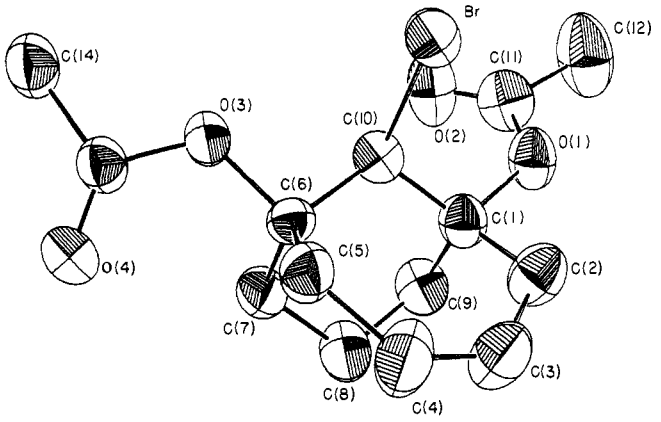
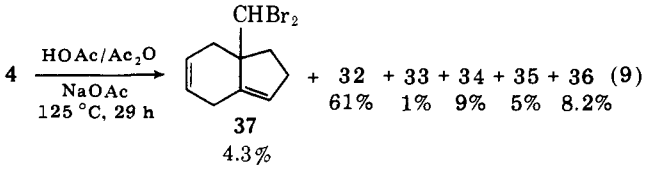
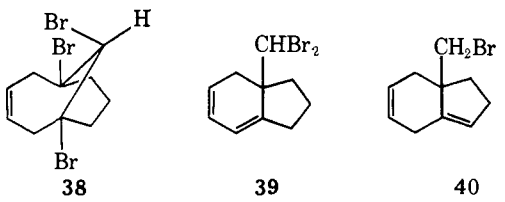


Figure 3. Computer generated drawing of the final x-ray model of **32.**



illustrated in eq 9 were isolated. The structure of **32** was firmly established by x-ray crystallography, as well as the usual spectroscopic and analytical means. Figure 3 is a drawing of the final model of **32.** Comparison of the bond distances (Tables X and XIII) and angles (Tables XI and XIV) shows that the ring structures of **22** and **32** are essentially identical. The six-membered ring is in the chair conformation; the seven-membered ring is also in a chair conformation, with six of the seven carbons being nearly coplanar. In both cases, the carbons comprising the double bond are tipped away from the above-lying bromine atoms. The dihedral angle between the six- and seven-membered rings is approximately 67° for **22** and 64° for **32.** The bond distances and angles agree with generally accepted values.

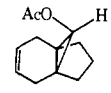
Compound **37,** which was undoubtedly formed, but not isolated, in the solvolysis shown in eq 8, is clearly an acid addition-elimination product. The analogous product was not observed in the acetolysis of **1** due to the faster ionization rate of **1,** making acetic acid addition noncompetitive. In fact, when **4** was acetolyzed in the absence of buffer (allowing HBr buildup), **37** became the major product (46%); among the many other products, tribromide **38** (9%) was identified. The structure of **37** was deduced from its mass spectrum, its ^1H and ^{13}C NMR (four olefinic, six aliphatic carbons) spectra, the presence of only end absorption in the UV spectrum, and its reduction with $(n\text{-Bu})_3SnH$ to give a substance (**40**) which

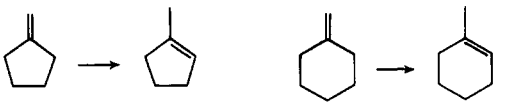


possessed an AB quartet (^1H NMR) for the two diastereotopic bromomethyl protons.

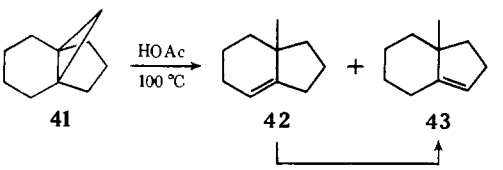
One might wonder about conjugated diene **39,** the absence of which was reinforced by the fact that the ^{13}C NMR spectrum of **37** showed only ten lines after 11 264 scans. From the following data,[20] one may calculate, neglecting conjugation, that the equilibrium between **39** and **37** should lie to the side of **37** by ca. 1.5 kcal/mol; conjugative stabilization of **39** could

Table III. Lanthanide Induced ^1H NMR Shifts for Some Cyclopropyl Acetates in $CDCl_3$ Solution

Compd	[Eu(fod)$_3$]/[Compd]	Lanthanide induced shift, ppm: Vinyl H's	Cyclopropyl H	Acetate H's
36	0.88	0.18		1.23
	1.75	0.25		2.00
	0.36	0.05	0.80	0.68
	0.91	0.10	2.10	1.77
	1.63	0.15	3.12	2.60
46				
	0.67	0.45	1.95	1.57
	1.69	0.80	3.70	2.94
47				

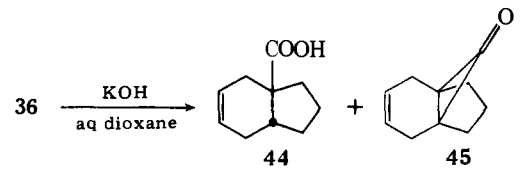


decrease this number by ca. 1 kcal/mol. But could such an equilibrium be established under the reaction conditions? Indeed, acetolysis of [4.3.1]propellane (**41**) produced a mixture of olefins **42** and **43,** where **42** isomerized to **43** under the re-



action conditions.[21] Thus some formation of **39** must be regarded as possible.

Cyclopropyl acetate **36** was the other isolated product which had no analogy from the solvolysis of **1.** The structure was assigned on the basis of a rather high infrared acetate absorption (1772 cm^{-1}), the symmetry plane apparent from the presence of only eight peaks in the ^{13}C NMR spectrum and the hydrolysis to a mixture of the known,[22] expected carboxylic acid **44** and a ketone tentatively assigned structure **45** ($\nu_{C=O}$

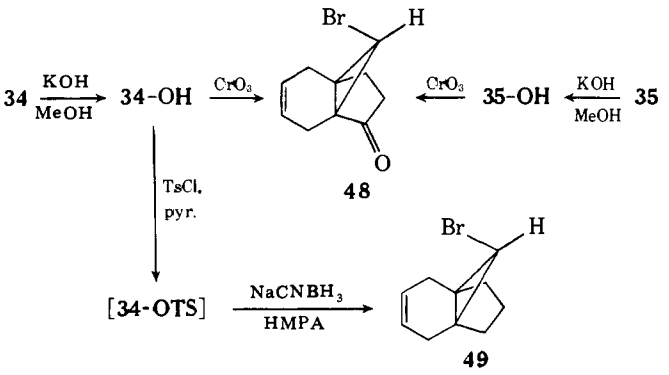


1825 cm^{-1}). The stereochemistry of **36** was assigned on the basis of a comparison of lanthanide induced ^1H NMR shifts for **36** with those for the known[23] epimeric acetates **46** and **47;** the data are summarized in Table III.

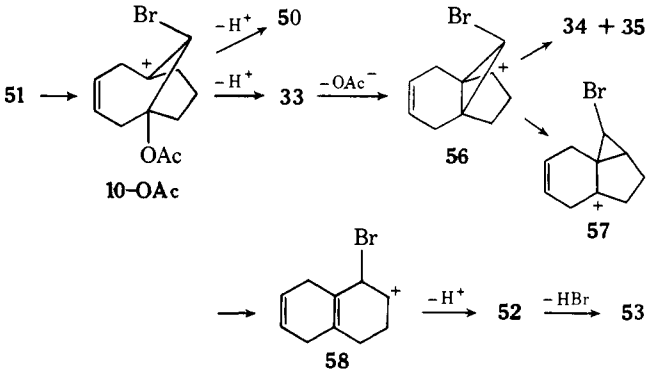
The remaining three acetolysis products, **33–35,** were separable by careful column chromatography. Bridgehead olefin **33** rearranged to **34** and **35** under the reaction conditions and showed only end absorption in the ultraviolet, wherefrom the location of the bridgehead double bond was gleaned. Additionally, hydrogenation of **33** gave **27,** completing the correlation with bridgehead olefin **24.**

The assignment of the major cyclopropylcarbinyl acetate (**34**) as exo was made on the basis of ^1H NMR evidence. From the known boat-like conformation[24] of bicyclo[3.1.0]hexane systems, Dreiding model examination and use of the Karplus equations led to the prediction that H(7-endo) (of **34**) should be coupled to both neighboring protons almost equally, with J = 7.5-8.5 Hz (observed: triplet, J = 8 Hz). On the other

Scheme III



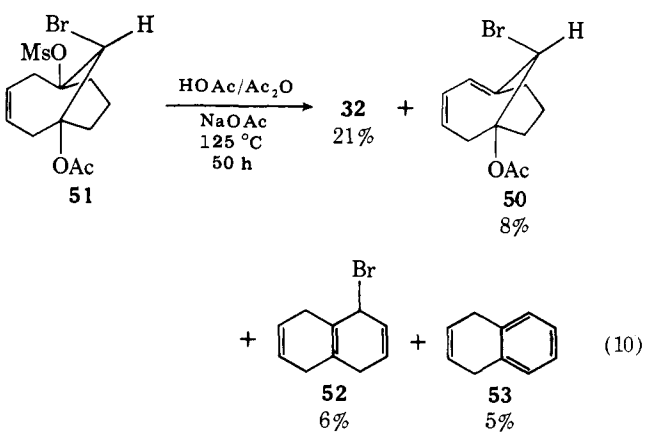
Scheme IV



hand, H(7-exo) (of **35**) was predicted to be coupled to H(8-exo) (J = 5 Hz), but not to H(8-endo) (observed: doublet, J = 3.5 Hz). Corroborative evidence for these assignments came from the cyclopropyl hydrogen chemical shifts. These were δ 3.30 for **34** and δ 2.92 for **35** (compare δ 2.85 for the corresponding proton of **49**), wherefrom the expected deshielding effect of the exo acetoxy group was apparent. The above spectral features were also observed in the corresponding alcohols, **34-OH** and **35-OH.** Further structural identification of **34** and **35** involved their separate hydrolysis and oxidation to the same ketone, **48,** whereby the epimeric nature of **34** and **35** was proven. Furthermore, the carbonyl infrared absorption of **48** at 1735 cm^{-1} was consistent with a five-membered ring ketone conjugated with a cyclopropane ring, but *not* with a cyclohexenone. Finally, **34** and **35** were correlated with the known[23] bromopropellane **49** via tosylation of **34-OH** in pyridine and subsequent in situ reduction with sodium cyanoborohydride. The in situ procedure had to be developed because **34-OTs** was too reactive to isolate [attempted isolation afforded primarily **34-OH,** and other deoxygenation methods failed (*e.g.*, sodium cyanoborohydride[25] or catechol borane[26] reduction of the tosylhydrazone of **48**)]. The above reactions are summarized in Scheme III.

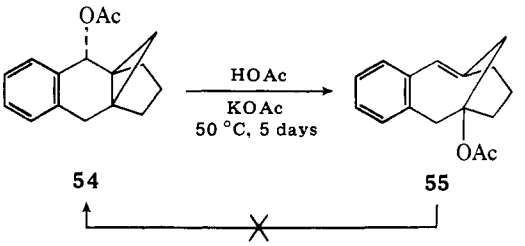
When **33** was subjected to the acetolysis conditions, in addition to the aforementioned **34** and **35,** some low-field peaks were seen in the ^1H NMR spectrum of the reaction mixture; these peaks could also be seen in the crude solvolysate from **4** (vide infra for their identification). This raised the question of the stability of **34** and **35** to the acetolysis conditions. A control experiment established that they neither interconverted nor isomerized in acetic acid.

