were calculated by reproducing transmittance *vs.* time oscillographs with an analog computer. Rapid scan features have been described previously.[16]

**Product of Kinetic Runs.** The effluent of the stopped flow was quenched on ice and the mixture was titrated to pH 7.0 with dilute $H_2SO_4$. The ether layer and an ether extract of the $H_2O$ layer were combined and washed with dilute $NaHCO_3$ and $H_2O$. The ether was dried ($Na_2SO_4$) and removed from the product on a rotary evaporator. Ir and nmr spectra of the product were consistent with expected properties of the addition and dehydration products.[15]

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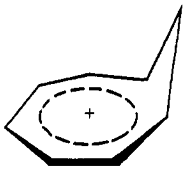
# Bishomotropylium Ions under Conditions of Long and Short Life[1]

**Per Ahlberg,*[2a] D. L. Harris, Mark Roberts, P. Warner, P. Seidl,**
**M. Sakai, D. Cook, A. Diaz, J. P. Dirlam, H. Hamberger, and S. Winstein[2b]**

*Contribution No. 2934 from the Department of Chemistry,*
*University of California, Los Angeles, California 90024.*
*Received February 14, 1972*

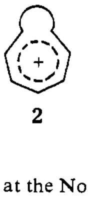
**Abstract:** The existence of three 1,4-bishomotropylium ions and one 1,3-bishomotropylium ion is demonstrated under conditions of long life, *i.e.*, in superacid media. The ions are the 1-methylbicyclo[4.3.0]nonatrienyl cation, the bicyclo[4.3.0]nonatrienyl cation, the bicyclo[4.3.1]deca-2,4,7-trienyl cation, and the 1,3-bishomotropylium ion, protonated *cis*-bicyclo[6.1.0]nona-2,4,6-triene. The electronic structure as inferred from the nmr is extensively discussed and the homoaromatic character of the ions emphasized. Evidence is presented for the existence of 1,4-bishomotropylium ions under conditions of short life, *i.e.*, solvolytic conditions.

In 1962 Pettit and coworkers[3] reported the first generation and direct observation of a homotropylium ion, the monohomotropylium ion **1**. The homoaromatic[4] character of **1** has been inferred from the nmr parameters of **1** and of its $Mo(CO)_3$ and $Fe(CO)_3$ complexes, taking advantage of the different electronic requirements of the metal tricarbonyls, as well as of the uv properties of **1**, etc.[4] Many substituted monohomotropylium ions with more or less pronounced homoaromatic character have been synthesized since that time. The discovery of the existence of the monohomotropylium ion has stimulated the search for polyhomotropylium[4] ions. Here we wish to report in a collective way some of the first discovered bishomotropylium ions.



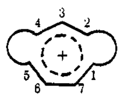
**1**

Because of the presence of only one homointeraction in monohomotropylium ions, there exists only one principle type of them, symbolized with structure **2**.

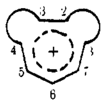


**2**

Depending on the relative position of the two bridges in bishomotropylium ions, we can distinguish three principally different types of ions, symbolized with structures **3**, **4**, and **5**. All three ions are six electron and, potentially, aromatic species and they are named 1,4-, 1,3-, and 1,2-bishomotropylium ions, respectively.



**3**



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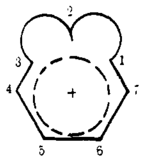
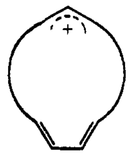
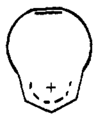


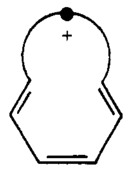
**5**



**6**



**7**



**8**

In **6**, **7**, and **8** we assume no interactions between the positively charged ionic part and the unsaturated part of the structures. Furthermore, if the assumption is made that the strain is the same in all three structures, the thermodynamic stability order is going to be **7** > **6** > **8**. If we allow interaction between the two parts in **6**, **7**, and **8** (through overlap intermediate between $\sigma$ and $\pi$), we obtain the structures **3**, **4**, and **5**. From relative estimates of the interaction between the highest occupied molecular orbital of the saturated part and the lowest unoccupied molecular orbital of the positively charged part of the three structures **6**, **7**, and **8**, we would expect **5** to be more stabilized than **3** and **3** more stabilized than **4** due to the intramolecular interactions. Again the strain is assumed to be the same in all three structures.

Thus, the stabilization order, due to intramolecular interaction, is the reverse of the thermodynamic stability

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[1] Presented in part by P. A. at the Nobel Workshop on aromaticity, especially in heterocyclic systems, held on Aug 20–22, 1971, at Väversunda, Östergötland, Sweden.

[2] (a) To whom inquiries should be addressed: Chemical Institute, Uppsala University, Uppsala 1, Sweden. (b) Deceased Nov 23, 1969. Supported in part by the National Science Foundation.

[3] (a) J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 2842 (1962); (b) C. E. Keller and R. Pettit, *ibid.*, **88**, 604 (1966); (c) J. D. Holmes and R. Pettit, *ibid.*, **85**, 2531 (1963).

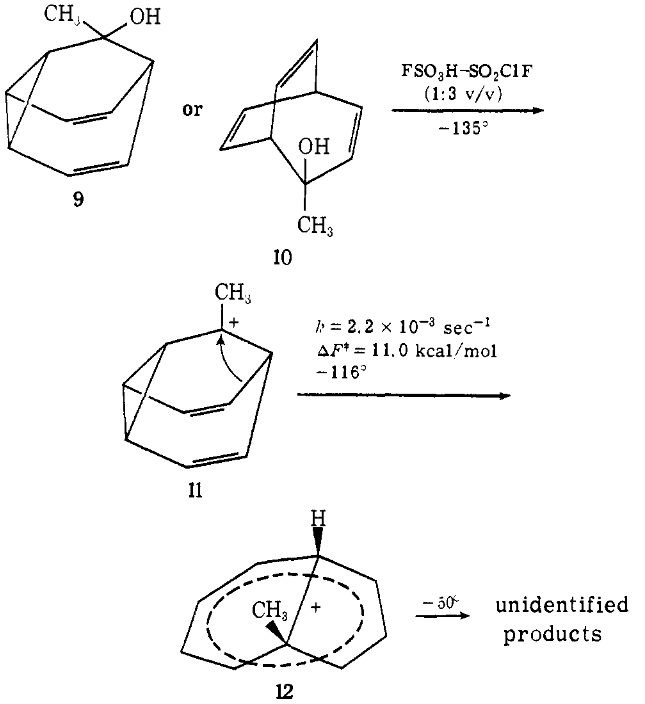
[4] S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969)

order for the corresponding structures without intramolecular interaction.

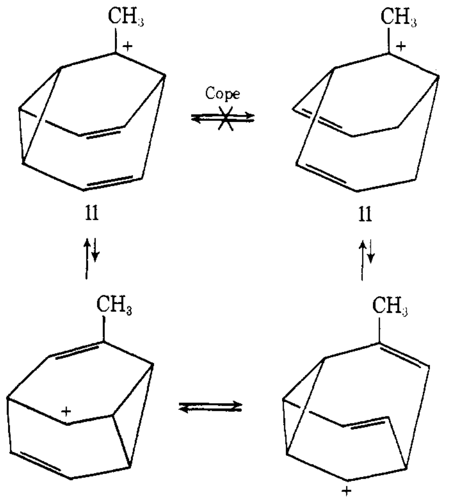
In this paper the existence of three ions of type **3** (1,4-bishomotropylium ions[5,6]) and one ion of type **4** (a 1,3-bishomotropylium ion[7]) is demonstrated under conditions of long life, *i.e.*, in superacid media. Their electronic structures are extensively discussed. The intermediacy of ions of type **3**,[8,9] under conditions of short life, *i.e.*, solvolytic conditions, is also discussed.

## Results and Discussion

**Experiments under Conditions of Long Life. 1,4-Bishomotropylium Ions.** When $CD_2Cl_2$ solutions of 9-methyl-9-barbaralol (**9**) or 2-methylbicyclo[3.2.2]nona-3,6,8-trien-2-ol (**10**) were mixed into a solution of $FSO_3H$-$SO_2ClF$ (1 :3 v/v) at *ca.* − 135° and observed by nmr at − 135°, the first ion observed was the 9-methyl-9-barbaralyl cation (**11**).[5a,b,d] This potentially very reactive ion was shown to undergo very fast non-Cope degenerate rearrangements: divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl cationic rearrangements (Scheme I).[5b–d] At − 116° **11** reacted completely through a quite rapid nondegenerate homoallylic rearrangement to give a new carbonium ion **12** having the following nmr spectrum (Figure 1). Of the eleven protons observed, seven appeared at quite low field, $\tau$ 1.99–3.73, one proton at $\tau$ 6.63, and the remaining protons, belonging to a methyl group, at $\tau$ 8.87.

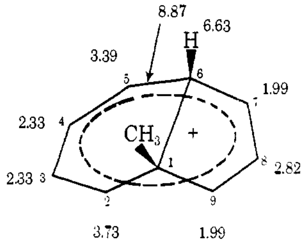


**Scheme I**



Among the seven low-field protons a three-spin system and a four-spin system with very weak intersystem coupling were disclosed through some decoupling experiments. From the nmr and a computer simulation of the four-spin system the coupling constants (Table I and Scheme II) and the chemical shifts (Table I and Chart I) were obtained. These parameters clearly indicate the structure of the observed ion.

