The aqueous fraction from the pentane extraction was evaporated to dryness under reduced pressure to leave solid which on recrystallization from water yielded 0.46 g of needles, mp 186–187°.

Anal. Calcd for monohydrate $C_{23}H_{26}O_3NSBr \cdot H_2O$: C, 55.83; H, 5.75. Found: C, 55.75; H, 5.84.

III-OBs. A 1.0-g quantity of this compound in 100 ml of dry pyridine was heated in a sealed tube at 100° for 3 days. By the same techniques as those used for I-OBs products, olefin VI, pure by vpc analysis,[16] was obtained in 0.15-g yield and a pyridinium salt in a yield of 0.25 g, mp 175–185°. Studies of the nmr spectrum of the crude pyridinium salt from this reaction indicated that the endo:exo pyridinium ratio was *ca.* 4:1. (Nmr of $CDCl_3$ solutions showed purified salt to have a single proton peak at τ 5.38 attributable to the α proton to the pyridinium group. The crude salt showed a smaller second band at τ 4.84 which was attributed to the proton α to an endo-substituted pyridinium group.) Recrystallization of the crude salt gave a product, mp 186–187°, undepressed by the salt from I-OBs.

IV-OBs. By an identical procedure to that used for III-OBs, this product was found to yield pure olefin VI and pure salt, mp 186–187°, undepressed by the salt from I-OBs.

ID-OBs. By the procedure described for I-OBs, olefin V was obtained. A deuterium analysis showed that the olefin contained 0.49 atom % D. The isomerized III-OBs from this reaction was further solvolyzed in pyridine by the procedure described for III-OBs. The olefin VI obtained was compared with authentic olefin VI by ir spectral analysis. The spectra, taken on neat samples at 0.025-mm path length with a Beckman IR4 spectrophotometer, showed the spectrum of the isomerized material to contain a strong C–D stretch band at 2350 cm^{-1}. Bands at 998 and 747 cm^{-1}, present in the authentic sample spectrum, were completely absent.

IIID-OBs. This compound was treated by an identical procedure to that described for III-OBs. Olefin VI was obtained with a deuterium analysis of 0.34 atom % D.

Kinetics. For all of the *p*-bromobenzenesulfonates other than I-OBs and ID-OBs, acetolysis rate measurements were carried out in the normal manner using standard sodium acetate solution in acetic acid which was prepared as described previously.[18]

For acetolysis rates of I-OBs and ID-OBs a more rapid, *in situ* titration technique was used. The rates were followed by continuously titrating thermostated solutions of *ca.* 0.010 *M* sulfonate in dry acetic acid with a solution of 0.020 *M* sodium acetate in dry acetic acid using Bromophenol Blue indicator.

For the pyridine solvolysis studies, Karl Fischer grade pyridine was allowed to stand over Linde 4A molecular sieves powder for 24 hr and then redistilled. Standard sodium methoxide solution was prepared by adding sodium to redistilled methanol at about 0.4 g/l. and the resulting solution was standardized by titration against aqueous acid. The kinetic studies were carried out with 0.010 *M* solutions of the *p*-bromobenzenesulfonates, aliquots being sealed in ampoules and placed in thermostated baths. After suitable time intervals aliquots were titrated against the standard sodium methoxide solutions using Thymol Blue indicator. In all cases single *p*-bromobenzenesulfonates gave good first-order rate plots.

Acknowledgement. Helpful discussions with Dr. R. Baker of Southampton University, Southampton, England, are gratefully acknowledged.

(18) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 826 (1948).

A Dibenzohomotropylium Ion[1]

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Contribution No. 2838 from the Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024. *Received June 1, 1971*

Abstract: The 2,3;5,6-dibenzo-*cis*-4-hydroxybicyclo[5.1.0]octa-2,5-diene (**16**-OH) and the corresponding *trans*-4-hydroxy isomer **17**-OH were prepared by the reaction of $C_6H_5HgCBr_3$ with 2,3;5,6-dibenzotropone to give the dibromo ketone **14**. $NaBH_4$ reduction of **14** gave the cis 4-hydroxy compound which was debrominated by way of the tetrahydropyranyl ether with the aid of *n*-Bu_3SnH. Equilibration between **16**-OH and **17**-OH occurred in acidified aqueous dioxane. The corresponding 4-acetoxy, 4-methoxy, 4-keto, and 4-hydro compounds were prepared by conventional techniques. Stereochemical assignments were made by detailed examination of the nmr spectra of the cis and trans series of compounds. The dibenzohomotropylium cation **9**, which was prepared by protonation of **16**-OH in FSO_3H or H_2SO_4, showed considerable evidence for the heavy involvement of the cyclopropane protons in electron delocalization. Collapse of **9** with a nucleophile occurred predominantly upon the same face of the cation as the bridging methylene group, which is consistent with the observation that the cis acetate **16**-OAc solvolyzed some 10^2 times more rapidly than **17**-OAc. The kinetically controlled methanolysis product distribution of either acetate was the same, very largely **16**-OMe. Comparison is made of the solvolysis rates with other related systems and possible reasons for the observed stereoselectivity are discussed.

The concept of homoaromaticity, advanced[3] formally somewhat more than a decade ago, has found ample fulfillment in the many homoaromatic systems which have since been prepared and studied.[4] Such cyclic electron delocalization has frequently been observed with both cationic and anionic species but is much less important in neutral molecules.[4] The general concepts of homoaromaticity can be equally well applied to the transition states of pericyclic reactions[5] of both neutral molecules and ions.[4,6]

The monohomotropylium cation **1** was the first monohomoaromatic cation to be characterized. It was obtained in 1962 by Rosenberg, Mahler, and Pettit[7]

(1) This research was supported by the National Science Foundation. A portion of this work was presented in preliminary form: R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6348 (1967).

(2) (a) Author to whom correspondence should be addressed at the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada; (b) deceased Dec 21, 1969; (c) deceased Nov 23, 1969.

(3) S. Winstein, *J. Amer. Chem. Soc.*, **81**, 6524 (1959); S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3244 (1961).

(4) S. Winstein, *Chem Soc., Spec. Publ.*, **No. 21**, 5 (1967); S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

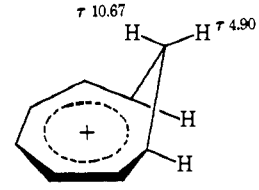
(5) R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(6) *Cf.* H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1563, 1566 (1966); M. J. S. Dewar, *Tetrahedron, Suppl.*, 8, 75 (1966); *Chem. Soc. Spec. Publ.*, **No. 21**, 177 (1967).

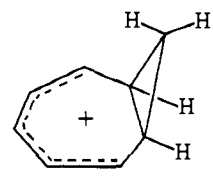
(7) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 2842 (1962).

on protonation of cyclooctatetraene with concentrated sulfuric acid, and could be isolated as the solid salt, $C_8H_9^+SbCl_6^-$, by reaction of cyclooctatetraene with HCl and $SbCl_5$. Subsequent investigations have fully confirmed[4] the six-electron cyclic delocalized nature of **1**.

A homotropylium structure, **1**, is uniquely able to account for the very large chemical-shift difference observed in the nmr spectrum of **1** between the "inside" and "outside" C_8 protons, one being shielded and the other deshielded by the induced diamagnetic ring current. The alternate classical bicyclic structure **2** is incompatible with the observed nmr spectrum. A good model for **2** is the bicyclo[3.1.0]hexenyl cation **3** in which there is no delocalization of the C_1C_5 bond, and in this cation the cyclopropylmethylene chemical shifts differ by less than 1 ppm.[8] When the 4π, 5C preference of an iron atom is used to lock the homotropylium cation into the bicyclic form **4**, the C_8 methylene protons have a very similar chemical shift.[9] That this is not due to an adventitious anistropy of the iron atom was demonstrated by preparing metal complexes with the metal having a 6π preference, for example, the molybdenum complex, **5**.[10]



1



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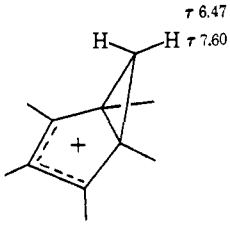

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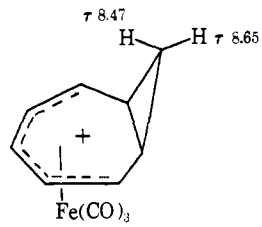

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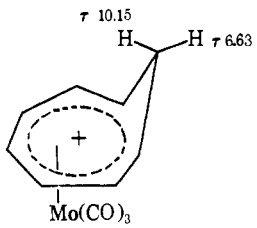

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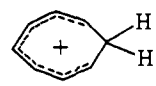


6

The planar cyclooctatrienyl cation **6**, in which the methylene protons are equivalent, is not only incompatible with the observed nmr spectrum of **1** but has been shown[11] to be at least 22.3 kcal less stable than the homotropylium ion **1**.