The absence of olefin **50** from the solvolysate was noteworthy, and the reason why not obvious. We thus sought to generate the presumed precursor cation, **10-OAc,** in a different manner. Acetolysis (1% acetic anhydride, 1 equiv sodium acetate, 125 °C, 50 h) of mesylate **51** proved slower than that of **4,** and produced the products shown in eq 10. The amount of



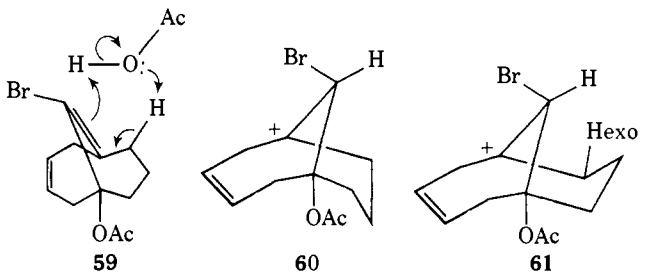
(10)

32 formed increased at higher sodium acetate concentrations. Products **52** and **53,** the aforementioned unidentified components of the crude solvolysate from **4,** are apparently the result of rearrangement of **33** (see Scheme IV). The absence of **34** and **35** among the identified products from **51** is not easily explained, but the low yield suggests they were missed (see Experimental Section for details). The most important point is the isolation of **50,** the structure of which was determined by a combination of mass spectral data, ultraviolet absorption of 255 (ϵ 515) nm, and especially the ^{13}C NMR spectrum (11 lines, with two olefinic carbons showing accidental equivalence, and two other low-field peaks δ 84.7 and 71.5, for C(6) and C(10), whereby a structure analogous to **29** was eliminated). The observed stability of **50** is in accord with the recently reported[27] stability of **55,** and eliminates the possibility that **33** arose from **50.**



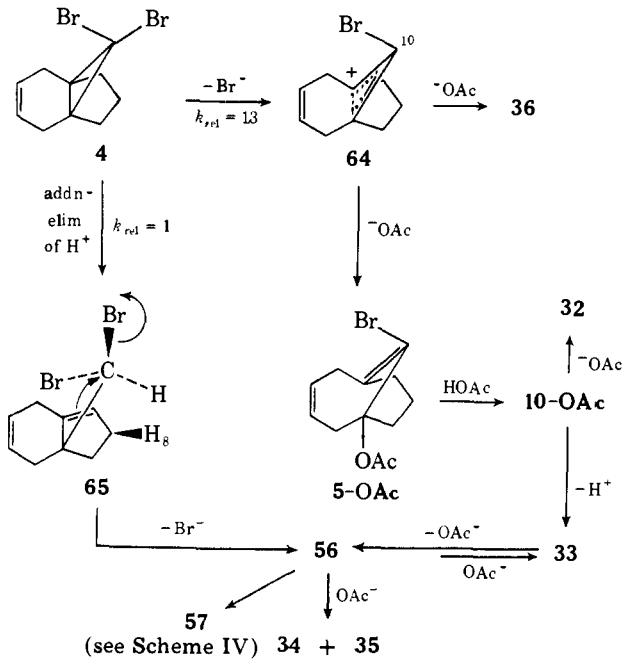
Why, then, does **50** not form in the acetolysis of **4**? It is reasonable to assume that since the kinetically more stable **50** is isomeric with and structurally similar to **33, 33** is actually more strained than **50.** At least three explanations for the sole formation of **33** remain:

(1) Bridgehead olefin intermediate **5-OAc** is directly converted to **33** via an acetic acid mediated process (see **59**). This would bypass ion **10-OAc,** and, at least where some water intervened, a similar ion (**10**) is necessary to explain the formation of **6.** We note that if the process depicted by **59** is at all nonsynchronous (i.e., if proton transfer from acetic acid is faster than proton loss from carbon), then **10-OAc** is an intermediate. We thus find process **59** unlikely.



(2) Protonation of **5-OAc** leaves an acetate ion on the side of the three-carbon bridge, wherefrom it preferentially plucks a proton. This would have to happen on an intimate ion pair level, exclude external acetate, and would imply that **32** comes

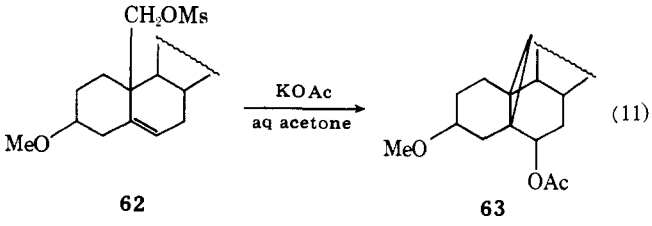
Scheme V



from a different ion or ion pair (because [**32**] depends upon external acetate).

(3) There are conformational differences between **10-OAc** formed from **4** and **51**. From the x-ray structure of **32**, it appears likely that **10-OAc** is formed from **51** in the conformation represented by **60**. In this conformation, the alignments of the four protons adjacent to the cationic center are similar. However, elimination in either direction without conformational change would yield a *trans*-cycloheptenoid or *trans*-cyclohexenoid, rather than the observed *trans*-cyclononenoid. Thus a conformational change must precede or coincide with proton loss from either side of the cationic center. On the other hand, the conformation of the bicyclohexane moiety of **4** is quite different, and should remain unchanged in the initial ion (**64**). If the six-membered ring of **5-OAc**, which is born in the boat conformation, retains its conformation through protonation, then the resulting **10-OAc** may look like **61**. In this conformation, the exo proton on the three-carbon bridge adjacent to the cationic center is uniquely well aligned for elimination to the observed product without any conformational change.

It would appear that we are now in a position to write a comprehensive mechanism for the solvolysis of **4** in acetic acid. That such might not be the case was indicated by the following reported[28] rearrangement (eq 11). Indeed, acetolysis of **37** led

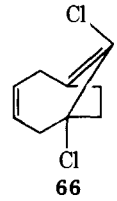


(11)

to 25% rearrangement to a mixture of (mainly) **34** and **33** (and perhaps some **35**). Thus, roughly 10% of the total amount of **33–35** came from **37**, while 90% arose via **5-OAc**. It is interesting that the rearrangement of **37** was stereospecific (with respect to bromine orientation). Structural formula **65** (Scheme V) is an attempt to indicate that this may be due to interaction with H(8) (**65** is the best conformation). In any event, this is a rare example of the same products forming via simultaneous, reconvergent pathways! From the total yield of products isolated, we calculate that the ratio of carbon-bromine heterolysis to proton-initiated cyclopropane cleavage is 13 for **4**. Scheme V presents a comprehensive mechanism for the acetolysis of **4**.

The saturated cyclopropyl acetate corresponding to **36** (**16-OAc**) was not found in the solvolysate from **1**, although it may have formed in minute amounts (cf. minor amount of **13** formed upon hydrolysis of **1**). More cyclopropyl acetate is formed from **64** than from **15** because of the inductive (and possibly electronic) positive charge-repelling effect of the double bond of **64**, making collapse at C(10) relatively more favorable. The stereochemistry of **36** suggests, but does not prove, that **64** is a nonplanar ion. This point is still under investigation.

To this point, the intermediacy of bridgehead olefins **2, 2-OAc, 5,** and **5-OAc** has not been demonstrated by the sort of dimerization or trapping experiments performed[4a,g] in the case of **66**. However, **66** did react with acetic acid[4g] in a manner



66

similar to **2-OAc** and **5-OAc**. Since **66** had not reacted with methanol, we thought dimerization of **2-OAc** might be observable if **1** were solvolyzed in a nonacidic solvent. Trifluoroethanolysis of **1** in the presence of urea or 2,6-lutidine did not, however, allow us to isolate any dimers of **2-OAc**; the products were of low molecular weight and were not further characterized. Although further work along these lines will be pursued, it is noteworthy that, from an examination of models, **2-OAc** and **5-OAc** possess bridgehead double bonds which are more twisted (~70-75°) than that of **66** (~60°).

Experimental Section

General. Infrared spectra were recorded on Beckman IR-12, IR-18A, and IR-4250 spectrometers. The ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. The ^1H NMR spectra were obtained on Varian A-60 and Hitachi Perkin-Elmer R-20B spectrometers, using carbon tetrachloride as the solvent and tetramethylsilane as the internal standard, unless otherwise specified. The ^{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 and High Resolution MS-9 mass spectrometers. Elemental analyses were performed by the Ilse Beetz Microanalytisches Laboratorium, Kronach, W. Germany and Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were measured on a Thomas-Hoover melting point apparatus, and are uncorrected. GLC analyses were conducted on a Varian Aerograph Model 90-P gas chromatograph equipped with a 6 ft × 0.25 in. 20% dinonyl phthalate on Chromosorb W column. All aqueous acetone solutions were made up on a volume basis. Glacial acetic acid was utilized without further drying, unless it is specifically noted that acetic anhydride was added.

Hydrolysis of 10,10-Dibromo[4.3.1]propell-3-ene[29] (4) in Aqueous Acetone. The amounts utilized in the following general procedure are given in Table IV. To the appropriate amount of a solution of **4** in ca. two-thirds of the total amount of solvent used in a round-bottomed flask equipped with a magnetic stirrer was added, all at once, a solution of silver perchlorate in the remaining amount of aqueous acetone. It is important to note that this all-at-once addition was only feasible when the silver concentration was below ca. 0.2 M. At much higher silver concentrations, the reaction occurred rapidly and became exothermic; however, dropwise addition of the silver perchlorate solution avoided problems at high concentrations.[10]

After stirring for the appropriate time, the acetone was removed on a rotary evaporator. Ether was then added to the mixture and the resulting mixture filtered through Celite to remove the precipitated silver bromide. Separation of the layers was followed by washing with

Table IV. Hydrolyses of 4 in Aqueous Acetone

% aq acetone	Amt 4, mg (mM)	Amt $AgClO_4$, mg (mM)	Vol solvent mL	Rxn time	Amt 4 recovered, mg	Amt 6, mg (%)	Amt 9, mg (%)
95	100 (0.34)	70.7 (0.34)	15	30 min	78		
95	100 (0.34)	141.4 (0.68)	15	30 min	74		
95	100 (0.34)	70.7 (0.34)	15	380 min	34	23 (45)	10 (18)
95[a]	100 (0.34)	70.7 (0.34)	15	380 min	21	27 (44)	12 (18)
90	1000 (3.4)	717 (3.5)	111	22 h	350	140 (27)	240 (44)

[a] This experiment was carried out in the presence of 1 equiv (20.6 mg) of urea as buffer.

water twice, then drying over potassium carbonate, and removal of the solvent. When the resulting oil was taken up in carbon tetrachloride, a precipitate was formed which proved to be 1,6-dihydroxy-10α-bromobicyclo[4.3.1]dec-3-ene (9): mp 174–176 °C (d, sealed tube); ^1H NMR already described.[4c] Anal. Calcd for $C_{10}H_{15}O_2Br$: C, 48.50; H, 6.12. Found: C, 48.47; H, 6.19. The material which dissolved was examined by ^1H NMR (*p*-dibromobenzene used as an internal standard); it proved to be a mixture of **4** and ketone **6** described by Reese.[4b]

Treatment of 9 under Hydrolysis Conditions. To simulate the reaction conditions, 23 mg (0.21 mM) of ethyl bromide dissolved in 0.25 mL of 90% aqueous acetone was added to 44 mg (0.21 mM) of silver perchlorate in 0.25 mL of the same solvent. Silver bromide precipitated instantly. To the resulting mixture was added 19 mg (0.08 mM) of 9 in 0.5 mL of 90% aqueous acetone. The resulting mixture was stirred for 38 h at room temperature. Workup as described for the hydrolysis of **4** left 15.2 mg (80%) of crystalline 9; no ketone **6** could be detected by IR or ^1H NMR.

Treatment of 6 under Hydrolysis Conditions. The reaction conditions were simulated as above, utilizing 25 mg (0.23 mM) of ethyl bromide and 42 mg (0.20 mM) of silver perchlorate, to which 10 mg (0.04 mM) of 6 (purified by column chromatography) was added; the total volume of 90% aqueous acetone was again 1 mL. After 38 h stirring at room temperature, the same workup as above gave 8 mg (80%) of 6; no diol 9 could be detected by ^1H NMR spectroscopy.

Hydrogenation of Diol 9. To 55 mg of 9 in 10 mL of ethyl acetate was added a catalytic amount of Pt/C, and the mixture hydrogenated at room pressure for 0.5 h. Filtration, followed by solvent evaporation, left 56 mg of crystalline material, which was identified as 1,6-dihydroxy-10α-bromobicyclo[4.3.1]decane (**11**): mp 148–150 °C (sealed tube, hexane), 154–155 °C (hexane/ether, material isolated by chromatography from hydrolysis of **1**); IR (CCl_4) 3570, 3455 cm^{-1}; ^1H NMR already described.[4c] Anal. Calcd for $C_{10}H_{17}O_2Br$: C, 48.21; H, 6.88. Found: C, 48.35; H, 6.77.

Hydrolysis of 10,10-Dibromo[4.3.1]propellane[29] (1) in 90% Aqueous Acetone. To 930 mg (3.16 mM) of **1** dissolved in 6 mL of 90% aqueous acetone was added dropwise, over a 5-min period, 700 mg (3.40 mM) of anhydrous silver perchlorate dissolved in 4 mL of 90% aqueous acetone, at room temperature. After a further 15 min of stirring, the precipitate was filtered off by suction filtration, followed by evaporation of the acetone in vacuo. The resulting mixture was diluted with ether, and the ether layer extracted thrice with water, once with a 5% sodium hydroxide solution, and then with a saturated sodium chloride solution. Drying of the ether layer over magnesium sulfate and evaporation of the solvent left a yellow oil (580 mg) which was chromatographed on a 20 × 0.5 in. column packed with silica gel (Baker, 60–200 mesh). In order of elution, the products were as follows.

a. Bicyclo[5.3.0]dec-1(7)-en-2-one[30] (7): ^1H NMR δ 2.75–2.20 (m, 8 H), 2.15–1.40 (m, 6 H); IR (CCl_4) 1644, 1624 cm^{-1}.

b. 5-Bromomethylenecyclononanone (3): IR (film) 1702, 1618 cm^{-1} (rep[4b] (film) 1702, 1618 cm^{-1}); ^{13}C NMR ($CDCl_3$): δ 215.2, 142.8, 106.7, 43.9, 41.4, 34.7, 33.3, 25.3, 23.9, 23.5.

c. 7-Hydroxybicyclo[5.3.0]decan-2-one (12): mp 94–95 °C (hexane/ether); IR (CCl_4) 3600, 3450, 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.03 (t, J = 8 Hz, H(1)), 2.80–1.20 (m, 15 H); lanthanide induced ^1H NMR shifts (LIS) for H(1) are given in Table V. Anal. Calcd for $C_{10}H_{16}O_2$: *m/e* 168.1150. Found: *m/e* 168.1152.

