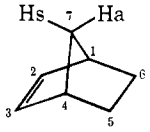
Synthesis and Nuclear Magnetic Resonance Spectra of Some Bridged Polyhydromethanonaphthalenes. Bridge Proton Assignments

John Haywood-Farmer,[1a] Herbert Malkus,[1b] and Merle A. Battiste*[1b]

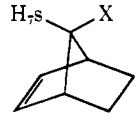
Contribution from the Department of Chemistry, Bishop's University, Lennoxville, Quebec, Canada, and the Department of Chemistry, The University of Florida, Gainesville, Florida 32601. *Received June 14, 1971*

Abstract: The stereospecific synthesis of a series of bridge-substituted polyhydromethanonaphthalenes is described. The nmr spectra of these compounds reveal that in all cases in which the substituent is anti to the exo-fused norbornyl ring the syn bridge proton is deshielded by that fragment. The corresponding syn-substituted epimers exhibit upfield shifts for the bridge proton although the values are generally close to those for the corresponding 7-norbornyl derivatives. The available nmr data on exo-endo fused polyhydrodi- and trimethanonaphthalenes are summarized and the chemical shifts of the bridge protons and the long-range shielding–deshielding effects of double bond and cyclopropyl groups in these molecules are discussed in the light of the present results. These results indicate that previous assignments for certain molecules in this series should be reversed.

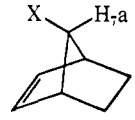
Over the past decade and a half the bicyclo[2.2.1]-heptane system has provided the spectroscopist with many examples of unusual magnetic resonance phenomena. While many examples could be quoted the recent controversy concerning the assignment of the correct chemical shift to the 7-syn (7s) and 7-anti (7a) protons in norbornene (**1**) is of particular interest to this report. Tori and coworkers[2] first assigned H-7s to the higher field multiplet but later, on the basis of deuterium labeling and spin decoupling experiments, reversed this assignment.[3] This reassignment has been independently confirmed by Franzus, *et al.*,[4] and by Marchand and Rose.[5]



1



2

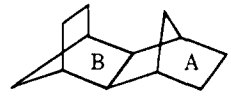


3

The original bridge proton assignment in **1** was undoubtedly prejudiced by the fact that in 7-substituted norbornenes, where stereochemistry (syn or anti) and H-7 assignments are unambiguous, H-7s in **2** absorbs at higher field than H-7a in **3**.[6]

The suggestion has been made[4] that H-7s in norbornene and substituted norbornenes lies very close to the border between the shielding and deshielding regions resulting from the magnetic anisotropy of the double bond.[7] In view of the spatial orientation of H-7s, relatively small changes in molecular geometry could lead to either a shielding or a deshielding effect on this proton relative to that found in **1**. Franzus suggests[4] that anti-7 substituents in norbornenes force the syn proton into the shielding zone of the double bond resulting in the observed anomaly between the chemical shifts of unsubstituted and substituted norbornenes.

While the bridge proton assignments in norbornene and benznorbornene systems would appear to have been resolved, if not explained, the situation for the closely related hexa-, octa-, and decahydrodimethanonaphthalene ring systems which are composed of two fused norbornyl fragments is still in a state of some confusion. Of the three geometrical isomers of this system, the one with exo-endo ring fusion (*e.g.*, **4**) is more frequently encountered and is of particular interest to this study. Several studies concerning nmr spectral assignments in this ring system and a variety of its derivatives have been published over the last 2–3 years and will be briefly reviewed below.



4

Complimentary to their study of norbornene Marchand and Rose[5] reported the spectra of the three compounds **5**–**7** and on the basis of chemical-shift arguments concluded that H-9s in **5** and **6** appears at higher field than H-9a as a result of the anisotropic effect of the $\Delta^{2,3}$ double bond. In the chlorinated insecticide aldrin (**7**), however, H-9s was found at lower field than H-9a as a result of anistropy and field effects of the chlorine atoms on C-2 and C-3 (Table I).[5]

Other groups have reported on the nmr spectrum of **7**. Parsons and Moore[8] and Bukowski and Cisak[9] as-

* Author to whom all inquiries should be addressed at the University of Florida.

(1) (a) Bishop's University; (b) University of Florida.

(2) K. Tori, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Can. J. Chem.*, **42**, 926 (1964).

(3) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966).

(4) B. Franzus, W. C. Baird, N. F. Chamberlain, T. Hines, and E. I. Snyder, *J. Amer. Chem. Soc.*, **90**, 3721 (1968).

(5) A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968). In this paper the captions under Figures 5 and 6 have been inadvertantly reversed as recently pointed out by these authors in a "corrections" note [*ibid.*, **92**, 5290 (1970)]. We wish to thank Dr. Marchand for informing us of this correction and for providing additional data regarding the nmr solvents for compounds **5**–**7**.

(6) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

(7) (a) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, pp 72–75; (b) J. W. ApSimon, W. G. Craig, P. V. Domarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, **23**, 2357 (1967).

(8) A. M. Parsons and D. J. Moore, *J. Chem. Soc. C*, 2026 (1966).

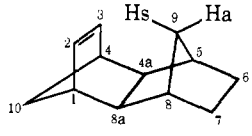
(9) J. A. Bukowski and A. Cisak, *Rocz. Chem.*, **42**, 1339 (1968).

Table I. Bridge Proton Chemical Shift Differences for Some Polyhydrodimethanonaphthalenes

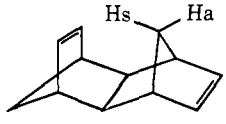
Compd	Hs (τ)	Ha (τ)	Δ, ppm[a]	Solvent	Ref
5[b]	9.52	8.03	1.49	CCl_4	*d*
6[b]	9.03	7.45	1.58	CCl_4	*d*
6	7.45	9.00	1.55	CCl_4	*e*
7	8.68[c]	8.44[c]	−0.24	$CDCl_3$	*f*
7	8.33	8.65	0.32	CCl_4	*d*
7	8.65[c]	8.44[c]	−0.21	CCl_4	*g*
7	8.42	8.68	0.26	$CDCl_3$	*h*
8	7.00	8.46	1.46	$CDCl_3$	*e*
9	6.95	9.04	2.09	$(CD_3)_2CO$	*e*
10	7.76	8.42	0.66	$(CD_3)_2CO$	*e*
11	7.76	9.25	1.49	$CDCl_3$	*i*
12	7.85 (s)	8.84 (a)	0.99	$CDCl_3$	*i*
12	7.72 (s′)	9.54 (a′)	1.82	$CDCl_3$	*i*
13	8.44	8.77	0.33	CCl_4	*j*
14	8.45	9.12	0.67	CCl_4	*j*
15	8.15	8.52	0.37	CCl_4	*j*
16	7.45	9.11	1.66	CCl_4	*j*
17	7.15	8.80	1.65	CCl_4	*j*
18	7.56	9.06	1.50	CCl_4	*j*
19	7.92	9.26	1.34	CCl_4	*j*
20	7.34	8.76	1.45	CCl_4	*j*

[a] $\Delta = \tau_{Ha} - \tau_{Hs}$. [b] These assignments are reversed by the results of the present work. [c] Believed to be in error. [d] Reference 5. [e] Reference 11. [f] Reference 8. [g] Reference 9. [h] Reference 10. [i] Reference 13. [j] Reference 14.

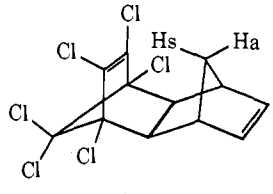
signed the high-field proton as H-9s but gave no reason for this assignment. On the other hand, Keith, Alford, and McKinney[10] agree with Marchand and Rose, assigning the high-field proton to H-9a, again based on extensive decoupling experiments.



5

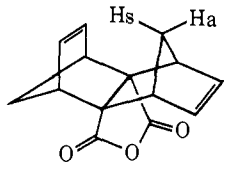


6

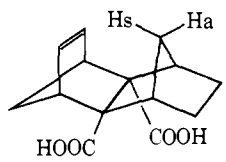


7

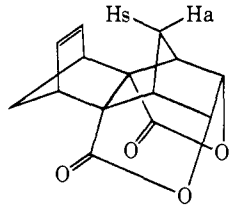
Shortly after the appearance of Marchand's paper,[5] Edman and Simmons reported the preparation and nmr spectra of the derivatives **8–10**.[11] For each of these compounds, the authors assign the higher field peak to H-9a clearly in disagreement with Marchand's work. These authors also report the nmr spectrum of **6** and, although it is not explicitly stated in their paper, they imply that H-9a is shielded relative to H-9s. Edman and Simmons offer two explanations of these chemical-shift values. First they suggest that H-9s may actually lie in the deshielding rather than in the shielding zone of the double bond. Alternatively steric compression may account for at least a portion of the observed shift. Related phenomena involving sterically compressed groups have been previously observed.[12]



8

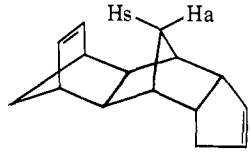


9

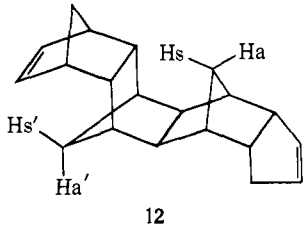


10

Also pertinent to this study are the papers concerning the nmr spectra of cyclopentadiene oligomers by Foster and McIvor.[13] Two of the compounds studied, trimer **11** and tetramer **12**, are of interest. For each pertinent geminal pair of bridge protons in these two molecules, one member of the pair, assigned as the syn proton by the authors,[13a] was shifted to anomalously low field. As with some of the compounds studied above[11] and with some in other ring systems,[12] this effect was attributed to steric compression.



