Protonation in Superacid Solution of Selected Exo-Methylene Polyunsaturated Alicyclics. Monomethyl 1,3-Bishomotropylium, Bicyclo[3.2.2]nonatrienyl, and Norbornadienyl Cations[1]

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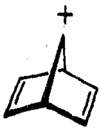
^{1}H NMR and ^{13}C NMR spectral studies of the protonation of 9-methylenebarbaralane (**7**), 5-methylenetricyclo[6.1.0.0^{4,9}]nona-2,6-diene (**8**), 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (**9**), 2-methylenebicyclo[3.2.2]nona-3,6,8-triene (**13**), 7-methylenequadricyclane (**18**), and 7-methylenenorbornadiene (**19**) in FSO_3H-SO_2ClF are reported. In the first three examples (isomeric $C_{10}H_{10}$ hydrocarbons), exposure to superacid at −135° gave exclusively the bishomoaromatic 1-methylbicyclo[4.3.0]nonatrienyl cation (**10**). In contrast, analogous treatment of **13** (a fourth $C_{10}H_{10}$) at −80° led cleanly to the stable 2-methylbicyclo[3.2.2]nonatrienyl cation (**14**), the first example of this heretofore elusive system. The stability and spectral features of **14** signify no obvious antibicycloaromatic character or other destabilization. With **18** and **19**, direct conversion to the 7-methylnorbornadienyl cation was observed. Spectral data concerning the ground-state polarization of the exo-methylene polyolefins are also presented and discussed.

Current interest in the electronic requirements for longicyclic stabilization[3] has prompted generation of several bi- and tricyclic carbocations under solvolytic conditions or in superacid solvents. The most intensely studied member of this group, the 7-norbornadienyl cation (**1**), is widely recognized to be highly stabilized.[4] Its distorted nature provides supportive evidence for the claim that homoaromatic interaction[5] is the major contributing factor to its "bicycloaromatic" character.[6] Various attempts to generate the bicyclo[3.2.2]nona-2,6,8-trienyl cation (**2**) have resulted instead in exclusive formation of the 9-barbaralyl cation (**3**).[6,7] The initial claim that this facile rearrangement arises because of inherent "antibicycloaromatic" destabilization in **2**[7a] has been refuted in favor of its access to a low-energy route leading to energetically favored **3**.[7d] The bicyclo[4.3.0]nonatrienyl (**4**) and bicyclo[4.3.1]deca-2,4,7-trienyl cations (**5**) enjoy charge delocalization of the bishomotropylium type.[7g,8] In fact, **4** is the ion to which **3** rearranges at temperatures of −125° and above.[7e] The bicyclo[4.2.1]nona-2,4,7-trienyl cation (**6**) is likewise very prone to skeletal isomerization with formation of dihydroindenyl cations,[9] despite its predicted "bicycloaromatic" nature.[3,10]



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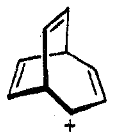

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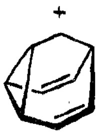

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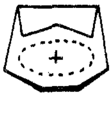

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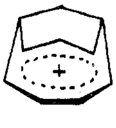

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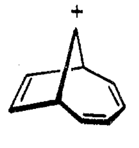

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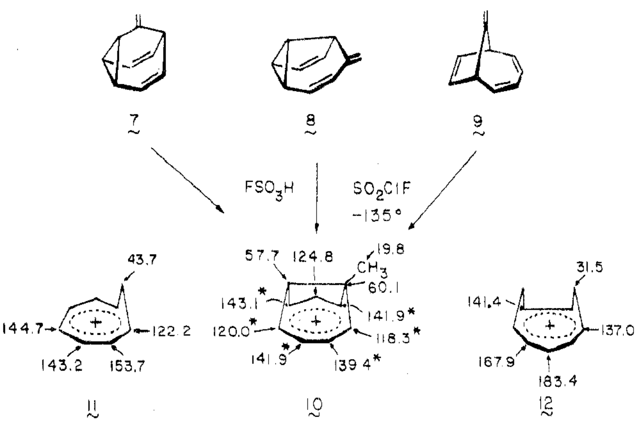
In recently published work,[11] one of our groups demonstrated that electrophilic addition to exocyclic methylene precursors of such cationic intermediates was a serviceable probe of possible longicyclic interactions. We have now investigated the protonation of several such alicyclic polyolefins under long-life conditions and wish to report the direct observation of the methyl-substituted carbocations. With but one exception, the 9-methyl-9-barbaralyl cation,[7g,12] no substituted derivatives of these ions have previously been investigated.