Table V. Lanthanide Induced ^1H NMR Shifts (LIS) for H(1) of Cis Fused Hydroxy Ketones **12** and **14**

Compd	[Eu(fod)$_3$]/ [Compd]	LIS, ppm	Compd	[Eu(fod)$_3$]/ [Compd]	LIS, ppm
12	0.17	−1.35	**14**	0.12	−1.43
12	0.33	−2.95	**14**	0.30	−3.90
12	0.45	−4.60	**14**	0.44	−5.30
12	1.10	−12.3	**14**	1.00	−11.0

d. 1,6-Dihydroxy-10α-bromobicyclo[4.3.1]decane (11). The aforementioned basic extract was acidified with 2 N hydrochloric acid solution, followed by ether extraction, drying (magnesium sulfate), and solvent evaporation to give ca. 3 mg of bicyclo[4.3.0]nonane-1-carboxylic acid (**13**): IR (CCl_4) 3600–2400, 1705 cm^{-1}; mass spectrum (70 eV) *m/e* (rel int) 168 (35, P), 151 (100, P − 17), 122 (76, P − 45). The yield of each product was determined by GLC and is given in Table I. The only discrepancy between GLC and isolated yields is for **13**, where the GLC yield quoted must be a lower limit; if the amount isolated were pure, the yield would be 0.6% (this must be an upper limit).

The above reaction was repeated as follows. To 280 mg (0.95 mM) of **1** in 3 mL of 90% aqueous acetone was added dropwise a 2 mL 90% aqueous acetone solution of 700 mg (3.4 mM) of silver perchlorate, at room temperature. After stirring for 5 h, workup as above afforded 150 mg of oil. GLC analysis gave the product yields shown in Table I.

Dehydration of Hydroxy Ketone 12. To 6 mg of **12** was added 1 mL of perchloric acid (70–72%), and the resulting solution allowed to remain at room temperature for 2.5 h. Workup involved dilution with water and ether, extraction with water, drying of the ether layer and solvent evaporation. IR analysis of the product indicated that enone **7** was formed.

Hydrolysis of Diol 11 in 90% Aqueous Acetone. A mixture of 20 mg (0.18 mM) of ethyl bromide and 76 mg (0.37 mM) of silver perchlorate in 0.5 mL of 90% aqueous acetone was allowed to stir for 10 min at room temperature. To the mixture was then added 45.5 mg (0.18 mM) of diol **11** in 2 mL of 90% aqueous acetone. After stirring for 20 min, the reaction was worked up as described for **4** to afford 36 mg of white solid; as determined by IR and ^1H NMR, this solid was a mixture of diol **11** and hydroxy ketone **12**.

Further reaction of the above-obtained solid with 700 mg (3.4 mM) of silver perchlorate in 5 mL of 90% aqueous acetone for 4 h at room temperature gave, upon workup, 22 mg of yellow oil which GLC analysis indicated was a 14:1 mixture of hydroxy ketone **12** and enone **7**.

Hydrolysis of Diol 9 in 90% Aqueous Acetone. To 300 mg (1.22 mM) of diol 9 in 15 mL of 90% aqueous acetone was added a solution of 2.5 g (12.2 mM) of silver perchlorate in 5 mL of 90% aqueous acetone. After stirring for 20 h, workup as described for the hydrolysis of **4** yielded a colorless oil (195 mg, 97%) which solidified upon cooling and proved to be 7-hydroxybicyclo[5.3.0]dec-4-en-2-one (**14**): mp 80–81.5 °C (pentane/ether); IR (CCl_4) 3600, 3410, 3030, 1708 cm^{-1};

^{1}H NMR δ 6.05-5.80 (m, 2 H), 3.35-3.02 (m, 3 H), 2.50-1.55 (m, 9 H); the lanthanide induced ^{1}H NMR shifts of H(1) are given in Table V; ^{13}C NMR ($CDCl_3$) δ 209.1, 128.0, 125.9, 87.9, 62.7, 45.8, 40.1, 37.2, 24.9, 23.5. Anal. Calcd for $C_{10}H_{14}O_2$: *m/e* 166.0994. Found: *m/e* 166.0993. Catalytic hydrogenation of 50 mg of **14** in ethanol (Pd/C) gave a quantitative yield of **12.**

Treatment of 3 under Hydrolysis Conditions. To 30 mg (0.13 mM) of **3** in 2 mL of 90% aqueous acetone was added 270 mg (1.3 mM) of silver perchlorate in 3 mL of 90% aqueous acetone. After stirring for 2 weeks at room temperature, no precipitate was detected. Workup, as described for the hydrolysis of **4**, returned **3** in 91% yield.

Treatment of Propellane 1 with Acid. To 54 mg (0.50 mM) of ethyl bromide in 1 mL of 90% aqueous acetone was added 82 mg (0.40 mM) of silver perchlorate in 1 mL of 90% aqueous acetone. After stirring at room temperature for 25 min, 147 mg (0.50 mM) of **1** in 5 mL of 90% aqueous acetone was added to the reaction mixture, and the resulting mixture left to stand at room temperature for 3 h. Workup as described for the hydrolysis of **1** left 140 mg (95%) of starting material (**1**).

Treatment of [4.3.1]Propellane with Silver Perchlorate. To 50 mg (0.45 mM) of ethyl bromide in 1 mL of 90% aqueous acetone was added 187 mg (0.90 mM) of silver perchlorate in 1 mL of 90% aqueous acetone. After stirring at room temperature for 40 min, 61 mg (0.45 mM) of [4.3.1]propellane 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 **4** gave 46 mg (76%) of starting material.

Preparation of 5-Bromomethylenecyclononanone-2,4-dinitrophenylhydrazone (19). Derivative **19** was synthesized via a literature procedure[31] in 85% yield: mp 164-165 °C (chloroform); IR (KBr) 3320, 1622, 1590, 1522, 1336, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.07 (d, 1 H, X portion of AMX, J_{MX} = 2.5 Hz), 8.25 (dd, 1 H, M portion, J_{AM} = 10 Hz), 7.87 (d, 1 H, A portion), 5.87 (s, 1 H), 2.9-1.5 (m, 14 H), 1.25 (s, NH). Anal. Calcd for $C_{16}H_{19}BrN_4O_4$: *m/e* 410.0590. Found: *m/e* 410.0572.

Transannular Cyclization of 3. To 5 mL of acetic anhydride containing 20 mg of anhydrous aluminum trichloride was added a solution of 93 mg (0.41 mM) of **3** in 1 mL of acetic anhydride under nitrogen. The resulting mixture was heated at 150 °C for 2.5 h, then cooled, and poured into a chilled saturated potassium carbonate solution. Subsequently, the mixture was extracted three times with ether, followed by washing with water and saturated sodium chloride solution, drying (magnesium sulfate), and removal of solvent under reduced pressure to afford 106 mg of an oil which solidified upon cooling. Recrystallization (hexane) yielded 71 mg (52%) of diacetate **20.**

Attempted Transannular Cyclization of 6-Chloromethylenecyclodecanone[4e] (21). To 5 mL of acetic anhydride containing 50 mg of anhydrous aluminum trichloride was added a solution of 50 mg (0.25 mM) of **21** in 1 mL of acetic anhydride under nitrogen. The resulting mixture was heated at 145 °C for 1 h and then worked up as described above for the cyclization of **3.** There resulted 53 mg of oil which was apparently an enol acetate on the basis of its IR spectrum (1768 cm^{-1}) and ^{1}H NMR spectrum (several olefinic absorptions). The oil was hydrolyzed in 5 mL of 90% aqueous methanolic potassium hydroxide solution (0.3 M) at room temperature for 30 min. The solution was then diluted with water and ether and the layers separated after shaking. The ether layer was washed with water, dried over sodium sulfate, and the solvent evaporated. There resulted 41 mg (82%) of starting ketone **21.**

Transannular Cyclization of Ketone 6. A series of experiments were performed in which ca. 1 mM (292 mg) of **4** was dissolved in 10 mL of acetic acid. To this solution was added, all at once, a solution of 1-5 equiv (200 mg to 1 g) of silver perchlorate in ca. 10 mL acetic acid. It is noteworthy that silver perchlorate is very hygroscopic, and the solutions undoubtedly contained some water. Upon addition, immediate copious precipitation of silver bromide occurred. The reactions were stopped, after from 1 min to 5.5 h, by pouring the reaction mixture into an ether/water mixture. The acetic acid was then neutralized by adding solid potassium carbonate (careful!) to the solutions in a separatory funnel. Subsequent washing with water, drying over potassium carbonate, and solvent evaporation left an oil which was chromatographed (silica gel) to give 3% of **36** and 67% of a mixture of **6, 22,** and **32** (vide infra for identification of **22, 32,** and **36**); products **33-35** were not identified, but could have been present. The ratio of **6:22:32** was best determined by internally standardized (*p*-dibromobenzene) ^{1}H NMR experiments, after it had been determined that this ratio changed with reaction time, but the overall yield was reasonably constant. The "kinetic" ratio (after 1 min—very little difference after 2 min reaction time) was 2.7:1.0:1.1 (**6:22:32**), while the "thermodynamic" ratio (almost the same after 1 or 5.5 h) was 0.1:1.0:0.2. It is not known if **6** went directly to **22** or funneled through **32.**

Silver Complexation of [4.3.1]Propell-3-ene.[29] To 80 mg of [4.3.1]propell-3-ene in an NMR tube was added 1 mL of acetonitrile containing 450 mg of dissolved silver nitrate. The mixture turned dark immediately. ^{1}H NMR spectroscopy revealed a cyclopropyl AB quartet centered at δ 0.38 ($\Delta\delta$ = 0.18 ppm, J = 5 Hz) and a broad olefinic peak at δ 5.87, whereas the [4.3.1]propell-3-ene itself showed[29] the cyclopropyl protons centered at δ 0.33 ($\Delta\delta$ = 0.07 ppm, J = 4.8 Hz) and the vinyl protons at δ 5.46 (carbon tetrachloride solution).

Buffered Acetolysis of Propellane 1. To 500 mg (1.7 mM) of **1** was added 10 mL of glacial acetic acid containing 280 mg (3.4 mM) of sodium acetate. The resulting solution was sealed in an ampule and heated at 125 °C for 1 h. After cooling, the solution was poured into an ice cold saturated potassium carbonate solution, which was then extracted three times with ether. The combined ether layers were washed with water, saturated sodium chloride solution, dried (magnesium sulfate), and concentrated under vacuum to give 460 mg of an oil. Column chromatography (20 × 0.5 in. column packed with silica gel) afforded the following products in order of elution.

a. 6-Acetoxy-10α-bromobicyclo[4.3.1]dec-1(9)-ene (24): 83 mg (18%); mp 85.5-86.5 °C (aqueous acetone); IR (CCl_4) 3020, 1734, 1632, 1250 cm^{-1}; ^{1}H and ^{13}C NMR already reported.[4f] Anal. Calcd for $C_{12}H_{17}O_2Br$: *m/e* 272.0412. Found: *m/e* 272.0411.

b. *exo*- and *endo*-7-Acetoxy-10α-bromo[4.3.1]propellane (25 and 26): 24 mg (5.1%, exo/endo = 1.7); IR (film) 1733, 1235 cm^{-1}; ^{1}H NMR δ 5.3-4.9 (m, H(7)), 3.18 (s, cyclopropyl H of **25**), 2.80 (s, cyclopropyl H of **26**), 1.98 (s, 3 H, OAc), 2.0-1.0 (m, 12 H). Anal. Calcd for $C_{12}H_{17}O_2Br$: *m/e* 272.0412. Found: *m/e* 272.0422.

c. 5-Bromomethylenecyclononanone (3): 21 mg (5.4%).

d. 1,6-Diacetoxy-10α-bromobicyclo[4.3.1]decane (20): 299 mg (53%), mp 73-74 °C (hexane); IR (CCl_4) 1730, 1250 cm^{-1}; ^{1}H NMR already reported;[4f] ^{13}C NMR ($CDCl_3$) δ 169.6, 124.4, 83.9, 66.2, 38.1, 36.3, 22.4, 20.9; mass spectrum (16 eV) parent ion not detected (*m/e* 332), but observed were peaks at *m/e* (rel int) 232 (4, P − Ac_2O), 230 (4, P − Ac_2O), 214 (17), 212 (17), 203 (6), 201 (6), 190 (19), 188 (19), 151 (95), 133 (37), 43 (100). Anal. Calcd for $C_{14}H_{21}O_4Br$: C, 50.59; H, 6.37. Found: C, 50.52; H, 6.20.

e. 1-Hydroxy-6-acetoxy-10α-bromobicyclo[4.3.1]decane (23): 12 mg (2.5%); mp 87-88 °C (ether/hexane); IR and ^{1}H NMR already reported;[4f] mass spectrum (14 eV) parent ion not detected (*m/e* 290), but observed peaks were at *m/e* (rel int.) 232 (12, P − HOAc), 230 (12, P − HOAc), 214 (7), 212 (7), 203 (19), 201 (20), 190 (37), 188 (37), 151 (100), 133 (20), 43 (69). Anal. Calcd for $C_{12}H_{19}O_3Br$: C, 49.65; H, 6.60. Found: C, 49.66; H, 6.79.

