Rearrangement of a Bicyclo[2.2.2]octadienol to a Dihydropentalene[1,2]

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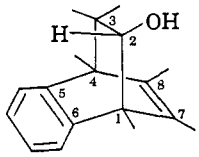
Abstract: Either of the epimeric alcohols **1** and **2** (1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ols), synthesized by addition of benzyne to hexamethyl-2,4-cyclohexadienone followed by hydride reduction, rearranged on dehydration with strong acid to the crystalline benzodihydropentalene **14**. The structure of **14** was deduced from its spectra and chemical transformations. In particular, **14** is hydrogenated preferentially at the "central" double bond, forms Diels–Alder adducts **21** and **22** with tetracyanoethylene and N-phenylmaleimide, and undergoes exclusive exchange in 80% D_2SO_4–D_2O at the C-3 methyl group. Treatment of **1** and **2** with strong acid for shorter periods and lower temperatures gave reduced yields of **14** and permitted the isolation of three isomeric methylenebicyclo[3.2.1]octadienes (**5**, **7** or **8**, and **25**), each of which with further acid treatment gave **14**. Reactions with deuterium-labeled precursors permitted the various methyl groups to be traced. A mechanism is suggested which involves rapid epimerization of **1** and **2** and the formation of equilibrating ions **37**, **38**, and **39** which may, by proton loss, furnish hydrocarbons **24**, **7** (or **8**), and **5**, respectively. Alternatively, prolonged treatment with acid permits opening of the bicyclo[3.2.1] system in **37**–**39**, leading to the bicyclo[3.3.0] system in **14**.

Acid-catalyzed rearrangements in bicyclo[2.2.2]octyl systems[5] most often yield bicyclo[3.2.1]octyl derivatives, although there are less frequent examples of reactions of the reverse kind.[6,7] A recent study has shown,[8] for instance, that benzobicyclo[2.2.2]octadienyl brosylates are solvolyzed to benzobicyclo[3.2.1]octadienyl acetates in which the vinyl or phenyl function *anti* to the brosylate group has shifted. Since most such studies have been performed under solvolytic conditions, we were interested in examining the behavior of suitable alcohols with the bicyclo[2.2.2]octyl skeleton in the presence of strong acids, where elimination would be expected to accompany rearrangement. We chose for study the readily available alcohols **1** and **2**[9] which of necessity must rearrange on dehydration. Under



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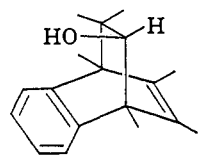

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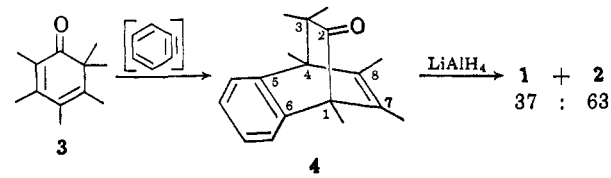
strongly acid conditions, **1** and **2** underwent a profound rearrangement to give a quite unexpected product. This reaction is the subject of the present paper.

Results

Preparation and Stereochemistry of the Starting Alcohols. Preparation of the 1,3,3,4,7,8-hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ols **1** and **2** was effected by a two-step procedure from 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dien-1-one[10] (**3**). Dienone **3** was subjected to reaction with benzyne[11] to give the bicyclooctadienone **4**. The nmr spectrum of this adduct



3 **4**

showed two methyl groups at τ 9.53 and 8.94 (*syn*- and *anti*-3-methyls), a six-proton signal at τ 8.38 (bridgehead methyls), and two mutually coupled (J = 1 Hz) methyl signals (allylic methyls) at τ 8.18 and 8.26. Comparison with the 7-d_3-bicyclooctadienone **27a** (see below) indicated that the τ 8.26 peak is due to the 7-methyl group, which presumably lies in the shielding region of the carbonyl group. Similarly the 4-d_3-bicyclooctadienone **27b** identifies the chemical shift of the 4-methyl as τ 8.38.

The ketone was reduced with lithium aluminum hydride to a 37:63 mixture of the epimeric alcohols **1** and **2**. Crystallization yielded the major epimer. The unchanged minor epimer was isolated in low yield from the mixture of 3,5-dinitrobenzoates prepared from the epimeric mixture of alcohols; its ester could not be separated from that of the major alcohol.

The nmr spectra of the epimers yielded the following data. The 2-proton in the minor epimer is at higher field (τ 7.10) than that in the major epimer (τ 6.97). A *syn* relationship with an aromatic nucleus has been noted to have this effect in other benzobicyclo[2.2.2]-octanyl systems.[12] The hydroxyl proton in the major epimer absorbs at the abnormally high position of τ 9.40, which may indicate a shielding interaction with the aromatic ring. The peaks at τ 8.28 and 8.30 are attributed to the allylic methyls, those at τ 8.37 (minor)

(1) Preliminary communication: A. C. G. Gray, T. Kakihana, P. M. Collins, and H. Hart, *J. Am. Chem. Soc.*, **89**, 4556 (1967).

(2) We are indebted to the National Science Foundation for their generous support of this research.

(3) We are grateful to Mr. T. Kakihana and Dr. P. M. Collins for their contributions in the early stages of this research. Experiments performed by them are indicated with their initials, in the Experimental Section.

(4) To whom inquiries should be addressed.

(5) For a review, see J. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 213–226.

(6) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Am. Chem. Soc.*, **87**, 2879 (1965).

(7) E. Cioranescu, A. Mihai, G. Mihai, M. Elian, and C. D. Nenitzescu, *Rev. Roumaine Chim.*, **10**, 175 (1965).

(8) H. Tanida, K. Tori, and K. Kitahonoki, *J. Am. Chem. Soc.*, **89**, 3212 (1967).

(9) Numbering used in this paper is shown in the formulas.

(10) H. Hart, P. M. Collins, and A. J. Waring, *J. Am. Chem. Soc.*, **88**, 1005 (1966).

(11) L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963); M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1005 (1963).

(12) K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1597 (1963).

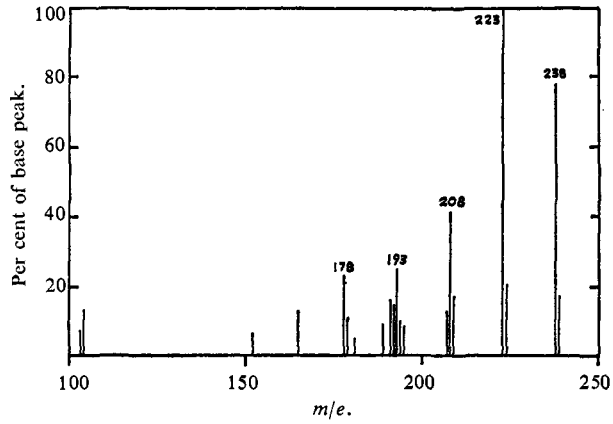


Figure 1. Mass spectrum of 1,4-dihydro-1,1,2,3,4,4-hexamethylbenzopentalene (**14**).

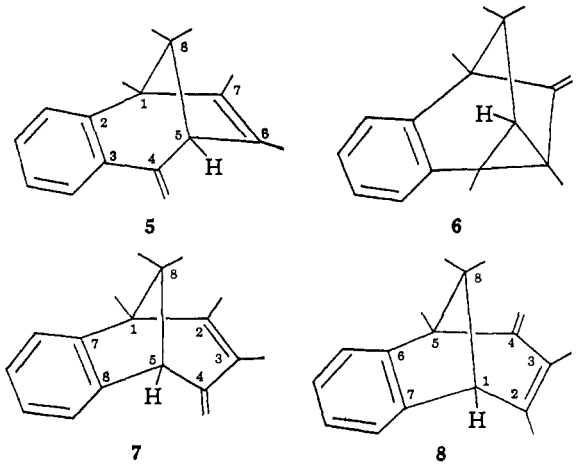
and 8.45 (major) to the bridgehead 1-methyls, and those at τ 8.51 and 8.50 to the bridgehead 4-methyls. The 3-*gem*-dimethyls are more widely separated in the major epimer (τ 9.05 and 9.63) than in the minor (τ 9.15 and 9.53). If in each compound the methyl *syn* to the aromatic ring is at higher field, assignment of the *syn* configuration to the major alcohol would imply that the hydroxyl group has a stronger deshielding effect on a *trans*- than on a *cis*-methyl group.[12a]

In the *syn* (major) epimer the hydroxyl stretching region in the infrared shows a strong band at 3580 and a weak one at 3635 cm^{-1}. In *syn*-5,6-benzobicyclo-[2.2.2]octen-2-ols, a band at 3586 cm^{-1} has been attributed to internal hydrogen bonding with the aromatic ring, whereas the 3620-cm^{-1} band in the *anti* epimer has been assigned to the free hydroxyl.[12] In our *anti* epimer the free hydroxyl band (3635 cm^{-1}) is stronger than in the *syn* compound, whereas the hydrogen-bonding band (3590 cm^{-1}) is weaker.

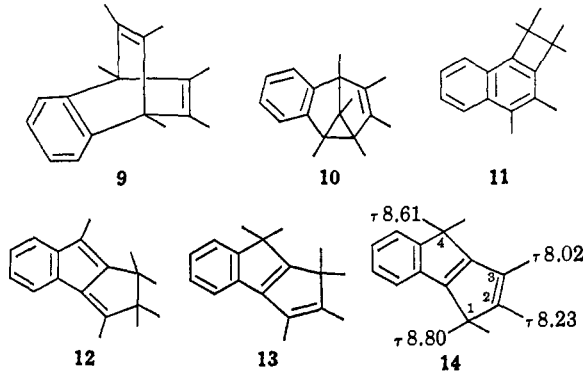
Formation of the *syn* alcohol **2** as principal product with lithium aluminum hydride is in accord with the results obtained with the homologous unsubstituted benzobicyclo[2.2.2]octadienone,[8] a result which may be attributed to "steric approach control."[13] Other homologs behave similarly.[14] In ref 1, the configurations of the two alcohols were reversed. In any case, the stereochemical assignment turns out not to be critical, since the dehydration is not stereoselective (*vide infra*).