11



12

Finally, McCulloch, Rye, and Wege recently reported the nmr spectra of several derivatives of **5**, **6**, and a benzo derivative of **6**.[14] Following the pattern established above all of these compounds (**13–20**) show a syn bridge proton in ring A which is deshielded compared with the corresponding anti proton and again this shift is explained on the basis of steric compression of that proton against the π cloud of the double bond. A summary of the bridge-proton resonances for all of the above dimethanonaphthalene systems is given in Table I.

Our interest in the foregoing nmr assignment question was initiated while engaged in the solvolytic study of neighboring cyclopropyl participation within the trimethanonaphthalene system **21**.[15] The nmr spectral features of **21** and its epimeric system **22** encouraged us to also prepare and examine the related anti–syn pairs **23–24** and **25–26** in hopes that these derivatives might provide additional insight into the problems associated with bridge-proton assignments in the *exo-endo*-octahydrodimethanonaphthalene ring system.[16] For nmr study the various derivatives of **21–26** offer two ad-

(10) L. H. Keith, A. L. Alford, and J. D. McKinney, *Tetrahedron Lett.*, 2489 (1970).

(11) J. R. Edman and H. E. Simmons, *J. Org. Chem.*, 33, 3808 (1968).

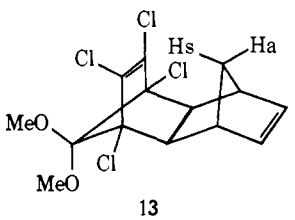
(12) (a) W. Nagata, T. Terasawa, and K. Tori, *J. Amer. Chem. Soc.*, 86, 3746 (1964); (b) S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *ibid.*, 87, 5247 (1965); (c) M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).

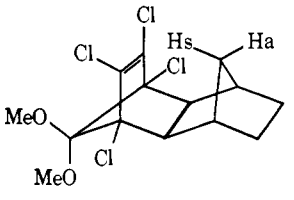
(13) (a) R. G. Foster and M. C. McIvor, *J. Chem. Soc. B*, 188 (1969); (b) *Org. Magn. Resonance*, 1, 203 (1969).

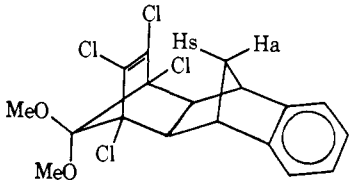
(14) R. McCulloch, A. R. Rye, and D. Wege, *Tetrahedron Lett.*, 5163 (1969).

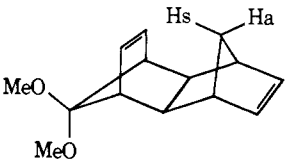
(15) M. A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl, and S. Winstein, *J. Amer. Chem. Soc.*, 92, 2144 (1970).

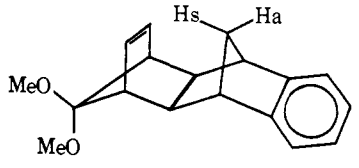
(16) The syntheses of **23** and **25** and several derivatives have been reported previously by other workers;[17] however, neither experimental details of their syntheses nor any nmr data were given.

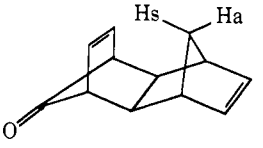

13

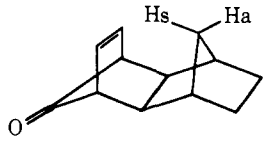

14

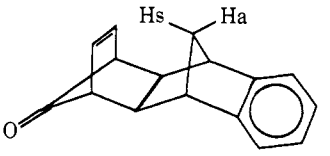

15


16

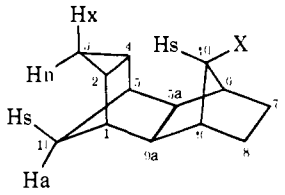

17

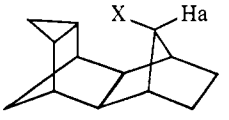

18

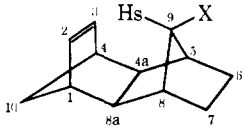

19

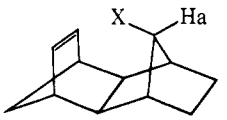

20

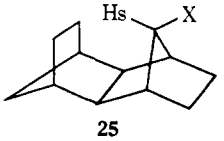
vantages over their unsubstituted parents: (i) there is only one pertinent methylene proton, whose stereochemistry is unambiguously known from the chosen method of synthesis; (ii) the proton of prime interest (geminal to the substituent) appears in a region of the spectrum which is free from the other proton signals in the molecule, thus avoiding the problem of peak assignment encountered by the previously cited workers. In addition, compounds **21** and **22** offer unique geometry for probing the magnetic anisotropy of the cyclopropane ring. At this time we would like to report the results of these synthetic and nmr spectral investigations.

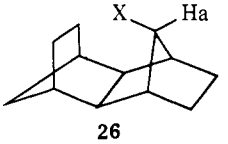

21


22


23


24

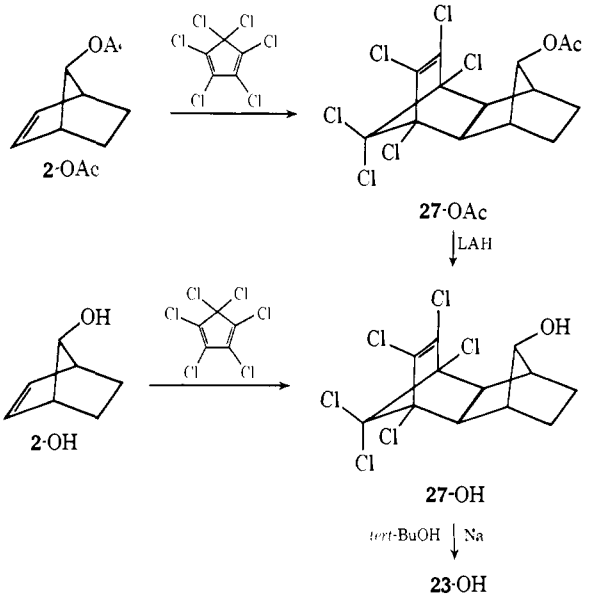

25


26

Results and Discussion

Syntheses. The syntheses of the various compounds of interest in this paper were standard to this area and proceeded stereospecifically as expected based on analogies to other polycyclic ring systems. Preparation of the key synthetic intermediate, alcohol **23**-OH, was initially attempted by Diels–Alder addition of cyclopentadiene to the tetrahydropyranyl ether of *anti*-7-norbornenol as had been accomplished previously by Winstein and Hansen.[17] This procedure led to viscous polymers from which only minor amounts of the desired ether product could be obtained. While hexachlorocyclopentadiene is much less prone to polymerization than is its dechlorinated parent, it readily functions as a Diels–Alder diene[18] and since its adducts can be readily dechlorinated,[19] we chose to synthesize **23**-OH using this diene as set forth in Scheme I. The

