Benzobicyclo[3.3.1]non-2-enes. I. Synthesis and Proton Magnetic Resonance Studies of 7-Substituted 1,3,5,5-Tetramethyl-4′-chlorobenzobicyclo[3.3.1]nonenes†

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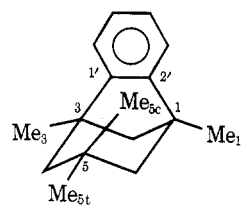
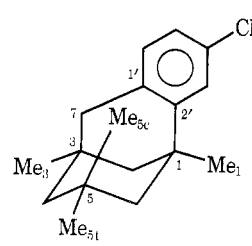
A new family of benzobicyclo[3.3.1]non-2-enes was prepared by the acid-catalyzed ring closure of *trans*-3-(*p*-chlorobenzyl)-1,3,5,5-tetramethylcyclohexanol. The benzobicyclic hydrocarbon so formed was readily converted to a series of compounds endo and exo substituted at C-7, the benzylic methylene carbon. The endo and exo alcohols and bromides all undergo rearrangements to yield a benzobicyclo[3.3.1]nona-2,8-diene and a benzobicyclo[3.2.1]nona-2,6-diene. In the benzobicyclo[3.3.1]non-2-enes, the high-field proton chemical shifts (δ_H 0.05–0.36) of Me_{5c} (the C-5 methyl group syn to the aromatic moiety) are primarily dependent upon aromatic ring current effects. The shifts in a particular derivative are also affected significantly by the nature and stereochemistry of the substituent at the benzylic methylene carbon; substitution results in both upfield and downfield shifts. The methyl ^1H NMR substituent effects in the benzobicyclo[3.3.1]nonene systems compare well with those which occur in the superficially similar adamantane ring system, and this is taken to imply that the steric interactions inherent in both systems are similar, i.e., the cyclohexane ring in the benzobicyclo[3.3.1]nonenes is chairlike in shape.

Previous and current work in this laboratory has been concerned with the synthesis and NMR studies of benzobicyclo[3.2.1]octenes such as 1.[1]



1

This family of compounds has proven interesting for a variety of NMR spectral studies, particularly those concerning the perpendicular diamagnetic shielding associated with aromatic substituents (the so-called "ring current" effect).[2] In compound 1, the proton resonance of Me_{5c} occurs at an unusually high field, δ −0.15, owing to this methyl being in the shielding region of the aromatic ring current.[1] Several chlorinated derivatives of 1 also show proton shifts similar to that of the parent hydrocarbon.[3] In naphtho analogues of 1, the Me_{5c} resonance appears at even higher fields, the range observed being δ −0.32 to −0.41, depending on the particular case.[1] As an extension of these studies, a new family of chlorobenzobicyclo[3.3.1]nonenes such as 2 and derivatives have been synthesized and are now reported.



2

Two theories concerning "ring current" effects have been proposed: the classical theory of Johnson and Bovey[2a] and the quantum mechanical theory of McWeeny.[2b] An extension of McWeeny's theory to include protons above the plane of the aromatic ring has recently been presented by Haigh.[2c] Predictions of the chemical shifts of protons in the plane of the aromatic ring have met with considerable success.[2d] However, the same method does not predict the chemical shifts of protons located above the ring with useful accuracy, as the chemical shifts are greatly underestimated.[2e] Part of the problem associated with such calculations involves a lack of experimental data on model compounds of well-defined geometries.

Since both the ring systems of 1 and 2 are essentially rigid, they can serve as suitable models for calculations of "ring current shifts". In addition, the benzobicyclo[3.3.1]nonene ring system 2 is strain-free (as judged from molecular models as well as from aromatic ring coupling constant data) in virtue of the additional carbon atom "inserted" between C-3 and the aromatic ring (as in 1). Therefore, these benzobicyclo[3.3.1]nonenes allow the study of perpendicular ring currents in systems which are not affected by any possible ring strain. (The possible effects of ring strain on aromatic ring current shifts remain to be assessed.) In this new family of compounds, these perpendicular ring current effects are also studied at slightly different geometrical positions relative to the aromatic moiety of 1.

Other reasons for the preparation and study of this series of compounds include (1) the investigation of the effect that substitution at the benzylic carbon (C-7) has upon the chairlike nature of the cyclohexyl ring; (2) the examination of the magnitude and direction of the shifting effect of other group (and bond) anisotropies, such as those of bromine and hydroxyl; and (3) the applicability of ^{13}C NMR substituent effects. This latter area will be reported separately, the present paper being confined to a discussion of the synthesis, characterization, and ^1H NMR studies of this new class of compounds.

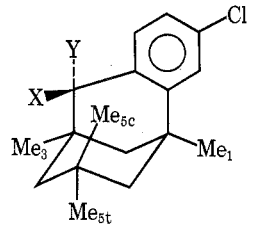
Synthesis. It was decided to study the 4′-chlorobenzobicyclo[3.3.1]non-2-enes rather than the unhalogenated analogue in order to obtain spectra whose aromatic proton patterns would be more conveniently analyzed, as well as to enhance desirable crystallinity in the compounds. No substantial ring current shift changes are introduced by the chlorine, as assessed by a less extensive study of the unchlorinated analogue.

The synthetic route used to obtain the parent compound of this family of benzobicyclo[3.3.1]nonenes, 2, is outlined in Scheme I. A two-step procedure was employed to prepare ketone 4 since the direct, copper(I)-catalyzed conjugate addition of *p*-chlorobenzylmagnesium chloride to iso-

† Taken in part from the Ph.D. Dissertation of M. J. Shapiro, Texas A&M University, 1974.

‡ Predoctoral Fellow of The Robert A. Welch Foundation.

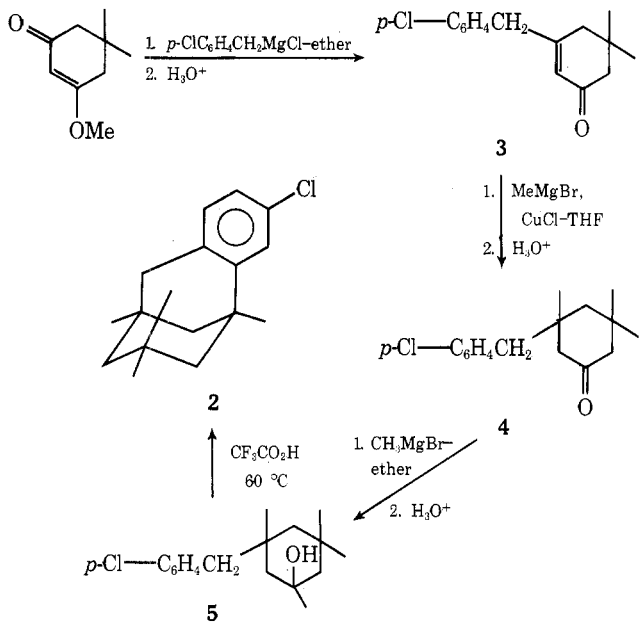
Table I. Proton Chemical Shifts (δ_H) for the Methyl Groups of the Benzobicyclo[3.3.1]non-2-enes[a]



Compd	X	Y	$\delta_{Me_{5c}}$	$\delta_{Me_{5t}}$	δ_{Me_3}	δ_{Me_1}	δ_X	δ_Y
2	H	H	0.30	0.82	1.01	1.30	2.72	2.61
6	Br	H	0.36	0.88	1.30[b]	1.32[b]		5.02
7	H	Br	0.12	0.84	1.30[b]	1.35[b]	5.30	
8	Br	Br	0.25	0.92	1.56	1.34		
9	H	OH	0.11	0.82	1.02	1.30	4.40	
10	OH	H	0.23	0.88	1.10	1.30		4.44
11	CO		0.29	0.90	1.11	1.38		
12	OMe	OMe	0.05	0.89	1.26[b]	1.30[b]	3.67	3.00
13	OH	Me	0.22	0.89	1.03	1.30		1.42

[a] Values refer to 5% w/v solutions in carbon tetrachloride. [b] Assignments in same row may be reversed; see text.

