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# 1,7-BRIDGED HOMOTROPYLIUM CATIONS

## NEW EVIDENCE ON THE DIMENSIONS OF THE HOMOCONJUGATION GAP IN HOMOTROPYLIUM CATIONS

LAWRENCE T. SCOTT* and MOHAMMED M. HASHEMI
Department of Chemistry and Center for Advanced Study, College of Arts and Science, University of Nevada, Reno, NV 89557, U.S.A.

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**Abstract**—Multistep syntheses, starting from the readily available propellane **14**, have provided access to the first 1,7-bridged homotropylium ions, **9** and **31**. From comparisons between the properties of these bridged ions and those of homotropylium ions with no bridge, it is concluded that the homoconjugation gap in unconstrained homotropylium ion must be relatively small, i.e. 1.5–1.7 Å; it cannot be as large as 2.1–2.3 Å.

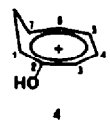
Among homoaromatic ions, the homotropylium ion **1** occupies a position comparable in prominence to that held by benzene within the family of aromatic molecules.[1] Cyclic conjugation of 6 $\pi$ electrons around a 7-carbon base in this system, despite an interruption in the $\pi$ framework, imparts a variety of physical and chemical properties to the homotropylium ion that qualify it as a genuine aromatic species. For more than 20 years, however, the actual structure of the homotropylium ion has remained obscure. Is it "open", with through-space overlap of p orbitals at the homoconjugation gap **2**, or is it "closed", with the cycle of conjugation being completed through the Walsh orbitals of a cyclopropane **3**?

**1**

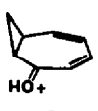
**2**

**3**

The ever-burgeoning body of theoretical and experimental data on this subject has been reviewed repeatedly since the mid 1960s,[1,2] with the most recent review by Childs[3] being quite thorough and up to date. Accordingly, rather than recount the entire history of the problem here, we simply note that structures **2** and **3** have both had their proponents over the years. The latest, most reliable *ab initio* molecular orbital calculations point to a relatively closed structure as the preferred geometry for homotropylium ion, with a remarkably short (1.58 Å) separation between C(1) and C(7) across the homoconjugation gap.†[4] The only published X-ray structure of an uncomplexed homotropylium ion is that reported by Childs *et al.* for the 2-hydroxyhomotropylium ion **4**, which can be viewed as a resonance structure of a protonated homotropone **5**.[5] A C(1)—C(7) distance of 1.63 Å was found in this ion; however, the extent to which the OH group perturbs the electronic structure, and therefore the geometry, away from that of the parent homotropylium ion is difficult to estimate. Solid salts of the parent ion have been known since 1962,[6] but crystals suitable for X-ray analysis have been difficult to grow. Thus, the nature of the bonding in the homotropylium ion remains an unsettled question.



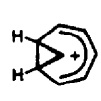
**4**



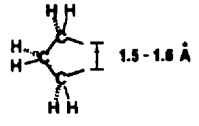
**5**

Efforts in our laboratory to shed new light on this problem have taken a course completely different from those of our predecessors. Our ambition was to measure the size of the homoconjugation gap with "molecular calipers". Top views of the open structure **6** and the closed structure **7** provide a fresh perspective. In both structures, the C—H bonds emanating from C(1) and C(7) *diverge* as they project away from the ion. If these two C—H bonds were to be replaced by a trimethylene chain, bridging C(1) to C(7), then the resulting ion should teach us something about the preferred structure of homotropylium ions.

**6**



**7**



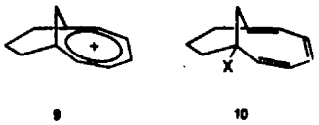

**8**

A trimethylene chain, our molecular calipers, **8**, will comfortably span the homoconjugation gap of the closed structure **7** but will not reach across the homoconjugation gap of the open structure **6** without serious distortions of normal bond angles. Therefore, if the natural geometry for the parent homotropylium ion is closed (or nearly so, i.e. C(1)—C(7) = 1.5–1.7 Å), then a trimethylene bridge should be accommodated with minimal geometric distortion, and the properties of the bridged ion should closely resemble those of the unbridged ion. If, on the other hand, the natural geometry for the parent homotropylium ion is open (or nearly so, i.e. C(1)—C(7) = 2.1–2.3 Å), then a trimethylene bridge should strongly perturb the geometry, either by squeezing the ion closed or by pyramidalizing C(1) and C(7) or both; in this case, the bridged and unbridged ions would be expected to have quite different properties.

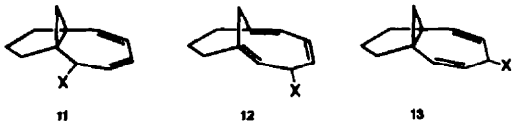
The challenge, then, was to synthesize a compound

† At higher energy, a local minimum was found for the open cyclooctatrienyl cation, with a homoconjugation gap of 2.30 Å.

from which a 1,7-trimethylene-bridged homotropylium ion (**9**) could be generated. Obvious target molecules included the unsaturated [5.3.1]undecane systems **10**–**13**, and the routes we have developed to such compounds are detailed below.



**9** **10**

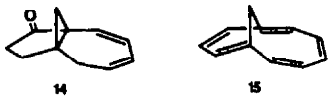


**11** **12** **13**

In keeping with the flavor of the "Symposium in Print" of which this paper is a part, we have eschewed the customary stilted style of scientific exposition and have attempted to relate some of the adventure that we enjoyed (and suffered through) along the way to our reward.

*Syntheses of homotropylium ion precursors*

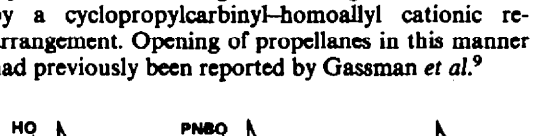
Some years ago, we developed an efficient method for preparing the tricyclic dienone **14**, a key intermediate in our synthesis of the novel nonbenzenoid aromatic hydrocarbon homoazulene, **15**, and derivatives thereof.[7,8] This propellane seemed an ideal starting point for the synthesis of compounds such as **10**–**13**. It is



**14** **15**

readily available on a multi-gram scale in just four steps from an inexpensive starting material, hydrocinnamic acid. It contains eleven carbon atoms already arranged in the [5.3.1]undecane framework which is common to all the target molecules under consideration; removal of the extra propellane bond would be necessary, of course, in any synthesis of **10** or **12**. The high degree of unsaturation already present in the seven-membered ring further enhanced its attractiveness. In fact, we anticipated relatively little difficulty in transforming **14** into one or another of the homotropylium ion precursors **10**–**13**.