**Table I.** Nmr Chemical Shifts and Coupling Constants for the 1-Methylbicyclo[4.3.0]nonatrienyl Cation in $FSO_3H$–$SO_2ClF$ (1 :3 v/v) at −85°; Internal Standard $CHDCl_2$ ($\tau$ 4.70)

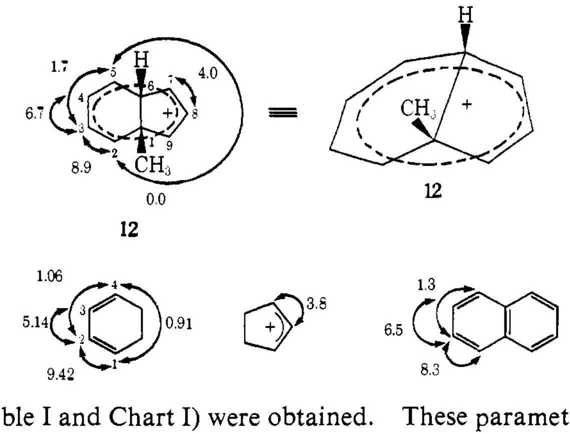


**12**

| | $\tau$ values | | | | | | |
|---|---|---|---|---|---|---|---|
| *J* | 2,3 | 2,4 | 2,5 | 2,9 | 3,4 | 3,5 | 3,6 |
| Hz | 8.9[a] | 0.1[a] | 0.0[a] | Small[b] | 6.7[a] | 1.7[a] | Small[b] |
| *J* | 4,5 | 4,6 | 5,6 | 5,7 | 6,7 | 7,8 | 8,9 |
| Hz | 7.7[a] | Small[b] | 4.9[b] | Small[b] | 2.0[b] | 4.0[b] | 4.C[b] |

[a] Calculated. [b] Measured.

**Scheme II.** Some Coupling Constants in Hertz for the 1-Methylbicyclo[4.3.0]nonatrienyl Cation in $FSO_3H$–$SO_2ClF$ (1 :3 v/v) at −85° and for Various Model Compounds



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(5) (a) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2146 (1970); (b) P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *ibid.*, **92**, 3478 (1970); (c) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 4454 (1970); (d) P. Ahlberg, unpublished work.

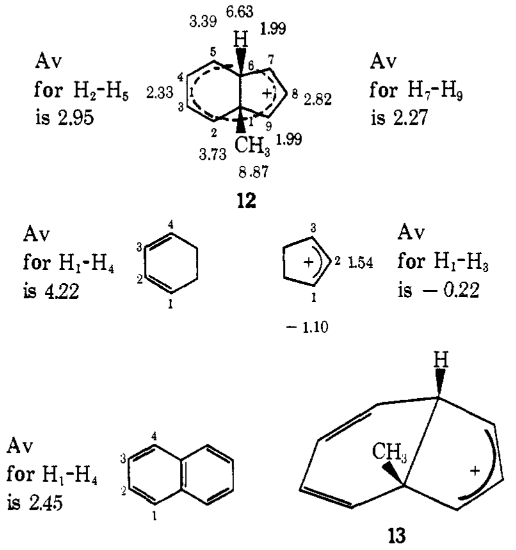
(6) (a) G. Schröder, U. Prange, N. S. Bowman, and J. F. M. Oth, *Tetrahedron Lett.*, 3251 (1970); (b) M. Roberts, H. Hamberger, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 6346 (1970); (c) G. Schröder, U. Prange, B. Putze, J. Thio, and J. F. M. Oth, *Chem. Ber.*, **104**, 3406 (1971) (this paper appeared when the present paper was in its completion and reports the direct observation of several 10-substituted bicyclo[4.3.1]deca-2,4,7-trienyl cations).

(7) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 1284 (1971).

(8) P. Seidl, M. Roberts, and S. Winstein, *ibid.*, **93**, 4089 (1971).

(9) D. Cook, A. Diaz, J. P. Dirlam, D. L. Harris, M. Sakai, S. Winstein, J. C. Barborak, and P. v. R. Schleyer, *Tetrahedron Lett.*, 1405 (1971).

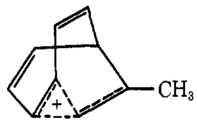
**Chart I.** Nmr Chemical Shifts ($\tau$) for the 1-Methylbicyclo[4.3.0]nonatrienyl Cation in $FSO_3H$-$SO_2ClF$ (1:3 v/v) at −85° and for Various Model Compounds



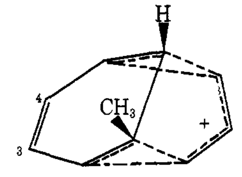
The three-spin system ($H_7$–$H_9$) showed a coupling constant $J_{7,8} = J_{8,9} = 4.0$ Hz. Comparison with the coupling constants in the cyclopentenyl cation, which is $J_{1,2} = 3.8$ Hz, indicates that $C_7$–$C_9$ are part of a five-membered ring. Furthermore, comparison of the coupling constants of the four-spin system ($H_2$–$H_5$) with those of cyclohexadiene and naphthalene indicates that $C_2$–$C_5$ is part of a six-membered ring. Thus the skeletal structure of the ion is indicated by the coupling constants. The proton chemical shifts clearly show that the electronic structure of the observed ion **12** is not that of structure **13**. The average chemical shifts of **12** (Chart I) compared with those of the cyclopentenyl cation and cyclohexadiene show that $C_7$–$C_9$ is not part of an isolated allylic cation but instead that a considerable amount of the positive charge has been donated from $C_7$–$C_9$ into the butadiene system ($C_2$–$C_5$). This extensive charge delocalization suggests the presence of homointeractions between $C_2$ and $C_9$ and between $C_5$ and $C_7$. Thus, the electronic structure of **13** is not a proper representation of the observed ion **12**.

It is worth mentioning here that donation of charge from one part of a molecule to another is a powerful probe of electronic structure. In this case it is reflected by the nmr chemical shifts of the protons. This structural probe is absent in the monohomotropylium ion **1** due to the presence of only one homointeraction.

The total deshielding of the "butadiene" protons of **12**, relative to those of cyclohexadiene, is *ca.* 5 ppm. This deshielding is accompanied by a total shielding of *ca.* 7 ppm of the protons of the "allylic" system relative to those of the cyclopentenyl cation. Taking into account probable shielding of the protons bonded to $C_2$, $C_9$, $C_5$, and $C_7$, due to the rehybridizations resulting from the homointeractions, the conclusion is that *ca.* 0.5 unit of positive charge[10] has been delocalized into the "butadiene" system from the "allylic" ion. That the structure **14**, like **13**, can be discarded as a good representation of the observed ion **12** is seen by the following reasoning. Structure **14** has two cyclopropylcarbinyl cationic structural elements, each one with a symmetrical type of charge delocalization. Thus, this has the implication that the "bridgehead" proton ($H_6$) should be substantially charge deshielded. On the contrary, the bridgehead proton in **12** has the chemical shift of a normal bridgehead proton that does not feel any excess charge. Furthermore, the olefinic protons ($H_3$ and $H_4$) of **14** should not carry any excess positive charge in analogy with what is observed for the 9-methyl-9-barbaralyl cation **11**. In the observed ion the "olefinic" protons ($H_3$ and $H_4$) do carry a substantial amount of positive charge.



**11**



**14**

A formulation of the observed ion with structure **12** yields an ion with two unsymmetrical cyclopropylcarbinyl cationic structural moieties, *i.e.*, homoallylic cationic segments, where mainly one side of the cyclopropane ring participates in the charge delocalization. The positive charge is exclusively (or almost so) delocalized onto the seven carbons $C_2$–$C_5$ and $C_7$–$C_9$ leaving the rest of the molecule with none or very little charge. Thus structure **12** is an excellent representation of the observed ion.