Catalytic Hydrogenation of 24. To a solution of 27 mg of **24** in 10 mL of absolute ethanol was added a catalytic amount of 10% Pd/C and the resulting mixture hydrogenated at room pressure for ca. 1 h. Subsequent filtration, solvent evaporation, and column chromatography (0.25 × 12 in. column, silica gel) yielded 26 mg (94%) of 1-acetoxy-10α-bromobicyclo[4.3.1]decane (**27**): IR (CCl_4) 1730, 1253 cm^{-1}; ^{1}H NMR δ 4.95 (d, J = 5 Hz, 1 H), 2.8-1.2 (m, 18 H); mass spectrum (16 eV) no parent ion observed, but highest peak was at *m/e* 214.0356; calcd for $C_{10}H_{15}Br$ (P − HOAc), 214.0357.

Base Hydrolysis of 24. To 4.5 mL of 90% aqueous methanol which was 0.4 M in potassium hydroxide was added 17 mg of **24.** After stirring at room temperature for 1 h, the solution was diluted with water and extracted with ether. The ether extracts were washed, dried (sodium sulfate), and the solvent evaporated. There resulted 12 mg (84%) of 10α-bromobicyclo[4.3.1]deca-1(9)-en-6-ol (**24-OH**): IR (CCl_4) 3560, 3020 cm^{-1}; ^{1}H NMR δ 5.72 (t, J = 5 Hz, H(9)), 4.85 (s, H(10)), 2.9-1.1 (m, 13 H).

Acetolysis of 24 in the Presence of Acid. As mentioned in the Results and Discussion section, prolonged buffered acetolysis of **1** led to a decrease in the amount of **24** and an increase in the amount of cyclopropylcarbinyl products (**25** and **26**). The following specific control was therefore carried out. Bridgehead olefin **24** (25 mg) was dissolved in 0.5 mL of glacial acetic acid containing 3 mg of *p*-toluenesulfonic acid. After heating at 45 °C for 11 h, the reaction mixture was worked up as described for the acetolysis of **1.** ^{1}H NMR examination of the resulting oil showed primarily a 1.7:1 ratio of **25:26,** as well as a trace of diacetate **20.**

Debromination of 24. To a solution of 21 mg of **24** in 0.5 mL of benzene was added 50 μL tri-*n*-butyltin hydride. The resulting solution was sealed in a ^{1}H NMR tube and heated at 125 °C for 10 min. The product was identified as 6-acetoxybicyclo[4.3.1]dec-1(9)-ene (**28**) on the basis of its ^{1}H NMR: δ 5.55 (t, J = 5.5 Hz, H(9)), 1.90 (s, OAc).

Base Hydrolysis of 20. To 5 mL of 90% aqueous methanol which was 0.4 M in potassium hydroxide was added 30 mg of **20.** After stirring at room temperature for 1 h, workup as described for the hydrolysis of **24** afforded 10 mg (45%) of diol **11**, mp 154–155 °C. Treatment of **20** as above at 55 °C for 30 min gave enone **7** quantitatively.

Acetylation of 23. To 20 mg of **23** was added a solution of 1 mL of acetyl chloride in 2 mL of pyridine. The resulting solution was stirred for 2 h at room temperature. The mixture was then poured into ice-water and extracted with ether. The ether extracts were then sequentially washed with 10% hydrochloric acid solution, saturated sodium bicarbonate solution, and saturated sodium chloride solution. Drying over magnesium sulfate followed by filtration and solvent evaporation left 18 mg (78%) of diacetate **20.**

Treatment of 3 under Acetolysis Conditions. In a ^{1}H NMR tube, 85 mg (0.37 mM) of ketone **3** was dissolved in 0.5 mL of glacial acetic acid containing 61 mg (0.74 mM) of sodium acetate. The tube was heated to 125 °C, and the contents monitored via ^{1}H NMR spectroscopy for a total reaction time of 1 h. Only starting material was observed. The reaction mixture was then worked up, as described for the acetolysis of **1,** to yield 81 mg (95%) of starting ketone **3.**

Buffered Acetolysis of 1 in the Presence of Acetic Anhydride. To 500 mg (1.7 mM) of **1** was added a solution of 4 mL of glacial acetic acid, 2 mL of acetic anhydride, and 280 mg (3.4 mM) of sodium acetate. The resulting solution was sealed in an ampule under nitrogen, and heated at 125 °C for 1 h. Upon cooling, the reaction mixture was worked up as already described for the acetolysis of **1.** There resulted 480 mg of colorless oil, column chromatography of which afforded 97 mg (21%) of **24** and 358 mg (63%) of **20.** Compounds **3, 23, 25,** and **26** were not formed in observable amounts. The above reaction was repeated, with the same result, in a solvent mixture which contained only 10% acetic anhydride and 2 equiv of sodium acetate.

Treatment of 20 under Dry Acetolysis Conditions. In a ^{1}H NMR tube, 120 mg of diacetate **20** was dissolved in 0.5 mL of glacial acetic acid (1% acetic anhydride) containing 2 equiv of sodium acetate. The tube was heated to 125 °C and the contents monitored via ^{1}H NMR spectroscopy for a total reaction time of 1 h. Only starting material was observed. Workup as described for the acetolysis of **1** afforded 93 mg (93%) of starting diacetate **20.**

Buffered Acetolysis of 1 in the Presence of Tetraethylammonium Bromide. The following ingredients were mixed and sealed in a tube: 100 mg (0.34 mM) of **1,** 56 mg (0.68 mM) of sodium acetate, 71 mg (0.34 mM) of tetraethylammonium bromide, 4 mL of glacial acetic acid, and 1 mL of acetic anhydride. The resulting solution was heated at 125 °C for 6 h. Workup as described for the acetolysis of **1** gave 107 mg of oil, which was analyzed via ^{1}H NMR spectroscopy. Only peaks attributable to **20, 24, 25,** and **26** could be seen; no low-field peaks which could have been due to **31a** or **dihydro-38** were detected.

1-Acetoxy-6-(3,5-dinitrobenzoyloxy)-10α-bromobicyclo[4.3.1]decane (31b). To a solution of 700 mg (2.4 mM) of **23** in 20 mL of dry pyridine was added 2.5 g (10.8 mM) of 3,5-dinitrobenzoyl chloride (recrystallized twice from ether/hexane). The mixture was stirred at room temperature for 3 days. The resulting mixture was poured into ice-water and extracted with ether. The combined ether layers were washed with 10% hydrochloric acid solution, saturated sodium bicarbonate solution, and lastly saturated sodium chloride solution. After drying (sodium sulfate), removal of solvent, and recrystallization (CCl_4/hexane), 720 mg (62%) of **31b** were obtained: mp 140–142 °C, IR (KBr) 3100, 1734, 1550, 1340 (NO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.1 (br s, 3 H), 5.45 (s, H(10)), 3.1–1.5 (m, 17 H with an acetate s at 2.13).

Buffered Acetolysis of 31b. Compound **31b** (200 mg, 0.46 mM) was dissolved in 3 mL of glacial acetic acid (1% acetic anhydride) containing 37.2 mg (0.46 mM) of sodium acetate. The mixture was heated at 125 °C and monitored by ^{1}H NMR. After the reaction had gone on for 5 days, the mixture was cooled and worked up in the manner described for the acetolysis of **1.** A yellow oil was obtained, to which was added 27 mg of dibromobenzene as an internal standard. Subsequent ^{1}H NMR examination of the products revealed a very complex array of low-field (vinyl and >CHOR) peaks; only **20** (7%) and a mixture of **25** and **26** (21%) could be identified.

The above reaction was repeated utilizing 24 mg (0.05 mM) of **31b,** 100 mg (1.2 mM, 24 equiv) of sodium acetate, and 0.1 mL of acetic anhydride in 0.5 mL of glacial acetic acid. The reaction mixture was heated at 125 °C for 4 days. After 26 h, monitoring via ^{1}H NMR spectroscopy served to detect **24** and **20.** Workup as above gave an oil which contained ≥80% **20,** some **25** and **26,** and a trace of **24.**

Acetolysis of 4. In a centrifuge tube was dissolved 525 mg (1.8 mM) of **4** in 3 mL of glacial acetic acid. The tube was tightly capped and placed in a 125 °C bath for 23 h. Upon removal and cooling, the contents of the tube were worked up as described for the acetolysis of **1.** Chromatography on silica gel gave a number (4–6) of unidentified acetates, one of which appeared to be the unsaturated analogue of **31a.** However, the first two compounds isolated were identified.

a. 1-(Dibromomethyl)bicyclo[4.3.0]deca-3,6-diene (37): 242 mg (46%); UV (hexane) end absorption only; IR (film) 3020, 1660, 1653, 782, 772, 755, 692, 654 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.05 (s, 1 H), 5.75–5.45 (m, 3 H), 3.0–2.2 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 140.6, 126.5, 125.8, 125.2, 58.3, 57.0, 37.4, 33.2, 29.8, 27.2. Anal. Calcd for $C_{10}H_{12}Br_2$: *m/e* 289.9306. Found: *m/e* 289.9298.

b. 1,6,10α-Tribromobicyclo[4.3.1]dec-3-ene (38): 58 mg (8.7%); mp 165–166.5 °C (sealed tube); IR ($CDCl_3$) 3040, 2975, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.45 (m, 2 H), 5.27 (t, J = 1.5 Hz, H(10)), 3.9–2.2 (m, 10 H). Anal. Calcd for $C_{10}H_{13}Br_3$: C, 32.21; H, 3.51. Found: C, 32.26; H, 3.55.

Debromination of 37 with Tin Hydride. In a ^{1}H NMR tube were placed 20 mg of **37** and 80 mL of tri-*n*-butyltin hydride. These were briefly heated with a heat gun, cooled, diluted with some deuteriochloroform, and the ^{1}H NMR spectrum obtained. A new narrowly split AB quartet (J = 10 Hz) at δ 3.50 (Δδ = 0.11 ppm) was observed, which was taken as evidence for the formation of 1-(bromomethyl) bicyclo[4.3.0]nona-3,6-diene (**40**).

Buffered Acetolysis of 4. In a centrifuge tube, 438 mg (1.5 mM) of **4** and 246 mg (3.0 mM) of sodium acetate were dissolved in 5.7 mL of glacial acetic acid. The resulting solution was tightly stoppered and placed in a 125 °C oil bath for 30.5 h. Removal and cooling of the tube was followed by the same workup described for the acetolysis of **1.** This procedure afforded 440 mg of crude oil, which was chromatographed on silica gel. The products, the yields of which are shown in eq 8, were eluted in the following order: **36, 33 + 34 + 35, 6, 32, 22.**

1-Hydroxy-6-acetoxy-10α-bromobicyclo[4.3.1]dec-3-ene (22): mp 88–89.5 °C; IR ($CDCl_3$) 3570, 3450, 3020, 1735, 1670, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.47 (m, 2 H), 5.08 (s, H(10)), 3.1–1.5 (m, with acetate s at 2.02, 14 H). Anal. Calcd for $C_{12}H_{17}O_3Br$: C, 49.99; H, 5.95. Found: C, 50.23; H, 5.93.

Buffered Acetolysis of 4 in the Presence of Acetic Anhydride. A sealed ampule, in which 700 mg (2.4 mM) of **4,** 390 mg (4.8 mM) of sodium acetate, and 0.5 mL of acetic anhydride had been dissolved in 5 mL of glacial acetic acid, was heated at 125 °C for 29 h. Upon removal, cooling, and opening of the tube, the contents were worked up, as described for the acetolysis of **1,** to give 690 mg of yellow oil. Column chromatography (0.62 × 24 in.) on silica gel afforded the following products in order of elution.

a. 1-(Dibromomethyl)bicyclo[4.3.0]deca-3,6-diene (37): 30 mg (4.3%).

b. 10α-Bromo-10β-acetoxy[4.3.1]propell-3-ene (36): 53 mg (8.2%); mp 51–52 °C (methanol); IR (CCl_4) 3025, 1772, 1217, 1200, 1184, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.57 (s, 2 H), 2.7–1.1 (m, 13 H); ^{13}C NMR ($CDCl_3$) δ 169.0, 123.3, 80.1, 36.0, 33.9, 27.9, 24.8, 21.0. Anal. Calcd for $C_{12}H_{15}O_2Br$: *m/e* 270.0255. Found: *m/e* 270.0265. Calcd: C, 53.14; H, 5.53. Found: C, 53.31; H, 5.67.

c. A mixture of **33, 34,** and **35** (100 mg, 15%) in a 1.0:8.7:4.7 ratio (^{1}H NMR analysis); see below for separation.

d. 1,6-Diacetoxy-10α-bromobicyclo[4.3.1]dec-3-ene (32): 480 mg (61%); mp 84–85.5 °C (hexane); IR (CCl_4) 3020, 1738, 1242 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.60 (s, H(10)), 5.49 (t, 2 H), 3.1–1.5 (m, with acetate s at 2.05, 16 H); ^{13}C NMR ($CDCl_3$) δ 169.6, 124.4, 83.9, 66.2, 38.1, 36.3, 22.4, 20.9. Anal. Calcd for $C_{14}H_{19}O_4Br$: C, 50.78; H, 5.77. Found: C, 50.91; H, 5.73.