(8) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968). The unsubstituted cation, very recently prepared by P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson (*ibid.*, **93**, 1551 (1971)), has the "inside" proton absorbing downfield of the "outside" proton. This striking result further reinforces the homoaromatic nature of 1.

(9) (a) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965); (b) G. N. Schrauzer, *ibid.*, **83**, 2966 (1961); A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

(10) For a detailed analysis of the nmr spectrum of **1** see P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970).

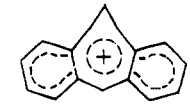
Volume susceptibility data obtained by Dauben and coworkers[12] provide more direct evidence for the presence of an aromatic ring current in the monohomotropylium cation. The ion **1** shows an exaltation, compared to the calculated nonaromatic value, almost as large as that of the tropylium ion. Comparison of the exaltation per unit area of the ring would indicate that the homotropylium ion is just as aromatic as the tropylium ion, or indeed benzene itself.

Many substituted homotropylium ions have been prepared (the 1-hydroxy-,[13] 2-hydroxy-,[14] 4-hydroxy-,[15] 1-methyl-,[14b] 1-phenyl-,[14b] and both the *exo*- and *endo*-8-chloro-[16]) and all exhibit considerable evidence of six-electron cyclic delocalization.[12b]

Recently the protonation of benzo-[17] and dibenzocyclooctatetraene[18] and 4,5-benzohomotropone have been reported to give **7**, **8**, and the corresponding benzohydroxyhomotropylium,[19] respectively.[20]

7

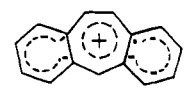
8



9

In order to probe the properties of the homotropylium ion further it seemed to us that it would be interesting to prepare the dibenzohomotropylium cation **9**, the homo counterpart of the 2,3,6,7-dibenzotropylium ion **10**.[21a] The two benzene rings in **10** considerably attenuate the properties of the tropylium cation[21b] and it would be instructive to determine the importance of homoconjugation in **9**.

In a previous study the rate-enhancing effect of the spirocyclopropyl group in the ionization[22] of **11** to the anthrylethyl-bridged ion **12**[22b] had been investigated and the preparation of **9** by ionization of covalent precursor would enable a comparison of spiro- to homoconjugation in these systems. The dampening effect



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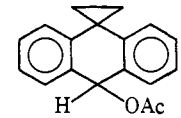

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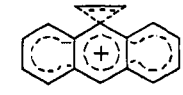


12

(11) S. Winstein, C. G. Kreiter, and J. I. Brauman, *J. Amer. Chem. Soc.*, **88**, 2047 (1966).

(12) (a) H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, *ibid.*, **90**, 811 (1968); **91**, 1991 (1969); (b) H. J. Dauben, J. Laity, and S. Winstein, unpublished work.

(13) M. Brookhart, M. Ogliaruso, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1965 (1967).

(14) (a) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963); (b) C. E. Keller and R. Pettit *ibid.*, **88**, 604, 606 (1966).

(15) O. L. Chapman and R. A. Fugiel, *ibid.*, **91**, 215 (1969).

(16) G. Bocke, W. Hechtl, H. Huber, and R. Huisgen, *ibid.*, **89**, 3344, 3345 (1967).

(17) W. Merk and R. Pettit, *ibid.*, 90, 814 (1968).

(18) G. D. Mateescu, C. D. Nenitzescu, and G. A. Olah, *ibid.*, **90**, 6235 (1968).

(19) Y. Sugimura, N. Soma, and Y. Kishida, *Tetrahedron Lett.*, 91 (1971).

(20) Several bishomotropylium cations have been reported: H. P. Löffler and G. Schröder, *ibid.*, 2119 (1970); G. Schroeder, V. Prange, N. S. Bowman, and J. F. M. Oth, *ibid.*, 3251 (1970); P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2147, 4454 (1970); M. Roberts, H. Hamberger, and S. Winstein, *ibid.*, **92**, 6346 (1970).

(21) (a) G. Berti, *Gazz. Chim. Ital.*, **87**, 293 (1957); (b) D. Meuche, H. Strauss, and E. Heilbronner, *Helv. Chim. Acta*, **41**, 57 (1958); G. Naville, H. Strauss, and E. Heilbronner, *ibid.*, **43**, 1221 (1960).

(22) (a) R. Leute and S. Winstein, *Tetrahedron Lett.*, 2475 (1967); (b) L. Eberson and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 3506 (1965).

of the benzene rings should permit a solvolytic study and so allow evaluation of the effectiveness of double bond **10** compared with cyclopropane (**9**) in cyclic electron delocalization.

Preparation and Characterization of the Dibenzohomotropylidenes

Synthesis. Repeated attempts to add methylene directly to a variety of dibenzo[*a*,*d*]cycloheptatrienyl systems were unsuccessful. Cyclopropylation of the double bond of **13** was eventually achieved in fair yield by reaction with phenylmercuric tribromomethane[23] in refluxing benzene. It was necessary to protect the ketone function of the product **14** before the two bromines could be removed, and to this end it was reduced with sodium borohydride to give **15**-OH. Only one stereoisomer was obtained upon this reduction and probably it has the hydroxy function cis with respect to the cyclopropyl ring (*vide infra*). The pyranyl ether **15**-OPy was formed from **15**-OH by reaction with dihydropyran in the presence of *p*-toluenesulfonic acid. Removal of the two bromines was affected in high yield with tri-*n*-butyltin hydride[24] at 55° for 84 hr. The protecting pyranyl ether group was removed from the reduced product with acidified 75% aqueous acetone to give a mixture of two isomeric alcohols which could be separated by column chromatography.

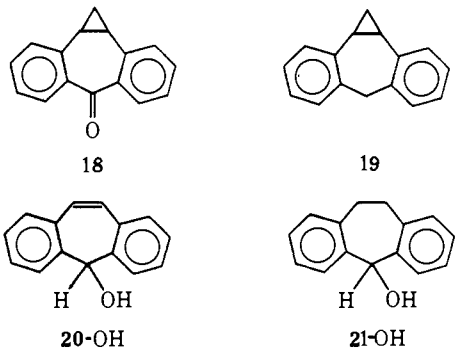
These two alcohols, which will be shown to have the stereochemistry indicated by **16**-OH, **17**-OH, were clearly structurally related. Their nmr spectra, apart from the resonance attributed to the proton α to the hydroxy function, were very similar and showed the distinctive chemical shifts and coupling constants of a cis-fused cyclopropane. In acidic 80% aqueous dioxane at 75° **16**-OH and **17**-OH were in equilibrium, the equilibrium composition, 80.8% **16**-OH and 19.2% **17**-OH, being determined by repeated integration of the proton resonances at τ 3.33 and 4.87, respectively.

Reaction of **16**-OH and **17**-OH with acetic anhydride–pyridine gave **16**-OAc and **17**-OAc, respectively. Heating either acetate at 100° in acetic anhydride gave rise to an equilibrium mixture of the two, comprising 46.5% **16**-OAc, and 53.5% **17**-OAc. As **16**-OAc solvolyzed in 80% aqueous acetone some 240 times more rapidly than **17**-OAc (*vide infra*) the most convenient large scale route to the latter compound was by partial solvolysis of the equilibrium mixture of acetates. The separation of the residual **17**-OAc from the alcohols formed as solvolysis products was readily achieved by column chromatography. This route possessed considerable advantage over the separation and acetylation of **17**-OH, particularly as the trans acetate, **17**-OAc, predominated in the acetate equilibrium mixture.