Scheme I

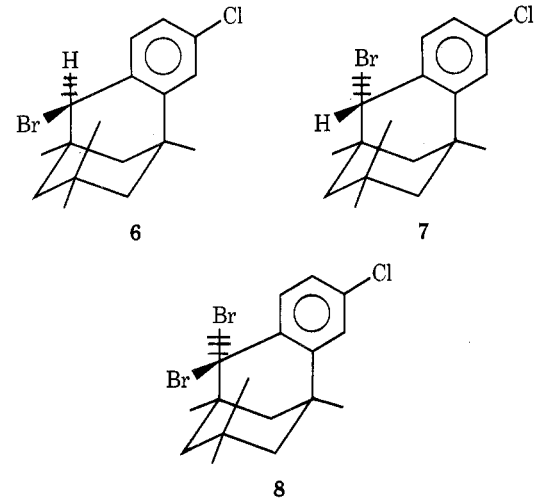


phorone does not proceed in adequate yield (in either diethyl ether or tetrahydrofuran as solvents). It was found that the direct copper(I)-catalyzed conjugate addition of methyl Grignard to 3 proceeded in markedly superior yield (50%) when tetrahydrofuran (THF) was used as a solvent rather than diethyl ether (yield 11%). This parallels the dramatic improvement in the yield of conjugate addition product of phenylmagnesium bromide and isophorone rather than the disappointing, negative results which obtain when THF is used in an analogous α-naphthyl Grignard addition to the same substrate.[4] The nature of this solvent effect remains, for the time being, obscure.

Addition of methylmagnesium bromide to 4 yielded a single tertiary alcohol 5, mp 52–54 °C. The isomer formed is the alcohol which is expected by minimal steric interaction in the transition state (i.e., the alcohol having an axial hydroxyl and an equatorial benzyl moiety), especially since the starting ketone has been shown via lanthanide-induced shift (LIS) data to be in a conformation where the benzyl group is equatorially disposed.[5] No trace (i.e., <1%) of the other alcohol isomer could be found. The lack of the other alcohol isomer is noteworthy in view of the results obtained when methylmagnesium bromide is added to the 3-aryl-3,5,5-trimethylcyclohexanones. In several such cases, *both* isomers are invariably produced in comparable yields.[6] The stereochemical implications of the present observation with 4 are under investigation.

The parent benzobicyclononene, 2, was prepared by the acid-catalyzed cyclization of alcohol 5, similarly to the method previously used to prepare the benzobicyclo[3.2.1]octenes.[1] It was found that excellent yields (ca. 80%) of the bicyclic hydrocarbon 2 could be obtained by adding the neat alcohol to trifluoroacetic acid heated to 60 °C.

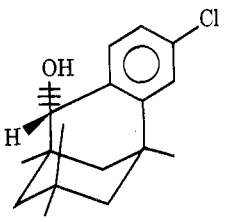
Compound 2 was found to be very susceptible to bromination at the benzylic methylene group (C-7). Thus, reaction with 1.2 molar equiv of bromine in carbon tetrachloride yielded a mixture of two monobrominated products, 6 and 7, and the *gem*-dibromo compound 8, as shown below. The relative yields were 65, 30, and 5%, respectively.



The dibromo compound, 8, could be produced exclusively either by brominating a mixture of 6 and 7 or by adding an excess of bromine to 2. In any event, 8, mp 142–144 °C, is easily isolated by crystallization, but 6 and 7 could not be obtained separately in pure condition. (Spectral data for these compounds, then, were obtained on mixtures of the two isomers.) Unsuccessful attempts to effect this separation included distillation, crystallization, and column, thin layer, and gas chromatographies.

In the case of column chromatography the mixture of monobromo compounds reacted on the alumina (or other)

column to yield an alcohol analogue, mp 133–134 °C, shown to be the exo isomer **9**, as well as two olefinic hydrocarbons (vide infra). The exo nature of the hydroxyl moiety in **9** is demonstrated by the NMR and LIS results presented below. The endo-hydroxyl isomer is probably formed on the column also, but is not isolated for reasons discussed below.



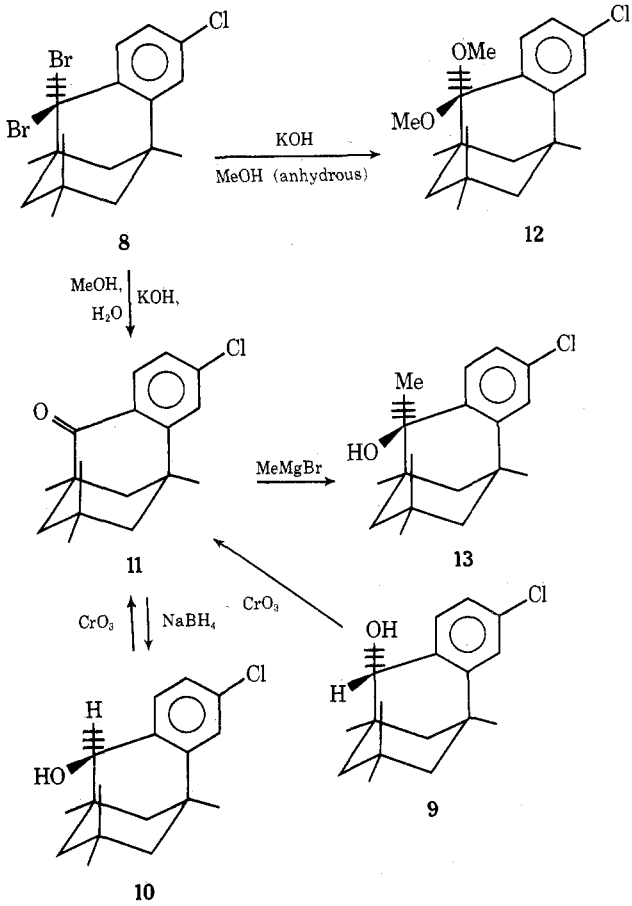
9

The isomeric endo alcohol, **10**, mp 102–104 °C, was prepared in quantitative yield by the sodium borohydride reduction of the corresponding ketone **11**, mp 74–75 °C, which itself was obtained in high yield by the acidic, aqueous methanol hydrolysis of **8**. When anhydrous conditions were maintained in the methanolysis of **8**, the dimethoxy ketal **12**, mp 79–80 °C, was obtained.