Structure of the Dehydration Product. Treatment of the epimeric mixture of alcohols with strong acid[15] at 25° gave up to 64% yield of a white crystalline hydrocarbon, $C_{18}H_{22}$. The nmr spectrum of this substance showed a broad asymmetric four-proton aromatic multiplet (τ 2.77–3.02), two mutually coupled (J = 1 Hz) allylic methyl peaks (τ 8.02 and 8.23), and two six-proton singlets (τ 8.61 and 8.80). The mass spectrum (Figure 1) showed that the parent ion (*m/e* 238) readily lost four *m/e* 15 fragments. The ultraviolet spectrum showed strong bands at λ_{max}^{EtOH} 238 mμ (log ϵ 4.10), 246 (3.89), 321 (4.35), suggesting an extended chromophore, and the infrared spectrum included bands at 1465 and 1445 (aliphatic and allylic methyl asymmetric deformation), 1395, 1365, and 1385 (geminal di- and allylic methyl symmetric deformation), and 765 cm^{-1} (*ortho*-disubstituted benzene).

On the basis of the spectroscopic data, a number of possible isomeric rearrangement products can immediately be excluded. Absence of vinyl proton signals in the nmr and presence of the 321-mμ band in the uv bar consideration of products of vinyl shift (**5**), ring closure (**6**), and phenyl shift (**7** and **8**). Possible products of methyl shifts (**9**) and more complex re-



arrangements (**10**) are also excluded by these spectra. Structures **11**–**14** each have extended chromophores, two different *gem*-dimethyl pairs and two different methyls on an unsaturated bond. The benzofulvene **12** should have a long-wavelength absorption,[17] but the



nmr spectrum should not show homoallylic coupling. Neither would the cross-conjugated compound **13** satisfy the uv requirement; for instance, *cis*- and *trans*-1-phenyl-1,3-butadienes absorb at λ_{max} 270 mμ (log ϵ 4.3) and 280 (4.35), 306 (3.65), respectively,[18,19] whereas 2-phenyl-1,3-butadiene has no strong absorption higher than 241 mμ (4.03).[20] Compounds **11** and **14** might both be expected to show absorption bands above 310 mμ; naphtho[*a*]cyclobutene,[21] 4-methyl-1-phenylcyclo-

(12a) NOTE ADDED IN PROOF. Such an effect is expected, according to a personal communication from Professor L. M. Jackman.

(13) H. C. Brown and J. Muzzio, *J. Am. Chem. Soc.*, **88**, 2811 (1966).

(14) T. Kakihana, M.S. Thesis, Michigan State University, 1966.

(15) Trifluoroacetic acid–98% sulfuric acid 1:1 w/w, $H_0 \sim -9$,[16] was the most satisfactory reaction medium; sulfuric acid alone was also effective.

(16) H. H. Hyman and R. A. Garber, *J. Am. Chem. Soc.*, **81**, 1847 (1959).

(17) Compare, for instance, A. Pullman, B. Pullman, E. D. Bergmann, G. Berthier, Y. Hirshberg, and Y. Sprinzak, *Bull. Soc. Chim. France*, 702 (1951).

(18) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

(19) N. B. Kupletskaya, A. V. Dombrovsky, and A. P. Terentyev, *J. Gen. Chem. USSR*, **27**, 3070 (1957).

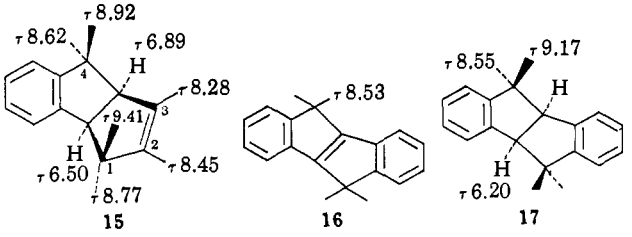
(20) I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1224 (1959).

pentadiene,[22] and 5,6-dimethyl-1-phenyl-1,3-cyclohexadiene[23] have bands at λ_{max} 322 mμ (log ε 3.39), 307 (3.57), and 309 (4.1), respectively.

Catalytic hydrogenation of the hydrocarbon gave principally a dihydro derivative which retained the two homoallylically coupled methyls but whose uv spectrum showed a broad structured band at 253–273 mμ. This last suggested a simple benzenoid chromophore and not the dihydronaphthalene expected from **11**.

Hence the product of acid-catalyzed rearrangement of **1** and **2** was deduced to possess a 1-phenylbutadiene skeleton, bearing a methyl group at either end of the terminal double bond, but having none on the intermediate unsaturation, where it is susceptible to hydrogenation. Additional links are provided by quaternary carbons bearing *gem*-dimethyls (structure **14**).

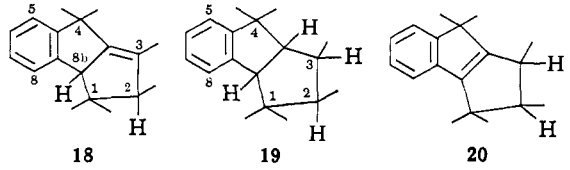
Substantiation for the structures 1,4-dihydro-1,1,2,-3,4,4-hexamethylbenzopentalene (**14**) for the rearrangement product and 1,1,2,3,4,4-hexamethyl-1,3a,4,8b-tetrahydrobenzopentalene (**15**) for its dihydro derivative was found in the nmr spectra reported for 5,10-dihydro- and 4b,5,9b,10-tetrahydro-5,5,10,10-tetramethylindeno-[2,1-*a*]indene (**16** and **17**).[24,25] In the former (**16**), the



gem-dimethyls are seen at τ 8.53; in **14** both pairs are at higher field (the 1-methyls markedly so) owing to the absence of the second benzene ring.[26] Molecular models show that in **17** the *endo*-methyls are thrust into the shielding region of the opposing aromatic ring, giving the signal at τ 9.17. In **15** there are four singlet methyl signals, of which those at τ 9.41 and 8.92 are assigned to the *endo*-1- and *endo*-4-methyls, respectively, having been shifted from τ 9.17 by the absence of the deshielding and shielding effects of the second aromatic nucleus.[26] The *exo*-methyls appear at τ 8.77 and 8.62, that at lowest field being adjacent to the aromatic ring. The structure of the allylic methyl peaks can be interpreted in terms of a mutual *cis*-homoallylic coupling of 0.9 Hz together with a Me(3)–H(3a) four-bond coupling in the 8.28 peak (0.9 Hz) and a Me(2)–H(3a) *trans*-homoallylic coupling of 1.8 Hz in the τ 8.45 peak.[27] When the analogous product was made by reduction of **14** with deuterium in place of hydrogen, the nmr spectrum showed simplification of the allylic signals to quartets, since these last two couplings were now absent.

(21) M. P. Cava, R. L. Shirley, and B. W. Erickson, *J. Org. Chem.*, 27, 755 (1962).
(22) M. Kolobielski and H. Pines, *J. Am. Chem. Soc.*, 79, 5820 (1957).
(23) F. S. Edmunds and R. A. W. Johnstone, *J. Chem. Soc.*, 2898 (1965).
(24) J. E. H. Hancock and D. L. Pavia, *J. Org. Chem.*, 26, 4350 (1961).
(25) J. E. H. Hancock and D. R. Scheuchenpflug, *J. Am. Chem. Soc.*, 80, 3621 (1958).
(26) The assignments of chemical shifts given for **14**, **15**, **21**, and **22** are confirmed and correlated by the results of deuterium-labeling experiments, described hereafter.
(27) Couplings of similar magnitude in comparable systems have been noted; see for instance S. Sternell, *Rev. Pure Appl. Chem.*, 14, 15 (1964); C. M. Cimarusti and J. Wolinsky, *J. Org. Chem.*, 31, 4118 (1966).

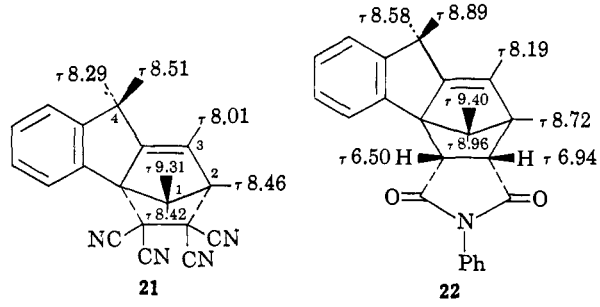
Two other hydrogenation products have also been found in minor amounts. Neither could be completely purified, but they are assigned the structures **18** and **19** on spectroscopic evidence.



Ultraviolet spectra showed that neither was the 2,3-dihydro compound **20**. One (**18**) showed one methyl as a doublet at τ 9.12 (J = 7.2 Hz) and another as a double doublet at τ 8.30 (J_1 = 1.6, J_2 = 2.6 Hz). These are assigned respectively to the vicinally coupled 2-methyl and to the 3-methyl, which suffers two different long-range couplings: a four-bond coupling with the 2-proton and a larger homoallylic coupling with proton **8b**.[27] The remaining four methyls (τ 8.48, 8.67, 8.75, and 9.48) appear as singlets.