Obviously this cyclic charge delocalization makes each one of the seven carbons carry a substantial part of the positive charge. The energy of the ion has very probably been lowered considerably by the cyclic delocalization. Presumably the stabilizing effect of the charge delocalization is the driving force for the reaction **11** → **12**. Thus **12** is an aromatic, bishomoaromatic, tropylium-like ion and should be named 1,4-bishomotropylium ion.[4]

The parent ion **15** of **12** has also been synthesized. First it was made from the 9-barbaralyl cation[5c] (**11′**), which had been generated from bicyclo[3.2.2]nona-3,6,8-trien-2-ol (**16**). The 9-barbaralyl cation was shown to undergo extremely rapid, totally degenerate rearrangements[5c] and appeared as a sharp singlet in the nmr even at −135°. Other precursors that have been used to generate **15** are *exo*-tricyclo[4.3.0.0$^{2,9}$]nona-4,7-dien-3-ol (**17**, *exo*-homosemibullvanol)[5c] and *exo-cis*-bicyclo-[4.3.0]nona-2,4,8-trien-7-ol (**18**, *exo-cis*-8,9-dihydroindenol).[9] For the generation of **15** the same procedure and similar conditions were used as for **12**. The very close relationship between **15** and **12** is shown by a comparison of the nmr data in Tables I and II and Figures 1 and 2. The dissymmetry in **12**, due to the methyl group, is removed in **15**, as reflected by the nmr spectra of the two ions (Figures 1 and 2). As in **12**, the proton chemical shifts of **15** demonstrate extensive cyclic charge delocalization with the result that each of the seven carbons $C_2$–$C_5$ and $C_7$–$C_9$ have a substantial amount of positive charge. The conclusion is that *ca.*

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[10] (a) The assumption is here adopted that the nmr shift (excluding ring current effects) is proportional to the charge on the carbon to which the hydrogen in question is attached with a proportionality constant of 10.[10b,c] Thus, with the shift estimates of the type used in present work, we get semiquantitative estimates of the charge donation from one part of the molecule to another which are to be compared with the theoretical estimates. (b) G. Fraenkel, R. E. Carter, A. D. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960); (c) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

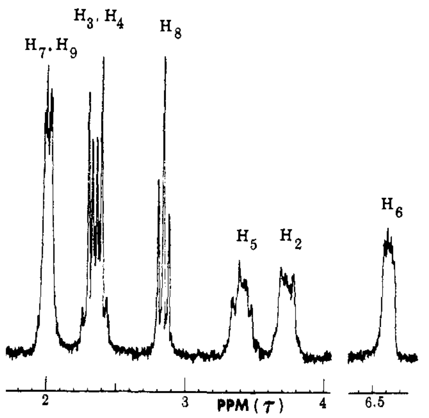
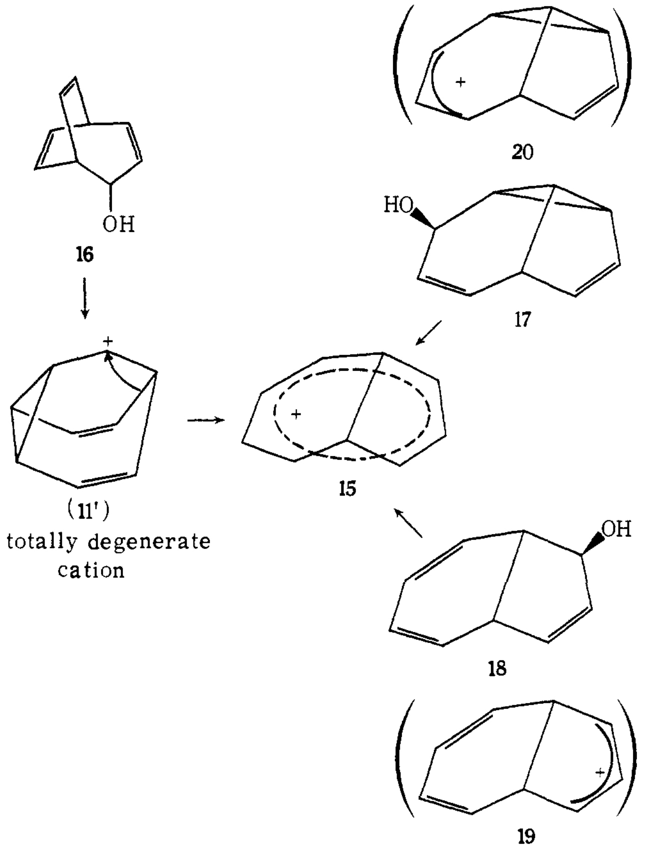


Figure 1. Nmr spectrum (100 MHz) of the 1-methylbicyclo[4.3.0]-nonatrienyl cation **12** in $FSO_3H$-$SO_2ClF$ (1:3 v/v) at −85° (the methyl absorption is not shown). $CDHCl_2$ was used as an internal standard, τ 4.70.



0.5 unit of the positive charge has been delocalized away from the "allylic" system into the "butadiene" system.

The ionic structures **20** and **19**, corresponding to *exo*-homosemibullvanol (**16**) and *exo*-dihydroindenol (**17**), were not observed together with **15**. This fact suggests that these structures are thermodynamically less stable than the observed ion **15**. As in **12** the reason for the stabilization of **15** is presumably the extensive cyclic charge delocalization yielding a tropylium-like ion. The aromatic ion **15**, since it is a bishomoaromatic species, should also be named the 1,4-bishomotropylium ion. The question arises whether structures like **19** and **20** have free-energy minima under the conditions used in the present investigation. Our data suggest no answers.

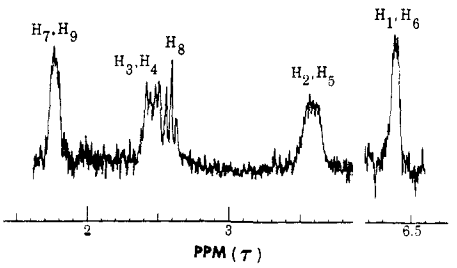
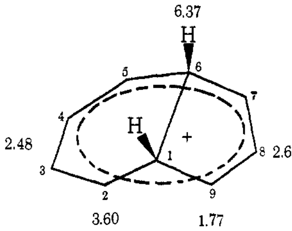


Figure 2. HA-100 nmr spectrum of the bicyclo[4.3.0]nonatrienyl cation **15** at −125°; $CHDCl_2$ internal standard at τ 4.70.

**Table II.** Nmr Chemical Shifts and Coupling Constants for the Bicyclo[4.3.0]nonatrienyl Cation in $FSO_3H$-$SO_2ClF$ (1:3 v/v) at −125°; Internal Standard $CHDCl_2$ (τ 4.70)



**15**

τ values

| J | 2,3 (4,5) | 2,4 (3,5) | 2,4 | 3,4 | 7,8 (8,9) | 1,3 (4,6) |
|---|---|---|---|---|---|---|
| Hz | 8.4 | 0.9 | 0.0 | 6.7 | 3.9 | 0.8 |

Quench experiments with either **12** or **15** using a solution of sodium methoxide in methanol at −75° were unsuccessful. This reflects an extraordinary reactivity of the ions toward base, probably due to the very acidic bridgehead protons ($H_1$ and $H_6$). These protons also ought to undergo hydride shifts easily. This is probably reflected by the relatively low barriers toward rearrangement for **12** and **15** ($\Delta F^{\ddagger}_{-80^\circ}$ = 12.9 kcal/mol).

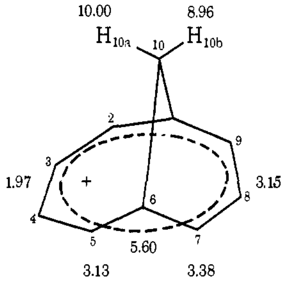
Another criterion for aromaticity, that often has been used, is that an aromatic system should be able to sustain an induced ring current.[4] However, in the present systems (**12** and **15**) it is difficult to estimate the size of the expected deshielding effect on the peripheral protons in the seven-membered ring due to a ring current. A sufficiently accurate estimate is complicated by shielding which accompanies the rehybridization of the homointeracting carbons. As expected, the average deshielding of the ring protons is smaller than for the monohomotropylium ion (Table III). Thus, there is a

**Table III**

| Ion | Average chemical shift for the seven-ring protons (τ) |
|---|---|
| Tropylium | 0.76[a] |
| Monohomotropylium (**1**) | 2.12[b] |
| 1,4-bishomotropylium (**12**) | 2.70[c] |
| 1,4-bishomotropylium (**15**) | 2.62[d] |

[a] In $FSO_3H$ with internal reference $CDHCl_2$ (τ 4.70).[4] [b] In $FSO_3H$-$SO_2ClF$ (1:1 v/v) with internal reference $CH_2ClCH_2Cl$ (τ 6.28) which was referenced to $CHDCl_2$ (τ 4.70): P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970). [c] **12** in $FSO_3H$-$SO_2ClF$ (1:3 v/v) with internal reference $CHDCl_2$ (τ 4.70). [d] **15** in $FSO_3H$-$SO_2ClF$ (1:4 v/v) with internal reference $CHDCl_2$ (τ 4.70).

**Table IV.** Nmr Chemical Shifts and Coupling Constants for the Bicyclo[4.3.1]deca-2,4,7-trienyl Cation in $FSO_3H$-$SO_2ClF$ (1:4 v/v) at −30°; $CDHCl_2$ Was Used as an Internal Standard (τ 4.70)



**21**

τ values

| $J$ | 1,2 | 1,9 | 1,10α | 1,10β | 2,3 | 2,4 | 2,5 | 3,4 | 2,10β | 7,10α | \|10α,10β\| |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Hz | ~4[b] | 5.9[b] | 0.0[b] | 4.5[b] | +9.9[a] | +1.2[a] | 0.0[a] | +9.4[a] | ~1[b] | Small | 14.2 |

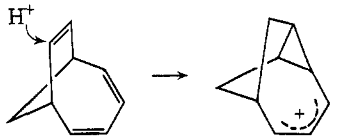
[a] Calculated. [b] Measured.

limited value of the ring current criterion for investigation of aromaticity in the present cases.