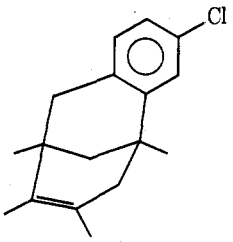
The exo–endo isomeric relationship of the two alcohols **9** and **10** was established by oxidation to the same ketone, **11**. In addition, a single tertiary methyl alcohol **13**, mp 79–80 °C, analogous to **10**, was formed on the addition of methyl Grignard to **11**. Only the one isomer is formed, as expected for steric reasons.

The structures of these benzobicyclo[3.3.1]non-2-ene derivatives are demonstrated by these and other chemical interrelations as summarized in Scheme II, as well as by the detailed ^1H NMR studies that follow and the ^{13}C NMR results to be presented anon.

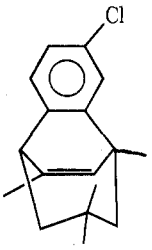
Scheme II



As mentioned above, all attempts to isolate the separate monobromo compounds **6** and **7** by column chromatography yielded two olefinic bicyclic hydrocarbons, **14** and **15**, shown to derive from either of the alcohols **9** and **10**. The same two olefins arise when either alcohol **9** or **10** is treated with *p*-toluenesulfonic acid in refluxing benzene.



14



15

The structures of olefins **14** and **15** are readily assigned on the basis of the mechanisms outlined in Scheme III, and by a detailed analysis of their observed NMR spectral properties.

The first step in the formation of **14** from the initially formed carbonium ion **16**, giving ion **17**, finds close analogy in the work of Berson et al.[7] The conversion of ion **17** to olefin **14** via ion **18**, as well as the ring expansion of ion **16** to olefin **15**, are, of course, completely unexceptional. The involvement of a carbonium ion intermediate in these reactions is further substantiated by the results of the treatment of **9** or **10** with trifluoroacetic acid, whereby the same mixture of epimeric trifluoroacetates is obtained.

The absence of alcohol **10** in the products of the chromatographic decomposition, then, is probably due to its carbonium ion forming much more rapidly owing to steric relief in the transition state. Similar results are observed on the dehydration of axial and equatorial cyclohexanols.[8]

Results and Discussion

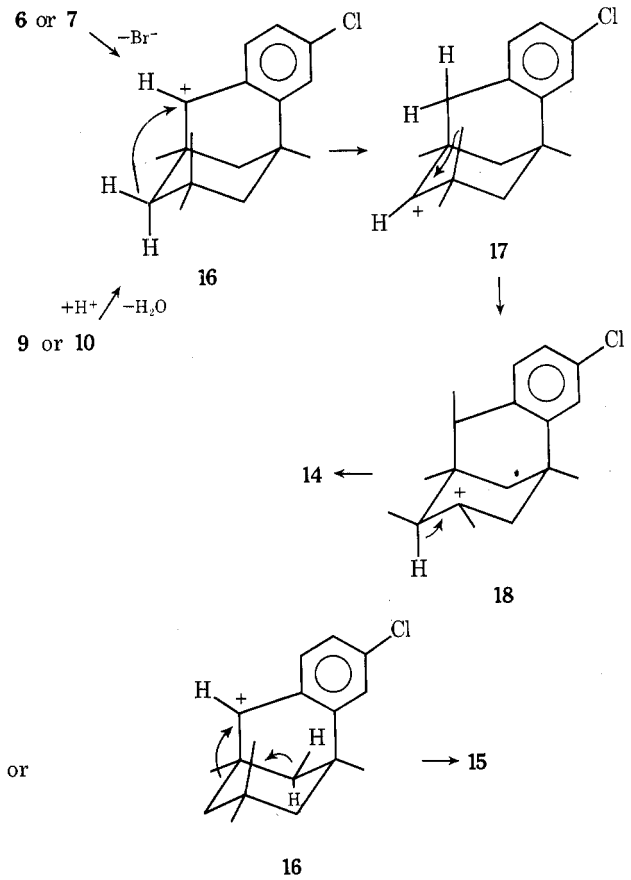
In this section are presented the methyl proton chemical shifts, along with data for the benzylic protons, and that for selected aromatic shifts. The cyclohexane-ring methylene proton shifts were not obtainable because of extensive overlap with each other and the very small shifts between the different proton types. Similar problems precluded the presentation of the aromatic proton shifts in most of the cases other than those cited herein. The methyl and benzyl proton chemical shifts for the benzobicyclo[3.3.1]non-2-enes are summarized in Table I.

The methyl proton resonances at highest and lowest fields are readily assigned to Me_{5c} and Me_1 by analogy with the data of the benzobicyclo[3.2.1]octenes and their precursors.[1] The high-field and low-field nature of these methyl shifts arise respectively from the "out-of-plane" diamagnetic and the "in-plane" paramagnetic ring current effects.[2]

The two remaining methyl group shifts, found at essentially normal positions, may be assigned by a consideration of substituent effects involving C-7. Regardless of the detailed weight of the different factors involved (vide infra), a substituent at C-7 would have a much greater effect on the resonance of Me_3 than it would have on Me_{5t}, for reasons of proximity. The other assignments in Table I, then, are based on the essential consistency of one methyl resonance (δ 0.84–0.92), which is then assigned to Me_{5t}. Because of the small shift differences observed for the Me_1 and Me_3 resonances in **6**, **7**, and **12**, the assignments may be reversed for these compounds.

On the basis of the methyl shift assignments of Table I, the interesting variation of the Me_{5c} chemical shift with the nature and orientation of the C-7 substituent may be ex-

Scheme III



amined. Of particular interest are the isomeric bromides **6** and **7** and the isomeric alcohols **9** and **10.**

The use of lanthanide-induced shifts (LIS) permitted the assessment of the orientation of the hydroxyl function in the two isomeric benzobicyclo[3.3.1]nonene alcohols **9** and **10.** Lanthanide shift reagent (LSR) binding is expected to be more facile in the exo case **9** because the binding site is more accessible sterically. Therefore, the LIS observed in the exo alcohol should be larger than that observed for otherwise comparable protons in the endo case, **10.** In Table II are presented the LIS, as λ values (slopes, in parts per million) for the methyl and benzyl proton types of **9, 10,** and **13.** Although detailed analyses of LIS curves were not performed for these compounds, insight into the benzyl substituent stereochemistry can be obtained by simple examination of λ values, the initial slopes of the LIS doping curves.[6] These semiquantitative experiments have been shown to be valid to explore stereochemical relationships. A larger λ value has the significance of greater LSR binding—for the same functional group (here, hydroxyl)—thus affording a direct, albeit qualitative, assessment of steric hindrance at the binding site.