Another acetolysis of **4** was conducted as above, utilizing 7.2 g of **4.** This produced 1.07 g of the mixture of **33, 34,** and **35.** These were resubjected to chromatography on the same column, where the eluting solvent was 0.5% ether in hexane. In order, the products were as follows.

a. 1-Acetoxy-10α-bromobicyclo[4.3.1]deca-3,6-diene (33): UV (hexane) no λ_{max} above 210 nm; IR (CCl_4) 3020, 1738, 1663, 1240

cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.66–5.40 (m, 4 H), 3.15–2.20 (m, 8 H), 2.07 (s, OAc). Anal. Calcd for $C_{12}H_{15}O_2Br$: *m/e* 270.0255. Found: *m/e* 270.0254.

b. 7-*exo*-Acetoxy-10α-bromo[4.3.1]propell-3-ene (34): IR (CCl_4) 3030, 1742, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.56 (s, 2 H), 5.32 (t, J = 8 Hz, H(7)), 3.30 (s, H(10)), 2.5–1.0 (m, with acetate s at 2.08, 11 H). Anal. Calcd for $C_{12}H_{15}O_2Br$: *m/e* 270.0255. Found: *m/e* 270.0251.

c. 7-*endo*-Acetoxy-10α-bromo[4.3.1]propell-3-ene (35): IR (CCl_4) 3030, 1742, 1660, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.62 (s, 2 H), 5.39 (d, J = 3.5 Hz, H(7)), 2.92 (s, H(10)), 2.8–1.2 (m, with acetate s at 2.10, 11 H). Anal. Calcd for $C_{12}H_{15}O_2Br$: *m/e* 270.0255. Found: *m/e* 270.0251.

Methanolysis of 36. In a round bottomed flask was dissolved, with magnetic stirring, 70 mg (0.26 mM) of **36** in 3 mL anhydrous methanolic potassium hydroxide (0.6 M) solution. After stirring for 5 min at room temperature, the solution was diluted with ether, whereupon a white precipitate formed. The contents of the flask were then "filtered" through a short silica gel column. Concentration of the filtrate gave 40 mg (86%) of an oil which appeared to be cleanly one product, namely the expected methyl bicyclo[4.3.0]non-3-ene-1-carboxylate (**44-OMe**): IR (CCl_4) 1728, 1650, 1194 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.6 (br s, 2 H), 3.65 (s, -COOMe), 2.8–1.1 (m, 11 H).

Hydrolysis of 36 in Aqueous Dioxane. Dissolved in 90% aqueous dioxane which was 0.8 M in potassium hydroxide was 14 mg (0.05 mM) of **36**. The resulting solution was stirred for 12 h at room temperature. The reaction mixture was then diluted with water and extracted thrice with ether. The combined ether extracts were washed with water and saturated sodium chloride solution, dried, and the solvent evaporated to yield 3 mg (39%) of an oil for which structure **45** ([4.3.1]propell-3-en-10-one) is proposed: IR (CCl_4) 1825 cm^{-1}.

The aqueous layer which remained after ether extraction was acidified and further extracted thrice with ether. The combined ethereal extracts were then washed with water and saturated sodium chloride solution, dried (magnesium sulfate), and stripped of solvent to yield 4 mg (47%) of *cis*-bicyclo[4.3.0]non-3-ene-1-carboxylic acid (**44**): mp 78–80 °C (aqueous acetic acid), lit.[22] 80–80.5 °C; IR (CCl_4) 1700 cm^{-1}.

Catalytic Hydrogenation of 33. To 20 mg of **33** dissolved in 25 mL of ethanol was added a catalytic amount of 10% Pd/C and the resulting mixture subjected to room pressure hydrogenation for 1 h. Filtration and solvent evaporation gave 19 mg (93%) of **27**, identical with that obtained from **24**.

Hydrolysis of 34. To 400 mg (1.5 mM) of **34** was added 40 mL of a 0.4 M potassium hydroxide in 90% aqueous methanol solution. The resulting solution was stirred for 1 h at room temperature, followed by workup as described for the hydrolysis of **24**, whereby 304 mg (90%) of 7-*exo*-hydroxy-10α-bromo[4.3.1]propell-3-ene (**34-OH**) was obtained: mp 84–85.5 °C (hexane); IR (CCl_4) 3620, 3320, 3020, 1662, 1048 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.60 (s, 2 H), 4.44 (t, J = 8 Hz, H(7)), 3.32 (s, H(10)), 2.5–1.0 (m, 9 H). Anal. Calcd for $C_{10}H_{13}OBr$: *m/e* 228.0150. Found: *m/e* 228.0150.

Oxidation of 34-OH. To 90 mg (0.39 mM) of **34-OH** in 4.5 mL of acetic acid was added 42 mg (0.42 mM) of chromium trioxide. After stirring the resulting solution for 2 h at room temperature, 2 mL of isopropyl alcohol was added to reduce the excess oxidant. The reaction mixture was then diluted with water, followed by the careful addition of solid potassium carbonate until the solution was basic. Extraction with ether, washing the extracts with water, drying (magnesium sulfate), and solvent evaporation left 72 mg (80%) of oil which solidified upon cooling and was identified as 10α-bromo[4.3.1]propell-3-en-7-one (**48**): mp 74–75 °C (aqueous methanol); IR (CCl_4) 3030, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.58 (s, 2 H), 3.40 (s, H(10)), 3.1–1.2 (m, 8 H). Anal. Calcd for $C_{10}H_{11}OBr$: *m/e* 225.9993. Found: *m/e* 225.9986.

Deoxygenation of 34-OH. To 30 mg (0.13 mM) of **34-OH** was added 0.5 mL of dry pyridine containing 50 mg (0.26 mM) of *p*-toluenesulfonyl chloride (recrystallized from hexane). Placement of the resulting solution in the freezer overnight led to the precipitation of pyridinium hydrochloride. Previous attempts to isolate **34-OTs** at this point had failed; essentially only **34-OH** had been isolated. Therefore the above-mentioned pyridine solution was diluted with 0.5 mL of dry hexamethylphosphoramide, and 83 mg (1.3 mM) of sodium cyanoborohydride added. The resulting mixture was stirred for 6 h at room temperature, whereafter it was diluted with water and extracted thrice with ether. The combined ether extracts were washed with dilute hydrochloric acid, dilute sodium bicarbonate solution, water, and saturated sodium chloride solution. Subsequent drying and concentration afforded 21 mg of oil. ^1H NMR analysis showed ca. 40% conversion to **49**.

Attempted Deoxygenation of 48. To 40 mg (0.18 mM) of ketone **48** in 10 mL of a 1:1 mixture of dimethylformamide–sulfolane was added 47 mg (0.25 mM) of *p*-toluenesulfonylhydrazine, 5 mg of *p*-toluenesulfonic acid, and 100 mg (1.6 mM) of sodium cyanoborohydride. The resulting mixture was heated for 20 h at 110 °C. Workup consisted of dilution with water, extraction with cyclohexane, drying, and evaporation. No identifiable products were observed.

To 30 mg (0.13 mM) of ketone **48** in 1 mL of ethanol was added 37 mg (0.20 mM) of *p*-toluenesulfonylhydrazine, and the resulting solution heated for 2 h at 60 °C. The tosylhydrazone was isolated by Hutchins' general procedure,[25] 34 mg (65%), mp 222–224 °C (d, ethanol). The tosylhydrazone was dissolved in 2 mL of methylene chloride and cooled to −10 °C. Catecholborane[26] (0.11 mL, 0.10 mM) was added and the solution stirred for 1.5 h. Sodium acetate (40 mg, 0.3 mM) was then added and the resulting mixture was stirred for 24 h at room temperature. After diluting with water, extracting with ether, drying (magnesium sulfate), and evaporating solvent, a yellow solid was obtained, and analyzed by ^1H NMR. There were no identifiable components.

Hydrolysis of 35. Exactly as described for **34**, 63 mg (0.23 mM) of **35** was hydrolyzed in 4.5 mL of 90% aqueous methanol (0.4 M in potassium hydroxide). There resulted 48 mg (91%) of 7-*endo*-hydroxy-10α-bromo[4.3.1]propell-3-ene (**35-OH**): mp 90–91 °C (hexane); IR (CCl_4) 3620, 3590, 3020, 1655, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.63 (s, 2 H), 4.29 (d, J = 3.5 Hz, H(7)), 2.90 (s, H(10)), 2.8–1.1 (m, 9 H). Anal. Calcd for $C_{10}H_{13}OBr$: *m/e* 228.0150. Found: *m/e* 228.0148.

Oxidation of 35-OH. To 30 mg (0.13 mM) of **35-OH** in 1.3 mL of acetic acid was added 14 mg (0.14 mM) of chromium trioxide. The oxidation and workup were performed as described for **34-OH**; 20 mg (75%) of ketone **48** was obtained.

Hydrogenation of 34 and 35. At room pressure, 36 mg (0.13 mM) of a mixture of **34** and **35** in 25 mL of ether were hydrogenated (5% Pt/C) for 1 h. Filtration and evaporation of solvent then afforded 35 mg of a mixture of **25** and **26**.

Hydrogenation of 32. At room pressure, 30 mg (0.09 mM) of **32** in 25 mL of ethanol was hydrogenated (10% Pd/C) for 1 h. Subsequent filtration and solvent evaporation left 27 mg (90%) of **20**.

Treatment of 34 and 35 under Acetolysis Conditions. In a tube which was subsequently sealed, 300 mg (1.1 mM) of **34** + **35** and 90 mg (1.1 mM) of sodium acetate were dissolved in 1.5 mL of glacial acetic acid. After heating the resulting solution at 125 °C for 47 h, the tube was cooled, broken open and worked up, as described for the acetolysis of **4**, to yield 290 mg (96%) of starting acetates **34** + **35**; ^1H NMR also showed that the ratio of **34**:**35** had not noticeably changed.

Treatment of 6 under Acetolysis Conditions. To 10 mg (0.04 mM) of **6** and 4.5 mg (0.05 mM) of sodium acetate was added 0.25 mL of glacial acetic acid in a ^1H NMR tube. The resulting solution was heated at 125 °C for a total reaction time of 21 h (monitored by ^1H NMR spectroscopy at 5-h intervals). While the solution became slightly yellow, the ^1H NMR did not indicate conversion to any of the acetolysis products (eq 8); indeed only **6** could be seen.

Treatment of 32 under Acetolysis Conditions. To 29 mg (0.09 mM) of **32** and 15.3 mg (0.19 mM) of sodium acetate was added 0.5 mL of glacial acetic acid. The resulting solution was heated at 125 °C for 23.5 h, whereafter it was worked up as described for the acetolysis of **4**. There resulted 26.3 mg (91%) of starting material, **32**. In another such experiment, 32 mg (0.10 mM) of **32** and 116 mg (1.4 mM) of sodium acetate were dissolved in 0.5 mL of acetic acid, and the resulting solution heated 36 h at 125 °C. Workup led to the recovery of 29.7 mg, the ^1H NMR of which showed a minor amount of **22**, in addition to **32**.

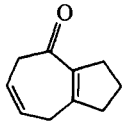
Hydrolysis of 32. To 30 mg (0.09 mM) of **32** was added 5 mL of an 80% aqueous methanolic potassium hydroxide (0.5 M) solution. The mixture was refluxed for 15 min, followed by workup as described for the hydrolysis of **24**. Obtained was 13.8 mg of oil which showed IR absorptions at 3580, 1653, and 1632 cm^{-1} and ^1H NMR absorptions at δ 6.17 (s), 5.40 (m), 4.55 (s), 3.1–1.2 (m). This implied the presence of **67** as well as **9**.