Even the bridgehead protons in **12** and **15** have limited use as ring current probes for they appear to be, judging from models of the ions, in regions of space that are neither shielded nor deshielded.

A third 1,4-bishomotropylium ion **21**, the methylene-bridged homolog to **15**, was first reported by Schröder and coworkers[6a] and later, but independently, by us.[6b]

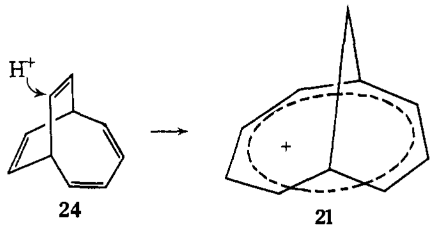
The idea for the synthetic route to the bicyclo[4.3.1]deca-2,4,7-trienyl cation **21** was the observation[6b] that bicyclo[4.2.1]nona-2,4,7-triene (**22**) was protonated to



**22** **23**

form **23**. The reason for this extraordinary reactivity of the isolated double bond is probably due to homoconjugative stabilization of the transition state.

Ion **21** was obtained, as predicted, when bicyclo[4.2.2]deca-2,4,7,9-tetraene (**24**) was protonated (Figure 3). This novel homoconjugative route was also used by Schröder and coworkers. The structure of **21**



**24** **21**

was elucidated *via* the nmr parameters (Table IV) analogously with what was done for the nonbridged ions **12** and **15**. The electronic structural similarity between **15** and **21** is striking even though some differences could be distinguished by comparing the proton chemical shifts of **15** with **21**.

The charge distribution, as reflected by chemical shifts of the seven tropylium-like protons, is more even in **21** than in **15**. The "butadiene" protons ($H_2$–$H_5$) in **21** are deshielded a total of *ca.* 7 ppm relative to those of the model compound, tricyclo[4.3.1.0$^{7,9}$]deca-2,4-diene (**25**), and the protons of the "allylic" part are

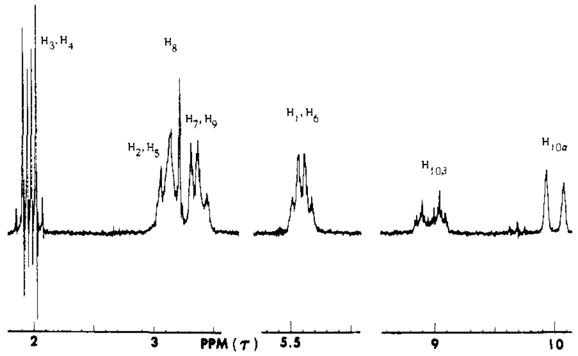
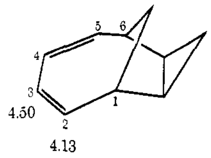
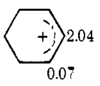


Figure 3. Nmr spectrum (100 MHz) of the bicyclo[4.3.1]deca-2,4,7-trienyl cation **21** in $FSO_3H$-$SO_2ClF$ (1:4 v/v) at −30°. $CDCl_2$ was used as an internal standard, τ 4.70.



**25**



**26**

τ values

shielded *ca.* 7.7 ppm relative to the corresponding protons of the cyclohexenyl cation **26**.[6b]

Thus the protons $H_2$–$H_5$ and $H_7$–$H_9$ of **21** are *ca.* 2 ppm more deshielded and *ca.* 0.7 ppm more shielded, respectively, relative to the corresponding protons of **15**. This indicates that the delocalization of charge from the "allylic" system into the "butadiene" system is more pronounced in **21** than in **15**. In **21** *ca.* 0.7 unit of the positive charge[10] has been donated into the "butadiene" system compared to *ca.* 0.5 in **15**.

As pointed out earlier in this paper, ion **15** was not equipped with any sensitive ring current probes. In striking contrast, **21** has ring current probing bridge protons as well as bridgehead protons. Thus the bridge protons in **21** are on the average shielded *ca.* 1 ppm relative to the bridge protons in hydrocarbon **27**. This extra shielding could be due to the presence of a ring current in the tropylium-like part of ion **21**. Also consistent with the presence of a ring current is the fact

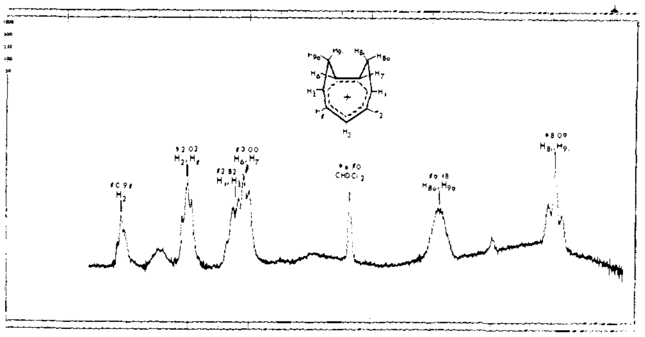
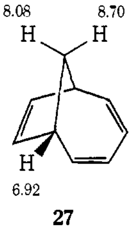


Figure 4. 100-MHz nmr spectrum of protonated *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**29**) at *ca.* −125° (sweep width = 1000 Hz).



**27**

τ values

that H$_1$ and H$_6$ appear at 1.3 ppm lower field than the bridgehead proton of **27**.

Ion **21** is considerably more stable than **15** or **12**; thus, **21** can be heated to +80° without significant change of its nmr spectrum. This is probably due to the absence of low-energy barrier routes, which are presumably present in **15** and **12**; moreover, the aromatic character should have a stabilizing effect on **21**. Let us now turn to another type of bishomotropylium ion, namely a 1,3-bishomotropylium ion.

**1,3-Bishomotropylium Ion.** The same technique and similar conditions as were used for the previously discussed 1,4-bishomotropylium ions also were used to protonate *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**28**) to give **29**.[7] Direct observation in the nmr gave the spectrum shown in Figure 4. Most of the chemical shifts and coupling constants were unambiguously[11] assigned *via* decoupling experiments; the nmr parameters are summarized in Table V.

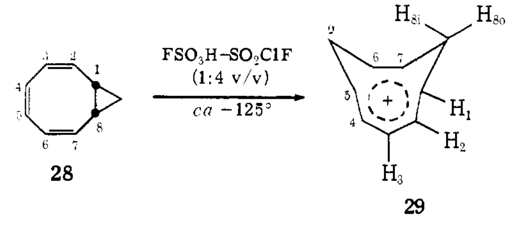
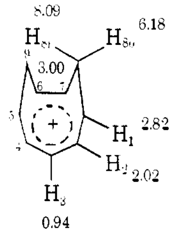


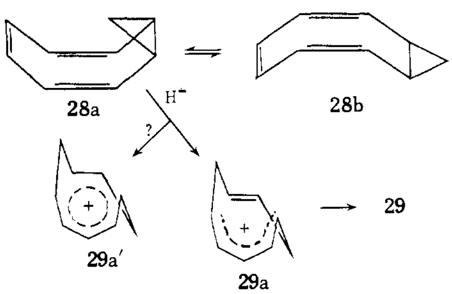
Table V. Nmr Chemical Shifts and Coupling Constants for Protonated *cis*-Bicyclo[6.1.0]nona-2,4,6-triene at *ca.* −125° in FSO$_3$H-SO$_2$ClF (1:4 v/v); CHDCl$_2$ Was Used as an Internal Standard (τ 4.70)



**29**

| | τ values | | | |
|---|---|---|---|---|
| *J* | 2,3 (3,4) | 1,2 (4,5) | 1,8o (5,9o) | 7,8o (6,9o) |
| Hz | 6.0 ± 0.5 | 9.0 ± 0.5 | 9.0 ± 0.5 | 9.0 ± 0.5 |
| *J* | 1,8i (5,9i) | 7,8i (6,9i) | 8i,8o (9i, 9o) | |
| Hz | 11.0 ± 0.5 | Small | 12.0 ± 0.5 | |

*A priori*, **28** could have been protonated at either one or more of C$_2$(C$_7$), C$_3$(C$_6$), C$_4$(C$_5$), C$_1$(C$_8$), and C$_9$. However, based on relative nucleophilicities, one would expect protonation at one or perhaps more of the double bond positions only. Protonation at C$_2$, C$_3$, or C$_4$ potentially could give 1,2-, 1,3-, or 1,4-bishomotropylium ion, respectively. As Paquette[12] has elegantly shown, only C$_3$ protonation of the syn conformer **28a** can give rise to an initially resonance-stabilized cation. The methylene groups of this initial ion necessarily have a trans orientation, and, therefore, **29a** must be formed almost immediately. Paquette's work[12] with CSI showed exo attack on **28a**, followed by internal collapse of ion-type **29a** to product. Deuteronation of **28a** led to a 70:30 mixture of **29**, with the deuteron mostly outside. This could be accommodated by "inside" (endo) attack on **28a** (similar to the type of attack seen in the cyclooctatetraenes[4]), followed by inversion to **29**.