Our work began with an $NaBH_4$ reduction of the tricyclic dienone **14** to the secondary alcohol **16**.† Solvolysis of the corresponding *p*-nitrobenzoate **17** in aqueous dioxane then gave the bridgehead alcohol **18** by a cyclopropylcarbinyl–homoallyl cationic rearrangement. Opening of propellanes in this manner had previously been reported by Gassman *et al.*[9]



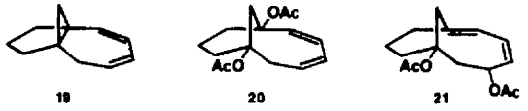
**16** **17** **18**

† A single stereoisomer was obtained. The OH group is presumed to be *exo*, but this assignment was not proven.

‡ Attempts to prepare trienol **10** (X = OH) by selective tosylation/elimination of the secondary OH group in diol **22** were not fruitful.

Isomerization of the conjugated triene system from its position in **18** to that in **10** was envisioned as the final step of a relatively short synthesis. Such a process, which moves the strained bridgehead double bond into a larger arm of the bicyclic carbon framework, should be exothermic and, therefore, we thought, easy to achieve. Unfortunately, all attempts to accomplish this isomerization either catalytically ($H^+$, $Ru^{3+}$, $Pd^{2+}$, etc.) or stepwise (initiated by oxymercuration of the bridgehead double bond) failed completely.

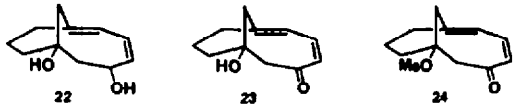
Frustrated at having come so close to our objective so quickly only to have it elude us, we turned our attention to alternative syntheses of the original target molecules. A completely different route was explored, beginning with the Wolff–Kishner reduction of tricyclic dienone **14**. The hydrocarbon obtained in this manner, **19**, was then treated with $Pb(OAc)_4$ to cleave the propellane bond oxidatively.[7] Diacetate **20**, the initial cleavage product, could be isolated when the reaction was conducted at room temperature or below, but an irreversible rearrangement of **20** to the more stable diacetate **21** was found when the reaction was conducted at higher temperatures in acetic acid.[7] Thus we were presented with a choice between two isomeric



**19** **20** **21**

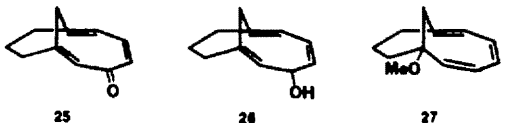
diacetates, **20** and **21**, either of which could have been used to carry on the synthesis. Since the latter resembles more closely the structures of target molecules **10** and **12**, we elected to optimize the experimental conditions for a one-pot conversion of **19** to **21**, and this was done.

Deacetylation of **21** with either KOH or MeLi then gave the corresponding diol **22**.‡ Oxidation with $MnO_2$ to the ketol **23** followed by mesylation of the bridgehead alcohol gave **24**, a highly reactive compound which was used without delay in the next step.



**22** **23** **24**

Brief exposure of mesylate **24** to 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) at room temperature in $CH_2Cl_2$ effected elimination to the bridged 3,4-homotropone **25**, our first compound in this series with a fully unsaturated 5-carbon bridge. It is interesting to note that this compound, like tropone itself, exhibits an extremely low-frequency C=O stretching band in the infrared spectrum (1594 $cm^{-1}$ for **25**, cf. 1582 $cm^{-1}$ for tropone).[10] Protonation of **25** to generate a bridged 3-hydroxyhomotropylium ion is discussed in the next section. Our ultimate goal, however, was the parent trimethylene-bridged homotropylium ion **9**, and one of the previously proposed precursors thereto, i.e. **12**, appeared finally to be within easy reach. Unfortunately, reduction of **25** to the corresponding alcohol **26** = **12** (X = OH) proved troublesome. Reagents such as $NaBH_4$, $(i\text{-}Bu)_2AlH$, and $(i\text{-}PrO)_3Al$ all gave over-reduction (at the strained enone C=C) or a myriad of unidentifiable products. Surprisingly, however, reduc-



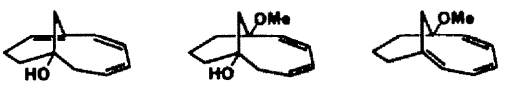
25 26 27

tion of **25** with $NaBH_4/CeCl_3$ in MeOH[11] gave the bridgehead ether **27** = **10** (X = OMe).

To explain this unexpected (though not unwelcomed) result, we reasoned that the reduction probably occurred in the desired fashion but that in the presence of $CeCl_3$, a Lewis acid, the labile alcohol **26** must have been transformed into cation **9** which was quenched by solvent at the bridgehead position. Careful monitoring of the reaction mixture by thin layer chromatography, in fact, did reveal the transient intermediacy of a slow-moving substance presumed to be the alcohol **26**. Subsequently, we have found that certain other enones also give allylic methyl ethers under these conditions.[12]

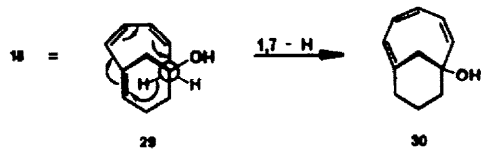
To summarize at this point, we note that our original objective of synthesizing a bridged homotropylium ion precursor of general structure **10** was accomplished in seven steps from the readily available dienone **14**. Throughout this work, however, we were continually haunted by the conviction that there must be an even shorter route to **10** based on isomerization of our previously abandoned intermediate **18**. Accordingly, **18** was resurrected at irregular intervals and subjected to new brandishments. In the end, our perseverance was rewarded by a most useful and unexpected discovery.

For many years it has been known that C=C bonds in six-membered rings will add MeOH in a Markovnikov manner under the influence of UV irradiation, presumably via a twisted excited state of the olefin.[13] It seemed plausible, therefore, that the recalcitrant trienol **18** might add MeOH to its already twisted cyclohexene double bond under the influence of UV irradiation to give the bridgehead ether **28**. Dehydration in a separate step could then complete the transformation of **18** into **27**. When this photoaddition was attempted, however, we saw no evidence for formation of **28**. Instead, *methoxytriene* **27** was isolated directly from the reaction mixture; the isomerization of **18** to **27** was accomplished in one step! With this discovery, our synthesis of **27** was reduced to just four steps from the starting ketone **14**.