Scheme I

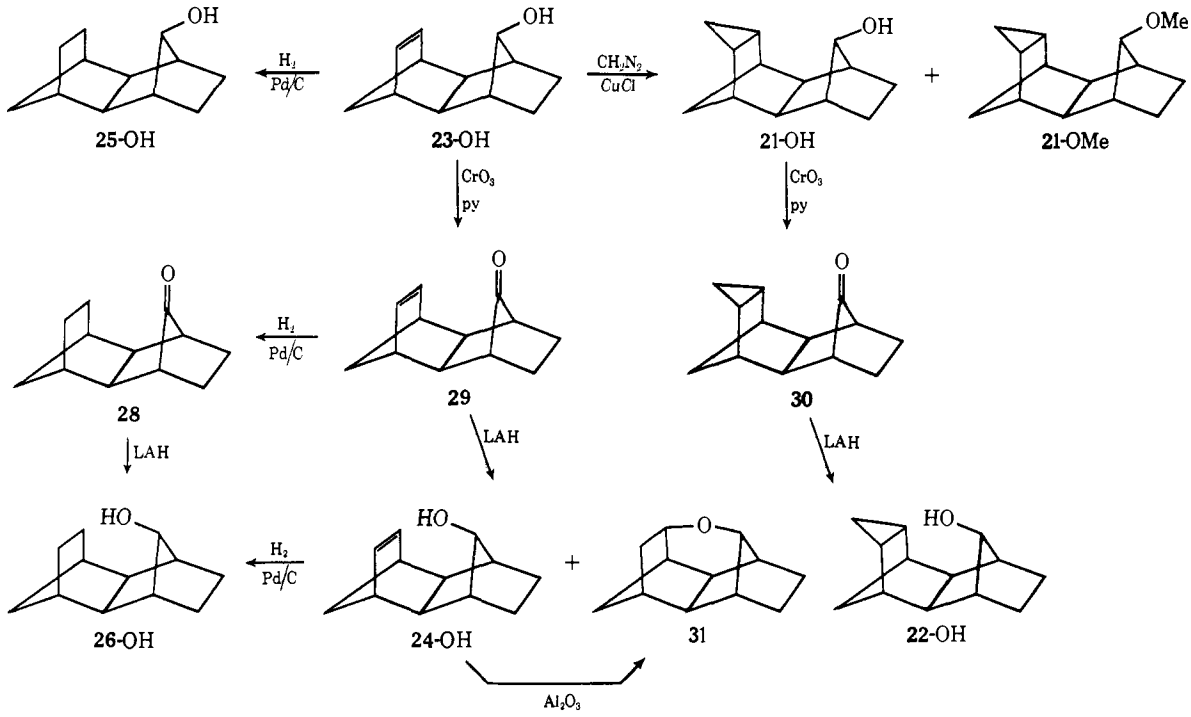


synthesis was accomplished in this manner without difficulty and in good yield. The Diels–Alder addition is stereospecific in the exo direction giving the desired exo-endo ring junction as anticipated.[20] Strangely, we found that lithium dechlorination of **27**-OH did not occur as had been reported previously,[17a] but that sodium dechlorination[19b] proceeded smoothly.

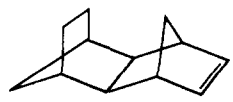
Conversion of alcohol **23**-OH into the known[17a] saturated alcohol **25**-OH, the cyclopropyl alcohol **21**-OH, and the unsaturated ketone **31** was accomplished as shown in Chart I. Cyclopropanation using the diazomethane–cuprous halide recipe[21] gave **21**-OH but the utility of this procedure was seriously hampered by the formation of large amounts (up to 50%) of **21**-OMe as well. It is known that diazomethane will insert methylene into the labile O–H bond of al-

(17) (a) S. Winstein and R. L. Hansen, *J. Amer. Chem. Soc.*, **82**, 6206 (1960); (b) *Tetrahedron Lett.*, **No. 25**, 4 (1960).
(18) C. W. Roberts, *Chem. Ind. (London)*, 110 (1958).
(19) (a) P. Bruck, D. Thompson, and S. Winstein, *ibid.*, 405 (1960); (b) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).
(20) (a) S. B. Soloway, *J. Amer. Chem. Soc.*, 74, 1027 (1952); (b) J. K. Stille and D. A. Frey, *ibid.*, 81, 4273 (1959); (c) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *ibid.*, 82, 5377 (1960).
(21) R. E. Pincock and J. I. Wells, *J. Org. Chem.*, **29**, 965 (1964).

Chart I



cohols,[22] but the authors are not aware of another instance in which this process interferes to this extent with the cuprous halide catalyzed addition of methylene to a double bond. Curiously no chromatographic peak for **23**-OMe or for any other product was observed. In the closely related addition to *anti*-7-norbornenol (**2**-OH), for example, methyl ether formation does occur, but only to a very minor extent, and even then only after prolonged reaction time.[23] This anomalous behavior can perhaps be explained as follows. It has been found[24] that cis additions to endo 5,6-disubstituted norbornenes (*e.g.*, **5**) are slower than the corresponding additions to exo 5,6-disubstituted norbornenes (*e.g.*, **32**). In the cyclopropanation of **23**-OH it is possible that the relative rates of reaction of diazomethane with the C=C and O—H bonds are much closer than in reaction with **2**-OH; hence, in **23**-OH insertion into the O—H bond competes more efficiently with addition to the C=C bond.



32

In order to overcome the difficulty of ether formation the alcohol function was protected as its acetate; then **23**-OAc was cyclopropanated cleanly and **21**-OAc reduced to **21**-OH in good yield.

$$\text{23-OH} \xrightarrow[\text{Py}]{\text{Ac}_2\text{O}} \text{23-OAc} \xrightarrow[\text{CuCl}]{\text{CH}_2\text{N}_2} \text{21-OAc} \xrightarrow{\text{LAH}} \text{21-OH}$$

The cyclopropanation reaction provides stereochemically pure product from expected exo addition to the norbornene moiety.[12c,23,25] Proof for this assignment lies in the observation that **21**-OH and its derivatives (acetate, brosylate, *p*-nitrobenzoate, methyl ether) all show an nmr signal at *ca.* τ 10.0 integrating for one proton. Such a high-field signal is characteristic of the *exo*-tricyclo[3.2.1.$0^{2,4}$]octane moiety (but not of the endo isomers)[26] and in **21** is assigned to H-3x as discussed below.

The oxidations of **23**-OH to **29** and of **21**-OH to **30** were accomplished using the Sarett procedure.[27] The saturated ketone **28** was synthesized by catalytic hydrogenation of **29** rather than by the more tedious oxidation of **25**-OH. As has been observed in the hydrogenation of 7-norbornenone,[19b] reduction of the carbonyl group does not compete with reduction of the double bond.

Reduction of the three ketones with LAH gave, as expected, the alcohols resulting from attack of the reagent from the less sterically hindered side of the molecule. Ketones **28** and **30** gave the corresponding alcohols **26**-OH and **22**-OH very cleanly, and, as shown by nmr, uncontaminated by their epimers (**25**-OH and **21**-OH). The unsaturated alcohol **24**-OH, however, could not be isolated in a pure form. The crude reduction mixture clearly contained an olefinic alcohol as the major component as was shown by nmr and infrared. That this must be the desired **24**-OH is shown by the differences in its nmr spectrum from that of the isomeric **23**-OH, with which **24**-OH was not contaminated, and by its facile hydrogenation to **26**-OH. Attempted esterification of **24**-OH gave unidentified nonolefinic products. Attempted chromatographic purification, either by glpc on a variety of columns or on a column of neutral alumina, gave as the only isolated product a saturated ether which,

(22) J. A. Kerr, B. V. O'Grady, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 897 (1967).
(23) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).
(24) J. K. Stille and D. R. Witherell, *J. Amer. Chem. Soc.*, **86**, 2188 (1964).
(25) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).
(26) J. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969), and references cited therein.
(27) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *ibid.*, **75**, 422 (1953).

Table II. Comparison of Bridge Proton Chemical Shifts for Some Substituted Methano-Bridged Polycyclic Ring Systems[a]

Compd	X = OH	OAc	OBs	OPNB	OMe	Δ[b]	Δ′[c]	Δ_{calcd}[d]
7-Norbornyl	6.01	5.37[g,h]	5.5[e]	4.95[i]	6.48			
2	6.55[e]	5.77		5.34[i]	6.88[j]	0.3	0.43	0.14
3	6.25[f]	5.50[f]			6.60		0.16	−0.12
21	5.00	4.25	4.33	3.88	5.48	−1.25	−1.08	−0.52
22	6.25						0.24	−0.09
23	5.20	4.47		4.12		−1.2	−0.85	1.34
24	6.40						0.39	0.25
25	5.58					−0.5	−0.43	
26	6.07						0.06	

[a] Values given in τ units with internal TMS at τ 10.0 or internal $CHCl_3$ at 2.73; solvent $CDCl_3$ unless otherwise noted. [b] Chemical-shift difference (parts per million) between bridge proton of anti isomer and that for its syn epimer. [c] Average chemical-shift difference (parts per million) between bridge proton of 7-substituted norbornane and related proton for the similarly substituted bridged polycyclic compound. [d] Olefinic shift values calculated by method of S. Yamaguchi, S. Okuda, and N. Nakagawa (*Chem. Pharm. Bull.*, **11**, 1465 (1963)), using Dreiding or Framework molecular models. Cyclopropyl anisotropic effects estimated by modified Johnson–Bovey method (see text). [e] J. I. Wells, M.S. Thesis, University of British Columbia, 1964. [f] Reference 6. [g] K. Tori, K. Aono, K. Kitahonoki, R. Muneyuki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 2921 (1966). [h] CCl_4 as solvent. [i] Reference 39. [j] T. Tsuji, private communication.

based on spectral data, was assigned structure **31**. The lability of syn alcohol **24**-OH is not surprising considering the compressional forces that must act on both oxygen and π-electron centers.