The nmr data of Table V are compatible, we believe, only with the arrangement of carbons and hydrogens shown in structure **29**.[11] We shall now consider different electron structure representations of **29**. Besides the bishomotropylium representation, **29**, the tricyclic

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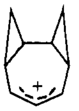
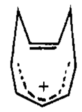
(11) (a) There is some uncertainty as to the assignment of H$_{8i}$(H$_{9i}$) and H$_{8o}$(H$_{9o}$) in **29**. While we feel reasonably sure that the coupling data have been correctly rationalized[7] on the basis of model inspection, we are pursuing further investigation of substituted 1,3-bishomotropylium ions; these results should finalize the "inner" proton–"outer" proton distinction. One possible reason for the small $J_{7,8i}$ may be that ion **29** is, in fact, the trans ion, **29a′**. Paquette's work[12] raises serious doubt as to the correct configuration for **29**. If **29** is, in fact, transoid (*i.e.*, **29a′**), it would be a double Möbius bishomotropylium ion; it would seem, from model examination, that considerable twisting of the 6,7 double bond would be required to obtain good homo overlap in **29a′**. We hope to obtain $J_{6,7}$ from substituted **29**'s in order to investigate this point. Alternatively, Paquette's work with the uniparticulate electrophile, CSI, could reflect attack on **28a** to give **29a** (the noninteracting pentadienyl cation), followed by collapse to product before inversion to **29** can occur. Some support for this interpretation comes from Paquette's study of the methylated derivatives of **28a**, wherein the ions formed behave as if they have the charge distribution expected for a pentadienyl ion[7] (*i.e.*, **29a**). However, we would not want to make a final distinction on just this point. For the remainder of this paper, we will assume that **29** is cisoid; the conclusions about electronic structure, however, would be similar for the transoid **29a′**. (b) Further structural evidence exists which supports the above assignments: P. Warner, unpublished results, Aug 1972.

(12) L. Paquette and M. Broadhurst, *J. Amer. Chem. Soc.*, **94**, 632 (1972). We thank Professor Paquette for informing us of his results prior to publication.

structure **29b** and the noninteracting monocyclic structure **29c** are conceivable.

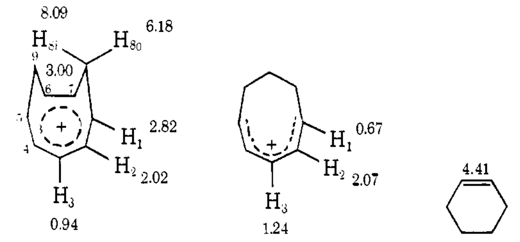


**29b**



**29c**

It is immediately possible to eliminate **29b** as an adequate representation for **29**, since the $|J_{\text{gem}}| = 12$ Hz is far too large for a cyclopropane ring. Also, the charge distribution at $C_2$, $C_3$, and $C_4$ observed for **29** is opposite of what one would expect for **29b**. Structure **29c**, with a simple pentadienyl unit and an isolated double bond, is not a representative structure of **29** as is seen by comparison with proper models.



**29** **30** **31**

τ values

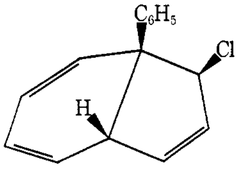
A comparison of the nmr data for **29** and **30** immediately reveals that **29c** is not an adequate representation for **29** either. In particular, $H_1$ and $H_5$ in **29** are each shifted some 2 ppm to higher field relative to their counterparts in **30**. Furthermore, the protons of the double bond (τ 3.00) are shifted *ca.* 1.4 ppm downfield relative to the appropriate model cyclohexene (**31**). Thus the shielding of the "pentadienyl" ion and the deshielding of the ethylene moiety indicate that positive charge has been donated from the cyclopentadienyl ion into the ethylene part of the molecule. The total shielding of the cyclopentadienyl ion part of **29** relative to **30** is *ca.* 4 ppm, and the total deshielding of the ethylene moiety relative to **31** is *ca.* 3 ppm, indicating that *ca.* 0.3 unit of the positive charge[10] has been dispersed into the ethylene moiety. Although the total amount of charge transferred to the olefinic part appears to be smaller than in the 1,4-bishomotropylium ions, the charge transfer per carbon is on the average approximately the same for the 1,3-bishomotropylium and for the 1,4-bishomotropylium ions (*ca.* 0.15 unit of positive charge).

Thus, there is also in this case considerable cyclic charge delocalization, which leaves a structure in which each of the carbons ($C_1$–$C_7$) in the seven-membered ring holds a substantial part of the positive charge. The mechanism for the delocalization is the same as for the 1,4-bishomotropylium ions: an unsymmetrical cyclopropylcarbinyl cationic (homoallylic) mechanism.

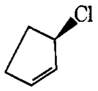
As **29** presumably is stabilized through the homointeractions, **29** is an aromatic species and should be named 1,3-bishomotropylium ion.

As in the bridged 1,4-bishomotropylium ion **21**, the present 1,3-bishomotropylium ion has potential ring current probes in the "inner" protons of the methylene groups. So far it is risky to make use of these probes because it is difficult to uniquely assign the "inner" protons of the methylene groups.[11b]

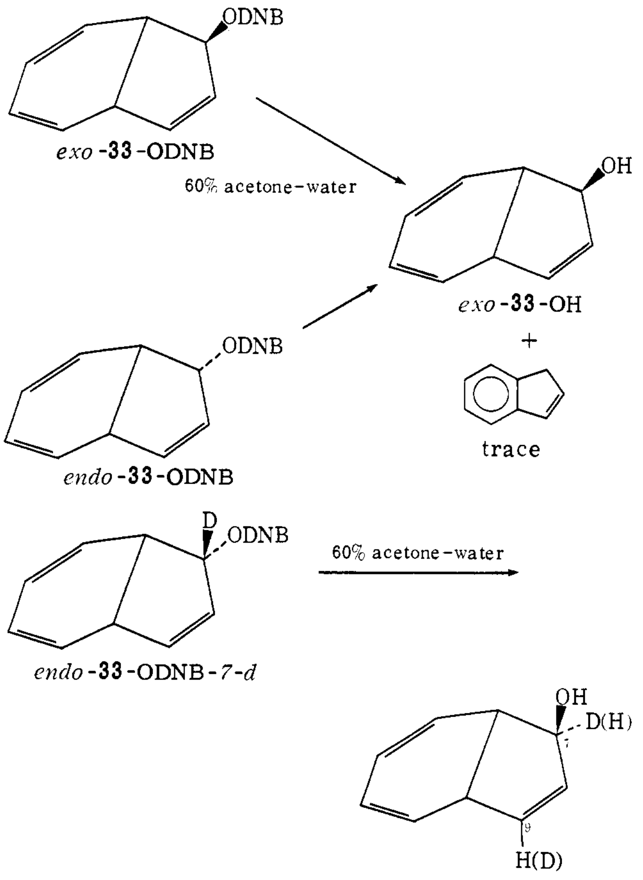
**Experiments under Conditions of Short Life. 1,4-Bishomotropylium Ions.** In 1967 Kende and Bogard[13] reported some preliminary results which showed that "unimolecular solvolysis of the chloride **32** in aqueous methanol has a slightly slower rate than solvolysis of the allylic 3-chlorocyclopentene. There is apparently no rate enhancement in this particular case from participation of the theoretically possible bishomotropylium ion."



**32**



The theoretically possible bishomotropylium ion, as we have demonstrated earlier in this paper, is now a reality under nonnucleophilic conditions. Now more extensive solvolysis work with the aim to search for the intermediacy of 1,4-bishomotropylium ions has been made.[9] Both *exo*- and *endo*-**33**-ODNB gave, when solvolyzed in 60% acetone–water, a quite nucleophilic media, *exo*-dihydroindenol and trace of indene. Furthermore, solvolysis of *endo*-**33**-*7-d* gave the following deuterium distribution in the product alcohol: no deuterium was found in the 1 and 6 position and 50 ± 5% D bonded to $C_7$ and 50 ± 5% D in the remainder of the molecule and was assumed to be $C_9$ bonded. These results suggest the intermediacy of a symmetric carbonium ion. The pertinent rate data are collected



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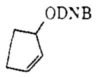
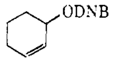
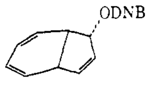
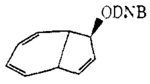
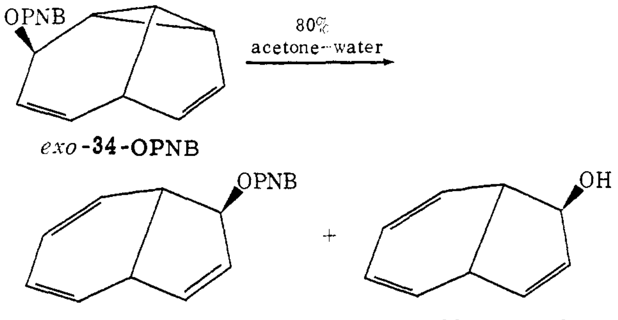
(13) A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, 3383 (1967).

in Table VI together with those for some model compounds.