The second compound (**19**) showed two methyl doublets at τ 9.16 (J = 7.1 Hz) and 9.01 (J = 6.4 Hz), assigned to the vicinally coupled 2- and 3-methyls, and four methyl singlets (τ 8.69, 8.83, 8.85, and 9.26).

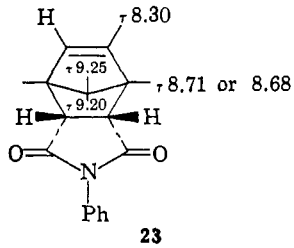
The benzodihydropentalene **14** gave crystalline Diels–Alder adducts with tetracyanoethylene (**21**) and N-phenylmaleimide (**22**). Both gave simple benzenoid ultraviolet spectra.



The nmr spectrum of **21** showed six distinct methyl signals. The two at τ 8.01 and 8.46 are sharp and are assigned to the allylic (C-3) and bridgehead (C-2) methyls, respectively. Two distinctly broader peaks at τ 8.29 and 8.51 are assigned to the 4-methyl groups, and the remaining two at τ 8.42 and 9.31 to the 1-methyls. These last share a small but clear splitting (~0.5 Hz) which seems to be a rare example of a *gem*-dimethyl four-bond coupling in a carbocyclic system.[26,28]

The N-phenylmaleimide adduct **22** also showed six methyl peaks which could be paired according to peak widths, and an AB quartet (J = 7.3 Hz, 2 H). The assignments given may be compared with those values noted for highly substituted cyclopentadiene–N-phenylmaleimide adducts (*e.g.*, **23**).[26,29] Adduct **22** is presumed to be the *endo* isomer, since it is formed under mild conditions. The τ 8.19 and 8.96 peaks are at low field compared to **23**, probably owing to proximity to the plane of the aromatic ring. The latter probably also shields the τ 9.40 methyl group somewhat.

(28) *Cf.* C. Pascual and W. Simon, *Helv. Chim. Acta*, 50, 94 (1967).
(29) S. McLean and P. Haynes, *Tetrahedron*, 21, 2313 (1965); 2343 (1965).



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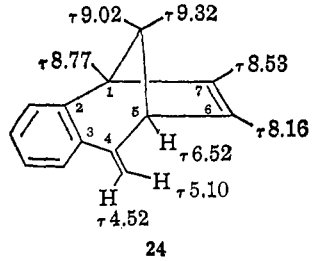
Intermediates in the Conversion of 1 and/or 2 to 14. Prolonged treatment of the alcohols **1** and **2** with strong acid at room temperature (55 min) gave good yields of **14** with only small quantities of other volatile products, but treatment at lower temperatures or for shorter periods gave reduced yields of **14** and larger amounts of the other products. Typical results are summarized in Table I. The compounds with retention times 12.8, 14.4, and 20.3 min were separated by vpc from the mixture of products formed at 0°. Mass spectra showed that all were isomers of **14**.

Table I. Yields[a] of Acid-Catalyzed Rearrangement Products of **1** and **2**

		14	**25**	**7** (or **8**)				**5**
Vpc ret time,[b] min	8.2	11.7	12.8	14.4	15.1	16.1	17.0	20.3[c]
0°, 15 min	<0.5	3	13	16	6	1	2	27
25°, 20 min	1	34	4	5	4	..	..	29
25°, 55 min	1	64	0.5	..	7	..	2	3

[a] Calibrated actual yields determined from the areas under the vpc curves. [b] 10-ft FFAP column at 200°. [c] Products of retention times 41.1 and 48 min were also found in small amounts.

The compound with a retention time of 20.3 min gave an ir spectrum (in CCl_4) which included bands at 1625 (double bond), 1715, 1400, and 905 cm^{-1} (exocyclic methylene). The uv spectrum suggested a styrene chromophore, *viz.*: λ_{max}^{EtOH} 301 mμ (log ε 3.76), 290 (3.76), 262 sh (4.07), and 252 (4.17). The nmr spectrum consisted of a four-proton aromatic multiplet, two sharp one-proton vinylic singlets (τ 4.52, 5.10), a broad one-proton peak (τ 6.52), three methyl singlets (τ 8.77, 9.02, 9.32), and two more complex methyl peaks at τ 8.16 and 8.53. Double-irradiation experiments showed that these signals were coupled with the τ 6.52 peak, the first by 0.9 Hz, the second by 1.8 Hz, and that they were mutually coupled by 1.0 Hz, so that the first appeared as an approximate quintet, the second as a sextet. When this product was separated from the rearrangement products of the labeled alcohol, **28a**, the τ 8.53 peak was a doublet, J = 1.8 Hz, and the τ 8.16 peak was diminished in area by half (**30a**). We consider this compound to be the expected primary rearrangement product of the *syn* alcohol[8] **2** (*i.e.*, **5**) and assign the nmr signals as in **24**.



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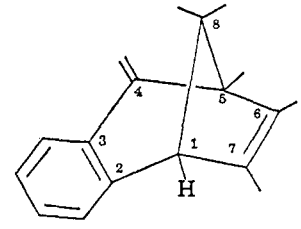
The compound with a retention time of 12.8 min had uv and nmr spectra similar to **5**. The band around 260 mμ (256, log ε 3.67) was still strong, but the bands around 300 mμ (~259 sh (3.08); 307 (2.95)) were considerably weaker, suggesting, perhaps, some steric distortion. In the nmr spectrum, the splitting in the allylic methyls was less distinct than in compound **5**, but that in the τ 8.60 peak could be interpreted as a double quartet (J_q = 1.1 Hz, J_d = 0.7 Hz), whereas the τ 8.43 peak was apparently a simple quartet, J = 1.1 Hz. The methylene protons were widely separated, as in **5** (τ 4.33, 4.98), suggesting proximity to the benzene ring. Singlet methyls appear at τ 8.88, 8.91, and 9.27, and the bridgehead proton at τ 7.45. This compound is assigned the structure **25**, which is readily derived from **7** by an acid-catalyzed bridge shift.



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The product with retention time 14.4 min could not be completely separated by vpc from the compound of retention time 15.1 min, which was not identified. However, the nmr spectrum of a 73% pure sample allowed identification as **7** (or **8**). The methylene protons were closer in chemical shift than in either **5** or **25** (τ 5.05 and 5.17) and the bridgehead proton appeared at about the same position as in **25** (τ 7.32). The allylic methyls were apparently simple quartets, (τ 8.15, 8.40, J = 0.8 Hz). Methyl singlets appeared at τ 8.68, 9.07, and 9.18.

Structures **5**, **7** and/or **8**, and **25** account, then, for most of the products of rearrangement of **1** and **2** under mild conditions.

Although compounds **7** and **25** are schematically derived from the *anti* alcohol, and **5** from the *syn* alcohol by simple rearrangements, the possible role of these in the more profound rearrangement to the dihydrobenzopentalene **14** needed to be probed. Treatment of each of the three hydrocarbons with strong acid under similar conditions to those employed for the preparation of **14** gave very similar mixtures of products in which **14** and **5** predominated (see Experimental Section). This result suggests that **5**, **7** (**8**), and **25** establish a more or less rapid equilibrium while the final product **14** is formed from one or more of them at a slower rate.

Since the stereochemistry of the alcohol precursor **1** or **2** might have been important, the course of the reaction was followed at 5° using as substrates the *syn* alcohol **2** and (in the absence of a sufficient quantity of the pure *anti* alcohol **1**) a 58.5:41.5 mixture of *anti* and *syn* alcohols. The results for the *syn* alcohol are given in Figure 2. The configuration of the 2-hydroxyl seems to make little difference to the result; the scheme for the *anti*-rich mixture is very similar, suggesting that a rapid epimerization of the protonated alcohol precedes all else. This epimeric mixture evidently forms some of the *anti* products **7** and **25** quite quickly, and the *syn* product **5** rather more slowly. The rate of formation of **14** appears to decrease as the concentra-