Nmr Spectra. The nmr spectral data recorded for the compounds prepared in this study are presented in Tables II–IV and the Experimental Section. The chemical shifts for the pertinent bridge protons of derivatives of **21**–**26** are collected in Table II. Inspection of the data in this table readily reveals that the bridge proton syn to the exo norbornyl ring (ring B) is at significantly lower field than the corresponding anti proton in its epimeric isomer (compare **21**, **23**, and **25** with **22**, **24**, and **26**, respectively). In contrast to what one might have naively predicted, the magnitude (Δ) of the deshielding effect is larger for the olefinic system **23** than for the saturated system **25** and about equal to that for the cyclopropane system **21**. In view of the magnitude of the deshielding effect in **23** it is considered highly unlikely that the relative positions of protons H-9s and H-9a in hydrocarbon **5** would be greatly altered from that of Hs and Ha in **23** and **24**, respectively. Therefore, the bridge proton assignments made by Marchand and Rose[5] for hydrocarbons **5** and **6** are clearly in error and should be reversed.

Large chemical-shift differences such as those observed for the epimeric systems in this study may be ascribed to magnetic anisotropy of neighboring C–C and C–H bonds,[28,29] polarization due to electric field effects around neighboring charge centers,[30] and intramolecular van der Waals interactions (steric compression).[12,31] Since the groups present in **21**–**26** are not highly polarizable (particularly the hydrocarbon parents) the importance of the polarization factors in these cases may be minimal. Thus, the syn-anti shifts (Δ) in Table II would preferably be assessed either in terms of anisotropic effects or compressional effects or a combination of both factors.

In discussion of the syn isomers it should be noted that the bridge proton (Ha) of saturated alcohol **26**-OH has a normal shift value very close to that for the corresponding proton in 7-norbornanol. Introduction of a double bond into both ring systems to give **24**-OH and **3**-OH produces an upfield shift (Δ′) of 0.39 and 0.16 ppm, respectively. Though the proton (Ha)–double bond distance is approximately the same (3.5 Å) in the two systems the greater shift for **24**-OH may be rationalized in terms of the conventional shielding cone picture for the carbon–carbon double bond as illustrated by the calculated shift values in Table II.[32] A similar shielding is observed for the anti proton Ha in hydrocarbons **5** and **11** and Ha′ in **12**; however, the magnitude of the effect relative to the bridge protons of norbornane (τ 8.80 in $CDCl_3$[2]) is sufficiently larger (0.45–0.74 ppm) as to suggest that other factors, such as steric compression of the corresponding syn protons (Hs or Hs′), may be operating in addition to double bond anisotropy.

The upfield shift of proton Ha in trimethanonaphthalene derivative **22**-OH is suprising since even a cursory examination of molecular models reveals that this nucleus is located in or near the plane of the cyclopropane ring. In terms of the currently accepted ring current model for cyclopropane, protons in or near the plane of the ring should experience deshielding, those above the ring shielding.[34] Application of the ring current model of Johnson and Bovey[35] with appropriate modification for the three-membered ring as recommended by Burke and Lauterbur (n = 3.5

(28) H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).
(29) J. A. Pople, *Proc. Roy. Soc., Ser. A*, **239**, 541, 550 (1957).
(30) A. D. Buckingham, *Can. J. Chem.*, 38, 300 (1960).
(31) T. Schaefer, W. F. Reynolds and Y. Yonemoto, *ibid.*, 41, 2969 (1963).

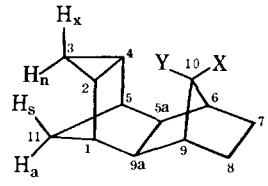
(32) The lack of agreement between predicted and observed shielding of H-7a in norbornene (3; X = H) has previously been noted without explanation.[3] The more recent conclusions of Franzus, *et al.*,[4] and Marchand and Rose[5] also provide little insight into the nature of this shielding observed for the parent as well as syn 7-substituted norbornenes. In this regard it is interesting that ApSimon[7b] has proposed a modification of the shielding–deshielding zone of the double bond which limits deshielding "to a restricted region at the ends of the double bond: outside this region a nucleus is shielded whether it lies in 'plane' of the double bond or above it." The latter view would appear to have merit; however, it has not received attention in the more recent texts on the subject.[7a,33]

(33) L. M. Jackman and S. Sternell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, pp 83–88.

(34) See ref 7a, p 71, and ref 33, pp 98–101, and references cited therein.

(35) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

Table III. Nmr Spectral Parameters (60 MHz) for Some 10-Substituted Decahydrotrimethanonaphthalenes in $CDCl_3$[a,b]



Compd	X	Y	H_{10}	$H_{6,9}$	$H_{5a,9}$[a]	$H_{1,5}$	H_{11s}	H_{11a}	$H_{7n,8n}$	$H_{7x,8x}$	$H_{2,4}$	H_{3x}	H_{3n}	Other
21-OAc	OAc	H	4.23 bs	8.30 m	7.73 m	7.70 bs	9.0 m	9.55 d J = 10.5	9.0 bm	8.30 bm	9.0 m	9.96 dt J = 5.8, 7.8	9.50 dt J = 5.8, 2.8	8.04 s (CH_3)
21-OH	OH	H	4.98 bs	8.31 m	7.95 m	7.69 m	9.05 bd $J \simeq 10$	9.51 bd	8.95 bm	8.07 bm	9.18 dd J = 7.2, 3.0	10.01 dt J = 5.5, 7.2	9.47 dt J = 6.0, 3.0	8.35 s (OH)
21-OMe	OMe	H	5.46 bs	8.30 m	7.80 bm		9.03 bd $J \simeq 11$	9.54 bd	9.0 bm	8.2 bm	9.21 dd J = 8.0, 2.7	9.97 dt J = 6.1, 8.0	9.48 dt J = 6.1, 2.7	6.78 s (CH_3)
21-OPNB	OPNB	H	3.88 s	8.23 m	7.60 bm		8.96 bd $J \simeq 11$	9.50 bd	8.8 bm	8.1 bm	9.02 dd J = 7.2, 2.6	9.90 dt J = 5.4, 7.2	9.45 dt J = 5.4, 2.6	
30	=O			8.04 bm		7.63 m	8.89 dt $J \cong 11$, 1.5	9.34 bd $J \cong 11$	8.60 bm	8.17 bm	9.23 dd J = 7.5, 2.9	10.09 dt J = 5.5, 7.5	9.56 dt J = 5.5, 2.9	
22-OH	H	OH	6.26 s	8.02 bm		7.63 bs	9.05 bd $J \simeq 11$	9.37 bd	9.0 bm	8.35 bm	9.0 m	9.97 dt J = 6.0, 7.2	9.46 dt J = 6.0, 2.9	7.15 s (OH)

[a] Chemical shifts given in τ units with internal $CHCl_3$ at τ 2.73. [b] Coupling constants (J) given in hertz with multiplicities represented by s (singlet), bs (broad singlet), d (doublet), bd (broad doublet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), and bm (broad multiplet); relative peak areas are in accord with assignments.

Table IV. Nmr Solvent Shifts and Spectral Parameters for **21**-OH and **30** at 100 MHz[a,b]

	$\delta_{1,5}$	$\delta_{6,9}$	$\delta_{5a,9a}$	$\delta_{7x,8x}$	$\delta_{7n,8n}$	δ_{11s}	$\delta_{2,4}$	δ_{3n}	δ_{11a}	δ_{3x}
21-OH										
In $CDCl_3$	231.3 bs	168.8 m	205.0 m	192.5 bm	105.4[c] bm	99.0[c] dt J = 10.1, 2.0	82.4 dd J = 7.2, 3.0	53.0[c] dt J = 6.0, 3.0	48.9[c] bd J = 10.1	*d*
In Benzene	218.4 bs	148.0 (q)	193.5 m	203.0 bm	93.5[c] bm	83.8[c] dt J = 10.8, 1.7	63.0 dd J = 7.2, 3.0	43.5 dt J = 5.7, 3.0	28.9 bd J = 10.8	−8.5 dt J = 5.7, 7.2
$\Delta\delta$ (Hz)[e]	12.9	20.8	11.5	−10.5	11.9	15.2	19.4	9.5	20.0	
30										
In $CDCl_3$	237.5 bs	195.5 m	195.5 m	183 bm	140 bm	111.0 dt J = 10.9, 1.5	76.8 dd J = 7.5, 2.8	44.0 dt J = 5.5, 2.9	66.0[c] bd J = 10.9	*d*
In Benzene	213.0 bs	173.0 (t)	147.5 (t)	152[c] bm	96[c] bm	[f]	85.2 dd J = 7.1, 2.5	30.0 dt J = 5.6, 3.2	35[c]	−13.5 dt J = 5.6, 7.2
$\Delta\delta$ (Hz)[e]	24.5	22.5	48.0	31	44		−8.4	14.0	31	

[a] Chemical shifts given in hertz downfield from TMS. In benzene TMS taken to be 716 Hz upfield from benzene. Proton H-10 not recorded on the 250-Hz sweep width employed for these spectra. [b] See footnote *b*, Table III; parentheses indicate irregular multiplicities, *i.e.*, number of lines. [c] Partially obscured by overlapping signal. [d] Obscured by TMS signal. [e] $\delta_{CDCl_3} - \delta_{C_6H_6}$. [f] Obscured by overlapping signals.

electrons; a = 1.10 Å)[36] allowed estimation of the shielding–deshielding contribution of the cyclopropane ring at proton Ha (and Hs of **21**) as recorded in Table II. The predicted effect (−0.09 ppm) is small but nevertheless opposite in direction to the observed shift. To explain this anomaly one must consider that either the above ring current model is inadequate or other factors must be operating.