Table VI

| | $k \times 10^5$ sec$^{-1}$, 60% acetone-water, 50° | $k_{rel}$, 50° |
|---|---|---|
|  | 57.8 | 64 |
|  | 0.32 | 0.35 |
| <br>*exo*-**33**-ODNB | 11.0 | 12 |
| <br>*endo*-**33**-ODNB | 0.904 | |

The exo/endo rate ratio is only 12, and, in addition, neither isomer reacts as fast as 3-cyclopentenyl-ODNB, an allylic model compound. Although the cyclobutadiene moiety in *exo*- and *endo*-**33**-ODNB may have an inductive rate-retarding effect, it seems clear that there is no evidence for a significant rate acceleration, suggesting none or very little participation in the transition state of the rate-determining step. However, the 1,4-bishomotropylium ion could nevertheless be the product-determining species.



*exo*-**34**-OPNB

*exo*-**33**-OPNB, 33% + *exo*-**33**-OH, 67%

+

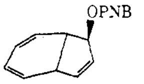
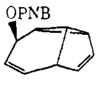
traces of two unidentified products

When *exo*-homosemibullvalenyl-OPNB (*exo*-**34**-OPNB) was solvolyzed in 80% acetone–water, the products were mainly *exo*-**33**-OH and *exo*-**33**-OPNB. Solvolysis of *exo*-**34**-OPNB is some 260 times faster than *exo*-**33**-OPNB, and most or all of this enhancement is probably due to the cyclopropane moiety of *exo*-**34**-OPNB (Table VII).

Overall, the rate data for the homosemibullvalenyl and dihydroindenyl systems do not provide much insight into the nature of the intermediates formed during solvolysis.

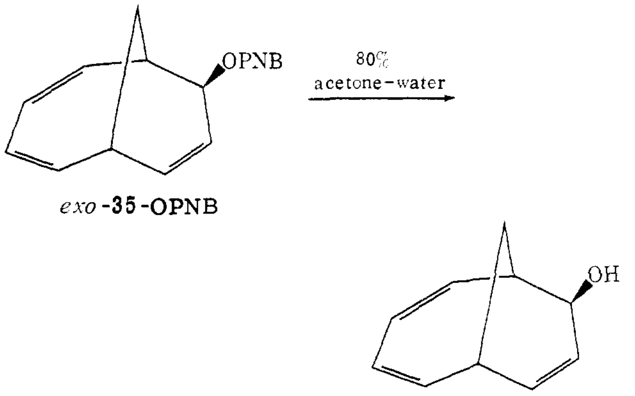
The nature of the solvolysis products from the two systems has more significance. Thus both epimers of the dihydroindenyl system yield only *exo*-**33**-OH.

Table VII

| | $k \times 10^5$ sec$^{-1}$, 80% acetone-water, 75° | $k_{rel}$, 75° |
|---|---|---|
| <br>*exo*-**33**-OPNB | 0.57 | |
| <br>*exo*-**34**-OPNB | 150 | 263 |

Coupled with the fact that *exo*-**34**-OPNB also yields *exo*-**33**-OH as the predominant carbinol product, this result suggests that the two systems pass through a common intermediate during solvolysis. Furthermore, the large percentage from internal return to *exo*-**33**-OPNB points to the intermediacy of a fairly stable intermediate as the *p*-nitrobenzoate ion is able to compete effectively with solvent three carbons away from the ionizing carbon. These results are consistent with the intermediacy of the 1,4-bishomotropylium ion in the solvolysis but not conclusive.

More enlightening with regard to the existence of a 1,4-bishomotropylium ion under conditions of short life, *i.e.*, solvolytic conditions, are the solvolysis results obtained when *exo*- and *endo*-7-bicyclo[4.3.1]deca-2,4,8-trienyl *p*-nitrobenzoate (*exo*- and *endo*-**35**-OPNB) were solvolyzed in 80% aqueous acetone. From both exo and endo compound, *exo*-**35**-OH was obtained as the only detectable product. The rate constants for the solvolysis of both *exo*- and *endo*-**35**-OPNB, as well as for proper model compounds, are collected in Table VIII.



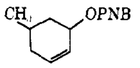
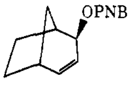
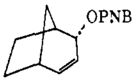
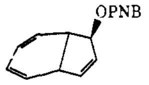
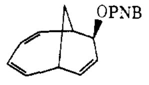
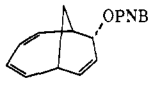
*exo*-**35**-OPNB

only detectable product

With this system we find an exo/endo rate ratio as high as 33,000. This ratio corresponds to a barrier difference of *ca.* 7.8 kcal/mol. This is to be compared with the exo/endo rate ratio of 12 (corresponds to a barrier difference of *ca.* 1.5 kcal/mol) obtained with the dihydroindenyl system. Although the butadiene moiety probably acts rate retarding, a value as high as 3000 is observed relative to **36**-OPNB.

These results demonstrate considerable participation in the transition state of the rate-determining step and

**Table VIII**

| | $k \times 10^5$ sec$^{-1}$, 80% acetone-water, 100° | $k_{rel}$, 100° |
|---|---|---|
|  | | 0.2 |
| <br>**36**-OPNB | | 1 |
|  | | 0.3 |
| <br>*exo*-**33**-OPNB | 6.7 | 9 |
| <br>*exo*-**35**-OPNB | 2200 | 3000 |
| <br>*endo*-**35**-OPNB | 0.066 | 0.09 |

suggest that the bridged bishomotropylium ion intervenes as an intermediate. The greater participation observed in solvolysis is in line with expectations based on the greater charge delocalization evidenced by the nmr studies of the cation. The large barrier difference between the *exo*- and *endo*-**34**-OPNB compound (*ca.* 7.8 kcal/mol) indicates that the 1,4-bishomotropylium ion intermediate is considerably stabilized, presumably through aromaticity.

**Bishomotropylium Ions, Monohomotropylium Ion, and Tropylium Ion. A Comparative and Theoretical Treatment.** First we want to compare two independent methods for estimation of the charge distribution in the ions **12**, **15**, **21**, and **29**. The measure used throughout this work has been nmr–proton chemical shifts for the ions compared to those of proper model compounds. Another method which in the present work only has been used for **21** is the following method. The uv spectrum of the ion, in combination with the HMO method and using the correlation between the HMO excitation energy and the frequency of long wavelength absorption,[4] has been used to calculate the charge distribution.

In Table IX $\lambda_{max}$ and log $\epsilon$ values for **21** are collected together with those of the tropylium and the monohomotropylium ion. The monohomotropylium ion and **21** have values close to each other. The long wavelength absorbtion maximum in **21** appears at 303.4 nm. It has been demonstrated that, for a large number of carbonium ions, a reasonably good correlation exists between the HMO excitation energy and the frequency of long wavelength absorption. In order that **21** will fit such a correlation, its HMO[14] excitation energy must be approximately $1.50\beta_0$ which corresponds to $\beta_{2,9} = \beta_{5,7} = 0.70\beta_0$. Using this value in a HMO calculation with neglect of overlap, a charge distribution shown in Chart II was obtained. In total 0.50 unit of the positive charge is delocalized away from the allylic ion into the butadiene part of the ion. This is to be compared to 0.7 unit of positive charge estimated from the total deshielding of the "butadiene" protons in the nmr.

Table IX. Uv Data for Different Cations in $H_2SO_4$

| Cation | $\lambda_{max}$, nm | log $\epsilon$ |
|---|---|---|
| Tropylium[a] | 217 | 4.61 |
| | 273.5 | 3.63 |
| Monohomotropylium (**1**)[a] | 232.5 | 4.52 |
| | 313 | 3.48 |
| Bicyclo[4.3.1]deca-2,4,7-trienyl (**21**) | 231.2 | 4.34 |
| | 303.4 | 4.25 |

[a] Reference 4.

In **12** and **15** *ca.* 0.5 unit of positive charge has been donated into the butadiene systems according to the nmr data. This suggests a smaller $\beta_{2,9} = \beta_{5,7}$ in **12** and **15** than in **21** which is also indicated by a comparison of models of the two ions.

Other results from HMO calculations are shown in Chart II. The value for $\beta_{1,7} = 0.73\beta_0$ used for the monohomotropylium ion is the value that has been obtained from uv data in the same way as is described for **21** above.

The charge donated to the ethylene moiety in the 1,3-bishomotropylium ion as estimated from the nmr chemical shift differences is *ca.* 0.3 unit of positive charge. This value is to be compared to 0.24 unit of positive charge obtained through a HMO calculation using a $\beta' = 0.70\beta_0$ for each homointeraction.

The delocalization energies (DE) for the reference ions **6**, **7**, and **8** vary considerably but in an expected way. On the contrary, the DE of the bishomotropylium ions is almost the same for all three bishomotropylium ions if a $\beta' = 0.70\beta_0$ is used in the calculations. Furthermore, it is interesting to see that the gain in DE obtained when going from the heptatrienyl cation to the tropylium cations is almost the same as that gained in going from **6** to **3**. Thus, the estimated gain of DE through homointeractions is larger in bishomotropylium ions ($\beta' = 0.70\beta_0$) than for the monohomotropylium ion ($\beta_{1,7} = 0.73\beta_0$).

The charge distributions of the bishomotropylium ions (Chart II) deviate considerably from the reference compounds and are closer to the distribution of the tropylium ion. The same is true for the calculated bond orders.