Treatment of **16**-OH with methanol–HCl gave an equilibrium mixture of the two methoxy ethers, **16**-OMe and **17**-OMe, which were separable by column chromatography. The same equilibrium composition, 56.4% **16**-OMe and 43.6% **17**-OMe, was obtained from pure **16**-OMe in acidic methanol at 65°.

Manganese dioxide oxidation of the alcohol **16**-OH in pentane gave the ketone **18** which still retained the cyclopropyl resonances in the nmr spectrum and had a carbonyl stretch at 1652 cm^{-1} (KBr). Reduction of **18** with sodium borohydride gave an alcohol mixture consisting of 98.8% **16**-OH and 1.2% **17**-OH. The analysis, as were other product analyses of a similar composition, was performed by a CAT technique.

The hydrocarbon **19** was obtained by reaction of **16**-OH with anhydrous HCl and solvolysis of the resulting chloride, which was not isolated, in aqueous dimethoxyethane containing sodium borohydride.[25]



The dibenzocycloheptatrienol **20**-OH and dienol **21**-OH were converted to the corresponding methoxy

(23) D. Seyferth, *et al.*, *J. Organometal Chem.*, **4**, 127 (1965); *J. Org. Chem.*, **27**, 1491 (1962); **28**, 1163 (1963).

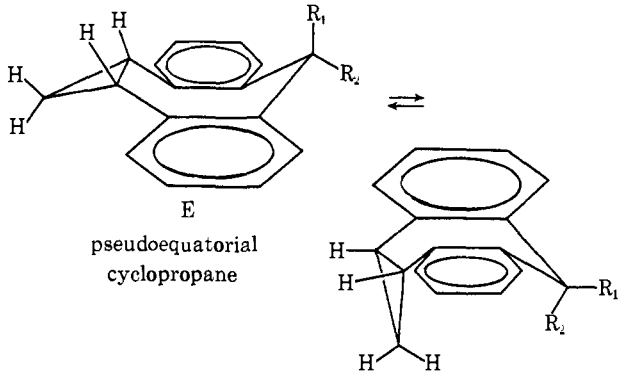
(24) D. Seyferth, H. Yamazaki, and D. L. Alleston, *ibid.*, **28**, 703 (1963).

(25) H. C. Brown and H. M. Bell, *ibid.*, **27**, 1928 (1962); H. M. Bell and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 1473 (1966).

ethers,[26] **20**-OMe and **21**-OMe, and acetates,[27] **20**-OAc and **21**-OAc, by conventional techniques.

Stereochemistry. The stereochemical assignments assumed in the preceding synthetic sequences were established by detailed examination of the nmr spectra of the two isomeric methoxy ethers, **16**-OMe and **17**-OMe, and other related systems.

The 3,4-homotropylidenes like cycloheptatriene exist in a boat conformation, the cyclopropane being either in the pseudoaxial, A, or pseudoequatorial position, E.[28] The nmr spectra of **16**-OMe and **17**-OMe, dissolved in CS_2–CD_2Cl_2, showed no temperature dependence on being cooled to −120 and −83°, respectively. The benzylic methylene protons of **19** give an AB quartet at room temperature and the AB chemical shift increases only slightly at −70°. Thus, either the energy barrier for the interconversion of the two conformations of the homotropylidene ring is very low, or these compounds exist predominantly in one conformation at room temperature. To assess the size of the energy barrier for conformational interconversion expected in these ring systems some related dibenzocycloheptatrienes were studied.



E
pseudoequatorial
cyclopropane

A
pseudoaxial
cyclopropane

Cooling the triene hydrocarbon **20**-H caused the singlet observed for the methylene protons in the nmr spectrum at room temperature to broaden, pass through a coalescence point[29] at −83°, and become an AB quartet below this temperature (at −123°, $\Delta\gamma_{AB}$ = 15.7 Hz, J_{AB} = 13.3 Hz). The spectrum of **20**-OMe was temperature invariant on cooling to −125°, pointing to the predominance of one conformation at room temperature.[30] Thus, any interconversion between the two boat forms of the dibenzohomotropylidenes could have been slowed sufficiently to have been observed, at least as line broadening, at the temperatures to which each compound was cooled.

The marked similarity in the nmr spectra of **16**-OMe and **17**-OMe, particularly of the cyclopropyl resonances, would strongly suggest that each exists in the same conformation. When the cyclopropane is in the pseudoaxial position A, there is steric hindrance between the "inside" C_8 methylene proton and the C_4 axial substituent, this becoming increasingly important when the C_4 substituent is other than a hydrogen.[28] As it has been established that the relative ground-state energies of the two ethers **16**-OMe and **17**-OMe are very similar (Table I), then the cyclopropyl group must occupy the pseudoequatorial position, E. The position of the equilibria between **16**-OH and **17**-OH and **16**-OAc and **17**-OAc further substantiates this assignment.

Table I. Thermodynamic Equilibria between *cis*- and *trans*-Dibenzohomotropylidenes

R	Composition, % 16-OR (cis)	17-OR (trans)	Temp, °C	K_{eq},[a] dihydropleiadenes
H[b]	80.8	19.2	75	0.3
Me[c]	56.4	43.6	65	2.2
$COCH_3$[d]	46.5	53.5	100	3.3

[a] K_{eq} = axial/equatorial substituent values taken from results of Lansbury.[32] [b] 80% aqueous dioxane–H^+. [c] MeOH–H^+. [d] Ac_2O.

Irradiation at τ 3.07 of the aromatic protons of a degassed solution of **17**-OMe in a double resonance experiment caused the area of the α-hydrogen signal (τ 5.32) to increase by 31 ± 3% with no apparent decrease in the half-width. No comparable increase in the area of the α-hydrogen resonance of **16**-OMe was detected upon irradiation of the aromatic protons. The presence of this intramolecular nuclear Overhauser effect[31] clearly demonstrates the proximity of the α-hydrogen and the two aromatic protons in **17**-OMe, a situation that only exists when this proton is in the pseudoequatorial position. The absence of an Overhauser effect in **16**-OMe would indicate that the α proton in this isomer is in the axial position. The low-field position of the pseudoaxial proton in these systems is entirely consistent with the results reported for the dihydropleiadenes,[32] dihydroanthracenes,[33] and 6,7-dichloroestrones.[34]

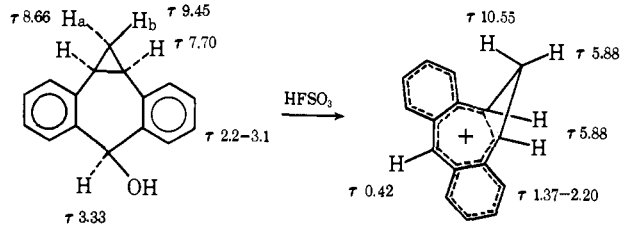
It can therefore be concluded that the cyclopropyl and methoxy groups of **16**-OMe are cis with respect to each other and conversely they are trans in **17**-OMe. The similarity in spectra of the two acetates **16**- and **17**-OAc and two alcohols **16**- and **17**-OH to the ethers **16**-OMe and **17**-OMe, respectively, allows their stereochemical assignment.[35]

It is instructive to note that Lansbury[32] has shown that there is an increasing preference for a substituent to be in the pseudoaxial position of the dihydropleiadenes in going from hydroxy, to methoxy, to acetoxy substituent. This same preference is exhibited upon equilibration of the substituted dibenzohomotropylidenes (Table I).