Partial Hydrolysis of 32. The following was utilized as a synthetic approach to **22**: a solution of 390 mg (1.13 mM) of **32** in 5 mL of

Table VI. Final Atomic Positional and Thermal Parameters with Their Standard Deviations for 19[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	5734(1)	6519(1)	-1678(1)	215(1)	168(1)	309(2)	103(1)	4(1)	-5(1)
O(1')	3267(6)	5522(6)	4521(8)	190(9)	158(7)	252(14)	58(7)	-30(9)	52(8)
O(2')	1420(7)	3713(7)	3592(8)	203(9)	181(9)	322(17)	66(8)	21(10)	113(10)
O(3')	-1064(7)	2114(6)	-2583(9)	232(10)	100(7)	347(16)	35(7)	-33(10)	14(8)
O(4')	-0941(6)	3447(6)	-4256(8)	186(9)	168(8)	228(13)	69(7)	-31(8)	16(8)
N(1')	4644(6)	8358(6)	1983(9)	108(8)	101(7)	307(17)	43(6)	11(10)	21(9)
N(2')	3968(7)	7165(7)	2423(10)	131(9)	119(8)	256(17)	53(7)	14(9)	15(9)
N(3')	2254(7)	4730(7)	3332(9)	154(10)	134(9)	238(16)	73(8)	37(11)	56(10)
N(4')	-0542(6)	3178(6)	-2877(9)	124(8)	97(8)	283(18)	49(7)	15(10)	6(9)
C(1)	5745(7)	9183(7)	3130(10)	113(9)	116(9)	247(17)	55(8)	21(11)	28(10)
C(2)	6452(9)	10458(8)	2626(14)	143(11)	108(10)	388(26)	61(9)	30(14)	34(13)
C(3)	7844(13)	10880(10)	2133(19)	278(20)	162(14)	631(45)	123(14)	161(25)	140(21)
C(4)	7862(17)	9945(11)	0555(16)	454(31)	200(16)	321(30)	192(20)	190(25)	140(18)
C(5)	8402(10)	9013(10)	0988(14)	192(14)	166(13)	344(25)	109(12)	33(16)	48(15)
C(6)	7495(9)	7972(8)	1347(11)	179(12)	124(10)	277(20)	95(10)	42(13)	62(12)
C(7)	7884(11)	8099(10)	3883(12)	243(16)	237(15)	255(22)	161(14)	6(15)	31(14)
C(8)	7771(13)	9117(14)	5124(14)	270(20)	351(24)	253(25)	201(20)	-52(17)	-6(18)
C(9)	6367(10)	9064(10)	5007(12)	140(11)	157(12)	213(19)	51(10)	16(13)	29(13)
C(10)	6450(11)	6911(10)	0886(12)	219(16)	117(12)	291(23)	100(13)	77(16)	76(13)
C(1')	2867(7)	6196(7)	1178(9)	118(8)	102(8)	211(16)	62(7)	31(10)	39(9)
C(2')	2043(7)	4987(7)	1510(9)	130(9)	116(9)	182(15)	70(8)	44(9)	53(9)
C(3')	0944(7)	3998(7)	0208(10)	134(10)	96(8)	243(18)	65(8)	43(11)	44(10)
C(4')	0652(7)	4191(7)	-1530(10)	125(10)	109(8)	216(17)	66(8)	20(10)	5(10)
C(5')	1434(8)	5364(7)	-1962(11)	134(10)	111(9)	219(17)	51(8)	35(11)	45(11)
C(6')	2534(7)	6357(7)	-0634(10)	131(10)	109(9)	247(18)	58(8)	23(11)	48(10)
H(2a)	644(10)	1104(8)	305(12)						
H(2b)	563(8)	1052(7)	152(10)						
H(3a)	787(8)	1178(8)	143(10)						
H(3b)	858(9)	1049(8)	159(12)						
H(4a)	792(9)	1026(9)	-038(13)						
H(4b)	697(9)	1008(8)	025(11)						
H(5a)	921(9)	923(8)	188(11)						
H(5b)	849(9)	854(8)	002(11)						
H(7a)	888(9)	818(7)	409(10)						
H(7b)	665(8)	764(8)	450(10)						
H(8a)	704(12)	939(10)	478(15)						
H(8b)	814(8)	923(8)	645(11)						
H(9a)	622(8)	975(8)	606(11)						
H(9b)	582(9)	826(9)	539(11)						
H(10)	612(9)	637(9)	145(12)						
H(N)	364(10)	734(9)	296(13)						
H(3')	321(8)	729(8)	-101(10)						
H(5')	118(9)	540(8)	-319(11)						
H(6')	036(8)	307(8)	029(11)						

[a] The heavy atom positional and thermal parameters are $\times 10^4$. The hydrogen atom positional parameters are $\times 10^3$; all hydrogen atoms were refined with fixed isotropic thermal parameters $B_H = 4.0$. The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. In this and succeeding tables, figures in parentheses correspond to standard deviations for the least significant figures. [b] Numbering as in Figure 1, with hydrogens receiving the same number as the heavy atom to which they are attached.



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methanol was mixed with 5 mL of a 90% aqueous methanolic potassium hydroxide (0.7 M) solution, and allowed to stir 1 min at room temperature. Dilution with ether was followed by neutralization with dilute hydrochloric acid solution. The ether layer was then washed with water and saturated sodium chloride solution, dried (magnesium sulfate), and concentrated to give 200 mg of oil, the ^{1}H NMR of which showed it to be mainly **22**. The oil was dissolved in hexane, and carbon tetrachloride was added, thereby precipitating the small amount of diol 9 present. Recrystallization of the remaining material from methylene chloride/hexane gave **22** (mp 89–91 °C).

1-Acetoxy-6-mesyloxy-10α-bromobicyclo[4.3.1]dec-3-ene (51). To

Table VII. Selected Bond Distances (Å) for 19

C(10)-Br	1.893 (9)	C(5′)-C(6′)	1.393 (10)
C(1)-C(2)	1.504 (12)	C(6′)-C(1′)	1.426 (10)
C(2)-C(3)	1.502 (15)	C(1)-N(1′)	1.269 (9)
C(3)-C(4)	1.517 (16)	N(1′)-N(2′)	1.399 (9)
C(4)-C(5)	1.540 (16)	C(1′)-N(2′)	1.356 (10)
C(5)-C(6)	1.501 (13)	C(4′)-N(4′)	1.450 (8)
C(6)-C(7)	1.506 (12)	N(4′)-O(3′)	1.210 (8)
C(7)-C(8)	1.484 (15)	N(4′)-O(4′)	1.221 (8)
C(8)-C(9)	1.514 (15)	C(2′)-N(3′)	1.460 (9)
C(9)-C(1)	1.546 (12)	N(3′)-O(1′)	1.225 (8)
C(10)-C(6)	1.295 (12)	N(3′)-O(2′)	1.216 (8)
C(1′)-C(2′)	1.406 (10)	N(2′)-O(1′)	2.610 (10)
C(2′)-C(3′)	1.382 (10)	C(1)-C(6)	3.059 (10)
C(3′)-C(4′)	1.384 (10)	C(1)-C(10)	3.431 (11)
C(4′)-C(5′)	1.395 (11)		

Table VIII. Selected Bond Angles (deg) for 19

C(1)-C(2)-C(3)	119.1 (10)	N(2′)-C(1′)-C(2′)	123.9 (7)
C(2)-C(3)-C(4)	114.0 (9)	C(1′)-C(2′)-C(3′)	123.3 (7)
C(3)-C(4)-C(5)	119.1 (11)	C(2′)-C(3′)-C(4′)	118.8 (7)
C(4)-C(5)-C(6)	115.6 (11)	C(3′)-C(4′)-C(5′)	120.9 (6)
C(5)-C(6)-C(7)	119.1 (7)	C(4′)-C(5′)-C(6′)	119.8 (8)
C(6)-C(7)-C(8)	116.8 (11)	C(5′)-C(6′)-C(1′)	121.0 (7)
C(7)-C(8)-C(9)	118.8 (8)	C(6′)-C(1′)-C(2′)	116.3 (5)
C(8)-C(9)-C(1)	114.5 (8)	C(1′)-C(2′)-N(3′)	121.0 (5)
C(9)-C(1)-C(2)	117.2 (6)	C(3′)-C(2′)-N(3′)	115.6 (6)
C(5)-C(6)-C(10)	122.7 (8)	C(2′)-N(3′)-O(2′)	117.9 (5)
C(7)-C(6)-C(10)	117.9 (8)	C(2′)-N(3′)-O(1′)	119.5 (7)
C(6)-C(10)-Br	126.3 (8)	O(2′)-N(3′)-O(1′)	122.6 (7)
C(2)-C(1)-N(1′)	114.4 (8)	C(5′)-C(4′)-N(4′)	119.9 (7)
C(9)-C(1)-N(1′)	128.1 (7)	C(3′)-C(4′)-N(4′)	119.0 (6)
C(1)-N(1′)-N(2′)	115.5 (7)	C(4′)-N(4′)-O(3′)	118.4 (7)
N(1′)-N(2′)-C(1′)	118.7 (7)	C(4′)-N(4′)-O(4′)	117.9 (6)
N(2′)-C(1′)-C(6′)	119.8 (8)	O(3′)-N(4′)-O(4′)	123.7 (5)

500 mg (1.74 mM) of **22** in 5 mL of methylene chloride and 1.5 mL of triethylamine was added 0.5 mL of freshly distilled methanesulfonyl chloride at −78 °C. As the mixture was warmed to 0 °C, the color changed from pale yellow to orange. After stirring at 0 °C for 2 h, the mixture was transferred to a dry ice-acetone chilled separatory funnel with the aid of cold methylene chloride. Washing with ice water, cold dilute hydrochloric acid, cold potassium carbonate solution, and saturated sodium chloride solution was followed by drying over potassium carbonate. Rotoevaporation of the solvent (water bath temperature kept below 20 °C) left an oil which solidified upon cooling. Recrystallization from methylene chloride/ether afforded 270 mg (42%) of mesylate **51**: ^{1}H NMR ($CDCl_3$) δ 5.5 (m, 2 H), 4.7 (s, H(10)), 3.18 (s, OMs), 3.1-1.2 (m, 10 H), 2.08 (s, OAc). The mesylate was thermally very labile, especially in the solid state; decomposition at room temperature was quite rapid. This instability probably accounts for the low yields and failure to clearly observe **34** and **35** in the following acetolysis.

Buffered Acetolysis of 51. From a preparation of **51** in which 1.0 g (3.48 mM) of **22** had been mesylated to give 660 mg of crude **51**, the unpurified mesylate was dissolved in 10 mL of glacial acetic acid (1% acetic anhydride) which contained 285 mg (3.48 mM) of sodium acetate. The resulting solution was heated at 125 °C for 50 h. Workup as described for the acetolysis of **4** produced 600 mg of crude material. Column chromatography of this material led to the following:

a. A mixture of **52** and **53** (70 mg) which was further separated by chromatography over alumina.

1. 1-Bromo-1,4,5,8-tetrahydronaphthalene (52): ^{1}H NMR δ 5.9 (s, 1 H), 5.6-5.4 (m, 4 H), 2.9-2.1 (m, 6 H). Anal. Calcd for $C_{10}H_{11}Br$: *m/e* 209.9972. Found: *m/e* 210.0041.

2. 1,4-Dihydronaphthalene[32] (53): ^{1}H NMR ($CDCl_3$) δ 7.9-7.2 (AA′BB′, 4 H), 5.5 (br s, 2 H), 2.9-2.6 (m, 4 H).

b. 6-Acetoxy-10α-bromobicyclo[4.3.1]deca-1,3-diene (50): 73 mg (7.8%); mp 88-90 °C; UV (hexane) λ_{max} 255 (ε 515) nm; IR (CCl_4) 3020, 1738, 1668, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.5-5.2 (m, 4 H), 3.1-2.2 (m, 8 H), 1.98 (s, OAc); ^{13}C NMR ($CDCl_3$) δ 170.0, 127.5, 126.1, 124.8 (2C), 84.7, 71.5, 45.9, 45.4, 36.4, 23.9, 22.7. Anal. Calcd for $C_{12}H_{15}O_2$: *m/e* 270.0255. Found: *m/e* 270.0258.

c. 1,6-Diacetoxy-10α-bromobicyclo[4.3.1]dec-3-ene (32): 244 mg (21%). It should be noted that the yields given are based on starting hydroxy acetate **22.**

Acetolysis of 37. In a ^{1}H NMR tube, 93 mg (0.32 mM) of **37** and 37 mg (0.45 mM) of sodium acetate were dissolved in a mixture of 1 mL of acetic acid and 0.3 mL of acetic anhydride. The solution was then heated at 125 °C for 24 h, whereafter it was worked up as described for the acetolysis of **4.** Recovered were 88 mg (>90%) of oil. ^{1}H NMR analysis indicated that ca. 25% of the starting **37** had disappeared, and primarily **34**, with some **33**, had been formed in its place.

Trifluoroethanolysis of 1. In a ^{1}H NMR tube, 147 mg (0.50 mM) of **1** and 120 mg (2.0 mM) of urea were dissolved in 0.5 mL of trifluoroethanol, and the solution heated at 90 °C for 30 min. The solution was then transferred to a flask with the aid of ethyl acetate, and the solvent evaporated. The residue was diluted with ethyl acetate, washed with water and saturated sodium chloride solution, and dried (magnesium sulfate). Solvent evaporation left 200 mg of a semisolid, which was analyzed on a Perkin-Elmer 270 GLC-mass spectral instrument. Three components, all below *m/e* 370, were observed; thus no evidence for a dimer of **2-OTFE** was obtained.

In a second experiment, 210 mg (0.71 mM) of **1** and 76 mg (0.71 mM) of 2,6-lutidine were dissolved in 0.5 mL of trifluoroethanol. The solution was heated at 90 °C for 30 min and worked up as above to afford 28 mg of oil which resisted all attempts to cause it to solidify. The oil was not investigated further.