Certainly one factor which should be taken into account in the series **22**, **24**, and **26** is the rather severe steric compression between the OH group and the opposing ethano, etheno, and cyclopropano bridges. This compression clearly manifests itself chemically in the instability of **24**-OH with respect to formation of the intercyclic ether **31**. While the cyclopropyl alcohol **22**-OH is chemically stable, the infrared spectrum of this alcohol (CCl_4, 0.1–0.5 M) in the 3300–3600-cm^{-1} region showed no evidence for a band characteristic of intramolecular cyclopropane–HO bonding.[37] The severe steric crowding in the cavity region of this alcohol apparently precludes formation of the proper conformation of the COH group for hydrogen bonding. Such compressional interactions in **24**-OH and **22**-OH may likewise give rise to significant distortions of the intramolecular electric fields associated with the hydroxyl and olefinic or cyclopropyl groups so as to produce dipolar shielding in the direction of Ha.

The anomalous deshielding of the syn protons (Hs) in the epimeric systems **21**, **23**, and **25** most assuredly cannot be explained on the basis of bond or ring anisotropies alone. Thus, in the olefinic system **23** one would have intuitively predicted abnormally high shielding for proton Hs, a factor which undoubtedly contributed to Marchand and Rose's misassignment in **5**. Other workers[11] have suggested that this inside proton may actually lie in the deshielding zone of the double bond. While precise X-ray crystallographic data are not available on **23**-OH, if one assumes a molecular geometry closely approximating that suggested by Dreiding or Framework molecular models, then the calculated shift (+1.34 ppm) definitely establishes that this proton lies in the strongly shielding, not deshielding, zone of the double bond. The only reasonable rationalization for the large deshielding effect would then appear to be steric deshielding. van der Waals repulsion between the olefinic and C–Hs charge clouds should appreciably distort the electronic environnment of proton Hs and lead to a low-field shift for this proton and a high-field shift for the corresponding anti proton (Ha) when the latter is present as in systems **5**–**20**.

(36) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 86, 1870 (1964). The parameter n represents the effective number of electrons circulating in a path of radius a. The deshielding effect (σ_g in parts per million) of this current is then given by the equation[35]

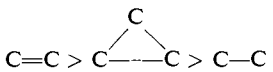
$$\sigma_g = \frac{10^6 ne^2}{6\pi Mc^2 a[(1+\rho)^2 + Z^2]^{1/2}} \times \left[K + \frac{1-\rho^2-Z^2}{(1-\rho)^2+Z^2}E\right]$$

where e and M are the charge and mass of the electron, respectively, c is the velocity of light, ρ and Z are the usual cylindrical coordinates, and K and E the complete elliptic integrals.

(37) L. Joris, P. v. R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, 90, 327 (1968), and references cited therein.

The smaller deshielding effect in saturated alcohol **35**-OH is consistent with diminished interaction between Hs and the C-2–C-3 σ bond. In this instance, however, hydrogen–hydrogen repulsion between Hs and H-2n,H-3n, should now play a significant role in steric deshielding, similar, in fact, to that orginally described by Winstein and Anet in the *endo,endo*-dimethanonaphthalene and half-cage compounds.[12b]

As indicated by the calculated shift in Table II, ring anisotropy apparently plays a major role in the observed deshielding of proton Hs in the cyclopropyl system **21**. The total downfield shifts for the various derivatives of **21**-OH are undoubtedly a combination of ring anisotropy and steric deshielding. With regard to the latter effect, the repulsive interactions between H-2,H-4 and Hs have been eased compared with **25**-OH; however, the protruding "banana bond" effect of the cyclopropyl C-2–C-4 edge bond enhances prospects for electrostatic distortion of the C–Hs charge cloud. Therefore, the order of electronic steric deshielding of Hs by the C-2–C-3(C-4) carbon–carbon bond in this ring system would appear to be



Curiously, this is also the order of solvolytic rate enhancements provided by these groupings in the systems **23**-OBs,[17b] **21**-OBs,[15] and **25**-OBs[17a] respectively.

The remaining proton assignments in the trimethanonaphthalene derivatives **21**–**22**, particularly the cyclopropyl and bridge methylene protons 3x, 3n, 11a, and 11s, are of interest and will be considered. The 60-MHz spectra of **21**-OH and its derivatives (Table III) are characterized by a trio of upfield multiplets A–C (A, the previously mentioned one-proton high-field doublet of triplets centered at about τ 9.9–10.0; B, a two-proton partially resolved multiplet at *ca.* 9.5; and C, a five-proton complex multiplet at 8.8–9.2) in addition to multiplet signals attributed to the bridgehead protons and a pair of ethano (7,8) protons. These spectra were rendered interpretable only with the aid of selective solvent shifts on **21**-OH and its analogous ketone **30** at 100 MHz. The data for the latter two compounds in benzene and deuteriochloroform are presented in Table IV while Figure 1 records the upfield portion of the spectrum (100 MHz) of **21**-OH in benzene.

In benzene at 100 MHz (Figure 1) the multiplets B and C for **21**-OH are clearly resolved into essentially their first-order components. The assignment of the exo cyclopropylmethylene proton 3x to the doublet of triplets at −8.5 Hz and the endo proton 3n to the quintet at 43.5 Hz is unambiguous based on analysis of the coupling constants:[26] $J_{3x,3n}$ = 5.6 Hz; $J_{3x,2}$ = $J_{3x,4}$ = 7.2 Hz; $J_{3n,4}$ = $J_{3n,2}$ = 3.0 Hz. The cyclopropyl bridgehead protons (2,4) appear as a slightly broadened doublet of doublets at 63.0 Hz while the bridge methylene protons 11s and 11a form a characteristic AB quartet at 28.9 and 83.8 Hz (J = 10.8 Hz). The inner member of the lower field portion of this AB pattern appears as a broadened triplet (^3J = 1.7 Hz). Both sets of triplets for this lower field AB signal are observed in the deuteriochloroform spectrum of ketone **30**. By contrast, the higher field signal of the same AB quartet in both **21**-OH and **30**

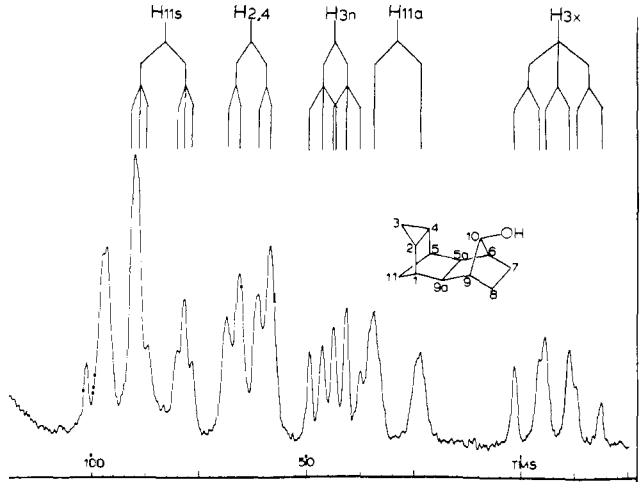
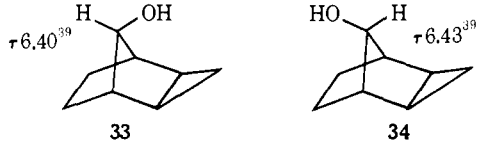


Figure 1. The high-field region of the ^1H nmr spectrum of **21-OH** in benzene at 100 MHz (250-Hz sweep width).

appears as a broadened doublet, each member showing at least quintet (probably septet) splitting indicative of stereospecific long-range coupling ($^4J \simeq 1$ Hz) with the cyclopropyl bridgehead (2,4) protons. On this basis the latter signal is assigned to the anti (11a) bridge proton while the syn (11s) proton is assigned to the lower field set of triplets.[38]

The apparent deshielding effect experienced by the syn bridge proton 11s is contrary to the prediction, based on the ring current model for cyclopropane, that protons above the ring should be shielded. On the other hand the rather severe van der Waals compression between the interior protons 3n and 11s and the resultant steric deshielding experienced by both protons must undoubtedly account for this reversal of the expected order of shifts for protons 11s and 11a. As an added consequence of this compressional effect the local diamagnetic shielding environment of the external pair of protons 3x,11a is enhanced, thus accounting for the appearance of these protons at highest field. A closer balance between compressional effects and ring anisotropy would likewise account for the surprising near equivalency of the bridge methinyl protons in the *exo-syn-* and *exo-anti*-tricyclo[3.2.1.$0^{2,4}$]octanols **33** and **34**.[21,23,39]