Of special interest is the LIS observed for H_7, which is equidistant from the binding site in **9** and **10.** It was found that the LIS for this proton was substantially larger in one isomer (**9**) than in the other (**10**). Also, the Me_1 and Me_3 λ values were larger in the compound having the larger H_7 λ value. The compound having the larger λ value for H_7, Me_1, and Me_3 is thus the exo isomer **9.** Conversely, the consistently smaller λ values observed for the other isomer support its configurational assignment as the more hindered endo alcohol, as indicated in structure **10.** Further support for these configurational assignments is found in the λ-value data for the tertiary alcohol analogue of **10,** viz., **13.** For **13,** which must surely have the endo hydroxyl configuration on mechanistic grounds, the λ values resemble those of **10** much more closely than those of **9,** at least for the larger Me_1 and Me_3 λ values. These conclusions derived from the LIS data are consistent with the chemical origin of these compounds, e.g., an endo alcohol is expected upon reduction of ketone **11,** via transfer of a hydride ion from the less hindered side of the molecule. Confirming the LIS and chemical results, the isomer **9,** assigned as exo, shows a singlet H_7 (benzylic) resonance as compared to **10,** assigned as endo, which shows a doublet signal for H_7 owing to slow exchange occurring in the more sterically hindered hydroxyl function.

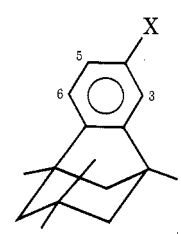
Table II. λ Values (Slopes, ppm) for Methyl and Benzyl Protons of 9, 10 and 13[a]

Compd	Me_1	Me_3	Me_{5c}	Me_{5t}	H_{X_7}
9	0.50	1.36	0.55	0.31	3.54
10	0.30	0.87	0.61	0.23	2.42
13	0.33	0.82	0.44	0.33	1.93[b]

[a] Values refer to $Eu(fod)_3$-doped solutions in carbon tetrachloride. [b] Me_7 (benzylic methyl group).

Assuming the stereochemical nature of the alcohols to be correctly assigned and that hydroxyl and bromine are grossly similar in aspects such as electronic and steric effects, the endo and exo structures (**6** and **7**, respectively) can be assigned for the bromo compounds on the basis of the proton chemical shift of Me_{5c}, i.e., the compound having the higher field methyl resonance is the exo isomer.

The *aromatic proton chemical shifts and coupling constants* for two representative benzobicyclo[3.3.1]nonenes, **2** and **8**, were obtained with the aid of the computer program ITRCL. (ITRCL is a two-part iterative computer program similar to LAOCN3,[9] and is available as part of the Nicolet 1085 data system in our JEOL PFT-100 Fourier transform spectrometer system.) These δ and *J* values are summarized in Table III, along with the data for similar benzobicyclo[3.2.1]octenes, **1** and **19.**



1, X = H
19, X = Cl

A detailed study of the aromatic coupling constants and chemical shifts for most of the other benzobicyclo[3.3.1]nonenes could not be performed owing to insufficient separation of the chemical shifts which in some cases led to deceptively simple spectra, while in other cases, too many unresolvable line frequencies were obtained. From the coupling constant data for **2** and **8** there is no evidence for ring strain in the bicyclo[3.3.1]nonenes analogous to that sometimes manifest in strained systems like the benzobicyclo[3.2.1]octenes (cf. studies of Cooper and Manatt[10a] and Castellano and Kostelnik[10b]). However, even in such strained systems as **1** and **19,** coupling constants are markedly substituent dependent, one chlorine serving to effect substantial changes which render the observed values near normal.

Evaluation of the Chemical Shift Data. As must obviously be the case, the proton chemical shift data in Table I serve to confirm that the benzobicyclo[3.3.1]nonenes all have essentially the same skeletal structure. The problem, then, is how to account for the considerable variation ob-

Table III. Chemical Shifts (δ_H) and Coupling Constants for 1, 2, 8, and 19

	δ_H			
	2	8	19[a]	1[b]
3	7.24	7.09	6.92	6.93
4				7.06
5	7.03	7.19	7.06	7.06
6	6.86	7.98	6.92	6.93
	Coupling constants, Hz			
$^3J(3,4)$				7.406
$^4J(3,5)$	2.309	2.248	1.993	1.117
$^5J(3,6)$	0.253	0.302	0.464	0.662
$^3J(4,5)$				7.497
$^4J(4,6)$				1.117
$^3J(5,6)$	8.241	8.636	7.873	7.406

[a] B. L. Shapiro and G. R. Sullivan, unpublished data. [b] Taken from the Ph.D. Dissertation of M. J. Gattuso, Texas A&M University, 1970.

served for $\delta_{Me_{5c}}$ with the nature and/or orientation of the substituent at the benzylic carbon, C-7. For instance, not only is there a substantial difference, 0.12 ppm, in the proton chemical shift for Me_{5c} in **9** and **10** but it is particularly noteworthy that the Me_{5c} resonance in both of these compounds have Me_{5c} shifts at *higher* fields than that of the parent compound **2**, by 0.19 and 0.07 ppm, respectively.

It is convenient to assess the changes in the Me_{5c} chemical shift in terms of the operation of one or more of the three factors of eq 1

$$\Delta\delta_{obsd} = \Delta\delta_E + \Delta\delta_A + \Delta\delta_G \quad (1)$$

where $\Delta\delta_E$, $\Delta\delta_A$, and $\Delta\delta_G$ are respectively the changes in the chemical shift due to electric field effects, anisotropy effects, and geometry effects. The first two of these effects are intended to have their usual connotations.

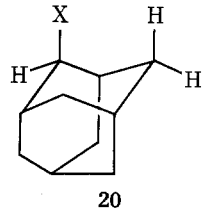
By "geometry effect" we mean the change in shift due to Me_{5c} having its position relative to the aromatic ring altered because of a change in steric crowding, here, because of the substituent at C-7. Since an upfield shift in the Me_{5c} resonances is observed, it is assumed that this alteration would be in a direction which places Me_{5c} closer to the face of the aromatic ring. An examination of Dreiding models indicates that a modest variability in the position of this methyl group due to a flexing of the cyclohexane ring is not energetically prohibitive.

In order to facilitate the discussion of the factors in eq 1, the endo and exo isomer pairs **6** and **7** and **9** and **10** will be discussed separately. Let us consider the exo isomers **7** and **9** first since it appears that their Me_{5c} chemical shifts can be the more easily understood. Of the three factors mentioned above, the "geometry effect" should be absent, because the exo nature of the substituent introduces no new steric interactions vis-à-vis Me_{5c}. In addition, since the C–O and C–Br bonds point away from Me_{5c}, the electric field effect is probably small. By process of elimination, this leaves some anisotropic effect (either atom or bond anisotropies) to be considered.