As we have seen, the experimental and HMO method descriptions of the bishomotropylium ions are qualitatively very similar and even the two types of bishomotropylium ions observed are quite similar to each other.

## Experimental Section

**Preparation of Ions.** The stable carbonium ion solutions were prepared by rapidly mixing a $CD_2Cl_2$ precursor solution into a mixture of $FSO_3H$ and $SO_2ClF$ at low temperature under dry nitrogen gas. The apparatus for maintaining low temperature and that for generating the ion solution is shown in Figure 5. By passing a current through the nichrome wire, cold nitrogen gas is boiled out of the apparatus through the upper vacuum-jacketed dewar. A test tube containing 2-methylbutane is cooled by the cold nitrogen gas

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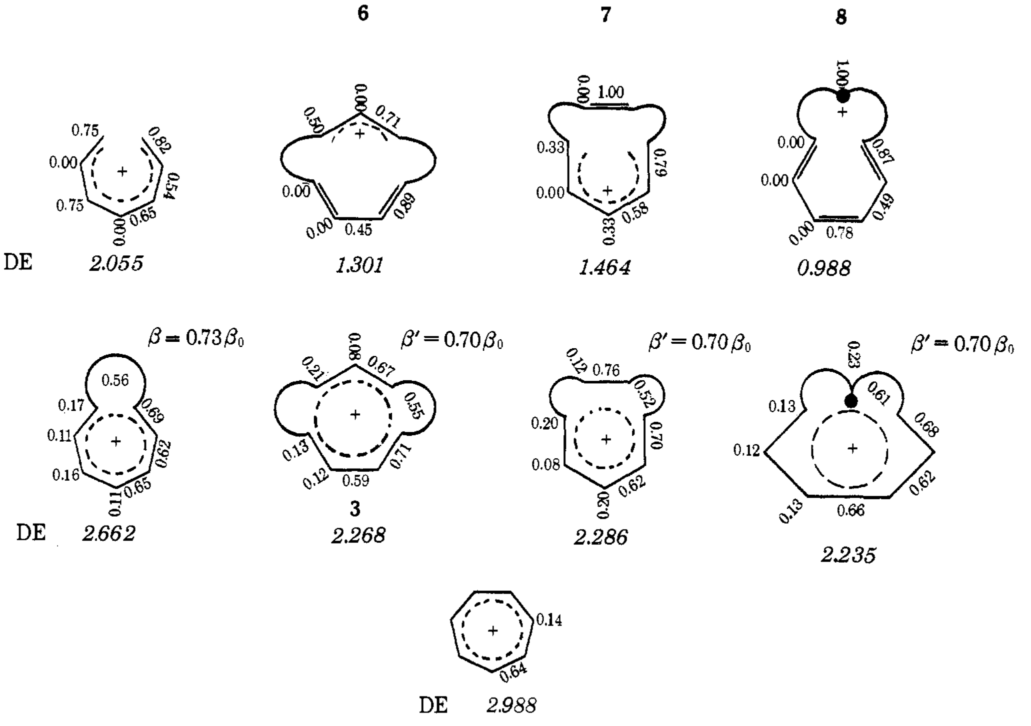
**Chart II**



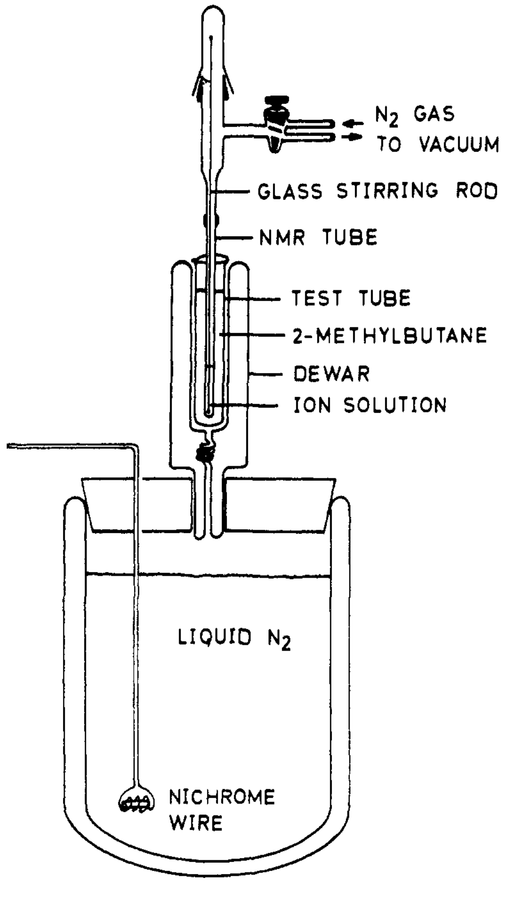


Figure 5. Cold temperature bath and ion-generating apparatus.

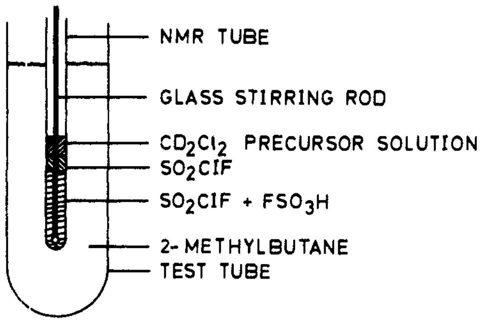


Figure 6. Scheme for preparing ion solutions.

and serves as a cold temperature bath. The bath temperature, as measured by a cold temperature thermometer, is controlled by varying the current through the nichrome wire. The ion solution is prepared as shown in Figure 6 in a nmr tube sealed to an apparatus which provides for either a dry nitrogen atmosphere or vacuum as needed. A mixture of $FSO_3H$-$SO_2ClF$ with a glass stirring rod already immersed is covered with a layer of neutral $SO_2ClF$ by condensing the gas into the cold tube. This layer serves to prevent premature contact between the acid solution and the room temperature precursor solution which is added on top of the $SO_2ClF$ layer by capillary pipet. The three layers are cooled to the desired temperature and then are mixed rapidly with the glass stirring rod. The apparatus is evacuated (followed by degassing if desired), and the nmr tube is sealed off and stored in liquid nitrogen.

**Nmr Spectra.** High-resolution nmr spectra at low temperature were obtained by tuning the Varian HA-100 nmr spectrometer at the desired temperature either using a sharp signal in the spectrum of the ion solution or using a homogeneity sample made up to approximate the properties of the ion solution. A solution of $FSO_3H$-$SO_2ClF$-$CD_2Cl_2$ has proven invaluable for tuning the instrument in preparation for studying dilute ion solutions. Temperatures were measured with a $CH_3OH$-$CHFCl_2$ solution which had been calibrated with a thermocouple.

**Preparation of 1-Methylbicyclo[4.3.0]nonatrienyl Cation from 9-Methyltricyclo[3.3.1.0$^{2,8}$]nona-3,6-dien-9-ol (9-Methyl-9-barbaralol).** Using the technique described above, 29.2 mg of 9-methyl-9-barbaralol[5d] dissolved in 140 mg of $CD_2Cl_2$ was mixed rapidly at *ca.* −135° into a *ca.* 0.4-ml solution of $FSO_3H$-$SO_2ClF$ (1:3 v/v). The ionic solution was observed in the nmr at −135°. The first ion observed was the degenerate 9-methyl-9-barbaralyl cation which, when the temperature was raised to −116°, rearranged with a first-order rate constant of $2.2 \times 10^{-3}$ sec$^{-1}$ to 1-methylbicyclo[4.3.0]-nonatrienyl cation, which at −50° rearranged to unidentified products.

**Preparation of 1-Methylbicyclo[4.3.0]nonatrienyl Cation from 2-Methylbicyclo[3.2.2]nona-3,6,8-trien-2-ol.**[5d] Using the technique described above, 12.6 mg of 2-methylbicyclo[3.2.2]nona-3,6,8-trien-2-ol[5d] dissolved in 110 mg of $CD_2Cl_2$ was mixed rapidly at −135° into a *ca.* 0.4-ml solution of $FSO_3H$–$SO_2ClF$ (1:3 v/v). The ionic solution was observed in the nmr at −135°. The first ion observed was the degenerate 9-methyl-9-barbaralyl cation, identical with the ion generated directly from 9-methyl-9-barbaralol. When the temperature was raised, the ion rearranged to 1-methylbicyclo[4.3.0]nonatrienyl cation, which at −50° rearranged to unidentified products.

**Preparation of Bicyclo[4.3.0]nonatrienyl Cation from Bicyclo[3.2.2]nona-3,6,8-trien-2-ol.**[15] Using the technique described above, 7.5 mg of bicyclo[3.2.2]nona-3,6,8-trien-2-ol[15] dissolved in 175 mg of $CD_2Cl_2$ was mixed rapidly at *ca.* −135° into a *ca.* 0.4-ml solution of $FSO_3H$–$SO_2ClF$ (1:4 v/v). The nmr at −135° showed the totally degenerate 9-barbaralyl cation, which quite rapidly at −125° rearranged with a first-order rate constant of $1.4 \times 10^{-3}$ $sec^{-1}$ to bicyclo[4.3.0]nonatrienyl cation, which at −90° reacted to give unidentified products with a first-order rate constant of $2.1 \times 10^{-3}$ $sec^{-1}$. Sometimes partial polymer formation was the result, when the $CD_2Cl_2$ solution was mixed into the superacid media.