(26) Belgian Patent 616,907 (1962); *Chem. Abstr.*, **58**, 4475 (1963).
(27) V. Mychazlyszyn and M. Protiva, *Collect. Czech. Chem. Commun.*, **24**, 3955 (1952).
(28) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).
(29) It is interesting to note that the energy barrier for the interconversion of the two boat conformations of **20**-H is considerably greater than that determined for the unsubstituted cycloheptatriene; F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964).
(30) In contrast, the sharp singlet of the proton α to the methoxy group of the less stereochemically rigid **21**-OMe broadened on cooling, coalescence temperature −65°, to give at −117° two resonances 57-Hz apart, the low-field absorption being approximately half the area of the high-field one. Only slight broadening of **21**-H was observed at −117°.
(31) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).
(32) P. T. Lansbury, *Accounts Chem. Res.*, **2**, 210 (1969).
(33) A. W. Brinkman, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Temay, Jr., *J. Amer. Chem. Soc.*, **92**, 5219 (1970).
(34) Y. Osawa and M. Neeman, *ibid.*, **85**, 2857 (1963).
(35) Apart from their spectral similarity, **16**-OH, **16**-OAc, and **16**-OMe are related chemically. Thus acetylation of **16**-OH gives **16**-OAc which on solvolysis in aqueous acetone gives very largely **16**-OH and in methanol **16**-OMe.

Results and Discussion

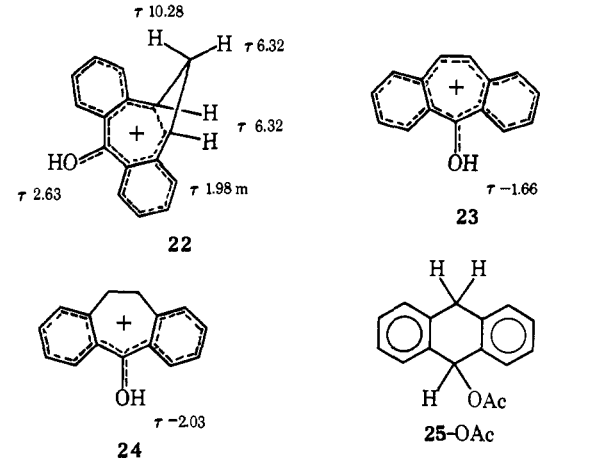
Direct Observation of the Dibenzohomotropylium Cation. Extraction of **16**-OH into fluorosulfuric acid at −78° or sulfuric acid at room temperature gave clean solutions of the dibenzohomotropylium ion, the nmr resonances of which are summarized in **9**. The chemical shifts of this cation, particularly of the cyclopropylmethylene resonances, demonstrated that the structure is best represented by a homoaromatic dibenzohomotropylium structure. Quenching the sulfuric acid solution of **9** in methanol–bicarbonate gave in high yield a mixture of **16**-OMe and **17**-OMe. The "inside" methylene proton H_b (τ 9.45 in the alcohol **16**-OH) moves to higher field (τ 10.55) in the cation while the "outside" proton H_a (τ 5.88) is deshielded by 2.78 ppm compared to **16**-OH. Thus, there is a difference of 4.7 ppm between these two methylene protons of the cation, a very considerable increase over the 0.8 ppm observed in **16**-OH. The magnitude of this chemical-shift difference compares favorably with the 5.8 ppm observed for the unsubstituted homotropylium ion **1** and indicates substantial involvement of the cyclopropane in cyclic electron delocalization.[7,9a,11] The chemical-shift differences between the bridging methylene protons of the monobenzohomotropylium **7** (Δ = 3.9 ppm) and dibenzohomotropylium **8** (Δ = 3.2 ppm) are both considerably less than that found for **9**; however, the different environment of the bridging methylene in **7** and **8** compared to **9** nullifies interpretation of the difference in terms of the magnitude of electron delocalization.



16-OH **9**

The ketone **18** was protonated by extraction from methylene chloride into fluorosulfuric acid to give a stable solution of **22**, with the nmr spectrum as indicated. Despite the extra stabilization the hydroxy group affords the cation **22** it is still decidedly homoaromatic. The nmr spectrum of **22** closely resembles that of **9** although the difference between the two C_8 methylene protons is now 4.0 ppm, the decrease in magnitude compared to **9** reflecting the tendency to localize charge on the hydroxy function.

The chemical shift of the C=O—H proton has been used as a measure of the stability of a cation: the greater the ability of the group or groups which are attached to the carbonyl to stabilize the positive charge the more the protonated carbonyl becomes a hydroxy cation, the position of the O–H resonance reflecting this change.[36] The O–H resonance of **23** (τ −1.66 at −75° in FSO_3H) obtained by protonation of dibenzotropone is upfield from the corresponding dibenzocycloheptadienone (**24**) (τ −2.03 at −75° in FSO_3H), which is indicative of greater charge delocalization in **23** than **24**. The protonated dibenzohomotropone O–H resonance could not be observed at −75° in $HFSO_3$, as exchange with solvent was still rapid at this temperature. At −90° a broad singlet was detected at τ −2.63 which is downfield of either of the hydroxy proton resonances of the two model compounds **23** and **24**. While it is not unexpected, perhaps, that there is less tendency to delocalize the charge into the dibenzohomotropyl system than with the dibenzotropyl system, the high-field position of the hydroxy proton of **24** compared to **22** is surprising. However, the choice of **24** as a model is open to question as there are not only conformational differences between **22** and **24** but the absence of a ring current in the saturated seven-membered ring of **24** could significantly alter the deshielding experienced by the hydroxy proton.



Solvolysis. Rate and Product Studies. The various acetate esters were hydrolyzed in 80% aqueous acetone and the developed acetic acid was determined by titration with methoxide in methanol. The first-order hydrolysis rate constants are summarized in Table II.

Table II. Solvolysis Rates in 80% Aqueous Acetone

ROAc	Temp, °C	k, sec^{-1}	Rel rate 25°
17-OAc	100.1	$(1.39 \pm 0.02) \times 10^{-5}$	
	75.0	$(9.61 \pm 0.19) \times 10^{-7}$	
	25.0[a]	1.23×10^{-9}	1
16-OAc	75.0	$(1.02 \pm 0.01) \times 10^{-4}$	
	50.0	$(6.86 \pm 0.15) \times 10^{-6}$	
	25.0[a]	2.94×10^{-7}	2.4×10^{2}
20-OAc	25.0	$(5.13 \pm 0.09) \times 10^{-5}$	4.2×10^{4}
21-OAc	100.1	$(4.00 \pm 0.06) \times 10^{-4}$	
	75.0	$(4.13 \times 0.09) \times 10^{-5}$	
	25.0[a]	1.45×10^{-7}	1.2×10^{2}
25-OAc[c]	25.0	1.26×10^{-5}	1.0×10^{4}
11-OAc[c]	25.0[b]	1.45×10^{-2}	1.2×10^{7}

[a] Extrapolated from data at higher temperatures. [b] Estimated from the rate constant in 90% acetone. [c] Reference 22a.

It is clear from these results that the cyclopropane in the dibenzohomotropyl systems (**16** and **17**-OAc) is less rate enhancing than the olefinic group of the dibenzotropyl system **21**-OAc. These rates, however, may not give a true reflection of the relative stabilities of the cations, for in both **16**- and **17**-OAc the cyclopropyl group is held in the equatorial position and as such is very poorly orientated to overlap with the π system. Indeed when a cyclopropyl is held in this position relative to a benzene ring it has been shown to

(36) M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1735 (1967); G. Levy, Ph.D. Thesis, University of California, Los Angeles, Calif., 1968.

Table III. Summary of Solvolysis Products from **16**-OAc and **17**-OAc

Compd	Solvent	Temp, °C	Products			Ratio of **16**-OMe:**17**-OMe
			16-OH, %	**17**-OH, %	**16** and **17**-OMe, %	
16-OAc	80% Me_2CO	75	94.4	0.6		
17-OAc	80% Me_2CO	100	83.4	16.6		
16-OAc	MeOH	100	2.9		97.2	98.9:1.1
17-OAc	MeOH	100		34.7	65.3	98.7:1.3
9[a]	MeOH	−78			79[b]	94.8:5.2

[a] Result of quenching H_2SO_4 solution of **9** in MeOH–HCO_3^- at −78°. [b] Per cent recovery based on starting **16**-OH.