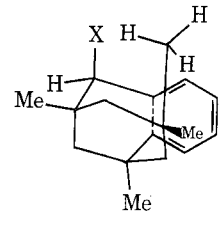
Anomalous shifts to higher field caused by the incorporation of an electronegative atom for hydrogen in a molecule are not without precedent, and have important structural implications. Several examples exist, dating from the earliest days of NMR, and although not completely understood, this effect has been attributed to the anisotropy of the substituent.[11] Schleyer found that the chemical shifts of protons in the δ positions of 1-substituted adamantanes are anisotropy controlled, i.e., a plot of substituent electronegativity vs. δ_{obsd} follows the order of the substituent atom anisotropies, that is, shifts to higher field with increasing electronegativity.[12] Similar shifts have been noticed in 2-substituted adamantanes.[13] The $\Delta\delta_H$ value (where $\Delta\delta_H = \delta_X - \delta_2$, negative values indicating upfield shifts) observed for the methylene protons at the δ positions in 1-hydroxyadamantane (−0.14 ppm) and 1-bromoadamantane (−0.05 ppm)[12] compare well with that found in **9** (−0.19 ppm) and **7** (−0.18 ppm), respectively. The bond pathway is different for the 1-substituted adamantane system than for **7** and **9**, but the spatial relationships between the exo substituent and the protons whose resonances are affected are similar in both types. Since anisotropic field effects are transmitted through space, one might expect that the chemical shift change for these systems would be similar, as is observed.

In any event, if anisotropy and electric field effects are important, then one should be able to predict the chemical shift of Me_{5c} using the additivity of substituent effects as, for example, in a dihydroxy-substituted compound. Although this particular molecule does not exist, a very similar compound, viz., the dimethyl ketal **12**, is in hand. Here the chemical shift of Me_{5c} is δ 0.05 and compares to a remarkable degree with the predicted value of δ 0.04. This value is arrived at by adding the $\Delta\delta_H$ values for **9** and **10** and adding this number to the chemical shift observed for Me_{5c} in **2**. Similarly, using the monobromo compounds to predict the shift of Me_{5c} for the dibromo compound **8**, one obtains δ 0.14 vs. δ 0.25 observed. Although the predicted value in this example is not as accurate as the first case, it is in the right direction. Perhaps the discrepancy can be at least in part accounted for by effective anisotropy changes arising from interactions between the two large and polarizable bromine atoms.

The observed shifts of the Me_{5c} resonance in the endo isomers **6** and **10** are much more difficult to evaluate because all three factors, geometry, anisotropy, and electric field effects, may play an important role. Here, the endo substituent is close in space to Me_{5c}. Thus, the position in space of Me_{5c} might be somewhat altered, causing $\Delta\delta_G$ to become important. However, since the Me_{5c} chemical shift in the endo bromo compound **6** is at lower field than that observed in both the endo hydroxy compound **9** and the parent compound **2**, the "geometry effect" is probably unimportant in these endo-substituted compounds also. A good model to assess the remaining two factors in eq 1 can be found in 2-hydroxyadamantane. Here an x-ray crystallographic study has shown that the hydroxyl function does not perturb the adamantane skeleton.[14] For comparison with the benzobicyclo[3.3.1]nonenes, one is particularly interested in the induced shift changes at the γ protons. As shown in the figure below, the *spatial* relationship between these protons and the functional group is very similar to that found (on a time-averaged basis) for the Me_{5c} protons in the endo-X bicyclo[3.3.1]nonenes. It was found that a



20



6, X = Br
10, X = OH

downfield shift was induced for the endo γ proton (syn to the substituent X) in the 2-substituted adamantane **20**, while for the corresponding exo proton an upfield shift is observed.[13] If we make the crude but simplifying assump-

tion that the protons of the methyl group Me_{5c}, in the endo-substituted benzobicyclo[3.3.1]nonenes, are in analogous position to the endo proton of **20** one-third of the time and in analogous position to the exo proton of **20** two-thirds of the time, then one should be able to predict (using the data for 2-substituted adamantanes[13]) the chemical shift of Me_{5c} in the endo benzobicyclononenes. Doing so, one obtains a chemical shift for Me_{5c} of δ 0.62 for **6** and δ 0.17 for **10**. The direction predicted for the induced shifts of both of these compounds is consistent with that observed, although the magnitude of the change clearly indicates at least the operation of additional factors. In **10** then, the anisotropic field effect is probably more important than the electric field effect (deshielding) and hence an upfield shift is observed. The situation in **6** is probably reversed with the electric field effect dominating. Final analysis concerning the nature of the $\Delta\delta_{Me_{5c}}$ awaits structure determinations by x-ray crystallography, so as to permit assessment of the possible importance of the $\Delta\delta_G$ factor of eq 1.

^{1}H NMR Chemical Shifts and Assignments for Benzobicyclononene Derivatives. The methyl proton chemical shifts of **14** and **15** are given in Table IV.

Table IV. Proton Chemical Shifts (δ_H) for the Methyl Groups of 14 and 15

	Me_{5c}	Me_{5t}	Me_3	Me_1	Other
14			1.12	1.34	1.54 (Me_4 and Me_5)
15	0.15	0.80	1.80	1.42	

Assignments for the methyl protons in **14** were made by comparison with **2**, i.e., Me_1 and Me_3 are in analogous positions to Me_1 and Me_3 in **2** and should have similar proton chemical shifts. The remaining doubly intense methyl resonance, δ 1.54, is assignable to the two olefinic methyl groups Me_4 and Me_5.

A similar procedure was used to assign methyl groups in **15**. Here, Me_1, Me_{5c}, and Me_{5t} are in analogous positions to the three methyl groups in **2**, and are readily assigned. The remaining methyl resonance at δ 1.80 is therefore assigned to the olefinic methyl group Me_3. The lower field resonance observed for this olefinic resonance as compared to those found in **14** is consistent with this methyl being near the edge of the aromatic ring.

Experimental Section

Capillary melting points were determined on a Mel-Temp melting point apparatus. All boiling and melting points reported below are uncorrected. Infrared spectra were determined with a Beckman Model IR 8 infrared recording spectrophotometer, calibrated by means of the 1603-cm^{-1} absorption of a polystyrene film. Microcombustion analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

All NMR spectra were run on a Varian HA-100 nuclear magnetic resonance spectrometer in the frequency sweep mode at an ambient probe temperature of 30 °C. Shifts were measured on carefully precalibrated chart paper and were estimated to be accurate to ±0.01 ppm or better.

The LAOCN3 and ITRCL analyses were carried out on samples vacuum degassed by means of several liquid nitrogen freeze–thaw cycles. Spectral parameters were obtained on an IBM 360-65 digital computer in the double-precision mode or a Nicolet 1085 data system to a root mean square error of less than 0.05 Hz.

The mass spectral data were obtained with a Consolidated Electronics Corp. Model 21-110B mass spectrometer, operated by Mr. G. Gabel of the Texas A&M University Department of Biochemistry.

3-(*p*-Chlorobenzyl)-5,5-dimethyl-2-cyclohexen-1-one (3). To 24.0 g (1 g-atom) of magnesium shavings in 200 ml of anhydrous ether was slowly added 170.0 g (1.05 mol) of *p*-chlorobenzyl chloride (Aldrich Chemical Co.) dissolved in 250 ml of ether. After all the magnesium had reacted, 100 g (0.67 mol) of dimedone methyl ether (DME) in 100 ml of ether was added slowly. The reaction mixture became very viscous and yellow in color. Stirring was continued overnight and the yellowish solution was hydrolyzed with 6 N hydrochloric acid. The solvent was removed and the crude product distilled. The fraction boiling at 130–144 °C (0.25 Torr) was collected and proved to be greater than 90% pure **3**, the impurity being *p,p'*-dichlorobibenzyl, yield 94.0 g (0.36 mol, 54%). This material was used without further purification. Recrystallization from hexane afforded pure material as needles: mp 84–85 °C; ir (CCl_4) 1660 cm^{-1} (C=O stretch); NMR (10% in CCl_4) δ (methyls) 0.94, δ (benzylic H) 3.22, δ (olefinic H) 5.80; mass spectrum *m/e* (rel intensity) 248 (74, M^+), 192 (100), 157 (50), 129 (50), 67 (32).