18 28 27

How does this remarkable transformation occur? The predicted product **28**, if ever formed, would likely survive the conditions of the reaction, so **18** must suffer some other unforeseen photochemical change. Molecular models reveal that **18** adopts a very rigid conformation which can be viewed to best advantage as a Newman projection down the saturated bridgehead C—C bond as shown in **29**. From this picture one can see that the atoms are almost perfectly arranged for an allowed suprafacial 1,7-sigmatropic shift on the underside of the molecule (see arrows). The product of that H migration would be the isomeric trienol **30**, but traces of acid in the MeOH could catalyze the

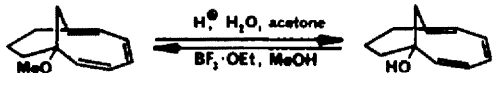


29 30

conversion of **30** to the corresponding ether **27** via the bridged homotropylium ion **9**. The ease of this $S_N1$ process is demonstrated in the following section.

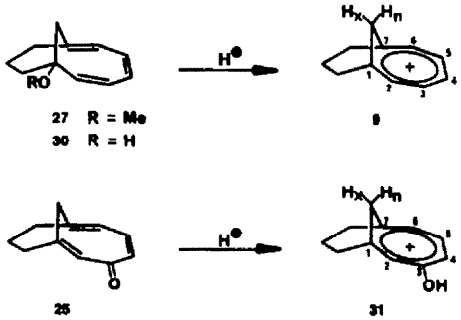
*1,7-Bridged homotropylium ions*

Evidence that the 1,7-bridged homotropylium ion **9** can be generated easily in hydroxylic media (MeOH) had already begun to accumulate during the synthesis phase of this project (*vida supra*). More direct evidence was obtained by subjecting the pure methoxytriene **27** to $CF_3COOH$ in aqueous acetone at room temperature; under these conditions, the methyl ether is transformed completely into the corresponding alcohol **30**. Treatment of **30** with $BF_3$–$OEt_2$ in MeOH regenerates the methoxytriene **27**.



27 30

These substitution reactions almost certainly occur via $S_N1$ reaction mechanisms involving the 1,7-bridged homotropylium ion **9**. The apparent ease with which this "bridgehead" carbocation is formed argues strongly for the presence of some special electronic stabilization, i.e. homoaromaticity, of ion **9**. The extraordinary stability of this cation is further demonstrated by the fact that "stable ion" solutions of **9** can be prepared (NMR discussed below) simply by dissolving one of the precursors, **27** or **30**, in $CF_3COOH$ (TFA) at room temperature. It is not necessary to employ "Magic Acid" at low temperatures, as in most other studies of stable carbocations.[14] In fact, stable solutions of the 1,7-bridged homotropylium ion **9** can be generated quantitatively even in chloroform just by adding one drop of TFA to a $CDCl_3$ solution of **27** or **30** at room temperature. This carbocation is amazingly stable! Protonation of the bridged homotropone **25**, either in 100% TFA or in $CDCl_3$, likewise generates solutions of the 1,7-bridged 3-hydroxyhomotropylium ion **31** which are stable indefinitely at room temperautre.[15] Quenching the solutions of **9** and **31** with water regenerates the precursors **30** and **25**, respectively.



27 R = Me
30 R = H

9

25 31

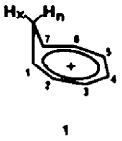
Treatment of methoxytriene **27** with $HBF_4$ in acetic anhydride gives a dark homogeneous solution from which the fluoroborate salt of the 1,7-bridged homotropylium ion **9** can be isolated by dilution with dry ether. The salt is soluble in acetonitrile, acetone, and 1,2-dichloroethane but insoluble in ether, ethyl acetate, and chloroform. After several abortive attempts to grow X-ray quality crystals of the salt, we sent samples of the precursor, **27**, to Professor Childs at McMaster University, but he, too, was unsuccessful at growing good crystals. Dissolution of the salt in methanol regenerates methoxytriene **27**. The fluoroborate salt of the 3-hydroxyhomotropylium ion **31** was likewise prepared but also failed to give decent crystals.

The 1,7-bridged homotropylium ion **9** was found to abstract hydride from cycloheptatriene in TFA to give tropylium ion. Thus, although ion **9** enjoys considerable stability, it is not as stable thermodynamically as the aromatic tropylium ion. In a similar experiment, ion **9** failed to abstract hydride from triphenylmethane. By approaching this latter reaction from the opposite direction, however, we were able to demonstrate that trityl cation will abstract hydride from diene **19** in TFA to give triphenylmethane. The other product, presumed to be ion **9**, apparently reacts with neutral diene **19** and could not be seen by NMR. These hydride transfer reactions place the 1,7-bridged homotropylium ion **9** somewhere between tropylium ion and trityl cation on the thermodynamic stability scale.[16]

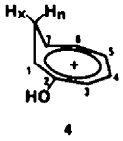
Complete $^1$H- and $^{13}$C-NMR data for the two new 1,7-bridged homotropylium ions **9** and **31** are reported in the experimental section; however, several features of these spectra deserve comment. We note first that protons 2–6 in ion **9** all resonate at essentially the same chemical shift ($\delta$ 8.14). The corresponding carbons, 2–6, in ion **9** likewise all resonate within a narrow range of one another ($\delta$ 140.4–146.6). These data provide compelling evidence for a very even distribution of positive charge among the five contiguous methine carbons in ion **9**.