33 **34**

The remaining proton assignments in **21-OH** and **30** were arrived at on the basis of anticipated coupling patterns and solvent shifts in $CDCl_3$ and benzene. Collision complexes between bicyclic ketones and benzene produce an upfield shift, with respect to $CDCl_3$, for those protons lying below an imaginary plane perpendicular to the carbon–oxygen bond and passing through the carbonyl carbon.[40] Protons lying above this plane exhibit downfield shifts as evidenced by H-2,H-4 in **30** (see Table IV). In addition the shifts are maximized for those protons oriented essentially perpendicular to this plane. Thus, of the three signals attributed to bridgehead protons in the benzene spectrum (100 MHz) of **30**, the one appearing as a virtual triplet at 147.5 Hz exhibited the largest upfield solvent shift ($\delta_{CDCl_3} - \delta_{C_6H_6} = 0.48$ ppm) and was assigned to the 5a,9a protons. Similarly the *endo* protons 7n,8n experience a larger solvent shift than the corresponding exo protons 7x,8x. Finally, protons 1,5 and 6,9 are readily distinguished on the basis of the known stereospecific coupling behavior of norbornyl type bridgehead protons.[6,41]

Experimental Section

General Procedures. Melting points were determined on a Hoover-Thomas apparatus and are uncorrected. Infrared spectra were recorded as mulls (Nujol), films, solutions (CCl_4), and solids (KBr) on Perkin-Elmer 137, 337, and 621 spectrophotometers. Only the band(s) important to structure characterization is (are) reported. Nmr spectra were recorded on a Varian A-60A (60 MHz) or XL-100 (100 MHz) spectrometer, tetramethylsilane being used as internal standard or lock in $CDCl_3$. Chemical shifts are reported in order of increasing τ, with multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, bs = broad singlet, and m = multiplet. Mass spectra were determined on a Hitachi RMU-6E spectrometer operating at 70 eV. Gas–liquid partition chromatographic (glpc) separations were performed on Varian Aerograph 600D or A-90P instruments. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Reaction of 2-OAc with Hexachlorocyclopentadiene. A mixture of 10.7 g (0.070 mol) of *anti*-7-norbornenyl acetate (**2**-OAc) and 76 g (0.28 mol) of hexachlorocyclopentadiene was degassed, sealed in a thick-walled glass tube and heated at 150° for 60 hr. The viscous yellow reaction mixture, which solidified on standing, was chromatographed on a column of silica gel using hexane (2 l.) to elute the unreacted hexachlorocyclopentadiene. Continued elution with hexane (3 l.) followed by recrystallization of the resulting solid from ether–petroleum ether (37–47°) afforded 22.7 g (76%) of **27**-OAc: mp 132–132.5°; ir (Nujol) 1735 (C=O) and 1590 cm^{-1} (ClC=CCl); nmr (CCl_4) τ 5.20 (bs, H_9), 7.31 (s, H_{4a} and H_{8a}), 8.0 (m, H_{6x} and H_{7x}), 8.05 (s, CH_3), and 8.9 (m, H_{6n} and H_{7n}).

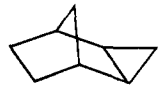
Anal. Calcd for $C_{14}H_{12}O_2Cl_6$: C, 39.57; H, 2.85. Found: C, 39.99; H, 2.91.

Hexachloro-*exo-endo* Alcohol (27-OH).[16,17] **A.** A mixture of 2.1 g (19 mmol) of *anti*-7-norbornenol (**2**-OH) and 7.6 g (27.8 mmol) of hexachlorocyclopentadiene was degassed and sealed under vacuum in a thick-walled tube which was then heated at 150° for 24 hr. The viscous yellow contents were removed from the tube and chromatographed on a column of 300 g of Fisher alumina. Elution in the order petroleum ether (750 ml), benzene (150 ml), and methanol (150 ml) afforded 3.44 g of hexachlorocyclopentadiene, 2.56 g of an unidentified fraction, and 3.68 g (50%) of **27**-OH. Recrystallization of the latter from acetone gave an analytical sample: mp 134.5–135°; ir (Nujol) 3250 (OH) and 1590 cm^{-1} (ClC=CCl); nmr ($CDCl_3$) τ 5.90 (bs, H_9), 7.27 (s, H_{4a} and H_{8a}), 7.74 (m, H_5 and H_8), 7.9 (m, H_{6x} and H_{7x}), and 8.8 (m, H_{6n} and H_{7n}).

Anal. Calcd for $C_{12}H_{10}OCl_6$: C, 37.64; H, 2.63. Found: C, 38.07; H, 2.70.

B. To a stirred slurry of 1.2 g (31.6 mmol) of lithium aluminum hydride in 50 ml of anhydrous ether under nitrogen at room temperature, was slowly added (about 0.5 hr) a solution of 6.82 g (16.0 mmol) of **27**-OAc in 50 ml of anhydrous ether. Following the addi-

(38) (a) To our knowledge this is the first reported assignment of relative chemical shifts to the bridge methylene protons of an *exo*-tricyclo[3.2.1.$0^{2,4}$]octane moiety. The nmr spectrum of the parent hydrocarbon i has been reported,[38b] but not analyzed. A more detailed examination of the nmr spectra of i and its derivatives is thus warranted and is currently underway in our laboratories. (b) H. E. Simmons and



i

R. D. Smith, *J. Amer. Chem. Soc.*, 81, 4256 (1959).

(39) J. Haywood-Farmer, Ph.D. Thesis, University of British Columbia, 1967.

(40) D. H. Williams and N. S. Bhacca, *Tetrahedron*, 21, 2021 (1965), and references cited therein. See also ref 33, pp 104–113.

(41) E. W. Garbisch, Jr., *Chem. Commun.*, 332 (1968), and references cited therein.

tion, the mixture was maintained at room temperature for about 1.5 hr and then refluxed for 0.5 hr. The mixture was cooled to 0° and water carefully added to destroy the excess reagent. The milky aqueous layer (about 100 ml) was acidified with 10% H_2SO_4 solution and extracted with three 200-ml portions of ether. The combined ether solutions were washed with 50-ml portions of water, 10% aqueous Na_2CO_3 solution, and brine. The organic extracts were combined, dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give 5.98 g (97%) of a yellowish pink solid. This solid was not further purified, but was shown by spectral analysis to be identical with the chlorinated alcohol obtained by method A.

Dechlorination of 27-OH. To a stirred solution of 2.26 g (5.9 mmol) of **27-OH** and 4.1 g (55 mmol) of *tert*-butyl alcohol in 28 ml of freshly distilled tetrahydrofuran at room temperature, was slowly added under nitrogen 3.15 g (0.14 g-atom) of finely cut sodium metal.[19b] The mixture was refluxed for a period of 10 hr, cooled to room temperature, and allowed to stand overnight. To the deep purple reaction mixture was slowly added about 30 ml of methanol to destroy the excess sodium. The aqueous layer formed by the addition of 200 ml of water was extracted with three 150-ml portions of ether. The combined ether fractions were washed with 30-ml portions of water and brine and the aqueous washings re-extracted with 150 ml of ether. The ether fractions were combined, dried ($MgSO_4$), and filtered. Removal of solvent by rotary evaporation afforded a viscous brown oil which was sublimed at 125° (14 mm) to give a colorless semisolid product. Crystallization from pentane afforded 0.25 g (24%) of white crystals, mp 104–106°. Preparative glpc gave pure **23-OH**: mp 107–109° (lit.[17b] 108–109°); ir (CCl_4) 3630 cm^{-1} (OH); nmr ($CDCl_3$) τ 3.90 (t, J = 1.7 Hz, H_2 and H_3), 5.20 (bs, H_9), 7.13 (irregular heptet, J = 1.7 Hz, H_1 and H_4), 7.95 (t, J = 2.0 Hz, H_{4n} and H_{8n}), 8.05 (m, H_8, H_5, H_{6x}, and H_{7x}), 8.50 (s, OH), 8.65 (dt, J = 8.0 Hz, 1.8 Hz, H_{10s}), 8.8 (d, J = 8.0 Hz, H_{10a}),[42] 8.90 (m, H_{6n} and H_{7n}).

Repetition of this reaction on larger scale followed by sublimation of the crude oily product gave higher yields (*ca.* 50%) of alcohol **23-OH** in sufficiently pure condition for further manipulations.