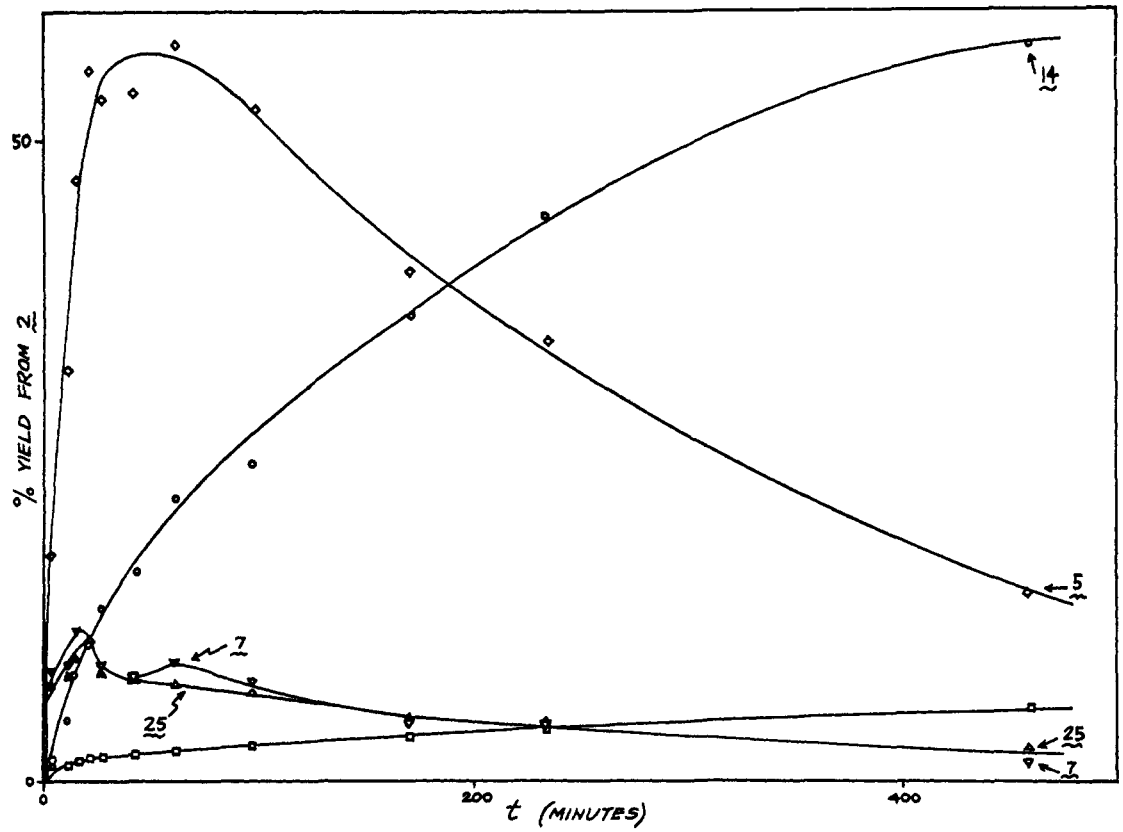
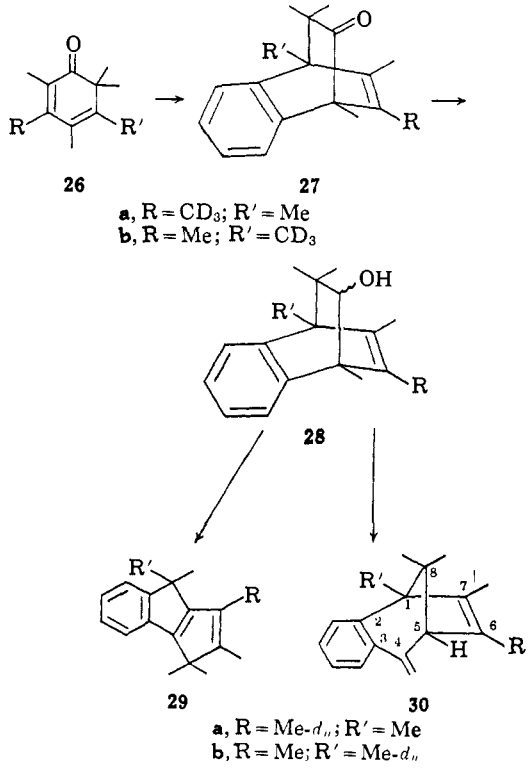


Figure 2. Progress of the reaction of alcohol **2** with 1:1 trifluoroacetic acid–sulfuric acid at 5°. The unlabeled curve is due to a minor unidentified product.

tion of **7** and **25** decreases. After about 60 min the "intermediates" **5**, **7**, and **25** settle down to a roughly constant ratio favoring **5**, and thereafter the rate of formation of **14** is similar to the rate of decay of **5**.

Deuterium-Labeling Experiments. Deuterium could be introduced into the dihydrobenzopentalene **14** by four different methods: (a) by acid treatment of the 7-d_3 alcohols **28a**, (b) by acid treatment of the 4-d_3 alcohols **28b**, (c) by exchange of the hydrocarbon **14** with 80% D_2SO_4–D_2O, and (d) by treatment of the alcohols **1** and **2** with 100% D_2SO_4.



The site of the label in the 3-d_3- and 5-d_3-hexamethylcyclohexadienones **26a** and **26b** has been unambiguously determined.[10] These dienones were converted to the 7-d_3- and 4-d_3-bicyclooctadienols **27a** and **27b**, respectively, and treated with sulfuric acid.

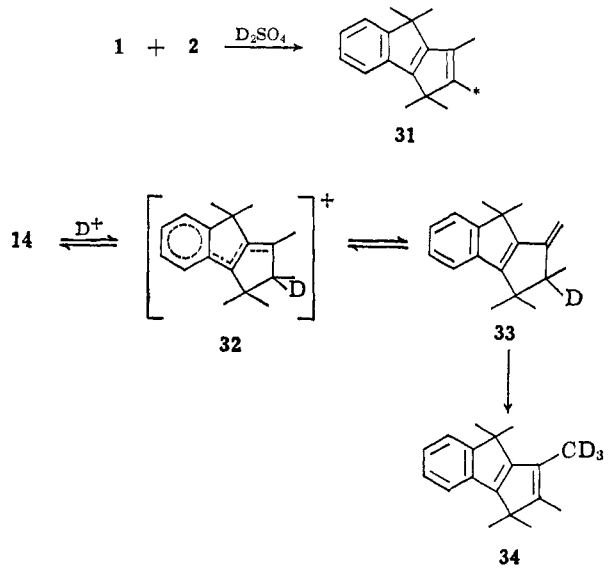
(a) The 7-d_3 alcohol gave a sample of the dihydrobenzopentalene in which the τ 8.02 peak was reduced to 1.0 proton (**29a**).

(b) The 4-d_3 alcohol gave a sample in which the *gem*-dimethyl signal at τ 8.61 was reduced to 5.2 protons (**29b**).

(c) From 80% D_2SO_4 the dihydrobenzopentalene was recovered with the τ 8.02 peak entirely eliminated, but no other peaks were affected (**34**).

(d) The alcohols **1** and **2** with D_2SO_4 gave dihydrobenzopentalene in which the peak areas corresponded (on average) to τ 8.02, 2.7 H; 8.23, 1.6 H; 8.61, 3.3 H; 8.80, 5.0 H (**31**).

Adducts of the products from c and d with TCNE, N-phenylmaleimide, and hydrogen were employed to establish the nmr assignments already noted. Thus in the adducts of **34**, in each case the lowest field methyl signal was absent or greatly diminished. In the 2,8b adducts **21** and **22** these have been assigned with some certainty to the allylic (3-) methyls; in the 3a,8b-dihydro compound **15** this is in accord with the long-range coupling constant H(3a)–Me(3) being smaller than H(3a)–Me(2). Proton–deuterium exchange at Me(3)

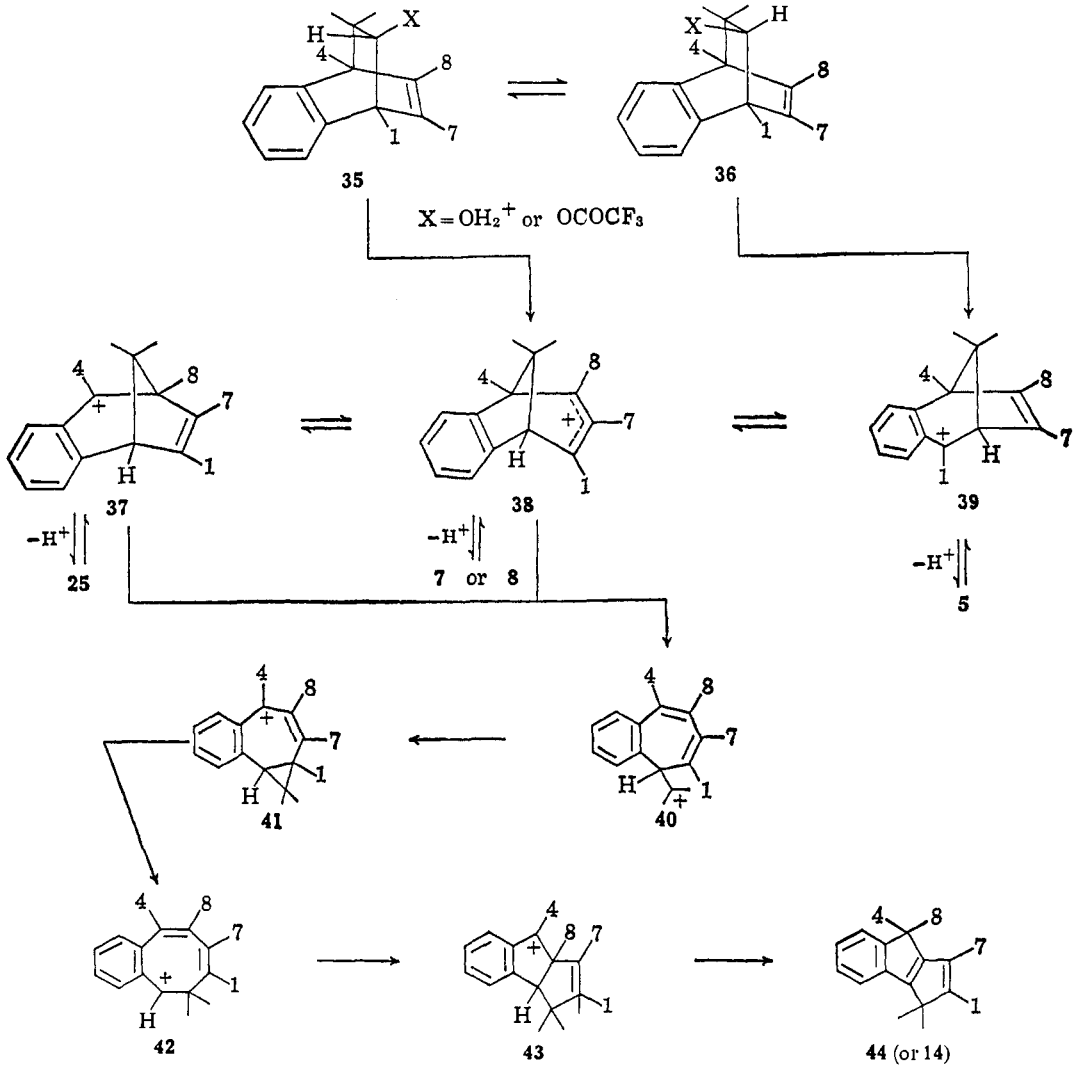


N-phenylmaleimide derivative of **31** retains almost unchanged the signals at τ 8.19, 8.96, 9.40 whereas those at 8.58, 8.89, and 8.72 are reduced by half. In the major hydrogenation product only the peaks τ 8.45, 8.62, and 8.92 are substantially reduced. Since the peak at τ 9.41 in **15** must belong to the one of the 1-methyls which was positioned over the aromatic ring, it follows that two of the reduced peaks, the singlets at τ 8.62 and 8.92, must belong to the 4-methyls. From these and the preceding data the nmr assignments given previously for **14**, **15**, **21**, and **22** are readily derived.