Second, we note that $H_n$ in ion **9** is abnormally shielded ($\delta$ 0.09) while $H_x$ is abnormally deshielded ($\delta$ 5.18). This large chemical shift difference between the *endo* and *exo* protons on the methylene bridge ($\Delta\delta$ = 5.08 ppm) is characteristic of homotropylium ions in general and has been ascribed to ring current effects.[6,17] Other factors have also been suggested to contribute to this unusual NMR feature of homotropylium ions.[18]

The $^1$H- and $^{13}$C-NMR spectra of ion **9** are quite similar to those of the parent homotropylium ion **1**,[19] although some differences can be seen. The large $\Delta\delta$ of the $-CH_2-$ bridge protons in ion **9** is about 13%




**1**




**4**

smaller than that in ion **1** ($\Delta\delta$ = 5.86 ppm). On the other hand, the distribution of positive charge among carbons 2–6 in the parent homotropylium ion **1** actually appears to be slightly *less even* than in ion **9**: the protons at these positions in ion **1** resonate over a wider range than those in ion **9** ($\delta$ 8.27–8.57 vs 8.14 singlet), and the same is true of the corresponding carbon resonances ($\delta$ 143.2–153.7 for ion **1** vs 140.4–146.6 for ion **9**). Finally, it can be seen from this same comparison that the $^1$H chemical shifts of the five methine hydrogens in the bridged ion **9** resonate at slightly higher field than those in ion **1** and that the same trend is observed in the $^{13}$C spectra. This fact indicates that carbons 2–6 all carry slightly less positive charge in ion **9** than in the parent homotropylium ion **1**. The residual positive charge must be found at the homoconjugation gap, i.e. at carbons 1 and 7. Indeed, the $^{13}$C chemical shift of these carbons in ion **9** ($\delta$ 170.2) is consistent with a higher positive charge density there than in the parent homotropylium ion **1** ($\delta$ 122.2). This large deshielding of carbons 1 and 7 in the 1,7-bridged ion **9**, relative to those in ion **1**, reflects also the substitution of an alkyl chain for a hydrogen atom and any strain effects introduced by the trimethylene bridge.

The 1,7-bridged 3-hydroxyhomotropylium ion **31** likewise exhibits NMR spectra characteristic of a true homotropylium ion. Other workers have previously reported on the properties of 1-hydroxy-,[20] 2-hydroxy-,[3b,5,21] and 4-hydroxyhomotropylium ions,[22] but ion **31** is the first homotropylium ion with an OH group in the 3-position to be observed spectroscopically, to the best of our knowledge.[23] In all cases, the OH group perturbs significantly the otherwise even distribution of positive charge in the homotropylium ion. In the $^1$H-NMR spectrum of the 1,7-bridged 3-hydroxyhomotropylium ion **31**, the protons attached to the unsaturated carbons resonate over a range from $\delta$ 7.00 to 7.77. The comparison protons in 2-hydroxyhomotropylium ion **4** resonate in essentially the same range ($\delta$ 7.0–7.7).

In the $^{13}$C-NMR spectrum of the 1,7-bridged 3-hydroxyhomotropylium ion **31**, carbons 2, and 4–6 resonate over the range from $\delta$ 126.1 to 149.4. This is a substantially broader range than that seen in the unsubstituted 1,7-bridged homotropylium ion **9** ($\delta$ 140.4–146.6) but is somewhat narrower than that in the unbridged 2-hydroxyhomotropylium ion **4** ($\delta$ 119.6–152.5). The average chemical shift for the four methine carbons in **31** (avg $\delta$ 134.6) relative to that in **4** (avg $\delta$ 138.7) reveals that these atoms carry slightly less positive charge in the 1,7-bridged ion than in the unbridged ion.

The three quaternary carbons in **31** (two bridgeheads plus the OH-substituted carbon) all resonate at similar chemical shifts ($\delta$ 175.9, 181.9, and 182.1), and no effort has been made to assign particular signals to particular carbons. By contrast, the OH-substituted carbon in ion **4** resonantes at $\delta$ 199.0, while carbons 1 and 7 resonate at 52.5 and 56.3. Clearly, the OH-substituted carbon in the 1,7-bridged ion **31** carries less positive charge than does the corresponding carbon in ion **4**. The bridgehead carbons in **31**, by contrast, are dramatically deshielded relative to the corresponding carbons in **4**. The effect is even larger than that noted above for the two homotropylium ions lacking an OH group (**9** vs **1**). This large deshielding presumably reflects a higher positive charge density at these positions in the 1,7-bridged ion as well as the effects of substituting an alkyl chain for a hydrogen atom and any strain effects introduced by the trimethylene bridge.

The other point of comparison between ions **31** and **4** is the chemical shift difference between the methylene

hydrogens $H_a$ and $H_s$. For 2-hydroxyhomotropylium ion **4**, $\Delta\delta = 3.08$, whereas for the 1,7-bridged 3-hydroxyhomotropylium ion **31**, $\Delta\delta = 2.53$ (82% as large). This same trend was also observed with the homotropylium ions lacking an OH group.

## CONCLUSIONS

An extra trimethylene bridge across the homoconjugation gap of homotropylium ion and 3-hydroxyhomotropylium ion has been found not to alter significantly the special properties associated with cyclic homoconjugation in these ions. Since these special properties depend on orbital interactions among the seven basal centers, and these orbital interactions depend in turn on molecular geometry, we conclude that the 1,7-bridged homotropylium ions must have geometries very similar to those of unconstrained homotropylium ions, espeically in the region of the homoconjugation gap.

In the introduction section of this paper, the case was made that an extra trimethylene bridge across the homoconjugation gap of a homotropylium ion could be accommodated without perturbing significantly the geometry of the ring *only if* the homoconjugation gap were relatively small, i.e. 1.5–1.7 Å. That argument, taken together with our new experimental findings, leads to the inescapable conclusion that *the homoconjugation gap in unconstrained homotropylium ion must be relatively small*, i.e. 1.5–1.7 Å; *it cannot be as large as* 2.1–2.3 Å.

Closer examination of the one big difference in the spectral properties of the 1,7-bridged homotropylium ions relative to those of the unconstrained parent ions further strengthens this conclusion. For the unbridged homotropylium ions, the $^{13}$C-NMR resonances of the two atoms that define the homoconjugation gap, C(1) and C(7), appear at unusually high field. In the $^{13}$C-NMR spectra of the 1,7-bridged homotropylium ions, on the other hand, these resonances appear at unusually low field. The difference in chemical shift between the bridged and unbridged ions is almost 50 ppm in the absence of an OH substituent and more than 100 ppm in the case of the OH-substituted ions. A smaller homoconjugation gap (more cyclopropane-like character) in the unbridged ions, relative to that in the bridged ions, would be consistent with these observations. If this is true, and the gap is actually smaller in the unbridged ions than in the bridged ions, as the $^{13}$C-NMR seems to indicate, and, as we have argued, the homoconjugation gap in the 1,7-bridged homotropylium ions is relatively small already, then the case is even stronger that the homoconjugation gap in unconstrained homotropylium ion must be relatively small. Our conclusion, which is based on a completely new approach to this problem, reinforces the conclusions reached independently from the most recent theoretical and experimental work in other laboratories.[3–5]