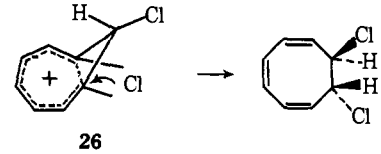
be inductively electron withdrawing.[37] This inductive withdrawal may be reflected in solvolysis rates of the cis and trans acetates, as the ethano compound **21**-OAc is only a factor of 2 slower than the cis compound **16**-OAc and 10^2 times more reactive than the trans acetate **17**-OAc. However, all the rate enhancements are beclouded in this series of compounds by the question of what model compounds to employ. Thus the rate of hydrolysis of the unsaturated system **20**-OAc is some 10^2 times greater than that of the saturated ethano compound **21**-OAc but is not appreciably faster than the saturated methano system **25**-OAc. Conformational and substituent effects in these model compounds are as important as the introduction of a double bond in place of an ethano bridge in the seven-membered ring. It is evident that the benzene rings in these compounds have very considerably attentuated the properties of the central ring. Despite this attentuation it is clear that the cyclopropane in the dibenzohomotropyl system is less rate enhancing than the spirocyclopropane group in **11**-OAc.[22a]

The difference in rate enhancement of the cis (**16**-OAc) and trans (**17**-OAc) dibenzohomotropyl systems of some 10^2 is also reflected in the distribution of products under kinetic control (Table III). The occurrence of alcohols as products of solvolysis in methanol indicates that an appreciable fraction of the ester hydrolysis occurs with acyl oxygen cleavage, particularly with the slowest ester, **17**-OAc. However, the ratio of cis:trans methoxy ethers (**16**-OMe:**17**-OMe) derived from either of the two acetates, **16** or **17**-OAc, within the limits of experimental error, is the same. The product ratio of **16**-OMe:**17**-OMe of *ca.* 10^2 is in line with the cis:trans reactivity ratio of 10^2 and a thermodynamic equilibrium ratio close to 1. The quench of the sulfuric acid solution of the dibenzohomotropylium cation **9** in methanol–bicarbonate gave the two methoxy ethers in a ratio of 94.8:5.2 cis:trans, which, allowing for some acid-catalyzed isomerization during the quench of the ether product, is in agreement with that observed from kinetic control in acetate methanolysis. It would seem evident, therefore, that the cation obtained during solvolysis of both the cis and trans acetates is the homotropylium cation **9** and that the difference in rates of formation of **9**, and its selectivity in collapse with a nucleophile, must arise from some intrinsic property of **9**.

As the nucleophile which attacks the dibenzohomotropyl system **9** does so predominantly from the most sterically congested side it does not seem possible to attribute the selectivity observed for the formation and capture of **9** to purely steric hindrance. It is pertinent to note in this context that the ketone **18**, which, although it may not be a perfect model, has a stereochemistry that must somewhat resemble that of the cation, undergoes predominantly trans attack when reduced with sodium borohydride. Analysis of the alcohol mixture so derived showed it to consist of 98.8% cis alcohol, **16**-OH, and 1.2% **17**-OH.

The participation and stereochemical control by a cyclopropyl bond, or bonds, during the formation and collapse of a carbonium ion are well documented. Systems investigated include the formation of an allyl cation upon heterolysis of a suitable cyclopropyl derivative,[38] cyclopropylcarbinyl systems, particularly when the stereochemistry is kept rigidly fixed,[37] and remote cyclopropyl as, for example, illustrated with the trihomocyclopropenium cations.[39] The dibenzohomotropyl system is somewhat different than these in that there is, formally, involvement and stereochemical control by a remote cyclopropane which is acting through a π system.[40] It is not clear as yet whether the stereospecificity observed with this system is a feature of the homotropylium cation or whether it will also be found as a characteristic of a rigid cyclopropyl–allyl system.

Huisgen[16] has reported a high degree of stereospecificity in collapse of the 8-chlorohomotropylium cations with chloride. Thus, **26** undergoes attack on the same side of the homotropylium ring as the bridging group, to give the trans dichloride. Between the C_1 and C_7



26

carbons of the homotropylium system there is an asymmetric electron distribution, each carbon atom being somewhere between sp^3 and sp^2 hybridized with the greatest electron density being on the opposite side of the seven-membered ring[41] to the bridging group. The attacking nucleophile, in this case chloride, approaches C_1 on that side of the atom which had the least electron density. One view of the results with the

(37) B. R. Lee and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970); P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880; (1969), and references cited therein.

(38) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedman, *ibid.*, **87**, 4006 (1965); C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966).

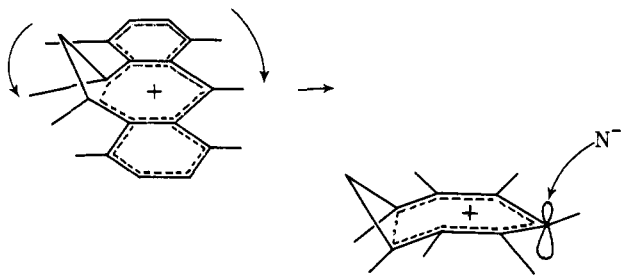
(39) M. A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl, and S. Winstein, *ibid*, **92**, 2146 (1970), and references cited thereln.

(40) The distance between the C_1C_7 cyclopropane bond and C_4, even when the seven-membered ring is in a boat conformation, is too great for the formation of a trishomocyclopropenium ion. The nmr spectrum of **9** is also inconsistent with such a formulation.

(41) The use of the term "seven-membered ring" is not meant to infer that there is a full bond between C_1 and C_7, but is used to denote those seven carbon atoms of the homotropylium cation over which the 6 electrons are principally delocalized.

dibenzohomotropyl system is that the unsymmetrical electron distribution between C_1 and C_7 of the cation is reflected at C_4, with a greater electron density being maintained upon the side of the seven-membered ring away from the bridging group. Thus the approach of a nucleophile, or departure of it from the covalent material, would be energetically more favorable when cis to the cyclopropyl, despite the increased steric interactions. A similar proposal has been made by Radlick to account for the stereospecific protonation of a homoaromatic anion.[42] Described as such the stereospecificity observed with **9** could be expected to be a general feature of homotropylium cations.

Alternatively it is conceivable that the steric preferences observed for the formation and collapse of **9** may be attributable to a steric interaction which is peculiar to **9**. If the dibenzohomotropyl cation, apart from the bridging methylene group, is planar then there is a steric interaction between the protons upon the bridgehead carbons, C_1 and C_2, and the two hydrogens in the adjacent positions on the benzene ring. This interaction can be minimized by allowing the seven-membered ring to adopt a shallow boat conformation, the bridgehead carbons (C_1 and C_7) and C_4 moving down from the plane of the cation and the two benzene rings tilting up, a movement which is exaggerated in the projections below.



Such a movement must be at the expense of overlap of the π system and this is particularly apparent at C_4. This could be partially offset by a rehybridization at C_4 to give some s character to the p orbital, the correct alignment for overlap being thus achieved but also an asymmetric π electron distribution at C_4, as such a nucleophile would be expected to attack at C_4 on the top face of the cation, cis to the C_8 bridge.

Experimental Section

General. Melting points were determined in open capillaries and are uncorrected. Elemental analyses were performed by Miss Heather King, University of California, Los Angeles, Calif. Ir spectra were obtained on a Perkin-Elmer Model 421 grating spectrometer as KBr discs. Nmr spectra were obtained on a Varian A-60 spectrometer and are referred to internal tetramethylsilane. Low-temperature spectra of the cations were recorded on a A-60 fitted with a variable-temperature probe, probe temperature being measured with a methanol sample. Variable-temperature spectra and Overhauser effects of the dibenzotropylidenes and dibenzohomotropylidenes were measured in a modified Varian HR-60. Samples were rigorously degassed by several pump–freeze–thaw cycles. Product composition was determined by multiple scanning of the appropriate area using a Varian C-1024 time averaging computer. Mass spectra were obtained on an AEI MS-9 double focusing mass spectrometer.