Anal. Calcd for $C_{15}H_{17}OCl$: mol wt, 248.906788. Found: mol wt, 248.907774.

3-(*p*-Chlorobenzyl)-3,5,5-trimethylcyclohexanone (4). Addition of *p*-Chlorobenzylmagnesium Chloride to Isophorone. To a flamed-out, 1000-ml, three-necked flask, equipped with a mechanical stirrer, condenser, and dropping funnel, and swept with a slow stream of nitrogen, were added 12.0 g (0.5 g-atom) of magnesium shavings and 300 ml of anhydrous ether. A solution of 80.0 g (0.5 mol) of *p*-chlorobenzyl chloride in 100 ml of ether was added dropwise with vigorous stirring over a period of 1 h. An additional 10 g of the benzyl chloride was added to allow all of the magnesium turnings to react. The reaction mixture was allowed to reach room temperature, 1.0 g (1 mol %) of freshly prepared cuprous chloride was added, and the resulting black solution stirred for 30 min. The reaction mixture was cooled by means of a dry ice–chloroform bath (maintained at ca. −40°), and stirred for 30 min. Isophorone (69.0 g, 0.5 mol) in 100 ml of dry ether was added dropwise, while maintaining the cooling bath. After addition of the isophorone was complete, the reaction mixture was stirred for an additional 4 h and allowed to reach room temperature and stirring continued overnight. The solution at this time was still black in color. (It has been our experience that when this black color is absent, the reaction did not proceed in the desired manner.)

Hydrolysis was effected by the slow addition of a saturated aqueous ammonium chloride solution to the stirred mixture. The ether layer was decanted and the residue washed several times with 50-ml portions of ether; the combined ether extracts were dried and the solvent removed in vacuo. The resulting yellow oil was distilled through a short Vigreux column at reduced pressure until the head temperature reached 120 °C (0.05 Torr) to remove the diene by-products. Chromatography of the remaining crude material (ca. 75% pure) on neutral alumina afforded 10.0 g (0.036 mol, 7.6%) of pure **4**.

The above synthetic procedure was also performed using tetrahydrofuran (THF) as the solvent. Analysis of the reaction product indicated that only *p,p'*-dichlorobibenzyl was formed from the coupling of the Grignard reagent.

Addition of Methylmagnesium Bromide to 3. The Grignard reagent was prepared by the standard method starting with 12.0 g (0.5 g-atom) of magnesium shavings in 200 ml of dry ether, to which methyl bromide was bubbled in until all the magnesium had reacted. [When commercially available methylmagnesium bromide (Alpha Chemical Co.) was used, the overall yield of **4** was reduced by one-half.] To the stirred solution was added 3 mol % of freshly prepared cuprous chloride. The reaction mixture was cooled in an ice–methanol bath (ca. −10 °C) for 1 h and then 70.0 g (0.28 mol) of **3** dissolved in ether was added dropwise with stirring. The reaction mixture was allowed to reach room temperature and stirred for an additional 36 h. Hydrolysis using cold dilute hydrochloric acid, separation of the organic layer, and evaporation in vacuo yielded a viscous yellow oil.

The crude reaction product was distilled at 0.025 Torr until the head temperature reached 110 °C, to remove dienes. The residue was chromatographed on neutral alumina, the ketone eluting in 25% benzene–hexane solution, yield 8.3 g (0.028 mol, 11.3%).

The above procedure was modified using THF as the solvent and 10 mol % of cuprous chloride, which was added *very slowly* owing to a vigorous reaction. An orange color appeared on the surface of the reaction mixture upon contact with the cuprous chloride but this color did not persist. Work-up in the usual fashion resulted in **4** being produced in 50% yield. This dramatic increase in yield is consistent with the observation (H. L. Pearce, in this laboratory) that the copper-catalyzed addition of phenylmagnesium bromide to isophorone using THF as the solvent proceeds in 95% yield while in ether only 30–40% yields are obtained.[4] Ir (CCl_4) 1710 cm^{-1} (C=O stretch); NMR (5% in CCl_4) δ (methyls) 0.98,

1.03, 1.06, δ (methylene H) 1.51, 1.64, 1.94, 2.07, 2.19, 2.47, 2.64, δ (aromatic H) 7.01, 7.20; mass spectrum: *m/e* (rel intensity) 264 (8, M^+), 139 (43), 125 (90), 83 (70), 55 (100).

Anal. Calcd for $C_{16}H_{21}OCl$: mol wt, 264.128088. Found: mol wt, 264.127473.

***trans*-3-(*p*-Chlorobenzyl)-1,3,5,5-tetramethylcyclohexan-1-ol (5).** To 60 ml of 3 M ethereal methylmagnesium bromide (commercially obtained solution) was added 4.0 g (0.015 mol) of **4** in 50 ml of ether. The reaction mixture was stirred at room temperature for 24 h, heated at gentle reflux for an additional 24 h, and hydrolyzed with a saturated ammonium chloride solution. After the ether layer was decanted, the solid residue was dissolved by addition of cold dilute hydrochloric acid and the organic layer extracted into ether. This was necessary since the solid residue was found to contain considerable amounts of product. The crude product (4.2 g, 0.015 mol) was dissolved in hexane and colorless crystals were deposited upon cooling, 2.6 g (9.3 mmol, 62% isolated), mp 52–54°: ir (CCl_4) 3610 cm^{-1} (OH stretch); NMR (5% in CCl_4) δ (methyls) 0.87, 1.25, 1.27, 1.27, δ (benzylic H) 2.38; mass spectrum *m/e* (rel intensity) 280 (2, M^+), 265 (6), 136 (100), 97 (95), 43 (67).

Anal. Calcd for $C_{17}H_{25}OCl$: mol wt, 280.159820. Found: mol wt, 280.160242.

1,3,5,5-Tetramethyl-4′-chloro-1′,2′-benzobicyclo[3.3.1]non-2′-ene (2). To 100 ml of trifluoroacetic acid (TFA) heated to 60 °C was slowly added 40.0 g (0.17 mol) of **5**, resulting in a homogenous solution. (The reaction of **5** at room temperature proceeds very slowly.) The temperature was maintained for 1 h and the TFA was removed in vacuo. The crude product was chromatographed on neutral alumina and distilled at 112 °C (0.025 Torr) to yield 35.8 g (0.14 mol, 80%) of pure **2** as a pale yellow liquid: ir (CCl_4) 2950, 2900 cm^{-1} (CH stretch); NMR (5% in CCl_4) δ (methyls) 0.30, 0.82, 1.01, 1.30, δ (benzylic H) 2.61, 2.72; mass spectrum *m/e* (rel intensity) 262 (8, M^+), 191 (100), 156 (33), 141 (41), 115 (22).