## EXPERIMENTAL

*General.* All solvents used for reactions described were freshly distilled. Ether and tetrahydrofuran (THF) were distilled under $N_2$ from the sodium ketyl of benzophenone. $CH_2Cl_2$ was distilled from $P_2O_5$; dimethyl sulfoxide (DMSO) was distilled from $Ca(OH)_2$; MeOH was distilled from anhyd $CaCl_2$. M.ps are uncorrected. $^1$H-NMR spectra were recorded on a Hitachi–Perkin–Elmer model R24-B 60 MHz High-Resolution spectrometer; 100 MHz $^1$H-NMR and 25 MHz $^{13}$C-NMR spectra were recorded on a JEOL FX-100 FT-NMR spectrometer. UV spectra were taken on a Beckman 25 UV–Vis spectrophotometer. IR spectra were recorded on a Perkin–Elmer IR 599 spectrophotometer. Prep TLC was performed on Woelm silica gel F, and Fisher activated alumina, 85 mesh, was used for alumina filtrations. Column chromatography was performed using Baker silica gel, 60–200. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan, and Galbraith Laboratories, Inc., Knoxville, Tennessee. High resolution mass spectra were recorded at the Facility for Advanced Instrumentation, University of California, Davis, California.

*Tricyclo*[5.3.1.0]*undeca*-3,5-*dien*-8-*ol* **16**. To a soln of 3.43 g (21.4 mmol) of **14**[24] in 60 ml of 2:1 THF–$H_2O$ was added 3.80 g (100 mmol) of $NaBH_4$. The resulting faint yellow soln was stirred for 2 h at room temp and then diluted with 50 ml of ether. The organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Prep TLC on silica gel (15% EtOAc–pet ether) afforded 3.08 g (89%) of **16** ($R_f = 0.20$): UV (EtOH) 265, 205 nm; IR (neat) 3370 (s), 3050 (s), 2925 (s), 1600 (m), 1450 (m), 1320 (m), 1050 cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 0.78 (d, 1H, cyclopropyl, J = 4 Hz), 1.31–1.90 (m, 6H, $CH_2CH_2$ cyclopropyl, and OH), 2.32 (d, 2H, $CH_2$—C=C, J = 6 Hz), 4.12 (t, 1H, CHOH, J = 8 Hz), 5.28–5.84 (m, 3H, vinyl), 6.06 (d, 1H, H(6), J = 12 Hz).

*Tricyclo*[5.3.1.0]*undeca*-3,5-*diene*-8-*yl p-nitrobenzoate* **17**. Tricyclic alcohol **16** (2.56 g, 15.8 mmol) was dissolved in 20 ml of freshly distilled pyridine at room temp, and 3.73 g (20.1 mmol) of *p*-nitrobenzoyl chloride dissolved in 30 ml of pyridine was added. The resulting green soln was stirred at 50° overnight to give a cloudy brown mixture. Quenching with 50 ml of 10% $NaHCO_3$ aq gave a heavy yellow ppt which was isolated by filtration and crystallized from 95% EtOH to give 3.86 g (78%) of **17**.

Alternatively, 13.5 ml of n-BuLi in hexane (2.6 M, 35.1 mmol) was added to a soln of **16** (5.54 g, 34.2 mmol) in 45 ml of dry ether at 0° and 6.8 g (36.6 mmol) of *p*-nitrobenzoyl chloride dissolved in 40 ml of ether was added dropwise. The soln became yellow and was stirred for 30 min at room temp. Water was added, and the organic layer was separated. The aqueous layer was washed with 10% $NaHCO_3$ aq and dried ($MgSO_4$). Removal of the solvent gave a yellow ppt which was crystallized from 95% EtOH to give 7.72 g (72%) of **17**: m.p. 140–142°; UV (EtOH) 260, 203 nm; IR (KBr) 3030 (w), 2950 (m), 1735 (s), 1620 (w), 1540 (s), 1280 (s) cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 1.10 (d, 1H, cyclopropyl, J = 4 Hz), 1.80–2.30 (m, 5H, cyclopropyl and $CH_2CH_2$), 2.55 (d, 2H, $CH_2$—C=C, J = 6 Hz), 5.35–5.83 (m, 4H, CH—OPNB and vinyl), 6.10 (d, 1H, H(6), J = 11 Hz), 8.15 (s, 4H, aromatic). (Found: C, 69.39; H, 5.52. Calc for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50%.)

*Bicyclo*[5.3.1]*undeca*-3,5,7-*trien*-1-*ol* **18**. A mixture of 1.2 g (3.9 mmol) of **17**, solid $NaHCO_3$ (338 mg, 4.0 mmol), and 70 ml of 60:40 *p*-dioxane–water was refluxed at 110° for 2 days. The resulting brown soln was extracted with ether (3 × 30 ml). The organic layer was washed with 10% $NaHCO_3$ aq, dried ($MgSO_4$) and concentrated. Column chromatography (silica gel, 15% EtOAc–pet ether) gave 560 mg (88%) of **18** ($R_f = 0.30$): UV (EtOH) 283 nm ($\varepsilon = 4400$); IR (neat) 3360 (s), 3020 (s), 2940 (s), 1460 (m), 1330 (s), 1270 (s) cm$^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 1.5–2.50 (m, 7H), 2.95 (d, 1H, J = 12 Hz), 5.42–6.25 (m, 5H); $^{13}$C-NMR ($CDCl_3$) $\delta$ 23.1, 31.7, 37.1, 41.7, 78.9, 123.1, 128.7, 129.8, 130.1, 131.5, 142.4; MS calc for $C_{11}H_{14}O$: 162.1045. Found: 162.1059.

*Tricyclo*[5.3.1.0]*undeca*-2,4-*diene* **19**. In a dry 250 ml three-neck flask equipped with a thermometer and a short path distillation head was mixed 120 ml of diethylene glycol, 6.83 g (42.7 mmol) of **14**, 5.25 ml of hydrazine hydrate (108 mmol) and 12.5 g (223 mmol) of KOH. The mixture was heated to 135° for 1 h during which time a mixture of water and some product as a clear oil distilled over. After being heated at 165° for an

additional 3 h, the mixture was cooled and extracted with pentane (3 × 20 ml). The pentane soln was combined with the distillate, and the mixture was washed with brine and dried ($MgSO_4$) to give a yellow soln. The yellow soln was filtered through alumina and concentrated under reduced pressure to give 2.43 g (39%) of **19** as a light blue oil. This material was used in the next step without further purification. A colorless analytical sample was prepared by molecular distillation at $10^{-5}$ Torr (40°): UV (EtOH) 238 (sh), 245 ($\varepsilon$ = 2900), 258 nm (sh); IR (neat) 3020 (m), 2910 (s), 2850 (s), 1600 (w), 1445 (m) $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 0.55 (d, 1H, cyclopropyl, J = 5 Hz), 1.30–2.10 (m, 7H), 2.40 (d, 2H, $CH_2$—C≡C, J = 6 Hz), 5.10–5.80 (m, 3H, vinyl), 5.95 (d, 1H, vinyl, J = 11 Hz). (Found: C, 90.34; H, 9.64. Calc for $C_{11}H_{14}$: C, 90.35; H, 9.65%.)