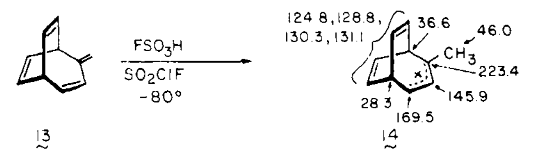
Results and Discussion

Protonation of $C_{10}H_{10}$ Isomers. When protonated in FSO_3H-SO_2ClF at −135°, hydrocarbons **7**,[11,13,14] **8**,[11,14] and **9**[9b,11,15] underwent ready conversion to the 1-methylbicyclo[4.3.0]nonatrienyl cation (**10**), the ^{1}H NMR spectral properties of which were identical with those previously reported by Winstein.[7g] The ^{13}C NMR spectrum of **10** was obtained at −90° using the Fourier transform technique and the carbon shifts (in parts per million relative to capillary TMS)[16] are shown alongside the structure. For comparison purposes, carbon shifts are also given for the mono- (**11**) and 1,3-bishomotropylium ions (**12**), recorded under similar conditions.[17] Of the seven "basal" carbons in **10**, four appear at rather low field (139–143 ppm) and the remaining three in more shielded environments (118–125 ppm). These shifts reveal that extensive charge delocalization is present in **10** such that the bishomoaromatic formalism suitably represents its electronic structure. However, even after account is taken of the rehybridization necessary for homointeraction, it is seen that the pair of methine bridges serve to reduce the level of delocalization as com-



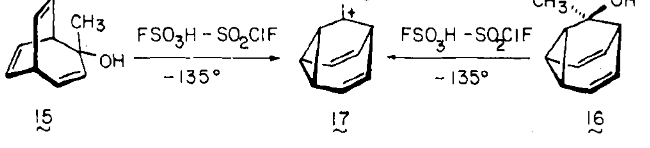
pared to **11**. In the latter case, the ring carbon shifts, exclusive of those due to C_1 and C_7, are more equally deshielded in accord with more equitable dispersal of the positive charge. The cyclic delocalization in **10** remains, however, at a higher level than in **12**, where the range of relevant carbon shifts is now greater than 40 ppm. That this ion possesses a ring current of lessened magnitude than that in **10** is also suggested by HMO calculations, which deduce that only 0.24 unit of positive charge is provided to the ethylenic moiety in **12** compared to 0.50 unit of positive charge donated away from the allylic part of **10** into its butadiene unit.[7g]

Treatment of 2-methylenebicyclo[3.2.2]nona-3,6,8-triene (**13**)[11,14] with FSO_3H-SO_2ClF at −135° gave a dark brown solution which was stable at −80° for days. ^1H NMR and ^{13}C NMR spectral analysis of this solution signaled the formation of **14**, the first example of the heretofore elusive[6,7] bicyclo[3.2.2]nonatrienyl class of cations. The charge distribution in **14**, as reflected by the chemical shifts of the peripheral protons and ring carbon atoms, is totally unlike that in **10** and **12** and as such can only be viewed as a *simple allylic ion*. Reference ions having allylic part structures have previously been described.[18] Of particular significance, the four olefinic protons on the two etheno bridges show normal olefinic character (Figure 1), as do the attendant carbon atoms. Consequently, the spectroscopic properties of **14** are uniquely concordant with the absence of interaction between the allylic cation moiety and the double bonds.