Discussion

The literature provides a few examples of cases in which bicyclo[2.2.2]- or -[3.2.1]octyl systems are rearranged under more or less severe conditions to bicyclo[3.3.0]octyl compounds.[20-32] However, these cases invariably involve facile eliminations or hydride shifts in the bicyclo[3.2.1]octane accompanied by bond

Scheme I



in **14** may be attributed to the stability of the carbonium ion **32** which would exchange the 3 protons readily *via* **33**.

The TCNE adduct of **31** showed signals at τ 8.01, 8.42, and 9.31 essentially undiminished compared with the adduct of **14**, whereas the peaks at τ 8.29, 8.46, and 8.51 are each diminished by about half. Similarly the shifts to the one-carbon bridge. In our case such a process is "blocked" by the *gem*-dimethyl group, unless

(30) S. J. Cristol, J. R. Mohring, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Am. Chem. Soc.*, **85**, 2675 (1963).
(31) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **82**, 4299 (1960).
(32) J. E. Germain and M. Blanchard, *Bull. Soc. Chim. France*, 473 (1960).

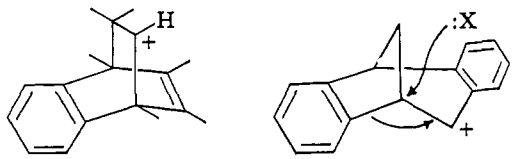
it can be preceded by a series of hydride and methyl shifts.

We consider the evidence presented in this paper as more satisfactorily explained by a mechanistic scheme such as Scheme I.

(1) The alcohols (or their esters) are quickly epimerized, as suggested by the insensitivity of the result to the stereochemistry of the substrate. Cristol, *et al.*,[6] have reported the epimerization of dibenzobicyclo[3.2.1]octadien-1-yl acetates under less strongly acid conditions.

(2) The epimeric mixture of **35** and **36** decays to the cations **37–39**, which quite quickly establish an equilibrium. From the results given in Figure 2, the ratio is about 8:1:1 in favor of **39**.

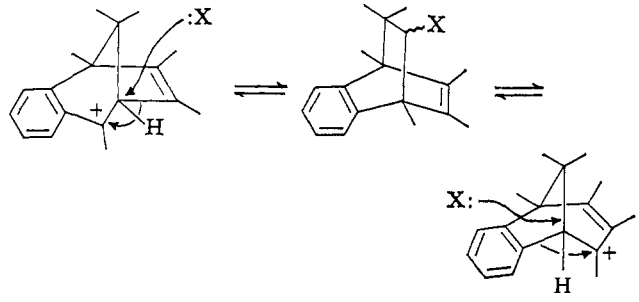
The rearrangement of **38** → **39** is most easily written as proceeding through the secondary [2.2.2] ion **45**. However, Cristol has dismissed[6] the possibility of the participation of the analogous dibenzobicyclo[2.2.2]-octa-2,5-dien-7-yl cation in the rearrangement of dibenzobicyclo[3.2.1]octadien-2-yl into -[2.2.2]octadien-7-yl acetates in acetic acid–perchloric acid in favor of



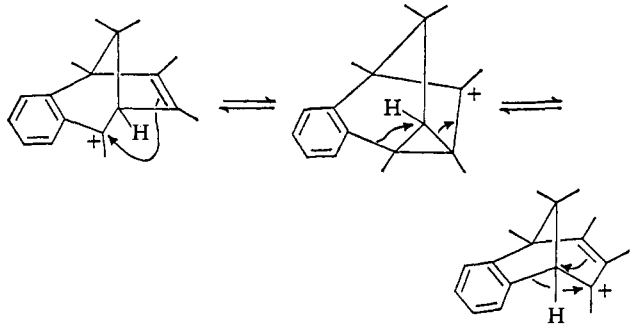
45 46

the "geitonodesmic" mechanism **46**. In our case the analogous reaction (Scheme II, X = CF_3CO_2–) may be responsible for this interconversion, *via* the epimerized esters **35** and **36**, or possibly Scheme III may be followed, since sulfuric acid alone seems to give similar results.

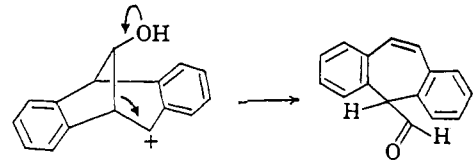
Scheme II



Scheme III



(3) Since no other "intermediates" are found in appreciable yields the next reaction (**37** or **38** → **40**) may be the slow step. This may be compared with a related rearrangement,[33] **47** → **48**. It is also possible



47 48

to write the process **37**, **38** → **41** as a direct 1,3- or 1,4-transannular shift.

The conversion **40** → **42** is analogous to the solvolytic rearrangement of 1,5-dibenzocyclohepta-1,3,5-trienyl-7-carbinyl tosylate to 1,5-dibenzocycloocta-1,3,5-trien-7-ol studied by Nenitzescu, *et al.*[34] These workers failed to observe the analog of the reverse of **40** → **37**, **38**, although such a ring closure has been noted in a simple monocyclic system.[35]

The cyclization of an eight-membered ring to a bicyclo[3.3.0]octyl system (**42** → **43**) is unusual,[36] but the driving force is undoubtedly the formation of a tertiary benzylic from a secondary benzylic cation. A methyl shift and loss of a proton complete the formation of the conjugated product.

The scheme also explains the labeling data. Thus the 4-d_3 alcohol (labeled at the position marked **4** in Scheme I) should give rise to 4-labeled dihydrobenzopentalene (**29b**). The 7-d_3 alcohol (labeled at position **7** in Scheme I) would yield 3-d_3-dihydrobenzopentalene (**29a**) and a 6-labeled methylenebicyclo[3.2.1]octadiene (**30a**). Both these results are as observed. A further consequence of this scheme is that in the comparatively long-lived intermediates **37–39** only the methyls at positions **1**, **4**, and **8** are situated at the sites of positive charge. This would demand that exchange of methyl protons during the reaction should take place predominately at these positions, *i.e.*, positions **2** and **4** in the product. That this is so is shown by the nature of the product **31** formed by the treatment of the alcohols **1** and **2** with deuterium sulfate, and by the partial loss of label in the formation of compound **29b**.

Experimental Section[37]

2,3,4,5,6,6-Hexamethylcyclohexa-2,4-dienone (3). This was prepared by a variant of the method of Hart, Collins, and Waring.[10] A chilled solution of peroxytrifluoroacetic acid (made from 21.6 ml of 90% hydrogen peroxide and 184.9 g of trifluoroacetic anhydride in 200 ml of dichloromethane) was added dropwise over 5 hr to a stirred solution of 116.4 g of hexamethylbenzene in 200 ml of dichloromethane at 0–5°. Boron fluoride–diethyl etherate (47% BF_3, 200 ml) was added simultaneously. After a further 12 hr at 0°, 400 g of ice was added, and the organic phase was separated and washed several times with water, 10% sodium bicarbonate, 5% sodium hydroxide, and water again, and finally dried ($MgSO_4$). Evaporation and distillation (93° (1 mm)) gave 115.0 g (93%) of an oil similar in all respects to the reported dienone; vpc (SE-30, 5 ft, 180°) showed less than 1% of volatile impurities.

1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (4) (T. K.).[3] Benzyne was generated by Friedman's method;[11] anthranilic acid (21.0 g) in 250 ml of acetone was added over 80 min

(33) S. J. Cristol and R. K. Bly, *J. Am. Chem. Soc.*, **82**, 6155 (1960).
(34) E. Cioranescu, A. Bucur, M. Elian, and C. D. Nenitzescu, *Rev. Roumaine Chim.*, **10**, 149 (1965).
(35) S. Winstein and P. Carter, *J. Am. Chem. Soc.*, **83**, 4485 (1961).
(36) Such cyclizations have been noted in the solvolyses of cyclooct-4-en-1-yl compounds; see A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 119 (1966), and references therein.
(37) Melting points and boiling points are uncorrected. Vpc separations and analyses were performed on Aerograph 200 and 350B chromatographs. The following spectrometers were used: nmr, Varian A-60; infrared, Unicam SP-200; ultraviolet, Unicam SP-800; mass spectra, Consolidated Electrodynamic 21-103C.

to a gently refluxing solution of 21 g of the dienone **3** and 19.2 g of isoamyl nitrite in 280 ml of dichloromethane. Gas evolution had ceased after a further hour under reflux, and the dark solution could be evaporated to an oil which crystallized on chilling. The solid was extracted with hot ether (600 ml) and the extract washed repeatedly with 10% sodium hydroxide and water and dried. Evaporation and crystallization from ethanol gave 22.1 g (74%) of white needles, melting point after further crystallization, 108–108.5°; λ_{max}^{EtOH} 220 mμ (log ε 3.79), 273 (2.97), and 300 (2.57); $\nu_{max}^{CCl_4}$ 1710 (s), 1670 (w), 1600 (m), and 700 cm^{-1} (m); nmr (CCl_4): τ 2.86 (singlet, 4 H), 8.18 (quartet, J = 1 Hz, 3 H), 8.26 (quartet, J = 1 Hz, 3 H), 8.38 (singlet, 6 H), 8.94 (singlet, 3 H), and 9.53 (singlet, 3 H); mass spectrum: *m/e* 254 (P).

Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.89; H, 8.78.

1,3,3,4,7,8-Hexamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ol (1 and 2) (T. K., in part).[3] The benzobicyclodienone **4** (32.5 g) in 150 ml of ether was added dropwise to a stirred slurry of 6 g of lithium aluminum hydride in 600 ml of ether at 0–5°. After being stirred for 1 hr, the mixture was treated with sufficient ice–water to hydrolyze the remaining hydride. By filtration, drying, and exhaustive evaporation of the solution, the product was isolated in virtually quantitative yield (34.6 g crude) as a colorless gum which tended to crystallize on prolonged chilling.

Comparison of the nmr spectrum of this product with those of the isolated epimers indicated a *syn*:*anti* ratio of 63:37. Tlc on silica gel was ineffective in separating the epimers. Crystallization twice from pentane gave the *syn* alcohol **2** as white crystals, mp 87–88°; $\nu_{max}^{CCl_4}$ 3635 (w), 3580 (s), 3450 (broad, w), and 1460 (s); nmr: τ 2.98 (narrow multiplet, 4 H), 6.97 (broad, 1 H), 8.30 (singlet, 6 H), 8.45 (singlet, 3 H), 8.51 (singlet, 3 H), 9.05 (singlet, 3 H), 9.63 (singlet, 3 H), and 9.40 (broad, 1 H; removed on shaking with D_2O).

Anal. Calcd for $C_{18}H_{24}O$: C, 84.30; H, 9.45. Found: C, 84.36; H, 9.41.

The 3,5-Dinitrobenzoate of 2. The mixture of alcohols **1** and **2** (1.62 g) was treated with 5 ml of pyridine and 1.5 g of 3,5-dinitrobenzoyl chloride in 15 ml of benzene and left to stand for 12 hr. Washing with water, drying, and evaporating gave a sticky solid which was crystallized from petroleum ether (bp 60–110°) to give the *syn*-dinitrobenzoate (0.94 g) as off-white platelets, mp 153–154°; nmr (CH_2Cl_2): τ 0.98, 1.27 (multiplet, 3 H), 2.78 (narrow multiplet, 4 H), 5.15 (singlet, 1 H), 8.18 (singlet, 6 H), 8.38 (singlet, 6 H), 8.80 (singlet, 3 H), and 9.62 (singlet, 3 H); ν_{max}^{Nujol} 1725 (ester carbonyl), 1560, and 1365 cm^{-1} (NO_2).

Anal. Calcd for $C_{25}H_{26}N_2O_6$: C, 66.65; H, 5.82; N, 21.31. Found: C, 66.70; H, 5.80; N, 21.26.

Saponification with aqueous alcoholic sodium hydroxide gave a solid identical with the *syn* alcohol. The nmr spectrum of the crystallization residues from the esterification suggested the presence of another product, presumably the *anti* ester, but this could not be isolated by tlc or crystallization. Chromatography on silica gel with benzene eluted the esters, and another compound (0.20 g) was eluted with dichloromethane. This product, an oil, was digested with aqueous alcoholic sodium hydroxide to remove esters, and was then identified as the *anti* alcohol; nmr: τ 3.00 (narrow multiplet, 4 H), 7.10 (broad, 1 H), 8.28 (singlet, 6 H), 8.37 (singlet, 3 H), 8.50 (singlet, 3 H), 9.15 (singlet, 3 H), and 9.53 (singlet, 3 H); $\nu_{max}^{CCl_4}$ 3635 (m), 3590 (m), 3480 (broad, m), and 1455 (s).

1,4-Dihydro-1,1,2,3,4,4-hexamethylbenzopentalene (14). a. The crude epimeric mixture of benzobicyclooctadienols **1** and **2** (5.02 g) in 10 g of chloroform was added dropwise over 15 min to a stirred solution of 100 g of sulfuric acid in 100 g of trifluoroacetic acid at 25°. After a total reaction time of 55 min, the brown solution was poured onto 500 g of ice. The purple mixture was extracted with dichloromethane and the extract washed with 10% sodium hydroxide solution, whereupon it quickly turned pale yellow. Washing with water, drying with magnesium sulfate, and evaporation gave yellowish sticky crystals (3.63 g). Vpc (10-ft 15% FFAP on Chromosorb W at 200°) indicated a yield of 64%, with about 13% of other products. Crystallization from ethanol gave **14** as white platelets (2.1 g, 45%), mp 101–102° after sublimation and recrystallization; $\nu_{max}^{CCl_4}$ 3100 (m), 2990 (s), 2950 (s), 2890 (m), 1600 (m), 1465 (s), 1445 (m), 1395 (m), 1385 (m), 1365 (m), and 1310 (m); in Nujol, 765 (s); λ_{max}^{EtOH} 238 mμ (log ε 4.10), 246 (3.89), and 321 (4.35); nmr (CCl_4): τ 2.77–3.02 (multiplet, 4 H), 8.02 (quartet, J = 1 Hz, 3 H), 8.23 (quartet, J = 1 Hz, 3 H), 8.61 (singlet, 6 H), and 8.80 (singlet, 6 H); mass spectrum: *m/e* 238 (P, 78%), 223 (P − 15, 100%), 208 (P − 30, 61%), 193 (P − 45, 25%), 178 (P − 60, 23%).

Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.74; H, 9.32.

b (T. K.).[3] Sulfuric acid (2 ml) was added dropwise over 15 min to a stirred solution of the benzobicyclodienols **1** and **2** (1.00 g) in 10 ml of carbon tetrachloride at 25°. After a further 15 min of stirring, the brown heterogeneous mixture was worked up as described in method a; vpc indicated that the product, a green tarry solid, 1.01 g, contained the same components in similar yields to those obtained above, *viz.*: **14**, 0.42 g (46%); other volatile products, 0.14 g (15%). Most of the remainder (~0.4 g) seemed to be involatile tars. The dihydrobenzopentalene **14** was refined by sublimation and crystallization and found to be identical with that obtained by method a.

Treatment of the Benzobicyclooctadienols 1 and 2 with Strong Acid at 0°. The epimeric mixture of alcohols **1** and **2** (5.02 g) in 10 ml of chloroform was added dropwise over 15 min to a stirred mixture of 100 g of trifluoroacetic acid and 100 g of sulfuric acid at 0°. The solution was immediately poured onto 500 g of ice and worked up in the manner described for **14** to give 4.22 g of a yellow oil which was distilled at 96–110° (0.2 mm). The pale yellow distillate (3.56 g) was separated by vpc (10-ft 15% FFAP on Chromosorb W at 230°). The major fractions were (retention time in minutes at 200°, estimated yield from benzobicyclooctadienol) 11.7, 3.3%; 12.8, 13.2%; 14.4, 16.2%; 15.1, 6.0%; 20.3, 27.3%.

The product, retention time 12.8 min, a colorless oil, was identified as **4-methylene-5,6,7,8,8-pentamethyl-2,3-benzobicyclo[3.2.1]-octa-2,6-diene (25)**; λ_{max}^{EtOH} 221 mμ (log ε 4.15), 228 (4.15), 256 (3.67), 295 sh (3.08), and 307 (2.95); $\nu_{max}^{CCl_4}$ 890 (s), 1120 (s), 1290 (m), 1380 (s), 1440 (s), 1455 (s), 1475 (s), 1605 (m), 1680 (s), 1700 (s), and 2850–3050 cm^{-1} (s); nmr (CCl_4): τ 2.8–3.1 (multiplet, 4 H), 4.33 (singlet, 1 H), 4.98 (singlet, 1 H), 7.45 (broad, 1 H), 8.43 (quartet, J = 1.1 Hz, 3 H), 8.60 (double quartet, J_q = 1.1, J_d = 0.7 Hz), 8.88 (singlet, 3 H), 8.91 (singlet, 3 H), and 9.27 (singlet, 3 H); *m/e* 238, 223, 208, and 193.

The product, retention time 14.4 min, a colorless oil, was assigned the structure **4-methylene-1,2,3,8,8-pentamethyl-** (or possibly 2,3,5,-8,8-pentamethyl-) **6,7-benzobicyclo[3.2.1]octa-2,6-diene (7 or 8)**. The uv spectrum showed no absorption above 285 mμ; $\nu_{max}^{CCl_4}$ 880 (s), 1210 (s), 1375 (s), 1460 (s), 1625 (w), 1720 (m), 2850–3050 cm^{-1} (s); *m/e* 238, 223, 208, and 193; nmr (CCl_4): τ 3.03 (narrow multiplet, 4 H), 5.05 (singlet, 1 H), 5.17 (singlet, 1 H), 7.32 (broad, 1 H), 8.15 (quartet, J = 0.8 Hz, 3 H), 8.40 (quartet, J = 0.8 Hz, 3 H), 8.68 (singlet, 3 H), 9.07 (singlet, 3 H), 9.18 (singlet, 3 H). This spectrum also showed the presence of 27% of the product with retention time 15.1 min.