1,7-*Diacetoxybicyclo*[5.3.1]*undeca*-2,4-*diene* **20**. Lead tetraacetate (3.98 g, 8.98 mmol) was added to a mixture of 20 ml of benzene and 10 ml of glacial AcOH to give a suspension which resulted in a clear soln after 10 min. Diene **19** (1.20 g, 8.22 mmol) was added, and the resulting light green soln was stirred at room temp for 30 min. The light brown mixture was then quenched with 25 ml of water and shaken with 30 ml of ether. The organic layer was separated, washed with water (3 × 20 ml), 10% $NaHCO_3$ aq (2 × 10 ml), brine (10 ml), dried ($MgSO_4$) and concentrated. Column chromatography (silica gel, 15% EtOAc–pet ether) gave 880 mg (40%) of **20** as a yellow oil ($R_f$ = 0.54): UV (EtOH) 234 nm; $^1$H-NMR ($CDCl_3$) $\delta$ 1.60–2.48 (m, 13H), 2.70 (d, 2H, $CH_2$—C≡C, J = 9 Hz), 3.39 (d, 1H, bridge, J = 12 Hz), 5.30–5.98 (m, 3H, vinyl), 6.15 (dd, 1H, vinyl, J = 4 and 11 Hz).

5,7-*Diacetoxybicyclo*[5.3.1]*undeca*-1,3-*diene* **21**. Diene **19** (2.05 g, 14.0 mmol) was dissolved in 50 ml of glacial AcOH at 15°. Lead tetraacetate (6.83 g, 15.4 mmol) was added, and the mixture was stirred at room temp for 30 min, then at 75° for 8 h. The resulting light brown mixture was quenched with 100 ml of water and extracted with ether (4 × 20 ml). The ether layer was washed with water (2 × 15 ml), 10% $NaHCO_3$ aq (20 ml), dried ($MgSO_4$) and concentrated. Column chromatography (silica gel, 15% EtOAc–pet ether) gave 2.24 g (60%) of **21** as a light yellow oil ($R_f$ = 0.6): UV (EtOH) 241 nm ($\varepsilon$ = 5900); IR (neat) 3020 (w), 2940 (m), 1735 (vs), 1450 (m), 1370 (s), 1240 (vs) $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 1.40–3.10 (m, 16H), 5.20–6.06 (m, 4H); $^{13}$C-NMR ($CDCl_3$) $\delta$ 21.2, 22.4, 27.0, 33.6, 34.9, 36.2, 40.6, 71.9, 85.8, 119.4, 126.9, 130.1, 141.4, 169.7, 170.3; MS calc for $C_{15}H_{20}O_4$: 264.1361. Found: 264.1348.

5,7-*Dihydroxybicyclo*[5.3.1]*undeca*-1,3-*diene* **22**. Diacetate **21** (683 mg, 2.59 mmol) was dissolved in 20 ml of 10:1 MeOH–$H_2O$. KOH (840 mg, 15 mmol) was added, and the soln was stirred at room temp for 1 h. The resulting orange soln was concentrated and the residue was dissolved in 40 ml of 50:50 ether–EtOAc. The soln was washed with water (5 ml), brine (4 ml) and dried ($MgSO_4$). Removal of the solvent left a light brown solid which was crystallized from anhyd ether to give 380 mg (81%) of **22** as a white solid.

Alternatively, a soln of 885 mg (3.35 mmol) of **21** in 20 ml of anhyd ether was added dropwise to 20 ml of ethereal MeLi (1.2 M, 24 mmol) in 20 ml of anhyd ether at 0° under $N_2$. The mixture was stirred at room temp for 30 min and was then quenched with 20 ml of $H_2O$. The organic layer was separated, the aqueous layer was washed with EtOAc (3 × 10 ml), and the combined organic layers were dried ($MgSO_4$). Removal of the solvent left a yellow solid which was crystallized from anhyd ether to give 485 mg (81%) of **22** as a white solid: m.p. 173–175°; UV (EtOH) 243 nm ($\varepsilon$ = 5600); IR (KBr) 3340 (s), 2940 (m), 1070 (m), 790 (vs), 760 (vs) $cm^{-1}$; $^1$H-NMR ($d_6$-DMSO) $\delta$ 0.95–2.64 (m, 10H), 3.15 (s, 2H, 2-OH), 4.32–4.64 (m, 3H), 5.28–5.48 (br s, 3H). (Found: C, 73.29; H, 8.95. Calc for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.)

7-*Hydroxybicyclo*[5.3.1]*undeca*-1,3-*dien*-5-*one* **23**. Diol **22** (569 mg, 3.16 mmol) was partially dissolved in 20 ml of dry $CH_2Cl_2$. $MnO_2$ (5.0 g, 57.4 mmol) was added, and the mixture was stirred at room temp for 12 h. The mixture was filtered through Celite, and the yellow filtrate was evaporated to dryness. Column chromatography of the yellow residue (25% EtOAc–pet ether, silica gel) gave 511 mg (91%) of shiny pale yellow crystals ($R_f$ = 0.36): m.p. 110–112°; UV (EtOH) 298 nm ($\varepsilon$ = 5700); IR (KBr) 3480 (s), 2940 (s), 2850 (m), 1650 (m), 1620 (s), 1570 (w) $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 1.70–2.50 (m, 8H), 2.68 (s, 1H), 2.85 (d, 1H, J = 10 Hz), 3.50 (d, 1H, J = 11 Hz), 5.70–6.00 (m, 2H), 6.50 (dd, 1H, J = 4 and 12 Hz). (Found: C, 74.11; H, 7.90. Calc for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.)