Furthermore, there is no evidence of inherent instability or unusual destabilization. Within narrow limits **14** gives every indication of being comparable to other allylic cations, notwithstanding the adverse inductive effect of the two additional double bonds. Cyclic charge delocalization involving one etheno bridge would make five of the carbon atoms carry a substantial part of the cationic character. However, this species would be electronically destabilized relative to the allylic moiety owing to its bishomocyclopentadienyl cation nature; as a result, it gains no importance. For similar reasons, antibicycloaromatic character is seen not to develop.

The observation that **7** and **13** do *not* undergo protonation to give the same cation contrasts significantly with the earlier finding that tertiary alcohols **15** and **16** are both ionized directly to the 9-methyl-9-barbaralyl ion (**17**) at −135° under otherwise comparable conditions.[7g,12] Rather, proton transfer to **13**, occurring as it does uniquely at the exo-methylene group, does not trigger homoallylic participation which would lead directly to **17**. Is methyl substitution at C_2 of the bicyclo[3.2.2]nonatrienyl cation as in **14** adequate to endow this cation with greater thermodynamic stability than its barbaralyl counterpart? This question is difficult to answer given only the present data. It would seem, however, that the direct conversion of **15** to **17** with resultant bypass of ion **14** arises by virtue of anchimeric assistance to C–O bond cleavage in the protonated alcohol. Since bond breaking is not involved in protonation reactions of exo-methylene compounds, energy requirements for cation formation are phenomenologically lessened and neighboring group participation is unnecessary. In principle therefore, protonation studies of exo-methylene derivatives are to be preferred to those involving tertiary methyl-substituted alcohols.



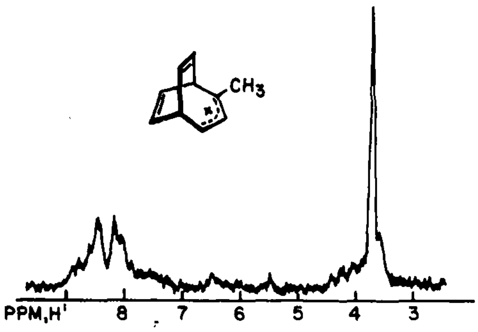
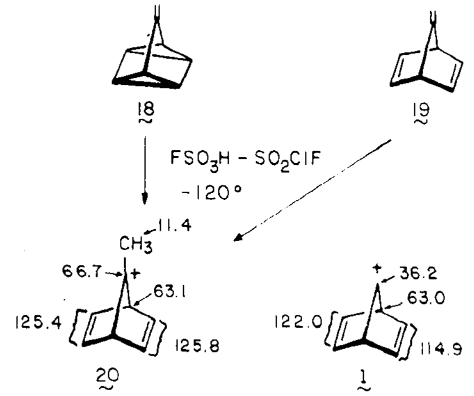


Figure 1. ^1H NMR spectrum (60 MHz) of the 2-methylbicyclo[3.2.0]nonatrienyl cation (**14**). The six olefinic protons appear downfield while the two bridgehead protons and the methyl group are seen at high field.

Methylenequadricyclane and Methylenenorbornadiene in Superacid. When **18**[11,19] and **19**[11,19] were carefully added to FSO_3H–SO_2ClF solutions at both −120 and −78°, solutions of the 7-methylnorbornadienyl cation (**20**) were formed. The ^1H NMR spectrum is as expected for this species,[20] showing a methyl singlet at δ 1.86 and multiplets for the bridgehead, olefinic, and homoaromatic protons at δ 5.18, 6.32, and 7.70, respectively. ^{13}C NMR data for the parent norbornadienyl cation have previously been reported (see **1**).[21] The ^{13}C NMR parameters evidenced by **20** compare favorably and point up an interesting additional feature. The presence of the methyl group at C_7 serves to make the signals due to C_2 and C_3 almost identical in their chemical shift with those of C_5 and C_6. This probably arises from the expectedly[22] lessened electronic demand at C_7, which in turn diminishes the need for homoaromatic stabilization and lessens conformational distortion.