Octahydro-*exo-endo*-dimethanonaphthalene Ketone (29). To the chromium trioxide–pyridine complex[27] prepared by careful addition of 1.8 g (18.0 mmol) of chromium trioxide to 10 ml of dry pyridine mechanically stirred under nitrogen at 0° was added, at room temperature, a solution of 600 mg (3.4 mmol) of **23-OH** in 10 ml of dry pyridine over a period of about 10 min. After a brief period of stirring, the reaction mixture was allowed to stand for 24 hr and then diluted with 200 ml of water. The aqueous solution was extracted with petroleum ether (20–40°) and the combined organic extracts were washed with water, 10% aqueous HCl solution, 10% aqueous Na_2Co_3 solution, and brine. The organic layer was dried and the solvent evaporated to give a pale yellow oil which solidified on standing. The ketone was purified by sublimation at 120° (10 mm) to give 540 mg (91%) of a sticky white solid: mp 54–56°; ir (Nujol) 1760 cm^{-1} (C=O); nmr ($CDCl_3$) τ 4.05 (t, J = 2.0 Hz, H_2 and H_3), 7.02 (irregular heptet, J = 1.9 Hz, H_1 and H_4), 7.79 (t, J = 1.9 Hz, H_{4n} and H_{8n}), 8.26 (m, H_5 and H_8), 8.49 (dt, J = 8.5, 1.8 Hz, H_{10s}),[42] 8.35 (m, H_{6x} and H_{7x}), 8.50 (m, H_{6n} and H_{7n}), 8.76 (d, J = 8.5 Hz, H_{10a}).[42]

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 80.1. Found: C, 82.56; H, 8.08.

After standing in the solid state for about 2 weeks this ketone had partially decomposed giving an ether-insoluble material presumably polymeric in nature.

***anti*-Octahydro-*exo-endo*-dimethanonaphthalenyl Acetate (23-OAc).** To a solution of 3.5 g (19.8 mmol) of **23-OH** in 10 ml of dry pyridine was added 10 g (85 mmol) of acetic anhydride and the mixture was heated on a steam bath for 40 min. The solution was cooled to 0°, an excess of water was added, and the mixture was stirred at 0° for 1 hr. The usual work-up afforded a pale yellow oil which on distillation gave 3.9 g (90%) of the pure acetate: bp 113–115° (3.1 mm); nmr ($CDCl_3$) τ 3.81 (t, J = 2.0 Hz, H_2 and H_3), 4.45 (bs, H_9), 7.10 (irregular heptet, J = 2.0 Hz, H_1 and H_4), 7.90 (m, H_8, H_5, H_{4a}, and H_{8a}), 8.07 (s, CH_3), 8.2 (m. H_{6x} and H_{7x}), 8.62 (dt, J = 8.3, 1.7 Hz, H_{10s}),[42] 8.90 (d, J = 8.3 Hz, H_{10a}),[42] 8.85 (m, H_{6n} and H_{7n}).

***anti*-Decahydro-1,4-*exo-endo*-5,8-dimethanonaphthalen-9-ol (25-OH).** Hydrogenation of **23-OH** (100 mg; 0.567 mmol) over 10% palladium-on-charcoal (30 mg) in 95% ethanol (6 ml) at room temperature quantitatively afforded pure **25-OH**, mp 127–128° (lit.[17a] mp 124–126°), after work-up and sublimation at 125° (9 mm): ir (CCl_4) 3640 cm^{-1} (OH); nmr ($CDCl_3$) τ 5.58 (bs, Hs), 7.73 (bs, H_1 and H_4), 8.1 (m, 4 H), 8.30 (s, OH), 8.3 (m, 2 H), 8.54 (bs, 4 H) 8.80 (bs, 2 H), 8.9 (m, 2 H).

Decahydro-1,4-*exo-endo*-5,8-dimethanonaphthalen-9-one (28). Hydrogenation of ketone **29** (116 mg; 0.665 mmol) over 10% palladium-on-charcoal (42 mg) in 95% ethanol solution (5 ml) afforded 108 mg (92%) of pure **28** after sublimation at 110° (14 mm): mp 87.5–89.0°; ir (Nujol) 1760 cm^{-1} (C=O); nmr ($CDCl_3$) τ 7.70 (bs, H_8 and H_5), 7.8–8.8 (broad multiplet, 14 H).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.69; H, 9.27.

***syn*-Decahydro-1,4-*exo-endo*-5,8-dimethanonaphthalen-9-ol (26-OH).** To a stirred slurry of 150 mg (3.95 mmol) of lithium aluminum hydride in 10 ml of anhydrous ether under nitrogen at room temperature was slowly added a solution of 110 mg (0.625 mmol) of **28** in 10 ml of anhydrous ether. The mixture was refluxed for 1.5 hr and then cooled to 0°. The excess hydride was destroyed by the cautious addition of water, and the resulting precipitated aluminum salts dissolved in 10% aqueous H_2SO_4 solution. The aqueous solution was extracted with ether (five 75-ml portions) and the combined ether solutions were washed with water, 10% aqueous sodium carbonate solution, and brine. The ether layer was dried ($MgSO_4$) and filtered and the solvent removed to leave a white solid which on sublimation at 130° (10 mm) gave 105 mg (95%) of product, mp 146.5–147.5°. Recrystallization from chloroform and resublimation at 125° (16 mm) gave an analytical sample of **26-OH**: mp 148–148.5°; ir (CCl_4) 3630 cm^{-1} (OH); nmr ($CDCl_3$) τ 6.07 (s, Ha), 7.70 (bs. H_8 and H_5), 8.0 (bs, H_{4a}, H_{8a}, H_1 and H_4), 8.1–9.3 (broad multiplet, 10 H), 8.32 (s, OH).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.13; H, 10.43.

Lithium Aluminum Hydride Reduction of Ketone 29. A. To a stirred slurry of 165 mg (4.35 mmol) of lithium aluminum hydride in 8 ml of anhydrous ether under nitrogen at room temperature was slowly added a solution of 80 mg (0.45 mmol) of freshly sublimed **29** in 7 ml of anhydrous ether. The mixture was stirred at room temperature for 45 min and cooled to 0° and water was slowly added to destroy the excess reagent. The snow-white mixture was separated and the aqueous portion (about 50 ml) extracted with ether (three 65-ml portions). The combined ether extracts were washed with water (two 40-ml portions) and brine (40 ml). The aqueous washings were back extracted with ether (50 ml). The ether solutions were combined and dried over magnesium sulfate. Removal of solvent afforded a pale yellow oil which solidified on cooling to 70°. The oil was sublimed as a liquid at 130° (15 mm) to give 74 mg (91%) of a liquid product which clearly contained, as the major component, the desired alcohol, **24-OH**: nmr ($CDCl_3$) τ 3.68 (t, J = 2.2 Hz, H_2 and H_3), 6.40 (s, H_9), 7.03 (irregular heptet, J = 2.0 Hz, H_1 and H_4), 7.63 (t, J = 1.5 Hz, H_{4a} and H_{8a}), 8.18 (bs, H_5 and H_8), 8.0–9.1 (m, unassigned).

This liquid defied all attempts at further purification. Gas chromatography on a variety of columns, all at *ca.* 180°, indicated that several components were present, one of them major. This component, however, was not an alcohol, as shown by the infrared spectrum. Attempted adsorption chromatography on Woelm neutral alumina eluting with ether–petroleum ether (36–48°) mixtures gave a glpc homogeneous oil which was shown to be the cyclic ether **31**: nmr ($CDCl_3$) τ 5.90 (m, H_2), 6.18 (bs, H_9), 7.7–9.2 (m, 14 H); mass spectrum, *m/e* (70 eV) 176 (M^+), 158, 91, 81 (100%), 79, 67, 66.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.91; H, 9.21.

A sample of crude **24-OH** (50 mg) was mixed with an equimolar amount of *p*-nitrobenzoyl chloride (53 mg) in a small volume (*ca.* 100 μl) of dry pyridine. The mixture was heated on a steam bath for 5 min, cooled to room temperature, and diluted with water. The gummy solid that was formed showed no olefinic peaks in its nmr spectrum.

B. To a stirred slurry of 252 mg (6.64 mmol) of lithium aluminum hydride in 8 ml of anhydrous ether under nitrogen at room temperature was slowly added a solution of 89 mg (0.51 mmol) of freshly sublimed **29** in 8 ml of anhydrous ether. After addition was complete, stirring was continued for 45 min, the mixture was cooled to 0°, and water was slowly added to destroy the excess metal hydride. The resulting snow-white mixture was extracted with three 100-ml portions of ether and the combined ether extracts were washed with water and brine and dried ($MgSO_4$). Filtration followed by removal of solvent gave 88.4 mg of an oil which was immediately dissolved in 3 ml of 95% ethanol and hydro-

(42) Assignments made in agreement with observed chemical shifts for C-7 protons in norbornene.[3-5]

genated with 35 mg of 10% palladium-on-charcoal as catalyst. After the catalyst was filtered and washed with ether, the solvent was removed from the filtrate to leave a white solid which was sublimed at 125° (14 mm) to give 77 mg (85%) of **26-OH**, mp 145–146°.