The cation solutions for direct nmr observation were prepared by extraction into FSO_3H or FSO_3H–SbF_5 from CH_2Cl_2 as previously described.[43] Chemical shifts were referred to internal CH_2Cl_2 taken at τ 4.7.

2,3;5,6-Dibenzo-8,8-dibromo[5.1.0]bicycloocta-2,5-dien-4-one (14). Dibenzo[*a*,*d*]cycloheptatrien-5-one (500 mg) and phenylmercuric tribromomethane[23] (5.2 g) were heated in benzene (6.5 ml) to 80–85° with stirring for 2.5 hr. The reaction was cooled and the precipitate of phenylmercuric bromide filtered off and washed with benzene. The filtrate and washings were evaporated to dryness *in vacuo* and the residue was treated with carbon disulfide (10 ml). The buff colored product crystallized on standing at 0°, mp 172–175° (560 mg). This material was used directly in the next stage. Recrystallization from acetone gave pure **14**: mp 177–178°; nmr (CS_2) τ 2.4–2.9 (m, 8, Ar*H*), 6.55 (s, 2, bridge *H*).

Anal. Calcd for $C_{16}H_{10}Br_2O$: C, 50.82; H, 2.67. Found: C, 50.81; H, 2.79.

2,3;5,6-Dibenzo-8,8-dibromo-*cis*-4-hydroxy[5.1.0]bicycloocta-2,5-diene (15-OH). The preceding ketone (3.7 g) was suspended in methanol (180 ml), water (9 ml), and aqueous sodium hydroxide solution (3.7 ml of a 1 *N* solution). Sodium borohydride (1.85 g) was added slowly and the reaction stirred until all the ketone had gone into solution (*ca.* 1 hr) and then for an additional 0.5 hr. Excess borohydride was destroyed by boiling the solution for 10 min. Water (200 ml) was added and the organic material was extracted into ether (two 50-ml portions). The ether extract was washed with water (three 100-ml portions) and dried over potassium carbonate, and the ether was removed *in vacuo*. The colorless residue was recrystallized from hexane–benzene to give **15**-OH (1.85 g): mp 160–161°; nmr (CS_2) τ 2.4–3.1 (m, 8, Ar*H*), 3.63 (s, 1, *H*-COH), 6.80 (s, 2, bridge *H*), 7.66 (s, 1, *OH*).

Anal. Calcd for $C_{16}H_{12}Br_2O$: C, 50.55; H, 3.18. Found: C, 50.71; H, 3.20.

2,3;5,6-Dibenzo-8,8-dibromo-*cis*-4-pyranoxy[5.1.0]bicycloocta-2,5-diene (15-OPy). The above alcohol (2.2 g) was stirred with dihydropyran (3 ml), ether (17 ml), and *p*-toluenesulfonic acid (10 mg) for 18 hr at room temperature. The reaction mixture was kept at 0° for 5 hr and the precipitate filtered off, it being washed with a little cold ether and then light petroleum ether (40–60°); yield 1.95 g. Recrystallization from ether gave analytically pure material: mp 181–182°; nmr (CS_2) τ 2.4–3.0 (m, 8, Ar*H*), 3.63 (s, 1, *H*-COPy), 6.72 (s, 2, bridge H), 5.27, 6.1–6.8, 8.0–8.7 (m, 9, Pr*H*).

Anal. Calcd for $C_{21}H_{20}Br_2O_2$: C, 54.33; H, 4.34. Found: C, 54.44; H, 4.24.

2,3;5,6-Dibenzo-*cis*-4-pyranoxy[5.1.0]bicycloocta-2,5-diene. The preceding ether (1.8 g) was treated with tri-*n*-butyltin hydride[44] (2.0 g) in anhydrous benzene (8 ml) at 55° for 24 hr. More of the tin hydride (1 g) was added and the reaction heated for a further 60 hr. The benzene was removed *in vacuo* and the oily residue seeded with a crystal of the product and then kept at 0° for 24 hr. (Scratching of the oil induced the crystallization of the oil in the first instance.) The product was filtered off, washed with light petroleum ether, and recrystallized from methanol to give a colorless crystalline product: mp 122.5–123.5° (0.87 g; 73%); nmr (CS_2) τ 2.4–3.1 (m, 8, Ar*H*), 3.34 (s, 1 *H*COPy), 5.18, 6.1–6.8, 8.0–8.7 (m, 9, Py*H*), 7.73 (q, 2, J_{cis} = 9 Hz, J_{trans} = 5.5 Hz, bridge *H*), 8.63 (1, J_{gem} = 4 Hz, J_{cis} = 9 Hz, cyclopropyl *H*), 9.52 (1, J_{gem} = 4 Hz, J_{trans} = 5.5 Hz, cyclopropyl *H*).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.22; H, 7.23. Found: C, 82.32; H, 7.24.

2,3;5,6-Dibenzo-4-hydroxy[5.1.0]bicycloocta-2,5-diene (16-OH and 17-OH). The preceding ether (585 mg) was dissolved in acetone (60 ml) and aqueous perchloric acid (20 ml of 0.2 *N*) was added. The solution was allowed to stand at room temperature for 36 hr, then water (300 ml) was added and the alcohols were extracted into ether (100 ml). The ether layer was washed with dilute aqueous bicarbonate (50 ml) and water (100 ml) and dried over magnesium sulfate. Removal of the ether *in vacuo* gave a white solid (345 mg).

Equilibration and Separation of 16-OH and 17-OH. The crude product from the previous experiment (100 mg) was dissolved in dioxane (12 ml) and aqueous perchloric acid (3 ml of 0.125 *N*) and kept at 75° for 19 hr. The reaction mixture was poured into aqueous sodium bicarbonate (30 ml) and extracted into ether (20 ml).

(42) R. Radlick and W. Rosen, *J. Amer. Chem. Soc.*, **89**, 5308 (1967). However, the solvent and counterion have been shown to be very important in determining the stereochemistry of collapse of the bicyclo[3.2.1]heptadienyl anion; J. M. Brown and E. N. Cain, *ibid.*, **92**, 3822 (1970).

(43) M. Brookhart, Ph.D. Thesis, University of California, Los Angeles, Calif., 1968.

(44) G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, 7, 366 (1957).

The ether layer was washed with water (20 ml), dried over potassium carbonate, and evaporated *in vacuo*. The product composition, determined by nmr, was found to be 80.8 ± 1.5% cis alcohol (**16**-OH) by integration of areas of the protons α to OH function.

The alcohols were separated by column chromatography (Woelm, neutral, activity 2.5). Eluting with petroleum ether (20–40°) gave **16**-OH: mp 142.5–144°; nmr (CS_2) τ 2.5–3.1 (m, 8, Ar*H*), 3.33 (s, 1, *H*-COH), 7.70 (2, J_{cis} = 9 Hz, J_{trans} = 5.5 Hz, bridge *H*), 8.66 (1, J_{gem} = 4 Hz, J_{cis} = 9 Hz, cyclopropyl *H*), 9.45 (1, J_{gem} = 4 Hz, J_{trans} = 5.5 Hz, cyclopropyl *H*).

Anal. Calcd for $C_{16}H_{14}O$: mass 222.10446. Found: mass 222.10419.

Eluting with 20% ether–petroleum ether gave **17**-OH: mp 135–137°; nmr (CS_2) τ 2.6–3.1 (m, 8, Ar*H*), 4.87 (s, 1, *H*-COH), 7.54 (2, J_{cis} = 9 Hz, J_{trans} = 5.5 Hz, bridge *H*), 8.46 (1, J_{cis} = 9 Hz, J_{gem} = 4 Hz, cyclopropyl *H*), 9.32 (1, J_{gem} = 4 Hz, J_{trans} = 5.5 Hz, cyclopropyl *H*).

Anal. Calcd for $C_{16}H_{14}O$: mass 222.10446. Found: mass 222.10419.