The product with retention time 20.3 min was identified as **4-methylene-1,6,7,8,8-pentamethyl-2,3-benzobicyclo[3.2.1]octa-2,6-diene (5)**, a white crystalline solid, mp 32–33°; $\nu_{max}^{CCl_4}$ 3150 (m), 3010 (s), 2920 (m), 1715 (m), 1625 (m), 1490 (s), 1480 (s), 1400 (s), 1130 (s), and 905 cm^{-1} (s); λ_{max}^{EtOH} 252 mμ (log ε 4.17), 262 (sh) (4.07), 290 (3.76), and 301 (3.76); nmr (CCl_4): τ 2.6–3.1 (multiplet, 4 H), 4.52 (singlet, 1 H), 5.10 (singlet, 1 H), 6.52 (broad, W_h = ~2.5 Hz, 1 H), 8.16 (double quartet, J_q = 1.0 Hz, J_d = 0.9 Hz, 3 H), 8.53 (double quartet, J_q = 1.0 Hz, J_d = 1.8 Hz, 3 H), 8.77 (singlet, 3 H), 9.02 (singlet, 3 H), 9.32 (singlet, 3 H); mass spectrum: *m/e* 238 (51%), 223 (P − 15, 100%), 208 (P − 30, 17%), and 193 (P − 45, 19%).

Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.40; H, 9.57.

Catalytic Reduction of the Dihydrobenzopentalene 14. a. With Hydrogen (P. M. C., in part).[3] The dihydrobenzopentalene (0.378 g, 1.59 mmol) was reduced in 12 ml of ethanol in the presence of 0.1 g of 5% palladium–charcoal catalyst at 20° and 1 atm. Hydrogen (1.62 mmol) was absorbed over 30 min. Filtration and evaporation gave a colorless oil: vpc (10-ft 20% FFAP on Chromosorb W at 190°) retention time 9 min, 35%; 10 min, 65%. The major product was separated, and gave the following spectra: $\nu_{max}^{liq\ film}$ 3100–2850 (s), 1485 (s), 1460 (s), 1385 (m), 1365 (m), and 760 (s); λ_{max}^{EtOH} 253 mμ (sh) (log ε 3.20), 260 (3.26), 266 (3.33), and 273 (3.33); nmr: τ 2.97 (narrow multiplet, 4 H), 6.50, 6.89 (AB quartet, broadened in high-field doublet, J = 9.9 Hz, 2 H), 8.28 (quintet, J = 0.9 Hz, 3 H), 8.45 (double quartet, J_q = 0.9, J_d = 1.8 Hz, 3 H), 8.62 (singlet, 3 H), 8.77 (singlet, 3 H), 8.92 (singlet, 3 H), 9.41 (singlet, 3 H); mass spectrum: *m/e* 240 (P), 225, 210, and 195. This compound is identified as **1,1,2,3,4,4-hexamethyl-1,3a,4,8b-tetrahydrobenzopentalene (15)**.

The minor product could not be completely purified; from samples containing 20% of the major product, the following spectra were deduced: nmr τ 2.95 (narrow multiplet, 4 H), 8.30 (double doublet, J_1 = 1.6 Hz, J_2 = 2.6 Hz, 3 H), 8.48 (singlet, 3 H), 8.67 (singlet, 3 H), 8.75 (singlet, 3 H), 9.12 (doublet, J = 7.2 Hz, 3 H), and 9.48 (singlet, 3 H). The uv spectrum was very similar to that

of the major product. This compound, which was also formed much more slowly when the dihydrobenzopentalene **14** was hydrogenated in the presence of platinum, is assigned the structure **1,1,2,3,4,4-hexamethyl-1,2,4,8b-tetrahydrobenzopentalene (18).**

On another occasion, hydrogenation with palladium on charcoal gave a product, retention time 12.2 min (10-ft 20% FFAP on Chromosorb W at 210°), as a 20% impurity in the major hydrogenation product (retention time 11.8 min). The former could only be refined to 60% purity by vpc; its uv spectrum closely resembled those of the other hydrogenation products, and its partial nmr spectrum was deduced to be as follows: τ 2.94 (probably 4 H), 8.69 (singlet, 3 H), 8.83 (singlet, 3 H), 8.85 (singlet, 3 H), 9.01 (doublet, J = 6.4 Hz, 3 H), 9.16 (doublet, J = 7.1 Hz, 3 H), 9.26 (singlet, 3 H); mass spectrum: parent *m/e* 242. This is apparently **1,2,3,-3a,4,8b-hexahydro-1,1,2,3,4,4-hexamethylbenzopentalene (19).**

b. With Deuterium. The dihydrobenzopentalene **14** took up 1 mol of deuterium under conditions similar to the first hydrogenation described above. The major product was refined in the same way, giving a colorless oil with very similar spectroscopic characteristics to the hydrogenated product. The ultraviolet spectrum was virtually identical; the infrared spectrum contained a weak band at 2180 cm^{-1} (ν_{C-D}) and was slightly different in the region <800 cm^{-1}. The nmr spectrum showed no signal in the region τ 6–7, and the peaks at τ 8.28 and 8.45 were now both quartets, J = 0.9 Hz. The mass spectrum showed a parent peak at *m/e* 242, strong peaks at 227, 212, and 197. This product is identified as **1,4-dihydro-3a,8b,-dihydro-d_2-1,1,2,3,4,4-hexamethylbenzopentalene.**

1,4-Dihydro-1,1,2,3,4,4-hexamethylbenzopentalene Labeled at the C-3 Methyl. a. From Unlabeled Dihydrobenzopentalene (14). The dihydrobenzopentalene **14** (0.25 g) was dissolved in 4 g of 4:1 w/w deuteriosulfuric acid–deuterium oxide. After standing for 3 hr, the solution was poured onto frozen deuterium oxide. Alkaline work-up and sublimation gave white crystals (0.16 g) of **1,4-dihydro-3-methyl-d_3-1,1,2,4,4-pentamethylbenzopentalene (34);** nmr (CCl_4) identical with **14**, except that the peak at τ 8.02 was totally absent, and that at τ 8.23 was now a singlet.

b. From Labeled Benzobicyclodienol (P. M. C.). 3-Methyl-d_3-2,4,5,6,6-pentamethylcyclohexa-2,4-dienone[10] **(26a**; 8.6 g) was treated with 8.6 g of isoamyl nitrite and 9.4 g of anthranilic acid in acetone–methylene chloride exactly as described for the unlabeled dienone **3**. Crystallization from ethanol gave **7-methyl-d_3-1,3,3,4,8-pentamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one (27a)** as white needles (8.1 g, 66%). The nmr spectrum resembled that of **4**, except that the τ 8.26 peak was nearly absent and the peak at τ 8.18 was now a singlet. A mass spectrum confirmed that the extent of labeling was 85% d_3.

Treatment of the 7-d_3-benzobicyclooctadienone **27a** with lithium aluminum hydride in the same manner as for **4** gave a high yield of **7-methyl-d_3-1,3,3,4,8-pentamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ol (28a).** Comparison of its nmr spectrum with that of **1** and **2** showed a decrease in the peak at τ 8.3 corresponding to about 75% label at the C-7 methyl. The mass spectrum is consistent with this value.

The benzobicyclooctadienol-7-d_3 **28a** (1.23 g) was treated with sulfuric acid by the second method described for preparation of **14.** Crystallization of the product from ethanol gave the dihydrobenzopentalene **29a** (0.38 g, 33%), mp 102–103°. The nmr spectrum showed the τ 8.02 peak reduced to 1.0 protons, with no change in the other peaks.

1,4-Dihydro-1,1,2,3,4,4-hexamethylbenzopentalene Labeled at the C-4 Methyl. 5-Methyl-d_3-2,3,4,6,6-pentamethylcyclohexa-2,4-dienone[10] **(26b)** with a little deuterium at the C-3 methyl was converted into 4-methyl-d_3-1,3,3,7,8-pentamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-one **(27b)** as described above for the preparation of **4.** The nmr spectrum showed 70% label at the C-4 methyl and 10% at the C-7 methyl. Reduction gave **4-methyl-d_3-1,3,3,7,8-pentamethyl-5,6-benzobicyclo[2.2.2]octa-5,7-dien-2-ol (28b)** with 67% label at C-4 and 7% at C-7, by nmr. A mass spectrum showed 82% d_3.[38]

Treatment of the benzobicyclodienol **28b** with sulfuric acid in carbon tetrachloride gave after crystallization and sublimation a sample of **29b** in which the τ 8.61 peak was reduced to 5.2 protons, with no significant reduction in any other peak.

Treatment of the Benzobicyclooctadienols 1 and 2 with Deuterium Sulfate. Unlabeled benzobicyclooctadienols **1** and **2** in 5 ml of carbon tetrachloride was treated with 1 ml of 100% deuterium sulfate as described in the second method for preparation of **14.** Sublimation gave white crystals of **31** (0.25 g, 52%). Three batches were made by this method, giving the following nmr spectra (methyl region) (values are for τ 8.02, 8.23, 8.61, and 8.80, respectively): (a) 2.8 H, 1.5 H, 2.9 H, 4.8 H; (b) 2.9 H, 2.1 H, 3.8 H, 5.5 H; (c) 2.4 H, 1.1 H, 3.2 H, 4.8 H.