Anal. Calcd for $C_{17}H_{23}Cl$: mol wt, 262.14871. Found: mol wt, 262.14819.

1,3,5,5-Tetramethyl-7,7-dibromo-4′-chloro-1′,2′-benzobicyclo[3.3.1]non-2′-ene (8). To 11.1 g (0.042 mol) of **2** in 50 ml of carbon tetrachloride, maintained at 50 °C, was added 18.2 g (0.12 mol) of bromine. The reaction mixture was allowed to stir overnight. After removal of the solvent and the excess bromine in vacuo, 16.7 g (0.04 mol, 95% yield) of crystals were deposited. Recrystallization from hexane afforded pure **8**: mp 142–144 °C; ir (CCl_4) 2950 cm^{-1} (CH stretch); NMR (5% in CCl_4) δ (methyls) 0.25, 0.92, 1.34, 1.56; mass spectrum *m/e* (rel intensity) 341 (100), 339 (85), 285 (45), 283 (38), 203 (92), 190 (73). A molecular ion peak for this compound could not be obtained even at low ionization voltages (cf. ref 15). The molecular weight determination was based upon the parent minus bromine peak (339). To this exact mass value was added the molecular weight of bromine for comparison with the calculated value.

Anal. Calcd for $C_{17}H_{21}Br_2Cl$: mol wt, 417.96706. Found: mol wt, 417.96851.

1,3,5,5-Tetramethyl-7(*endo*- or *exo*-)bromo-4′-chloro-1′,2′-benzobicyclo[3.3.1]non-2′-ene (6 and 7). An analogous procedure used to prepare **8** was used to prepare these compounds starting with 800 mg (3.1 mmol) of **2** and 1.2 molar equiv of bromine. The small amount of **8** (ca. 50 mg) which was formed was removed by crystallization from hexane, leaving 1.0 g (2.9 mmol) of crude product, ca. 70:30 mixture of **6** and **7**, respectively. All attempts at separating these compounds were unsuccessful. These attempts included chromatography on acidic, neutral, and basic alumina, silica gel, and Florisil, gas chromatography, and short-path distillation: NMR (10% in CCl_4) δ (methyls) 0.36, 0.88, 1.30, 1.35 (**6**); 0.10, 0.84, 1.30, 1.35 (**7**), δ (benzylic H) 5.30 (**6**); 5.02 (**7**).

1,3,5,5-Tetramethyl-7-keto-4′-chloro-1′,2′-benzobicyclo[3.3.1]non-2′-ene (11). The above compound was prepared by the hydrolysis of 4.0 g (9.6 mmol) of **8** with excess aqueous KOH–methanol solution. This reaction mixture was heated for 2.5 h. The organic material was extracted into methylene chloride and the solvent removed in vacuo, yielding **11** quantitatively. An independent synthetic preparation involved the Jones oxidation[16] of either **9** or **10**. Recrystallization from hexane yielded colorless crystals: mp 74–75 °C; ir (CCl_4) 1690 cm^{-1} (C=O stretch); NMR (5% in CCl_4) δ (methyls) 0.29, 0.90, 1.11, 1.38; mass spectrum *m/e* (rel intensity) 276 (100, M^+), 261 (40), 243 (30), 206 (30), 191 (15).

Anal. Calcd for $C_{17}H_{21}OCl$: mol wt, 276.128069. Found: mol wt, 276.128088.

1,3,5,5-Tetramethyl-7-*endo*-hydroxy-4′-chloro-1′,2′-benzobicyclo[3.3.1]non-2′-ene (10). To 2.75 g (9.8 mmol) of **11** in 50 ml of absolute ethanol was added an excess of sodium borohydride. The solution was stirred overnight and then diluted with an equal amount of water. The reaction mixture was extracted by ether and the solvent removed in vacuo to yield 2.64 g (9.5 mmol, 95%) of **10**. Recrystallization from hexane yielded colorless crystals: mp 102–104 °C; ir (CCl_4) 3620 cm^{-1} (OH stretch); NMR (5% in CCl_4) δ (methyls) 0.23 0.88, 1.10, 1.30, δ (benzylic H) 4.44; mass spectrum *m/e* (rel intensity) 278 (100, M^+), 245 (85), 243 (76) 207 (45), 181 (90), 139 (32).

Anal. Calcd for $C_{17}H_{23}OCl$: mol wt, 278.14362. Found: mol wt, 278.14421.

1,3,5,5-Tetramethyl-7,7-dimethoxy-4′-chloro-1′,2′-benzobicyclo[3.3.1]non-2′-ene (12). To 4.0 g (9.5 mmol) of **8** in 150 ml of anhydrous methanol was added 3.0 g (0.05 mol) of fresh potassium hydroxide pellets and the resulting mixture refluxed for 25 h. Half of the methanol was removed in vacuo and replaced by an equal amount of water. The organic material was extracted by three 100-ml additions of CCl_4. The solvent was dried and removed in vacuo. Crystallization from anhydrous methanol gave 1.0 g (3.1 mmol, 33%) of crystalline **12**: mp 79–80 °C; ir (CCl_4) 2950 (CH stretch), 1150 cm^{-1} (OCH_3 stretch); NMR (5% in CCl_4) δ (methyls) 0.05, 0.89, 1.26, 1.30, 3.00, 3.67; mass spectrum *m/e* (rel intensity) 291 (100), 276 (30), 225 (27). See discussion concerning mass spectrum of compound **8**.

Anal. Calcd for $C_{19}H_{27}O_2Cl$: mol wt, 322.16522. Found: mol wt, 322.16299.

1,3,5,5-Tetramethyl-7-*exo*-hydroxy-4′-chloro-1′,2′-benzobicyclo[3.3.1]non-2′-ene (9). This compound (108 mg) was isolated from the chromatography of 800 mg of a mixture of **6** and **7** on alumina by elution with a benzene–methanol solution. Recrystallization from hexane afforded crystals: mp 133–134 °C; ir (CCl_4) 3580 cm^{-1} (OH stretch); NMR (5% in CCl_4) δ (methyls) 0.11, 0.82, 1.02, 1.30, δ (benzylic H) 4.40; mass spectrum *m/e* (rel intensity) 278 (100, M^+), 245 (62), 243 (50), 207 (60), 181 (75), 139 (30).

Anal. Calcd for $C_{17}H_{23}OCl$: mol wt, 278.14362. Found: mol wt, 278.14339.

1,3,5,5,7-Pentamethyl-7-*endo*-hydroxy-4′-chloro-1′,2′-benzobicyclo[3.3.1]non-2′-ene (13). To 0.105 mol of methylmagnesium bromide solution was added 2.0 g (7.3 mmol) of **11** and the reaction mixture allowed to stir for 3 h. Hydrolysis in the usual manner and removal of the ether yielded 2.1 g (7.2 mmol) of crude product. This material was dissolved in hexane and upon cooling 0.90 g (3.5 mmol, 47%) of crystals was isolated, mp 79–80 °C. The remaining 1.2 g of viscous oil was chromatographed on alumina, but decomposed into unidentified material. Ir (CCl_4) 3570 cm^{-1} (OH stretch); NMR δ (methyls) 0.22, 0.89, 1.03, 1.30, 1.42; mass spectrum *m/e* (rel intensity) 292 (2, M^+), 277 (100), 221 (15), 203 (10), 43 (23).