2,3;5,6-Dibenzo-*cis*-4-acetoxy[5.1.0]bicycloocta-2,5-diene (16-OAc). **16**-OH (170 mg) in pyridine (1 ml) was treated with acetic anhydride (0.3 ml) for 24 hr. The solution was poured into water (5 ml) and extracted into ether (5 ml) and the ether layer was washed with dilute hydrochloric acid (5 ml) and water (5 ml) and then dried over potassium carbonate. The material obtained on evaporation of the ether was twice recrystallized from hexane to give colorless crystals (130 mg): mp 150–151°; nmr (CS_2) τ 2.4 (s, 1, *H*-COAc), 2.7–3.1 (m, 8, Ar*H*), 7.78 (s, 3, $OCOCH_3$), 7.59 (2, J_{cis} = 9 Hz, J_{trans} = 5.5 Hz, bridge *H*), 8.56 (1, J_{cis} = 9 Hz, J_{gem} = 4 Hz, cyclopropyl *H*), 9.46 (1, J_{gem} = 4 Hz, J_{trans} = 5.5 Hz, cyclopropyl *H*).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.89; H, 6.25.

Equilibration of Cis and Trans Acetates (16-OAc and 17-OAc). The cis acetate (30 mg) was heated in acetic anhydride (0.5 ml) at 75° for 90 hr and then for 6 hr at 100°, the equilibration being followed by nmr. Repeated integration of the two methyl resonances of the acetates, τ 7.78 cis and 8.07 trans, showed 53.5% **17**-OAc and 46.5% **16**-OAc at equilibrium.

Partial Solvolysis of the Cis–Trans Acetate Mixture and Separation of 17-OAc. The above mixture (160 mg) dissolved in 80% acetone–20% water (80 ml) was sealed in ampoules and heated at 75° for 22 hr. Removal of the solvents *in vacuo* gave a colorless residue which was chromatographed on neutral alumina (Woelm, activity 2.5). Elution with 10% ether–petroleum ether gave **17**-OAc and then **16**-OH. The acetate was recrystallized from hexane: mp 140.5–142°; nmr (CS_2) τ 2.6–3.0 (m, 8, Ar*H*), 3.74 (s, 1, *H*-COR), 8.07 (s, 3, OCH_3), 7.55 (2, J_{cis} = 9 Hz, J_{trans} = 5.5 Hz, bridge *H*), 8.55 (1, J_{cis} = 9 Hz, J_{gem} = 4 Hz, cyclopropyl *H*), 9.35 (1, J_{gem} = 4 Hz, J_{trans} = 5.5 Hz, cyclopropyl *H*).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.88; H, 6.19.

The same product was obtained by acetoxylation of **17**-OH by the same procedure as that used for **16**-OAc.

2,3;5,6-Dibenzo[5.1.0]bicycloocta-2,5-dien-4-one (18). The cis alcohol (**16**-OH) (150 mg) dissolved in ether (60 ml) and pentane (60 ml) was stirred for 24 hr with manganese dioxide (10 g). The organic material was decanted from the inorganic residue and the latter washed with ether (five 75-ml portions). Evaporation of the solvent *in vacuo* gave crude ketone. Recrystallization from hexane gave **18** (129 mg): mp 83.5–85°; nmr (CH_2Cl_2) τ 2.3–2.9 (m, 8, Ar*H*), 7.2–8.0 (m, 3, bridge *H* and cyclopropyl *H*), 9.51 (1, cyclopropyl *H*).

Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.39; H, 5.53.

Borohydride Reduction of 18. The preceding ketone (33 mg) in methanol (5 ml), water (0.25 ml), and 1 *N* sodium hydroxide solution (0.1 ml) was treated with sodium borohydride (50 mg) at room temperature for 1 hr. Excess borohydride was removed by boiling the solution for 5 min, then the solution was poured into water (50 ml) and the alcohol was extracted into ether (two 10-ml portions). The ether layer was washed with water (three 10-ml portions) and dried over potassium carbonate and the ether was removed *in vacuo* to give 31 mg of a mixture of **16**-OH and **17**-OH. The alcohol composition was determined by nmr (CS_2), 70 scans with CAT, over the *H*-COR region; found, 1.2% **17**-OH; 98.8% **16**-OH.

2,3;5,6-Dibenzo[5.1.0]bicycloocta-2,5-diene (19). The cis alcohol (**16**-OMe) (50 mg) was dissolved in ether (15 ml) and the solution cooled to −78°. Dry hydrochloric acid gas was bubbled through the solution for 15 min and the reaction kept at this temperature for a further 30 min. The saturated solution was allowed to warm up to −25° before the acid was neutralized with ice-cold sodium bicarbonate solution. The ether layer was separated, washed with ice cold water, and dried over potassium carbonate (all manipulations were carried out rapidly), and the ether was evaporated to give an oily residue. The ir spectrum showed the absence of OH stretch.

The oil was dissolved in dry dimethoxyethane (1 ml) and slowly added to sodium borohydride (200 mg) in dimethoxyethane (3.2 ml) and 1 *N* sodium hydroxide solution (1.8 ml). The mixture was kept at 55° for 3 hr and then poured into water (50 ml) and the organic material extracted into ether (20 ml). The ether layer was washed with water (two 50-ml portions), dried over potassium carbonate, and evaporated to give the crude hydrocarbon (**19**).

Chromatography on alumina (Woelm, neutral activity 2.5) with pentane as the solvent gave the hydrocarbon **19** which was recrystallized from ethanol: mp 63–65° (20 mg); nmr (CS_2) τ 2.7–3.0 (m, 8, Ar*H*), 5.34 and 6.77 (each d, 1, J = 13 Hz, $ArCH_2Ar$), 7.77 (2, J_{cis} = 9 Hz, J_{trans} = 5.5 Hz, bridge *H*), 8.63 (1, J_{cis} = 9 Hz, J_{gem} = 4 Hz, cyclopropyl H), 9.43 (1, J_{trans} = 5.5 Hz, J_{gem} = 4 Hz, cyclopropyl *H*).

Anal. Calcd for $C_{16}H_{14}$: mass 206.10954. Found: 206.10953.

Preparation, Separation, and Equilibration of Methoxy Ethers (16-OMe and 17-OMe). The cis alcohol (**16**-OH) (60 mg) was refluxed in anhydrous methanol (10 ml) with a drop of concentrated hydrochloric acid (0.5 *N* in HCl) for 20 min. The cooled solution was poured into water (25 ml) and extracted into ether; the ether was washed with sodium bicarbonate solution and water and then dried over potassium carbonate. Removal of the solvent *in vacuo* gave an oil. Nmr (CCl_4) showed there to be 56.2% **16**-OMe and 43.8% **17**-OMe (integration of two methyl resonances).

The same ratio of cis to trans was obtained if the reaction was carried out for a further hour, or by starting with essentially pure cis methoxy ether, and allowing it to react under the same conditions.

Chromatography of the oil on neutral alumina (Woelm, activity 2.5), eluting with petroleum ether (20–40°), gave 2,3;5,6-dibenzo-*cis*-4-methoxy[5.1.0]bicycloocta-2,5-diene (**16**-OMe) as a colorless solid: mp 93.5–94°; nmr (CS_2) τ 2.6–3.1 (m, 8, Ar*H*), 3.89 (s, 1, *H*-COMe), 6.42 (s, 3, O*Me*), 7.66 (2, J_{cis} = 9 Hz, J_{trans} = 5.5 Hz, bridge *H*), 8.63 (1, J_{cis} = 9 Hz, J_{gem} = 4 Hz, cyclopropyl *H*), 9.47 (1, J_{gem} = 4 Hz, J_{trans} = 5.5 Hz, cyclopropyl *H*).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.43; H, 6.75.