Catalytic Hydrogenation ot the Labeled Dihydrobenzopentalenes 31 and 34. The 3-d_3-dihydrobenzopentalene **34** derived from treatment of the unlabeled hydrocarbon with 80% deuterium sulfate and the 2,4-labeled hydrocarbon **31** prepared by treatment of the alcohols **1** and **2** with deuterium sulfate (batch a) were hydrogenated by the method described for the unlabeled compound **14.** The major products (structure **15**, except for deuterium label) gave the following nmr: from **34**, τ 8.28 greatly reduced, other peaks not affected; from **31**, τ 8.28, 2.8 H; 8.45, 1.0 H; 8.62, 8.92, equal, total 2.5 H; 8.77, 9.41, equal, total 5.2 H. The high-field doublet of the AB spectrum (τ 6.89) was sharper than in the unlabeled compound.

Diels–Alder Adducts of the Dihydrobenzopentalenes. a. With TCNE. Typically, dihydrobenzopentalene (0.06 g) in 1 ml of benzene was mixed with 0.04 g of tetracyanoethylene in 3 ml of benzene and left for 3 days before evaporating and crystallizing from ethanol. The adducts displayed the following characteristics: from **14** (adduct **21**), colorless prisms, mp 192–193° dec; $\lambda_{max}^{CHCl_3}$ 273.5 mμ (log ϵ 3.19), 266 (3.16), 258 (2.99); nmr (CH_2Cl_2): τ 2.43 (multiplet, 4 H), 8.01 (singlet, 3 H), 8.29 (slightly broadened singlet, 3 H), 8.42 (slightly split, $J \sim 0.5$ Hz, 3 H), 8.46 (singlet, 3 H), 8.51 (slightly broadened singlet, 3 H), 9.31 (slightly split, $J \sim 0.5$ Hz, 3 H); from **34**, nmr (CH_2Cl_2) lacks τ 8.01 peak but is otherwise as above; from **31** (batch b) (CH_2Cl_2), τ 8.01, 3 H; 8.29, 1.9 H; 8.42, 2.8 H; 8.46, 1.9 H; 8.51, 1.7 H; 9.31, 3.0 H.

Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.62; H, 5.96; N, 15.34.

b. With N-Phenylmaleimide. Typically, the dihydrobenzopentalene (0.15 g) was dissolved with 0.14 g of N-phenylmaleimide in 5 ml of benzene and left 2 days before evaporating and crystallizing the residue from ethanol. The preparation could also be effected in refluxing benzene. The adducts had the following characteristics: from **14** (adduct **22**), white needles, mp 184.5–185°; λ_{max}^{EtOH} 259 mμ (log ϵ 3.49), 266 (3.55), 273 (3.53); nmr (CCl_4): τ 2.5–3.0 (multiplet, 9 H), 6.50, 6.94 (AB quartet, J = 7.3 Hz, 2 H), 8.19 (singlet, 3 H), 8.58 (singlet, 3 H), 8.72 (singlet, 3 H), 8.89 (singlet, 3 H), 8.96 (singlet, 3 H), 9.40 (singlet, 3 H); from **34**, nmr (CCl_4) lacks τ 8.19 peak but is otherwise as above; from **31** (batch c), nmr (CCl_4): τ 8.19, 2.3 H; 8.58, 1.4 H; 8.72, 1.5 H; 8.89, 1.4 H; 8.96, 2.5 H; 9.40, 2.5 H.

Anal. Calcd for $C_{28}H_{29}NO_2$: C, 81.72; H, 7.10; N, 3.40. Found: C, 81.63; H, 7.17; N, 3.46.

4-Methylene-1,6,7,8,8-pentamethyl-2,3-benzobicyclo[3.2.1]octa-2,6-diene Labeled at the C-6 Methyl Group (30a). To the 7-d_3-benzobicyclooctadienol **28a** (0.53 g) in 5 ml of carbon tetrachloride at 0° was added 1 ml of sulfuric acid over 10 min. The solution was allowed to warm up to 20° over 10 min before alkaline work-up in dichloromethane as described for **14.** The product, an oil, was shown by vpc to contain a component of the same retention time as **5** as 60% of the volatile products. This was isolated and shown to give an nmr spectrum similar to **5**, except in the following: τ 8.20 (double quartet, J_q = 1.0 Hz, J_d = 0.9 Hz, 1.2 H) and 8.57 (doublet, J = 1.8 Hz, 3 H).

Treatment of the Methylenebenzobicyclo[3.2.1]octadienes 5, 7 (or 8), and 25 with Strong Acid. Compounds **5**, **7**, and **25** were each treated with 1:1 trifluoroacetic acid–sulfuric acid at 25°. For example, **5** (10.9 mg) in chloroform (487.5 mg) was treated with 1 g of the mixed acid and left to stand for 25 min at 25° before pouring onto ice and extracting with chloroform. The weighed extract was analyzed by vpc, using the original solution for calibration. The three compounds gave the yields of products under the conditions shown in Table II.

Table II

	Ret time, min: 11.7	12.8	14.4	15.1	20.3
	Compound, %: **14**	**25**	**7** (or **8**)		**5**
From **5**	39%	3	1	6	16
From **7** (or **8**)	28	3	0	5	11
From **25**	39	3	0	4	10

(38) Both this and the previous mass spectral analysis are based on the tetramethylnaphthalene peak (P − 72), the parent peak not being detectable.

Study of the Progress of the Reaction at 5°. A solution of the *syn*-benzobicyclooctadienol **2** in chloroform (1 ml, 237.8 mg/ml) was added over 1 min to a stirred mixture of trifluoroacetic acid and 98% sulfuric acid (exactly 1:1, 20 ml, 32.6 g) maintained at 5°. At intervals 1-ml portions were withdrawn, quenched with ice, and extracted with 200 μl of a solution of hexamethylbenzene in chloroform (5.343 mg/ml). The extracts were analyzed by vpc (10-ft 15% FFAP on Chromosorb W at 200°); the results are given in Figure 2.

In the absence of a pure sample of the *anti* alcohol **1**, a mixture of 58.7% **1** and 41.5% **2** was examined by the above procedure, with closely similar results.

Carbonium Ion–Silane Hydride Transfer Reactions. I. Scope and Stereochemistry

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Abstract: Carbonium ions varying in stability over a range of greater than 24 pK units were readily reduced to the corresponding hydrocarbons by hydride transfer from organosilanes. 2,6,2′,6′,2″,6″-Hexamethoxytriphenylmethane (**9**) was formed in 95% yield from the alcohol and triethylsilane in acetic acid but fragmented to *m*-dimethoxybenzene and 2,6,2′,6′-tetramethoxydiphenylmethyl cation in methylene chloride–trifluoroacetic acid. Reduction of either *cis*- (**15**) or *trans*-4-*t*-butyl-1-phenylcyclohexanol (**16**) afforded mixtures of *cis*- and *trans*-4-*t*-butyl-1-phenylcyclohexanes in which the *trans*/*cis* ratio was independent of the isomer used and the nature of the groups bonded to silicon. The *trans*/*cis* ratio did depend on the number of groups other than hydrogen bonded to silicon, being *ca.* 1.8 for triorganosilanes and *ca.* 4.0 for diorganosilanes and phenylsilane. The relative reactivity of the silanes used was triethyl > trioctyl ~ diethyl > diphenyl ~ triphenyl > phenyl. The results are interpreted as requiring carbonium ion intermediates for hydride transfer to occur and the stereoselectivity rationalized on the basis of "product development control." The higher percentage of elimination from equatorial alcohol (axial phenyl) than from axial alcohol (equatorial phenyl) is believed to result from the higher ground-state energy of the former.

Since silicon is more electropositive than carbon, silanes are good donors of hydride to carbonium ions. The reaction

$$(CH_3)_3SiH + (CH_3)_3C^+ \longrightarrow (CH_3)_3Si^+ + (CH_3)_3CH$$

has been calculated to be exothermic by 8 kcal/mol in the gas phase from electron impact measurements of bond energies.[1] Experimental evidence regarding the effectiveness of silanes as hydride donors to carbonium ions can be found in the observation made some time ago that *n*-hexyl chloride is converted to *n*-hexane and neopentyl chloride to isopentane by triethylsilane in the presence of aluminum chloride.[2] More recently the hydrogen–halogen exchange between trityl chloride and triphenylsilane in ionizing solvents has been studied and a mechanism proposed involving a four-center transition state between the carbonium chloride ion pair and the silane.[3]

$$R_3CCl + R_3SiH \longrightarrow \begin{matrix} R_3C^+\cdots H \\ Cl^-\cdots SiR_3 \end{matrix} \longrightarrow R_3CH + R_3SiCl$$

R = Ph

Consistent with this description is the report that the reaction proceeds with complete retention of configuration at asymmetric silicon.[4]

Intermolecular hydride transfer reactions *between carbons* are generally considered to involve a linear array of atoms in the transition state and to require a true carbonium ion ("open sextet") in order to occur.[5,6] Deno has discussed this requirement and pointed out that the capacity to abstract hydride from a neutral donor appears to be the unique reaction of carbonium ions not allowed their covalent precursors such as protonated alcohols. Thus, while *t*-butyl alcohol will undergo ^{18}O exchange with solvent, alkylate olefins and nitriles, and eliminate to olefin in 60% sulfuric acid, a medium in which the alcohol is protonated but negligible carbonium ion formation takes place, it does not abstract hydride from xanthene. Hydride transfer does take place, however, in 96% sulfuric acid where the equilibrium concentration of the *t*-butyl and derived cations is significant.[7]

We were interested in determining if similar restrictions applied to hydride transfers from silanes and investigating these reactions as probes for carbonium ion behavior. This paper reports our study of the scope of carbonium ion–silane hydride transfer reactions and some observations regarding their stereoselectivity and stereospecificity.

Results

The survey of carbonium ions reduced to the corresponding alkanes presented in Table I strikingly demonstrates the efficiency of silanes in donating hydride to carbonium ions. These carbonium ions were chosen to

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