7-*Methanesulfonatobicyclo*[5.3.1]*undeca*-1,3-*dien*-5-*one* **24**. A soln of 90 mg (0.50 mmol) of **23** in 10 ml of $CH_2Cl_2$ was stirred at 0° under $N_2$ with $Et_3N$ (210 $\mu$l, 1.40 mmol) and 114 $\mu$l (1.08 mmol) of methanesulfonyl chloride was added. The dark yellow mixture was stirred 20 min at 0° and then 30 min at room temp. The soln was diluted with 20 ml of $CH_2Cl_2$, washed with 10% $NaHCO_3$ aq (2 × 10 ml), brine (2 × 10 ml) and dried ($MgSO_4$). Solvent was removed to yield 136 mg (100%) of crude **24** as a pale yellow oil. This unstable material was used immediately without further purification: IR (neat) 3010 (w), 2940 (m), 2860 (w), 1660 (s), 1640 (s), 1590 (m), 1320 (s), 1175 (s), 910 (s) $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 1.65–2.70 (m, 8H), 3.10 (s, 3H), 3.39 (d, 1H, J = 12 Hz), 5.65–6.02 (m, 2H), 6.30–6.67 (m, 1H).

*Bicyclo*[5.3.1]*undeca*-1,3,6-*trien*-5-*one* **25**. To a mixture of 283 mg (1.10 mmol) of freshly prepared **24** in 20 ml of $CH_2Cl_2$ was injected 240 $\mu$l (1.90 mmol) of diazabicyclononene. The mixture was stirred for 30 min at room temp, then diluted with 30 ml of ether, washed with water (2 × 5 ml), 10% $NaHCO_3$ aq (2 × 5 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Prep TLC on silica gel (30% EtOAc–pet ether) gave 107 mg (61%) of **25** as a pale yellow oil ($R_f$ = 0.37): UV (EtOH) 324 nm ($\varepsilon$ = 3800); IR (neat) 3010 (w), 2950 (m), 2860 (w), 1645 (s), 1594 (s), 1335 (m) $cm^{-1}$; 100 MHz $^1$H-NMR ($CDCl_3$) $\delta$ 1.5–2.5 (m, 6H), 2.70 (d, 1H, J = 9.2 Hz), 3.44 (d, 1H, J = 9.2 Hz), 5.81 (d, 1H, J = 4.1 Hz), 5.97 (s, 1H), 6.54 (s, 1H), 6.57 (d, 1H, J = 4.1 Hz); $^{13}$C-NMR ($CDCl_3$) $\delta$ 37.1, 37.2, 41.2, 41.8, 117.4, 123.6, 135.0, 137.6, 159.6, 163.9, 192.5.

7-*Methoxybicyclo*[5.3.1]*undeca*-1,3,5-*triene* **27** (*by reduction of trienone* **25**). To a soln of 220 mg (0.83 mmol) of $CeCl_3 \cdot H_2O$ in 5 ml of MeOH was added 91 mg (0.57 mmol) of **25** with stirring. After 5 min, 22 mg (0.57 mmol) of $NaBH_4$ was added over a period of 4 min. TLC (40% EtOAc–pet ether) of the resulting colorless soln showed only one spot ($R_f$ = 0.39, corresponding to **26**. Stirring was continued, and a second spot on TLC began to develop ($R_f$ = 0.66) and became more intense as time went on. After a total reaction time of 15 min, the two spots on the TLC slide had almost the same intensity, and the mixture was quenched with water (6 ml) and diluted with ether (25 ml). The ether layer was separated, washed with water (3 ml), brine (3 ml), dried ($MgSO_4$) and concentrated to give 74 mg of a yellow oil. The yellow oil was diluted with 3 ml of MeOH, and 200 $\mu$l of $BF_3$-etherate was added. Stirring the mixture for 6 min caused the lower spot on TLC to disappear and the top spot to become larger. The mixture was worked up as above to give a yellow oil. Prep TLC on silica gel (40% EtOAc–pet ether) gave 33 mg (33%) of **27** as a colorless oil ($R_f$ = 0.66): UV (EtOH) 245 nm ($\varepsilon$ = 2400); IR (neat) 2940 (s), 2850 (m), 1650 (m), 1445 (m), 1270 (m), 1070 (s) $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 0.90–2.36 (m, 7H), 2.77 (d, 1H, J = 12 Hz), 3.06 (s, 3H), 5.27 (dd, 1H, J = 2, 12 Hz), 5.67 (s, 1H), 5.97 (m, 3H); $^{13}$C-NMR ($CDCl_3$) $\delta$ 29.8, 35.9, 37.1, 39.7, 48.8, 119.1, 126.0, 127.7, 128.0, 135.7, 149.9; MS calc for $C_{12}H_{16}O$: 176.1201. Found: 176.1234.

7-*Methoxybicyclo*[5.3.1]*undeca*-1,3,5-*triene* **27** (*by irradiation of* **18** *in methanol*). A soln of **18** (300 mg, 1.85 mmol) in 15 ml of MeOH contained in a soft glass vessel was irradiated with a 450 W medium pressure mercury arc through a Corex filter. After 12 h, TLC showed that the reaction was completed, and the solvent was removed under reduced pressure. Prep TLC of the resulting dark yellow oil on silica gel (40% EtOAc–pet ether) gave 92 mg (28%) of **27** as a colorless oil identical in all respects to the material prepared by reduction of **25**.

*Interconversion of methoxytriene* **27** *and hydroxytriene* **30**. To a soln of 32 mg (0.18 mmol) of **27** in 3 ml of acetone and 2 ml of water was added 10 drops of $CF_3COOH$. The mixture was stirred overnight at room temp. Acetone was removed under reduced pressure, and the aqueous soln was extracted with

$CH_2Cl_2$ (3 × 5 ml). The organic soln was washed with water (5 ml), 10% $NaHCO_3$ aq (2 × 5 ml), dried ($MgSO_4$) and concentrated to give a pale yellow oil. Prep TLC on silica gel (20% EtOAc–hexane) gave 23 mg (78%) of **30** as a pale yellow oil ($R_f$ = 0.29): UV (EtOH) 245 nm; IR (neat) 3370 (s), 3010 (m), 2940 (s), 2860 (m), 1650 (w), 1450 (m) $cm^{-1}$; $^1$H-NMR ($CDCl_3$) $\delta$ 1.02–2.35 (m, 8H), 2.69 (d, 1H, J = 10 Hz), 5.38–5.72 (m, 3H), 5.78–6.08 (br s, 2H).