**Preparation of Bicyclo[4.3.0]nonatrienyl Cation from *exo*-Tricyclo[4.3.0.0$^{2,9}$]nona-4,7-dien-3-ol.** Using the technique described above, 2.8 mg of *exo*-tricyclo[4.3.0.0$^{2,9}$]nona-4,7,-dien-3-ol in 261.0 mg of $CD_2Cl_2$ was mixed rapidly at −130° into a *ca.* 0.4-ml solution of $FSO_3H$–$SO_2ClF$ (1:4 v/v). The nmr spectrum of bicyclo[4.3.0]nonatrienyl cation was obtained in one scan on the HA-100 nmr spectrometer at −120°; however, time averaging was necessary in order to determine the coupling patterns. Higher quantities of alcohol led to immediate polymer formation. The ion reacted to give unidentified products at −90°.

**Preparation of Bicyclo[4.3.0]nonatrienyl Cation from *exo-cis*-Bicycol[4.3.0]nona-2,4,8-trien-7-ol (*cis*-8,9-Dihydroindenol).** Using the technique described above, 2.7 mg of *exo-cis*-bicyclo[4.3.0]nona-2,4,8-trien-7-ol dissolved in 153.6 mg of $CD_2Cl_2$ was mixed rapidly at −125° into a *ca.* 0.4-ml solution of $FSO_3H$–$SO_2ClF$ (1:4 v/v). Partial polymer formation was observed; however, the nmr spectrum matched that obtained from *exo*-tricyclo[4.3.0.0$^{2,9}$]nona-4,7-dien-3-ol and from rearrangement of barbaralyl cation.

**Preparation of Tricyclo[3.2.2.0$^{7,8}$]non-2-enyl Cation from Bicyclo[4.2.1]nona-2,4,7-triene.**[16] Using the technique described above, 46.3 mg of bicyclo[4.2.1]nona-2,4,7-triene dissolved in 173.0 mg of $CD_2Cl_2$ was mixed rapidly at −120° into *ca.* 0.4 ml of $FSO_3H$–$SO_2ClF$ (1:4 v/v) or $FSO_3D$–$SO_2ClF$. The nmr spectrum of tricyclo[3.2.2.0$^{7,8}$]non-2-enyl cation, obtained on the HA-100 nmr spectrometer at −90°, was clean with the exception of trace amounts of polymer in the $\tau$ 8.0–9.0 region. The ion reacted to give unidentified products at −70°. Quenching experiments were unsuccessful.

**Preparation of Bicyclo[4.3.1]deca-2,4,7-trienyl Cation from Bicyclo[4.2.2]deca-2,4,7,9-tetraene.**[17] Using the technique described above, 25.2 mg of bicyclo[4.2.2]deca-2,4,7,9-tetraene dissolved in 193.4 mg of $CD_2Cl_2$ was mixed rapidly at −128° into a *ca.* 0.4-ml solution of $FSO_3H$–$SO_2ClF$ (1:4 v/v). The nmr spectrum of the bicyclo[4.3.1]deca-2,4,7-trienyl cation was observed at temperatures varying from −110 to +20°. The spectrum was clean except for a trace amount of impurity at $\tau$ 9.70.

**Protonation of *cis*-Bicyclo[6.1.0]nona-2,4,6-triene.**[18] Using the technique described above, 16 mg of *cis*-bicyclo[6.1.0]nona-2,4,6-triene dissolved in *ca.* 100 mg of $CD_2Cl_2$ was mixed rapidly at −125° into a *ca.* 0.4-ml solution of $FSO_3H$–$SO_2ClF$ (1:4 v/v) or $FSO_3D$–$SO_2ClF$. Some polymer formation occurred which could be seen as broad absorptions in the nmr spectral base line. The ion was observed to decompose at *ca.* −90°.

**Protonation of Cycloocta-1,3,5-triene.** Using the technique described above, 15 mg of cycloocta-1,3,5-triene dissolved in *ca.* 100 mg of $CD_2Cl_2$ was mixed rapidly at −120° into a *ca.* 0.4-ml solution of $FSO_3H$–$SO_2ClF$ (1:3 v/v). Mostly polymer was obtained from the protonation; however, sufficient ion was produced to obtain an nmr spectrum using a time-averaging computer.

**Preparation of Cyclohexenyl Cation from Cyclohex-2-en-1-ol.** Using the technique described above, 10 mg of cyclohex-2-en-1-ol (Aldrich) dissolved in *ca.* 100 mg of $CD_2Cl_2$ was mixed rapidly at −120° into a *ca.* 0.4-ml solution of $FSO_3H$–$SO_2ClF$ (1:3 v/v). Cyclohexenyl cation was produced with little attendant polymer formation and gave a clean nmr spectrum.

**Tricyclo[4.3.0.0$^{2,9}$]nona-3,7-diene (Homosemibullvalene).** A solution of 2.0 g of KOH, 3 ml of 99% hydrazine hydrate (Matheson Coleman and Bell), and 0.8 g of bicyclo[4.2.1]nona-2,4,7-trien-9-one in 20 ml of diethylene glycol was refluxed for 2 hr. The bath temperature was allowed to climb to 210°. The solution was stirred at this point for 2 hr and the distillate was collected (bp 120–122°), poured into water, and extracted with pentane. The pentane layer was washed, dried, and concentrated. Distillation at reduced pressure afforded 0.6 g (86%) of homosemibullvalene, bp 55–57° (30 mm). Vpc showed this product to be 95% pure. An analytical sample was collected *via* preparative vpc using a 10% DEGS column (0.25 in., 2 m) at 90° with 10 psi He pressure (retention time 4.3 min): nmr spectrum ($CCl_4$, $\tau$) 4.0–5.0 (4 H, broad multiplet, olefinic), 7.00 (1 H, narrow multiplet, bridgehead), and 7.5–9.0 (5 H, broad multiplet, cyclopropyl and methylene); ir spectrum ($CCl_4$, $cm^{-1}$) 3030 (s), 2985 (w), 2920 (s), 2897 (s), 2840 (m), 1632 (w), 1601 (w), 1437 (w), 1358 (s), 1175 (m), 1036 (m), 937 (m), 920 (m), 903 (m), 869 (m), 839 (m), 701 (s), 681 (m), and 662 (s). The ir and nmr spectra as well as the vpc retention time of the hydrocarbon were identical with those of authentic homosemibullvalene prepared by G. Petrowski.[19]

***exo*-3-Hydroxytricyclo[4.3.0.0$^{2,9}$]nona-4,7-diene.** A solution of 2.0 g of homosemibullvalene and 15 mg of Rose Bengal in 100 ml of anhydrous methanol was bubbled with oxygen and irradiated with an $I_2$ lamp; the reaction was stopped after the absorption of oxygen ceased (calcd, 200 ml; obsd, 350 ml). The reaction mixture was reduced with 10 g of $NaBH_4$ at room temperature and then quenched with 100 ml of 20% KOH solution and extracted with ether. The ether layer was dried over $K_2CO_3$ and evaporation of the ether gave a viscous oil. The oil was chromatographed on a column of 100 ml of SilicaAR with 10% ether–pentane and was divided into 20 fractions of 150 ml each. After evaporation of the solvent, fractions 6, 7, and 8 gradually crystallized on standing at room temperature to give white needles. mp 87.0–88.0°. These were recrystallized from pentane to give 800 mg of white needles: mp 88.5–89.5°; the nmr spectrum is described in the text; ir spectrum ($CCl_4$, $cm^{-1}$) 3620 (m), 3601 (m), 3050 (s), 2915 (m), 2840 (w), 1586 (w), 1376 (m), 1341 (m), 1205 (m), 1038 (s), 997 (s), 970 (m), 956 (m), 942 (w), 919 (m), 910 (m), 892 (m), 853 (w), 727 (m), and 693 (s). The mass spectrum shows a parent peak at *m/e* 134 ($C_9H_{10}O^+$) and a base peak at *m/e* 43. *Anal.* Calcd for $C_9H_{10}O$: C, 80.56; H. 7.51. Found: C, 80.45; H, 7.56.

***exo*-8,9-Dihydroinden-1-ol.** 1-Chloro-8,9-dihydroindene[20] (5 g), prepared by the method of Katz and Garratt, was solvolyzed in a solution of 3 g of sodium bicarbonate in 650 ml of 60% aqueous acetone by heating for 30 min at 50°. The solution was cooled to room temperature and the bulk of the acetone was removed by rotary evaporation. The aqueous solution was then extracted with ether. The ether solution was washed with dilute potassium carbonate solution and dried over potassium carbonate yielding 3.7 g (86%) of the alcohol. No further purification was performed: nmr ($CCl_4$, $\tau$) 4.0–4.7 (6 H, broad multiplet olefinic), 5.42 (1 H, narrow multiplet), 6.38 (1 H, multiplet, bridgehead), 7.30 (1 H, multiplet bridgehead). *Anal.* Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 78.55; H, 7.58.

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