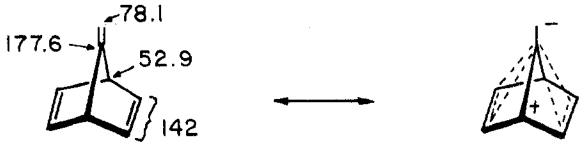


Ground-State Polarization of the Exo-Methylene Hydrocarbons. To infer longicyclic interaction in the neutral exo-methylene compounds would require that polarization of the exocyclic double bond operate in a direction which would electronically stabilize the particular molecule. In more classical systems such as fulvene (**21**) and heptafulvene (**22**), their differing reactivity characteristics have been ascribed to the existence of appreciable dipolar character which places opposite charge on the respective methylene groups. Access to cyclopentadienide and tropylium ion character underlies the otherwise energetically unrewarding charge separation.

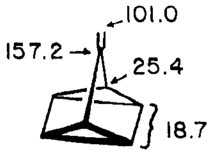
21a 21b

22a 22b

The excessive shielding of the methylene carbon in 7-methylenenorbornadiene (**19**) relative to 7-methylenequadricyclane (**18**) and 7-methylenenorbornane (**23**) has previously been commented upon.[11,19] The appearance of the methylene proton signal in **19** (δ 3.63) approximately 0.9 ppm to higher field than those in **18** and **23** is believed to point up the strong shielding arising from polarization which orients the negative terminus of the dipole away from the bicyclic framework. That structure **19b** contributes significantly to the ground state is suggested further by its dipole moment (0.71 D) and ^{13}C NMR parameters.[19] In particular, the magnitude of $\Delta\delta$ (>C=CH$_2$) for **19** (99.5 ppm) is enormously larger than those for **18** (56.2 ppm) and **23** (61 ppm).



19a 19b



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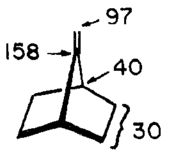

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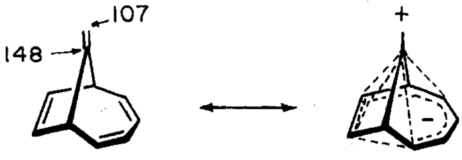
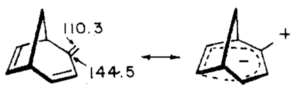
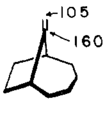
The ^{13}C NMR spectrum of **9**[15] was seen to exhibit a chemical shift difference for the methylene group of 41 ppm, a value far smaller than that for **19** and actually distinctly less than the average $\Delta\delta$ value of approximately 50–60 ppm seen for nonpolarized cyclic methylene compounds such as **23** and **25**. This can be accounted for in terms of contributions from zwitterion **9b**, an interpretation which compares favorably with that offered in explanation of the ^{13}C NMR data for 2-methylenebicyclo[3.2.1]-octa-3,6-diene (**24**, $\Delta\delta$ = 34.2 ppm, μ = 0.59 D).[23] By way of comparison, **26** exhibits a quite normal $\Delta\delta$ value of 47.8 ppm.[23b]



9a 9b



24a 24b



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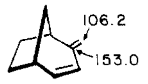

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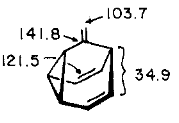
Judging from the ^{13}C NMR spectrum of 9-methylenebarbaralane (**7**), where a $\Delta\delta$ of 38.1 is seen, it would appear that the exocyclic double bond is in this instance also giving up a small portion of its charge density to the remainder of the π system.



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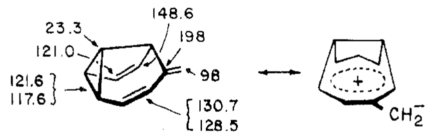

8a 8b

On this basis, the large $\Delta\delta$ for **8** (100 ppm) would appear to be a direct consequence of an inherent tendency for development of ground-state 1,4-bishomotropylium ion character. Interestingly, the substitution pattern in **8b** is not the same as that which is ultimately realized upon protonation.

Experimental Section

Materials. The preparation of the hydrocarbons has been previously described.