Anal. Calcd for $C_{18}H_{25}OCl$: mol wt, 292.159385. Found: mol wt, 292.158804.

1,3,4,5-Tetramethyl-4′-chloro-1′,2′-benzobicyclo[3.3.1]nona-2′,4-diene (14). To 50 mg (0.18 mmol) of **9** (**10** may also be used) in 30 ml of dry benzene was added 50 mg of *p*-toluenesulfonic acid. The reaction mixture was refluxed for 4 h and neutralized with a saturated sodium bicarbonate solution. The organic layer was removed and washed with another portion of the base. After removal of the solvent, the crude product was dissolved in hexane and placed in the freezer, upon which time crystals were deposited: yield 42 mg (0.16 mmol, 89%) of pure **14**, mp 99–101 °C; ir (CCl_4) 2950, 2900 cm^{-1} (CH stretch); NMR (5% in CCl_4) δ (methyls) 1.12, 1.34, 1.54, 1.54; mass spectrum *m/e* (rel intensity) 260 (96, M^+), 245 (100), 191 (66), 153 (30), 135 (19).

Anal. Calcd for $C_{17}H_{21}Cl$: mol wt, 260.133178. Found: mol wt, 260.133759.

1,3,6,6-Tetramethyl-4′-chloro-1′,2′-benzobicyclo[3.2.2]nona-2′,2-diene (15). This compound (ca. 1 g) was isolated as a colorless liquid from the chromatography of 3.3 g of a mixture of **6** and **7** on alumina: ir (CCl_4) 2870 cm^{-1} (CH stretch); NMR (5% in CCl_4) δ (methyls) 0.15, 0.80, 1.43, 1.80, δ (benzylic H) 3.02; mass spectrum *m/e* (rel intensity) 260 (15, M^+), 245 (33), 190 (100), 189 (80), 175 (50), 152 (50).

Anal. Calcd for $C_{17}H_{21}Cl$: mol wt, 260.13318. Found: mol wt, 260.13350.

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Registry No.—**2,** 58240-96-3; **3,** 58240-97-4; **4,** 58240-98-5; **5,** 58240-99-6; **6,** 58241-00-2; **7,** 58267-55-3; **8,** 58241-01-3; **9,** 58341-82-5; **10,** 58249-35-7; **11,** 58241-02-4; **12,** 58241-03-5; **13,** 58241-04-6; **14,** 58241-05-7; **15,** 58241-06-8; *p*-chlorobenzyl chloride, 104-83-6; dimedone methyl ether, 4683-45-8; isophorone, 78-59-1; methyl bromide, 74-83-9.

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Zero Bridge Cleavage and a Neighboring Hydroxyl Group Effect in the Oxymercuration of Bicyclo[3.1.0]hexanes

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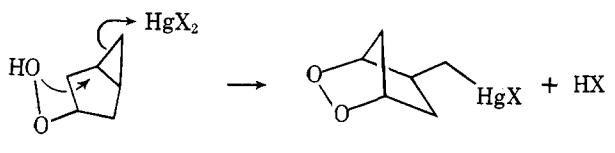
Cleavage of the zero bridge is a major pathway in the oxymercuration of all bicyclo[3.1.0]hexanes examined. Though a 3-acetoxy substituent has no effect on the competition between peripheral and bridge C–C bond cleavage, a cis or trans 3-hydroxyl group markedly promotes the latter. Thus, oxymercuration–acetylation–demercuration of *cis*-3-hydroxybicyclo[3.1.0]hexane (**3b**) gives mainly *cis*-1,3-diacetoxycyclohexane (83%). The intermediate mercurial from zero bridge cleavage of **3b** gives *cis*-1,3-diacetoxy-*cis*-5-chlorocyclohexane upon reaction with chlorine in pyridine. Hence, the electrophilic addition leading to zero bridge cleavage involves inversion of stereochemistry at the center of electrophilic attack as well as at the center of nucleophilic attack.

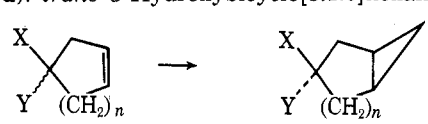
This study of the oxymercuration of bicyclic cyclopropanes is part of our general examination of the utility of oxymercuration reactions for the total synthesis of prostaglandin endoperoxides.[1] These biological precursors of prostaglandins are base-sensitive derivatives of 2,3-dioxabicyclo[2.2.1]heptane. Peroxymercuration of olefins[2] or cyclopropanes[3] which can be performed under neutral or mildly acidic conditions is especially attractive for the synthesis of base-sensitive secondary alkyl peroxides. Since inversion of configuration at the site of nucleophilic attack is strongly favored for oxymercuration of cyclopropanes,[18] intramolecular peroxymercuration of **1** is expected to lead to **2** by cleavage of a peripheral C–C bond of the three-membered ring. Moreover, oxymercuration of bicyclo[3.1.0]hexane is reported to result in the desired cleavage of a peripheral rather than bridge C–C bond of the three-membered ring.[4] However, we now report that cleavage of the bridge bond is a major pathway for oxymercuration of bicyclo[3.1.0]hexanes. We have also uncovered a novel neighboring group effect on the electrophilic cleavage of a cyclopropane. Thus, some substituents promote almost exclusive cleavage of the zero bridge in bicyclo[3.1.0]hexanes. Moreover, these bridge cleaving oxymercurations are stereospecific and provide an effective new route for the stereospecific synthesis of polysubstituted cyclohexanes.



1 2

Results

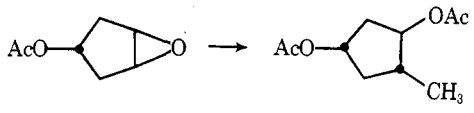
A. Syntheses of Oxymercuration Substrates and Products. Bicyclo[3.1.0]hexane (**3a**),[5] *cis*-3-hydroxybicyclo[3.1.0]hexane (**3b**),[6] and *cis*-3-hydroxybicyclo[4.1.0]heptane (**3c**)[7] were prepared by Simmons–Smith methylenation of the corresponding olefins. Acetylation of **3b** gave the acetate (**3d**). *trans*-3-Hydroxybicyclo[3.1.0]hexane (**3f**)[6] was



X=H or OH
n=1 or 2

3a, X = Y = H; n = 1
b, X = OH; Y = H; n = 1
c, X = OH; Y = H; n = 2
d, X = OAc; Y = H; n = 1
e, X, Y = O; n = 1
f, X = H; Y = OH; n = 1

obtained from the cis epimer (**3b**) by oxidation to the ketone (**3e**) with chromium trioxide–pyridine complex in methylene chloride followed by reduction with aluminum isopropoxide in 2-propanol. *cis*-1,3-Diacetoxycyclohexane (**4b**) and *trans*-1,3-diacetoxycyclohexane (**4c**) were prepared by acetylation of the commercially available diols. 1,3-Diacetoxy-4-methylcyclopentane (**5b**) was prepared by



6 5b