To a soln of 42 mg (0.26 mmol) of **30** in 8 ml of dry MeOH was added 300 $\mu$l of $BF_3$–$Et_2O$. The mixture was stirred overnight at room temp and then diluted with 20 ml of $CH_2Cl_2$, washed with water (5 ml), 10% $NaHCO_3$ aq (5 ml), and dried ($MgSO_4$). The solvent was removed, and a light yellow oil was obtained. The oil was purified as before to give 31.6 mg (70%) of **27**, identified by $^1$H-NMR.

*Generation of bridged homotropylium cation* **9** *and bridged 3-hydroxyhomotropylium cation* **31** *in trifluoroacetic acid (TFA).* In an NMR tube was placed 36 mg of **25** and 0.5 ml of TFA to give a light brown transparent soln: 100 MHz $^1$H-NMR (TFA) $\delta$ 1.63 (d, 1H, J = 8 Hz), 2.18–3.13 (m, 7H), 4.16 (d, 1H, J = 8 Hz), 7.00 (d, 1H, J = 7 Hz), 7.19 (s, 1H), 7.25 (d, 1H, J = 13 Hz), 7.77 (dd, 1H, J = 13 and 7 Hz); $^{13}$C-NMR (TFA) $\delta$ 40.1 (t), 40.7 (t), 51.4 (t), 52.9 (t), 126.1 (d), 130.6 (d), 132.1 (d), 149.4 (d), 175.9 (s), 181.9 (s), 182.1 (s).

Similarly, 41 mg of **27** was dissolved in 0.5 ml of TFA to give a light brown soln: 100 MHz $^1$H-NMR (TFA) $\delta$ 0.09 (d, 1H, J = 7 Hz), 2.38–3.38 (m, 6H), 5.18 (d, 1H, J = 7 Hz), 8.14 (s, 5H); $^{13}$C-NMR (TFA) $\delta$ 39.2, 41.0, 55.6 (OMe), 57.5, 140.2, 142.3, 146.6, 170.2 (singlet in off-resonance spectrum).

*Generation of bridged homotropylium cation* **9** *and bridged 3-hydroxyhomotropylium cation* **31** *in* $CDCl_3$. To a mixture of 28 mg of **25** and 0.5 ml of $CDCl_3$ in an NMR tube was added 2 drops of TFA; the resulting light brown soln was kept at room temp for 2 min, during which time no change was observed: $^1$H-NMR ($CDCl_3$) $\delta$ 1.80 (d, 1H, J = 7 Hz), 2.28–2.96 (m, 7H), 3.90 (d, 1H, J = 7 Hz), 6.71 (d, 1H, J = 6 Hz), 7.00 (s, 1H), 7.08 (d, 1H, J = 12 Hz), 7.30–7.76 (dd, 1H, J = 6 and 12 Hz). The mixture was then hydrolyzed, and 23.0 mg of the starting material was recovered.

The above experiment was repeated, using 33 mg of **27** in 0.5 ml of $CDCl_3$. Addition of 1 drop of TFA to the mixture at room temp gave **9** without any trace of starting material: $^1$H-NMR ($CDCl_3$) $\delta$ 0.30 (d, 1H, J = 7 Hz), 2.06–3.40 (m, 6H), 3.60 (s, 3H, OMe), 4.94 (d, 1H, J = 7 Hz), 8.04 (s, 5H); $^{13}$C-NMR $\delta$ 38.0, 49.4, 54.5 (OMe), 56.4, 139.2, 141.2, 145.7, 167.7.

*Hydride transfer to cation* **9** *from cycloheptatriene.*[26] Bridged cation **9** was generated from **27** (35 mg, 0.20 mmol) in TFA. To this mixture was added 18.4 mg (0.20 mmol) of cycloheptatriene to give a light brown soln. $^1$H-NMR spectra of the mixture were taken periodically (*ca* 5 min intervals). After 5 min, the NMR showed that much of **9** had disappeared and a new singlet corresponding to the tropylium cation at 9.0 ppm appeared. Based on the integration of the peaks at $\delta$ 9.0 (tropylium) and $\delta$ 8.14 (bridged homotropylium) the molar ratio of these two species after 5 min was *ca* 65 : 35; after 10 min it was *ca* 80 : 20. After an additional 5 min, no further change was observed, so more cycloheptatriene was added. The disappearance of **9** was complete in less than 5 min thereafter.

*Attempted hydride transfer to homotropylium cation* **9** *from triphenylmethane.* In an NMR tube was placed 37 mg (0.21 mmol) of **27** and 0.5 ml of TFA to generate the **9**. To this mixture was added 47 mg (0.21 mmol) of triphenylmethane, and the mixture was shaken until all the solid dissolved (*ca* 5 min). A $^1$H-NMR spectrum was then taken, but no change was observed (no hydride transfer). The mixture was heated to 100° for 10 min, during which time **9** gradually disappeared while triphenylmethane remained unchanged.

*Hydride transfer from diene* **19** *to trityl cation.* In an NMR tube was placed a mixture of 65 mg (0.5 mmol) of triphenylmethanol and 1 ml of TFA to give trityl cation as a yellow soln: $^1$H-NMR (TFA) $\delta$ 7.42–8.30 (singlet with several shoulders). To this soln was added 36.5 mg (0.25 mmol) of **19** which resulted in a light brown soln. The $^1$H-NMR spectrum of the mixture still showed peaks at 7.42–8.30 ppm, but the following new peaks appeared: 0.82–2.82 (m), 3.83 (br s), 5.38 (s), 7.02 (s). The last two peaks (*ca* 1 : 15) correspond to those of triphenylmethane. Addition of another 36.5 mg (0.25 mmol) of **19** to the mixture resulted in complete conversion of the trityl cation to triphenylmethane. No trace of bridged cation **9** ($\delta$ 8.14) could be detected. The mixture was then poured into 10 ml of MeOH, stirred for 15 min at room temp, and then hydrolyzed with water (10 ml). The aqueous mixture was extracted with ether (3 × 10 ml), and the ether soln was dried ($MgSO_4$) and concentrated. Prep TLC on silica gel (4% EtOAc–pet ether) gave 120 mg of triphenylmethane contaminated with a saturated hydrocarbon impurity, presumably polymerized **19** ($R_f$ = 0.5).

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Subsequent to our 1978 publication in this area, it has been found that compounds 3 and 5 in the paper cited do not have bicyclo[5.3.1]undecane skeletons [L. T. Scott and W. R. Brunsvold, unpublished work]. Thus, there is no evidence for circumambulatory rearrangements in 1,7-bridged homotropylium ions.

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