Crystallographic and X-Ray Data. A. 5-Bromomethylenecyclononanone-2,4-dinitrophenylhydrazone (19): (2,4-DNP)$C_{10}H_{12}N_2Br$, mol wt 394.9, triclinic $P\bar{1}$, a = 11.048 (5), b = 11.997 (6), c = 7.514 (2) Å, α = 98.42 (3), β = 97.09 (3), γ = 116.70 (4)°, V = 859.73 Å^3, ρ_{calcd} = 1.35, Z = 2, Mo Kα (λ 0.709 54 Å) μ = 25.7 cm^{-1}.

Bright orange, irregularly shaped crystals were obtained by slow evaporation of a $CHCl_3$ solution. The crystals were observed to be air stable, and a single crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was mounted on a glass fiber with Duco cement and attached to a standard goniometer head. Both preliminary data and intensity data were collected using an automated four-circle diffractometer interfaced to a PDP 15 computer.[33] From six preliminary ω-oscillation photographs taken at various χ and φ settings, 13 independent reflections were chosen for input into an automatic indexing algorithm.[34] The resulting reduced cell and reduced cell scalars indicated triclinic symmetry. This was confirmed by inspection of axial ω-oscillation photographs. The unit cell parameters and their standard deviations were obtained by a least-squares fit[35] to 14 independent high angle reflections whose centers were determined by half-height techniques on a previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.709 54 Å).

Four octants of data (hkl, $hk\bar{l}$, $h\bar{k}l$, $h\bar{k}\bar{l}$) were collected within a 2θ sphere of 50°. Intensities were measured by the stationary crystal, stationary counter method, and background counts were taken at the beginning and end of each measurement by offsetting in ω-2θ. As a check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 75 reflections. The standards did not vary significantly during the course of data collection, indicating that no crystal decomposition occurred. A total of 3368 unique reflections were collected. The intensity data were corrected for Lorentz, polarization, and background effects; however, no corrections for absorption or secondary extinction were made. There were 1920 reflections having $|F_o|^2 > 3\sigma_1$, where

$$\sigma_1^2 = C_T + 2C_B + (0.03C_T)^2 + (0.03C_B)^2$$

C_T and C_B being the total count and the background count, respectively, while the factor 0.03 represents an estimate of nonstatistical errors. The estimated standard deviation in each structure factor was calculated by the finite difference method.[36]

Solution and Refinement. On the basis of a Howells, Phillips, and Rogers statistical test,[37] the unit cell was indicated to be centrosymmetric and the space group was assumed to be $P\bar{1}$, with one independent molecule per asymmetric unit. The position of the bromine atom was unambigously revealed by analysis of a sharpened Patterson map.[38] The remaining nonhydrogen atoms were located by successive structure factor[39] and electron density map calculations.[38] Approximate positions for the aromatic and methylene hydrogens were cal-

Table IX. Final Atomic Positional and Thermal Parameters with Their Standard Deviations for 22[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	$\beta\beta_{13}$	β_{23}
Br	1580(1)	3761(1)	-0417(1)	117(2)	93(1)	121(2)	-19(2)	-0(2)	-3(2)
O(1)	-0070(8)	4178(6)	2668(1)	69(10)	31(5)	192(19)	-0(6)	34(11)	5(7)
O(2)	-0280(10)	2627(6)	3121(13)	130(12)	30(5)	231(21)	-6(7)	70(13)	-6(9)
O(3)	3958(9)	2732(8)	1475(13)	85(10)	55(6)	194(20)	19(8)	24(12)	-13(9)
C(1)	3488(12)	3526(8)	2307(16)	65(13)	28(8)	147(22)	12(8)	19(14)	9(9)
C(2)	4193(15)	4358(11)	1647(22)	62(16)	50(10)	261(3C)	-9(10)	20(19)	9(15)
C(3)	3900(19)	5328(14)	2208(27)	120(28)	50(12)	205(31)	-12(13)	14(23)	1(15)
C(4)	2810(17)	5674(10)	2598(19)	104(20)	19(8)	206(30)	-3(12)	38(19)	13(12)
C(5)	1514(14)	5279(11)	2641(22)	74(16)	33(8)	229(35)	2(10)	26(19)	-3(13)
C(6)	1339(12)	4248(8)	3006(16)	58(13)	30(7)	162(23)	-5(8)	12(14)	-3(11)
C(7)	1694(20)	4032(11)	4855(29)	78(14)	49(11)	234(40)	-3(12)	38(19)	-20(16)
C(8)	3107(16)	4007(13)	5259(19)	91(19)	61(12)	167(28)	16(11)	-23(20)	-6(15)
C(9)	3769(17)	3341(15)	4166(23)	104(20)	67(11)	195(33)	22(13)	6(21)	9(16)
C(10)	2047(13)	3574(9)	1978(15)	91(4)	29(7)	107(20)	-2(8)	3(13)	-3(10)
C(11)	-0696(14)	3389(10)	2793(15)	121(18)	28(7)	109(21)	-6(10)	54(16)	-19(10)
C(12)	-2099(15)	3558(14)	2402(26)	70(16)	64(14)	287(4E)	-11(11)	23(20)	-5(18)
H(2a)	257(16)	382(10)	-003(19)						
H(2b)	510(18)	445(12)	178(23)						
H(3)	447(24)	549(18)	227(31)						
H(4)	250(20)	633(12)	239(23)						
H(5a)	088(19)	550(14)	315(23)						
H(5b)	100(17)	542(12)	183(21)						
H(7a)	148(18)	442(12)	564(21)						
H(7b)	107(27)	361(14)	502(33)						
H(8a)	322(16)	469(12)	513(19)						
H(8b)	333(19)	380(13)	612(24)						
H(9a)	444(17)	347(14)	443(23)						
H(9b)	342(16)	283(12)	404(21)						
H(10)	176(16)	294(13)	205(20)						
H(12a)	-267(18)	340(13)	322(22)						
H(12b)	-237(19)	398(13)	220(26)						
H(12c)	-189(16)	390(10)	074(21)						
H(O)	459(18)	278(13)	208(23)						

[a] The heavy atom positional and thermal parameters are $\times 10^4$. The hydrogen atom positional parameters are $\times 10^3$; all hydrogen atoms were refined with fixed isotropic thermal parameters $B_H = 4.0$. The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbering as in Figure 2, with hydrogens receiving the same number as the heavy atom to which they are attached.

Table X. Selected Bond Distances (Å) for **22**

C(1)-C(2)	1.54 (2)	C(10)-C(6)	1.50 (2)
C(2)-C(3)	1.50 (3)	C(10)-Br	1.99 (1)
C(3)-C(4)	1.31 (2)	C(1)-O(3)	1.43 (2)
C(4)-C(5)	1.47 (2)	C(6)-O(1)	1.49 (2)
C(5)-C(6)	1.53 (2)	C(11)-O(1)	1.32 (2)
C(6)-C(7)	1.56 (2)	C(11)-O(2)	1.21 (2)
C(7)-C(8)	1.51 (2)	C(11)-C(12)	1.51 (2)
C(8)-C(9)	1.49 (3)	C(1)-C(6)	2.58 (2)
C(9)-C(1)	1.55 (2)	O(2)-O(3)	2.94 (2)
C(10)-C(1)	1.52 (2)		

Table XI. Selected Bond Angles (deg) for **22**

C(1)-C(2)-C(3)	121.5 (14)	C(1)-C(10)-Br	111.0 (8)
C(2)-C(3)-C(4)	128.3 (15)	C(1)-C(10)-C(6)	117.1 (11)
C(3)-C(4)-C(5)	132.9 (14)	C(2)-C(1)-O(3)	106.7 (11)
C(4)-C(5)-C(6)	120.1 (12)	C(10)-C(1)-O(3)	108.9 (11)
C(5)-C(6)-C(7)	111.1 (12)	C(9)-C(1)-O(3)	106.0 (11)
C(6)-C(7)-C(8)	112.2 (13)	C(10)-C(6)-O(1)	111.8 (11)
C(7)-C(8)-C(9)	112.0 (14)	C(7)-C(6)-O(1)	109.5 (11)
C(8)-C(9)-C(1)	113.8 (14)	C(5)-C(6)-O(1)	99.1 (10)
C(9)-C(1)-C(2)	114.4 (13)	C(6)-O(1)-C(11)	122.3 (11)
C(9)-C(1)-C(10)	107.8 (12)	C(12)-C(11)-O(2)	121.5 (12)
C(2)-C(1)-C(10)	112.9 (11)	C(12)-C(11)-O(1)	109.1 (12)
C(5)-C(6)-C(10)	116.5 (12)	O(2)-C(11)-O(1)	129.4 (14)
C(7)-C(6)-C(10)	108.5 (10)		
C(6)-C(10)-Br	110.9 (9)		

culated from the carbon atom positions, using typical C-H distances and H-C-H angles. The remaining hydrogen atom positions were obtained by analysis of electron density difference maps. The positional parameters for all atoms, as well as the anisotropic thermal parameters for all nonhydrogen atoms, were refined by a full-matrix least-squares procedure,[39] minimizing the function $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma_F^2$. Analysis of the weights was performed via the requirement that $\omega\Delta^2$ should be a constant function of $|F_o|$.[40] The analysis indicated that very low and very high values of $|F_o|$ were slightly overweighted, and the weights were subsequently adjusted. Successive iterations of refinement using the adjusted weights reduced the conventional discrepancy index to 0.078 for the 1920 observed reflections. The scattering factors used were those of Hanson et al.,[41] except for hydrogen, where the values used were those of Stewart et al.[42] The scattering factor of bromine was modified for the real and imaginary parts of anomalous dispersion.[43]

A computer generated[44] drawing of the final model is given in Figure 1. Table VI lists the positional and thermal parameters along with their estimated standard deviations. Bond distances and angles

Table XII. Final Atomic Positional and Thermal Parameters with Their Standard Deviations for 32[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	-0051(1)	2904(1)	0725(1)	39(0)	72(1)	259(3)	-3(1)	9(1)	-23(1)
O(1)	1260(4)	1028(5)	1565(9)	63(3)	57(5)	226(15)	-1(3)	19(5)	1(7)
O(2)	1119(5)	1179(7)	4587(10)	105(6)	95(7)	229(17)	-25(5)	21(7)	2(9)
O(3)	0920(3)	4788(4)	2926(7)	42(2)	48(4)	191(14)	-6(2)	20(4)	-14(6)
O(4)	1636(4)	6369(6)	2874(9)	46(3)	77(5)	299(17)	-12(3)	31(6)	-19(7)
C(1)	1636(5)	2118(8)	1318(10)	43(3)	62(6)	184(19)	2(5)	10(6)	7(11)
C(2)	1647(7)	2082(10)	-0763(13)	56(5)	78(8)	210(23)	13(6)	22(8)	13(14)
C(3)	1907(7)	3031(10)	-1761(13)	64(5)	92(11)	187(22)	13(6)	45(8)	-7(14)
C(4)	1823(8)	4081(10)	-1525(14)	59(5)	82(10)	205(27)	13(6)	26(10)	-36(13)
C(5)	1384(7)	4633(8)	-0060(14)	45(5)	52(7)	249(25)	1(5)	36(9)	-13(11)
C(6)	1472(5)	4139(6)	1886(10)	33(3)	43(6)	153(18)	5(4)	18(6)	-1(9)
C(7)	2346(6)	4143(9)	3008(15)	33(4)	90(9)	226(23)	-0(5)	4(8)	-12(13)
C(8)	2905(6)	3246(9)	2398(15)	39(5)	82(10)	291(28)	7(5)	-3(9)	-9(13)
C(9)	2496(6)	2128(10)	2501(15)	44(5)	80(8)	275(24)	8(6)	0(9)	12(14)
C(10)	1107(5)	3010(8)	2022(12)	35(3)	58(7)	166(18)	1(4)	2(7)	10(10)
C(11)	1047(6)	0644(8)	3149(17)	62(5)	45(7)	283(30)	-6(5)	4(10)	24(13)
C(12)	0664(11)	-0433(11)	2876(24)	99(10)	82(13)	414(42)	-21(10)	-55(19)	20(19)
C(13)	1069(6)	5868(8)	3297(11)	42(4)	62(7)	150(19)	1(5)	9(7)	-8(10)
C(14)	0425(8)	6310(9)	4355(15)	58(5)	68(8)	242(25)	-15(6)	36(10)	-16(13)
H(2a)	194(7)	148(10)	-086(15)						
H(2b)	114(7)	196(10)	-146(15)						
H(3)	218(7)	267(10)	-264(16)						
H(4)	177(10)	421(13)	-060(19)						
H(5a)	068(8)	480(9)	-053(14)						
H(5b)	145(7)	532(10)	-012(17)						
H(7a)	228(7)	403(10)	424(16)						
H(7b)	267(7)	483(10)	272(14)						
H(8a)	458(7)	261(9)	160(14)						
H(8b)	329(7)	318(10)	328(15)						
H(9a)	294(7)	167(10)	225(15)						
H(9b)	245(7)	181(10)	379(16)						
H(10)	108(7)	285(10)	335(15)						
H(12a)	046(7)	-065(10)	402(16)						
H(12b)	103(8)	-076(12)	260(21)						
H(12c)	013(8)	-034(10)	264(17)						
H(14a)	043(7)	598(10)	538(16)						
H(14b)	054(7)	698(11)	427(15)						
H(14c)	-023(8)	630(9)	377(15)						

[a] The heavy atom positional and thermal parameters are $\times 10^4$. The hydrogen atom positional parameters are $\times 10^3$; all hydrogen atoms were refined with fixed isotropic thermal parameters $B_H = 4.5$. The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Numbering as in Figure 3, with hydrogens receiving the same number as the heavy atom to which they are attached.

are given in Tables VII and VIII, respectively. A complete list of calculated and observed structure factor amplitudes is available (Table XV).[46]

B. 1-Hydroxy-6-acetoxy-10α-bromobicyclo[4.3.1]dec-3-ene (22): $C_{12}H_{17}O_3Br$, mol wt 289.1, monoclinic $P2_1/n$, $a = 10.45$ (2), $b = 14.38$ (4), $c = 8.06$ (2) Å, $\beta = 93.81$ (2)°, $V = 1208.6$ Å^3, $\rho_{calcd} = 1.59$, $Z = 4$, Mo Kα (λ 0.709 54 Å), $\mu = 35.4$ cm^{-1}.