The second product to be eluted was 2,3;5,6-dibenzo-*trans*-4-methoxy[5.1.0]bicycloocta-2,5-diene (**17**-OMe): mp 56–58°; nmr (CS_2) τ 2.6–3.1 (m, 8, Ar*H*), 5.32 (s, 1, *H*COMe), 6.72 (s, 3, O*Me*), 7.66 (2, J_{trans} = 5.5 Hz, J_{cis} = 9 Hz, bridge *H*), 8.63 (1, J_{cis} = 9 Hz, J_{gem} = 4 Hz, cyclopropyl *H*), 9.47 (1, J_{trans} = 5.5 Hz, J_{gem} = 4 Hz, cyclopropyl *H*).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.19; H, 7.10.

Kinetic Procedures. The acetates were solvolyzed in 80% acetone–20% water[45] (by volume) at the temperatures indicated in Table II. At 25° the acetate (~0.2 mmol) was dissolved in the solvent mixture in a 50-ml volumetric flask and allowed to come to temperature equilibrium for 30 min, before the initial points were taken. The reaction was followed by taking aliquots (5 ml) at appropriate times and stopping the reaction by running the aliquot into a precooled flask. The developed acetic acid was titrated with sodium methoxide in methanol (*ca.* 0.01 *M*) with *p*-hydroxyazobenzene as the indicator. At higher temperatures sealed ampoules were used, nine being made up from a 50-ml *ca.* 0.01 *M* solution of the appropriate acetate. The ampoules were equilibriated in a constant temperature bath for at least 5 min before the first point was taken and the reaction was stopped by rapidly cooling the sample. Five-milliliter aliquots were taken and titrated as described before. The infinity points were taken after at least 10 half-lives. Each rate measurements was repeated at least once.

The first-order rate constants were calculated in the usual manner, the average rate constant, k_a, recorded in Table II being given by

$$k_a = \frac{\sum_1^n kn}{n}$$

(45) Acetone purified and diluted as described by S. G. Smith, Ph.D. Thesis, University of California, Los Angeles, Calif., 1968.

and the error by

$$\sum_{1}^{n} \frac{(kn - ka)}{n}$$

Product Analysis. This was performed by nmr using a CAT, triggering from internal tetramethylsilane. The purity of each acetate (**16**- and **17**-OAc) was determined by scanning the methyl resonances (τ 7.78 and 8.07, respectively) 100 times. The amount of **17**-OAc in the sample of **16**-OAc used was shown to be less than 0.25% by cutting and weighing the appropriate peaks. Likewise **17**-OAc contained less than 0.25% **16**-OAc and less than 0.5% of either **16**-OH or **17**-OH. The latter was determined by scanning the *H*-COR resonances. These same signals were used to estimate the ratio of **16**-OH and **17**-OH present upon solvolysis of the acetates in aqueous acetone. The OMe resonances of the methoxy ethers obtained upon methanolysis of the acetates were used in the same manner. The error in the analyses is ±0.25%. Results are given in Table III.

Solvolysis of 16-OAc in 80% Acetone. The cis acetate (**16**-OAc) (23 mg) dissolved in acetone (4 ml) treated with saturated sodium bicarbonate solution (1 ml) was heated at 75° in an ampoule for 21 hr. The solution was poured into water (25 ml) and extracted with ether (two 15-ml portions), the combined extracts being washed with water (20 ml). Removal of the ether gave 20.5 mg of residue which was dissolved in CS_2 for nmr analysis with the CAT–TMS trigger.

Methanolysis of 16-OAc. The cis acetate (**16**-OAc) (22 mg) was dissolved in methanol[46] (5 ml), with sodium bicarbonate (100 mg) added, heated at 100° for 10 hr in an ampoule, and worked up in a similar manner to that described above to give 16 mg of recovered material, which was dissolved in CS_2 for assay.

(46) E. C. Evans and A. G. Knox, *J. Amer. Chem. Soc.*, 73, 1739 (1951).

Solvolysis of 17-OAc in Aqueous Acetone. The trans acetate (**17**-OAc) (21 mg) in 6 ml of 80% acetone–20% water with sodium bicarbonate (100 mg) was heated at 100° for 9 days in an ampoule and worked up as previously described giving 16.5 mg (93.5%) of alcohols, **16**- and **17**-OH.

Methanolysis of 17-OAc. The trans acetate (**17**-OAc) (26 mg), sodium bicarbonate (100 mg), and anhydrous methanol[46] (8 ml) were heated at 100° for 18 days and worked up as before giving 20 mg (86%).

Product Analysis of 7-Acetoxy-1,2;5,6-dibenzocycloheptа-1,3,5-triene. The acetate **20**-OAc (51 mg) was heated in 12 ml of 80% acetone–20% water and sodium bicarbonate (13 mg) at 50° for 12 hr and worked up as described before; 40 mg of **20**-OH was obtained with nmr and ir spectra identical with an authentic sample.

Product Analysis of 7-Acetoxy-1,2;5,6-dibenzocycloheptа-1,5-diene. The acetate (**21**-OAc) (50 mg) in 10 ml of 80% acetone–20% water with sodium bicarbonate (130 mg) was heated at 100° for 18 hr and worked up as described above to recover 42 mg of **21**-OH with nmr and ir spectra identical with authentic material, melting point, and mixture melting point, 88–89°.

The Formation and Quench of the Dibenzohomotropylium Ion. Cis alcohol (**16**-OH) (25 mg) was dissolved in the minimum amount of methylene chloride added to concentrated sulfuric acid (0.5 ml) at room temperature. The mixture was stirred and the two layers allowed to separate and the organic layer was removed. The nmr spectrum indicated essentially complete formation of the homotropylium ion. The sulfuric acid solution was slowly added to a rapidly stirred suspension of sodium bicarbonate (4 g) in methanol (30 ml) at −78°. After warming to room temperature the methanol was poured into water (100 ml) and the products were extracted into ether (20 ml). The ether layer was washed with water (two 50-ml portions) and dried over potassium carbonate. Evaporation gave 21 mg of an oil which was assayed by nmr as before.

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1-Isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene. Synthesis and Reactions

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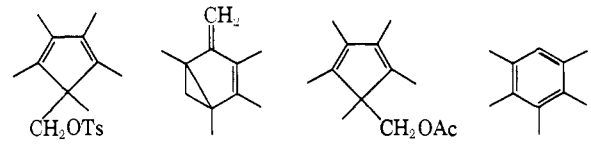
Abstract: Dehydration of the isomeric umbellulols **5** and **6** gives 1-isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**). Acetolysis of diene **7** produces the bicyclic acetates **9** and **10** as well as the cyclopentadienylmethyl acetate (**11**) under more drastic conditions. Under acidic conditions, diene **7** gives a mixture of *p*- and *m*-cymene. This system is contrasted to the analogous pentamethylcyclopentadienylmethyl system studied by Winstein and Battiste.

Winstein and Battiste[3] have reported the acetolysis of pentamethylcyclopentadienylmethyl *p*-toluenesulfonate (**1**) gives predominantly olefin **2** and only a small amount of acetate **3**. On standing, **2** adds acetic acid, **3** becoming the major component of the mixture. Pentamethylbenzene (**4**) was not observed except under more vigorous acidic conditions, when it then became the major product.



1 2 3 4

Treatment of the bicyclic umbellulols **5** (and/or **6**)[4] with dimethyl sulfoxide at elevated temperatures gives 1-isopropyl-4-methylenebicyclo[3.1.0]hex-2-ene (**7**) as well as ketone **8**[5] if oxygen is not excluded from the

(1) Abstracted from the M.S. Theses of R. H. Chung, 1968, Grace J. Lin, 1969, Anna Tseng, 1970, and Otis Tucker, 1971.

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(3) S. Winstein and M. Battiste, *J. Amer. Chem. Soc.*, 82, 5244 (1960); L. de Vries, *ibid.*, 82, 5242 (1960); R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, 90, 7144 (1968).

(4) J. W. Wheeler and R. H. Chung, *J. Org. Chem.*, 34, 1149 (1969).

(5) The structure of the α,β-unsaturated ketone **8** was confirmed by converting it to diene **7** by a Wittig reaction. Ketone **8** is an air-oxidation product of diene 7 and may be prepared in that manner.