Cyclopropanation Reactions with Diazomethane–Cuprous Chloride–23-OAc. The diazomethane required for this preparation was generated according to the procedure of Pincock and Wells.[21] A stirred solution of 3.8 g (17.4 mmol) of **23**-OAc in 40 ml of anhydrous ether containing 1.5 g of suspended cuprous chloride was treated with a steady stream of diazomethane in nitrogen gas. The progress of the reaction was followed by glpc and was allowed to proceed until less than 1% starting ester remained. The grey reaction mixture was filtered to give a clear colorless filtrate. The solvent was removed and the resulting yellow oil distilled to give 3.75 g (92.5%) of homogeneous **21**-OAc: bp 124–125° (2.0 mm); ir (film) 1725 cm^{-1} (C=O). The nmr spectral data for this and other trimethanonaphthalene derivatives are listed in Table III.

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.97; H, 8.83.

23-OH. As above, a steady stream of diazomethane gas was passed through a stirred solution of 290 mg of **23-OH** in 10 ml of anhydrous ether containing 0.25 g of cuprous chloride and held at 0°. The reaction was followed by glpc and continued until the starting material had been consumed. The reaction mixture was filtered and the solvent evaporated to give 400 mg of a cloudy yellow oil. Gas–liquid chromatography showed the presence of two major products. The longer retention time peak was collected and shown to be **21-OH** by comparison of spectral properties with an authentic sample as obtained below. The shorter retention time peak was also collected and identified as the ether **21**-OMe by spectral analysis. Acceptable elemental analyses for this ether could not be obtained primarily due to the limited amount of sample; however, the nmr spectrum (Table III) left no doubt as to the structure.

anti-**Decahydro-*exo-endo*-trimethanonaphthalene Alcohol (21-OH).** To a stirred slurry of 1.2 g (31.6 mmol) of lithium aluminum hydride in 50 ml of anhydrous ether under nitrogen was slowly added a solution of 3.56 g (15.3 mmol) of **21**-OAc in 50 ml of anhydrous ether. After addition was complete, the mixture was refluxed for 3 hr and water slowly added to decompose excess hydride. The aqueous layer was separated and extracted with ether, and the combined ether solutions were washed with water and brine and dried over magnesium sulfate. The drying agent was removed by filtration, the solvent evaporated, and the residue sublimed at 125° (11 mm) to give 2.75 g (94%) of pure **21-OH**: mp 118.5–120.5°; ir (CCl_4) 3630 cm^{-1} (OH).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.31; H, 9.81.

The *p*-nitrobenzoate derivative was prepared from 300 mg (1.58 mmol) of **21-OH** and 297 mg (1.60 mmol) of *p*-nitrobenzoyl chloride in 0.6 ml of dry pyridine. The mixture was heated to boiling for about 1 min and cooled, and the solid triturated with an excess of water before filtration. After washing well with water, aqueous sodium carbonate solution, and water again, the solid was dried to give 519 mg (97%) of pale yellow crystals. Recrystallization from acetone gave pure **21**-OPNB: mp 152.5–152.8°; ir (Nujol) 1710 cm^{-1} (C=O).

Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.62; H, 6.41; N, 4.12.

anti-p-**Bromobenzenesulfonate (21-OBs).** A mixture of 1.51 g (7.95 mmol) of **21-OH** and 2.06 g (8.05 mmol) of *p*-bromobenzenesulfonyl chloride was dissolved in 4.5 ml of pyridine with slight warming and allowed to stand at 0° for 5 hr. The solid mass was triturated with water, filtered, washed well with water, aqueous sodium carbonate solution, and water, and dried to give 3.02 g (93%) of white crystalline material. Recrystallization from petroleum ether (65–110°) afforded pure **21**-OBs: mp 118.5–119°; nmr ($CDCl_3$) τ 2.32 (s, 4 H, aromatic), 4.18 (bs, H_{10s}), 7.7 (m, H_1, H_5, H_{5a}, and H_{9a}), 8.3 (m, H_6, H_9, H_{7x}, and H_{8x}), 8.8–10.2 (m, 8 H).

Anal. Calcd for $C_{19}H_{21}SO_3Br$: C, 55.75; H, 5.17; Br, 19.52. Found: C, 55.89; H, 5.03; Br, 19.80.

Decahydro-*exo-endo*-trimethanonaphthalene Ketone (30). To 10 ml of ice-cooled, mechanically stirred, dry pyridine under nitrogen was slowly added 1.7 g (17.0 mmol) of chromium trioxide.[27] The resulting pasty yellow complex was warmed to room temperature causing it to darken considerably. A solution of 400 mg (2.1 mmol) of **21-OH** in 10 ml of dry pyridine was slowly added to the complex. Stirring was continued for an additional 20 min and the dark solution allowed to stand for 24 hr. The reaction mixture was diluted with 200 ml of water and the aqueous solution extracted with ether (20–40°). The combined organic extracts were thoroughly washed with water, 10% aqueous sodium carbonate solution, water, and brine, and dried ($MgSO_4$). After filtration and concentration, the slightly yellow oil which remained solidified on standing and was sublimed at 110° (9 mm) to give 365 mg (91%) of pure white, crystalline ketone: mp 60.5–62°; ir (Nujol) 1760 cm^{-1} (C=O).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.79; H, 8.64.

syn-**Decahydro-*exo-endo*-dimethanonaphthalene Alcohol (22-OH).** A solution of 20 mg (1.06 mmol) of **30** in 15 ml of anhydrous ether was added dropwise to a stirred mixture of 500 mg (13.1 mmol) of lithium aluminum hydride in 7 ml of ether under nitrogen. The mixture was refluxed for 2 hr and the same work-up procedure followed as with ketone **29**. Sublimation (130° (11 mm)) of the yellow solid that remained after removal of solvent gave 195 mg (96%) of pure white crystals: mp 62–63°; ir (CCl_4) 3635 cm^{-1} (OH).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.97; H, 9.62.

syn-**7-Norbornenyl Methyl Ether (3-OMe).** This ether was prepared by a method similar to that described by Meinwald, *et al.*,[43] for the anti isomer **2**-OMe. A 2.6-g portion of a 50% dispersion of sodium hydride in mineral oil was washed repeatedly with small portions of pentane, the residual pentane removed by suction, and the light tan residue slurried with 17 ml of benzene under nitrogen. To this slurry was added, over a period of about 10 min, a solution of 2.1 g of *syn*-7-norbornenol[44] in 5 ml of benzene. The mixture, which foamed considerably during the addition, was stirred at room temperature for 3.5 hr during which time, it solidified. An additional 10 ml of benzene was added; the mixture was heated to 80° for 1 hr and then cooled to room temperature. Following an additional stirring period of 1.5 hr, 5.0 g of freshly distilled methyl iodide was slowly added followed by about 4 ml of benzene. The mixture was heated at 80° for 3 hr, cooled to 0°, hydrolyzed with water, and extracted with ether. The ether fractions were washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Distillation of the residual yellow oil gave 1.02 g of a colorless liquid, bp 100–102° (165 mm), estimated to contain *ca.* 65% of **3**-OMe by glpc (28% yield). Samples for analytical and spectral purposes were obtained by preparative glpc: nmr ($CDCl_3$) τ 3.98 (m, H_2 and H_3), 6.60 (m, H_7), 6.80 (s, CH_3), 7.13 (m, H_1 and H_4), 8.3 (m, H_{5x} and H_{6x}), 9.1 (m, H_{5n} and H_{6n}).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.52; H, 9.87.

7-Norbornyl Methyl Ether.[45] A mixture of 613 mg of the crude distilled fraction of **3**-OMe, 25 mg of 10% palladium-on-charcoal, and 15 ml of diethyl ether was exposed to hydrogen gas at *ca.* 1.1 atm and room temperature until gas uptake ceased. The catalyst was removed and the solvent evaporated to leave 500 mg (80%) of a volatile colorless oil. Analysis by glpc clearly showed the absence of olefinic ether in the product. Samples for spectral purposes were obtained by preparative glpc: nmr ($CDCl_3$) τ 6.48 (m, H_7), 6.70 (s, CH_3), 7.88 (m, H_1 and H_4), 8.0–9.1 (m, 8 H).

Acknowledgment. Financial support of this work by the National Science Foundation (Grants No. GP-9412 and GP-27411) is gratefully acknowledged. One of us (M. A. B.) acknowledges his personal indebtedness to the late Professor Saul Winstein for his encouragement and friendly counsel during the course of this and related work over the past few years.

(43) J. Meinwald, Y. C. Meinwald, and T. N. Baker, *J. Amer. Chem. Soc.*, 86, 4074 (1964).

(44) W. C. Baird, Jr., *J. Org. Chem.*, 31, 2411 (1966).

(45) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, 88, 864 (1966). These authors report the preparation of this ether, but no spectral data or experimental details are given.