White, irregularly shaped crystals were obtained by recrystallization from a $CHCl_2$/hexane solution. The crystals were observed to be reasonably air stable (decomposing slowly if left standing at room temperature for an extended period of time), and a single crystal of approximate dimensions 0.2 × 0.2 × 0.1 mm was mounted on a glass fiber with Duco cement and attached to a standard goniometer head. Both preliminary data and intensity data were collected using an automated four circle diffractometer interfaced to a PDP-15 computer.[33] From four preliminary ω-oscillation photographs taken at various χ and φ settings, ten independent reflections were chosen for input into an automatic indexing algorithm.[34] The resulting reduced cell and reduced cell scalars indicated monoclinic symmetry. The unit cell parameters and their standard deviations were obtained by a least-squares fit[35] to 20 independent high angle reflections whose centers were determined by half height techniques on a previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.709 54 Å).

Two octants of data (hkl, $hk\bar{l}$) were collected within a 2θ sphere of 50°. Intensities were measured by the stationary crystal, stationary counter method, and background counts were taken at the beginning and end of each measurement by offsetting in ω-2θ. As a check on electronic and crystal stability, the intensities of three standard reflections were measured every 50 reflections. The standards did not vary significantly during the course of data collection, indicating that no crystal decomposition occurred. A total of 1933 unique nonzero reflections were collected. Examination of the data revealed systematic absences of $h0l$ reflections for $h + l = 2n + 1$ and $0k0$ reflections for $k = 2n + 1$, thus uniquely defining the space group as $P2_1/n$. The intensity data were corrected for Lorentz, polarization, and background effects; however, no corrections for absorption or secondary extinction were made. There were 1044 reflections having $|F_o|^2 >$

Table XIII. Selected Bond Distances (Å) for **32**

C(1)-C(2)	1.52 (1)	C(10)-Br	1.98 (1)
C(2)-C(3)	1.47 (2)	C(1)-O(1)	1.50 (1)
C(3)-C(4)	1.32 (2)	O(1)-C(11)	1.34 (1)
C(4)-C(5)	1.53 (2)	C(11)-O(2)	1.23 (1)
C(5)-C(6)	1.53 (1)	C(11)-C(12)	1.47 (2)
C(6)-C(7)	1.53 (1)	C(6)-O(3)	1.49 (1)
C(7)-C(8)	1.54 (1)	O(3)-C(13)	1.37 (1)
C(8)-C(9)	1.54 (2)	C(13)-O(4)	1.19 (1)
C(9)-C(1)	1.53 (1)	C(13)-C(14)	1.50 (1)
C(10)-C(1)	1.53 (1)	C(1)-C(6)	2.55 (1)
C(10)-C(6)	1.52 (1)		

$3\sigma_I$, where

$$\sigma_I^2 = C_T + 2C_B + (0.03C_T)^2 + (0.03C_B)^2$$

C_T and C_B being the total count and the background count, respectively, while the factor 0.03 represents an estimate of the nonstatistical errors. The estimated standard deviation in each structure factor was calculated by the finite difference method.[36]

Solution and Refinement. The position of the bromine atom was determined by analysis of an unsharpened Patterson map.[38] The remaining nonhydrogen atoms were located by successive structure factor[39] and electron density map calculations.[38] Approximate positions for the methylene hydrogens were calculated from the carbon atom positions using typical C-H distances and H-C-H angles for the C-CH_2-C group. The remaining hydrogen atom positions were obtained by analysis of electron density difference maps. The positional parameters for all atoms, as well as the anisotropic thermal parameters for all nonhydrogen atoms, were refined by a full-matrix least-squares procedure,[39] minimizing the function $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma_F^2$. Analysis of the weights was performed via the requirement that $\omega\Delta^2$ should be a constant function of $|F_o|$.[40] The analysis showed the reflections at large $|F_o|$ to be overweighted, and the weights were subsequently adjusted. Successive iterations of refinement using the adjusted weights reduced the conventional discrepancy index to 0.084 for 1044 observed reflections. The scattering factors used were those of Hanson et al.,[41] except for hydrogen, where the values used were those of Stewart et al.[42] The scattering factor of bromine was modified for the real and imaginary parts of anomalous dispersion.[43]

A computer generated[44] drawing of the final model is given in Figure 2. Table IX lists the positional and thermal parameters and their estimated standard deviations. Bond distances and angles are given in Tables X and XI, respectively. A complete list of calculated and observed structure factor amplitudes is available (Table XVI).[46]

C. 1,6-Diacetoxy-10α-bromobicyclo[4.3.1]dec-3-ene (32): $C_{14}H_{19}O_5Br$, mol wt 332.2, monoclinic $P2_1/a$, a = 16.220 (11), b = 12.325 (5), c = 7.268 (4) Å, β = 98.81 (7)°, V = 1435.85 Å^3, ρ_{calcd} = 1.53, Z = 4, Mo Kα (λ 0.709 54 Å), μ = 30.3 cm^{-1}.

White, prismatic crystals were obtained by recrystallization from hexane. The crystals were observed to be air stable, and a single crystal in the shape of a monoclinic prism with approximate dimensions 0.1 × 0.15 × 0.2 mm was mounted on a glass fiber with Duco cement and attached to a standard goniometer head. Both preliminary data and intensity data were collected using an automated four-circle diffractometer interfaced to a PDP-15 computer.[33] From three preliminary ω-oscillation photographs taken at various χ and φ settings, 11 independent reflections were chosen for input into an automatic indexing algorithm.[34] The resulting reduced cell and reduced cell scalars indicated monoclinic symmetry. The unit cell parameters and their standard deviations were obtained by a least-squares fit[45] to ten independent reflections whose centers were determined by half-height techniques on a previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.709 54 Å).

Two octants of data (hkl, $hk\bar{l}$) were collected within a 2θ sphere of 50°. Intensities were measured by the stationary crystal, stationary counter method, and background counts were taken at the beginning and end of each measurement by offsetting in ω-2θ. As a check on electronic and crystal stability, the intensities of three standard reflections were remeasured every 50 reflections. The standards did not vary significantly during the course of data collection, indicating that no crystal decomposition occurred. A total of 2240 unique nonzero reflections were collected. Examination of the data revealed systematic absences of $h0l$ reflections for $h = 2n + 1$ and $0k0$ reflections for $k = 2n + 1$, thus uniquely defining the space group as $P2_1/a$. The intensity data were corrected for Lorentz, polarization, and background effects; no correction for absorption was made. There were 1405 reflections having $|F_o|^2 > 3\sigma_I$, where

$$\sigma_I^2 = C_T + 2C_B + (0.03C_T)^2 + (0.03C_B)^2$$

C_T and C_B being the total count and background count, respectively, while the factor 0.03 represents an estimate of the nonstatistical errors. The estimated standard deviation in each structure factor was calculated by the finite difference method.[36]

Solution and Refinement. The position of the bromine was revealed by analysis of an unsharpened Patterson map.[38] The remaining atoms were located by successive structure factor[39] and electron density map calculations.[38] The hydrogen atom positions were located by inspection of electron density difference maps. The positional parameters for all atoms, as well as the anisotropic thermal parameters for all nonhydrogen atoms, were refined by a full-matrix least-squares procedure,[39] minimizing the function $\Sigma\omega(|F_o| - |F_c|)^2$, where $\omega = 1/\sigma_F^2$. Analysis of the weights was performed via the requirement that $\omega\Delta^2$ should be a constant function of $|F_o|$ and $(\sin\theta)/\lambda$.[40] The analysis indicated that the reflections at very high $(\sin\theta)/\lambda$ values were overweighted, and the weights were subsequently adjusted. Successive iterations of refinement using the adjusted weights reduced the conventional discrepancy index to 0.063 for the 1405 observed reflections. The scattering factors used were those of Hanson et al.,[41] except for hydrogen, where the values used were those of Stewart et al.[42] The scattering factor of bromine was modified for the real and imaginary parts of anomalous dispersion.[43] A comparison of the observed and calculated structure factors for the most intense reflections indicated that secondary extinction effects, while small, were significant enough to warrant correction. An extinction correction based on the relation

$$I_c/I_o = 1 + 2gI_c$$

where g is an isotropic empirical correction factor, was carried out. Three cycles of refinement with the corrected data produced a final discrepancy index of 0.062.

A computer generated[44] drawing of the final model is given in Figure 3. Table XII lists the positional and thermal parameters along with their estimated standard deviations. Bond distances and angles are given in Tables XIII and XIV, respectively. A complete list of calculated and observed structure factor amplitudes is available (Table XVII).[46]

Supplementary Material Available: a listing of observed and calculated structure factor amplitudes, Tables XV-XVII (21 pages). Ordering information is given on any current masthead page.

Table XIV. Selected Bond Angles (deg) for **32**

C(1)-C(2)-C(3)	121.2 (9)	C(1)-C(10)-C(6)	112.9 (7)
C(2)-C(3)-C(4)	132.2 (11)	C(2)-C(1)-O(1)	99.3 (8)
C(3)-C(4)-C(5)	126.7 (11)	C(10)-C(1)-O(1)	110.1 (7)
C(4)-C(5)-C(6)	118.9 (9)	C(9)-C(1)-O(1)	107.2 (7)
C(5)-C(6)-C(7)	116.3 (8)	C(1)-O(1)-C(11)	125.7 (7)
C(6)-C(7)-C(8)	112.7 (8)	O(1)-C(11)-C(12)	111.2 (11)
C(7)-C(8)-C(9)	110.5 (9)	O(1)-C(11)-O(2)	122.8 (9)
C(8)-C(9)-C(1)	110.2 (9)	O(2)-C(11)-C(12)	125.8 (12)
C(9)-C(1)-C(2)	114.4 (8)	C(10)-C(6)-O(3)	100.7 (6)
C(9)-C(1)-C(10)	108.6 (8)	C(7)-C(6)-O(3)	108.0 (6)
C(2)-C(1)-C(10)	116.6 (8)	C(5)-C(6)-O(3)	106.2 (7)
C(5)-C(6)-C(10)	116.2 (7)	C(6)-O(3)-C(13)	121.1 (6)
C(7)-C(6)-C(10)	108.0 (6)	O(3)-C(13)-O(4)	125.0 (8)
C(6)-C(10)-Br	112.5 (7)	O(3)-C(13)-C(14)	109.8 (8)
C(1)-C(10)-Br	109.6 (6)	C(14)-C(13)-O(4)	125.2 (9)

References and Notes

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(2) Taken, in part, from the Ph.D. Dissertation of Shih-Lai Lu.
(3) Fellow of the Alfred P. Sloan Foundation, 1976-1978.
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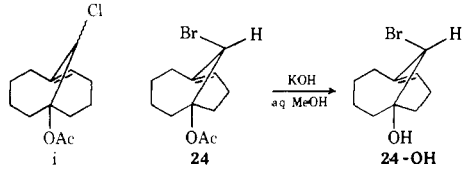

On the Mechanism of Reductive Cleavage of Aryl Phosphates[1a]

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Abstract: Evidence is presented which strongly indicates that cleavage of aryl phosphates with electron donors may occur either by a one-electron or two-electron pathway. Thus, high concentrations and greater reducing power of the electron donor favor production of arene (C-O cleavage product) while low concentrations and/or lower reducing power of the electron donor favor production of phenol (P-O cleavage product) from aryl phosphates. A rationale based on the intermediacy of a trigonal bipyramidal phosphate ester anion radical which either undergoes P-O (α) scission or is reduced further and undergoes C-O (β) scission, is presented. Comparison is also made with the electron transfer chemistry of sulfonate esters.

In our studies of the reaction of sulfonyl derivatives with electron donors we have discovered several rather different types of cleavage mechanisms. With arenesulfonamides (**1**) the initial electron transfer step is rate controlling and results in exclusive S-N cleavage.[2] This is followed by rapid further reduction resulting in overall formation of arenesulfinate and amide anions. With alkyl alkanesulfonates (**2**) initial electron transfer apparently results in a metastable substrate anion radical which, if nothing further transpires, undergoes C-O cleavage yielding alkyl radical and alkanesulfonate anion.[3] If,