Proton Nuclear Magnetic Resonance Spectroscopy. ^{1}H NMR spectra were obtained using Varian Associates Model A56/60A and HA 100 NMR spectrometers equipped with variable-temperature probes. External tetramethylsilane (capillary) was used as reference.

Carbon-13 nuclear magnetic resonance spectra were obtained using a Varian Associates Model XL-100 nmr spectrometer equipped with a Fourier transform accessory, a spin decoupler, and a variable-temperature probe as previously described.[24]

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Registry No.—**7**, 37816-60-7; **8**, 38898-44-1; **9**, 38898-39-4; **10**, 53906-74-4; **13**, 38898-40-7; **14**, 53821-39-9; **18**, 38898-42-9; **19**, 37846-63-2; **20**, 19005-48-2.

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Benzidine Rearrangements. XIII. The Role of Reductive Scission. Reactions of *N,N'*-Dimethylhydrazobenzenes in Acid Solutions[1,2]

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N,N'-Dimethyl-*p*-hydrazoanisole (**6b**) in acetonitrile containing a small amount of hydrochloric acid underwent reductive scission to *N*-methyl-*p*-anisidine (**7b**, 70%). Other products formed were 2-amino-4-chloro-4',5-dimethoxy-*N*-methyldiphenylamine (the monodemethylated chloro-*o*-semidine, **10**, 5%), 2,7-dimethoxyphenazine (**9b**) and 3-chloro-2,7-dimethoxyphenazine (**11**) as a mixture which could not be separated quantitatively, and traces of 4,4'-dimethoxyazobenzene (**12b**). A radical was detected by ESR and is identified as the cation radical of 2,7-dimethoxy-5,10-dimethyl-5,10-dihydrophenazine (**18b**). Anodic oxidation of **6b**, its *o*-semidine (**8b**), and *N*-methyl-*p*-anisidine each gave rise to the same ESR spectrum, also attributed to **18b**$\cdot^+$. *N,N'*-Dimethyl-*p*-hydrazobiphenyl (**6d**) in acetonitrile–hydrochloric acid underwent reduction to *N*-methyl-*p*-aminobiphenyl (90%) along with other unidentified products, some of which contained chlorine. Molecular chlorine was not detected during reaction, and succinonitrile could not be found as a reaction product. A radical was detected during reaction under flow conditions only and its spectrum is attributed to **6d**$\cdot^+$ rather than to the analogous dihydrophenazine (**18d**$\cdot^+$). *N,N'*-Diethyl-*p*-hydrazoanisole (**16b**) in acetonitrile–hydrochloric acid gave rise to an ESR signal attributed to 2,7-dimethoxy-5,10-diethyl-5,10-dihydrophenazine (**20b**$\cdot^+$). In contrast the spectrum obtained with *N,N'*-diethyl-*p*-hydrazobiphenyl (**16d**) is attributed to **16d**$\cdot^+$. Our results suggest that the major reducing agent in reductive scission of **6b** is the first-formed rearrangement product, the *o*-semidine (**8b**), which is in turn oxidized successively to **18b**, **9b**, and **11**. Analogous reactions are believed to occur with **6d**. Oxidative demethylation of **6b** and **6d** also occurs. The results show, also, that the solvent is not a reducing agent in these reactions. The oxidizing agent is either the cation radical (e.g., **7b**$\cdot^+$) formed by homolytic scission of the diprotonated hydrazo compound or the protonated hydrazo compound itself.

In spite of the large effort that has been made by numerous research groups over the last few decades, the mechanism of the acid-catalyzed benzidine rearrangements remains unsolved. Of the several mechanisms that have been proposed, the polar transition state one from Ingold, Hughes, and Banthorpe remains the most attractive, although it is by no means universally accepted.[4-6] In recent years, indeed, new proposals for the participation of ring-protonated rather than N-protonated intermediates have been made,[7,8] although there is no direct experimental evidence in support of them as has been pointed out by Banthorpe[9] and by Shine.[10] Apart from the problem of explaining the benzidine rearrangements there are the problems also of accounting for two reactions which accompany benzidine rearrangements. One of these reactions is disproportionation. This accompanies all acid-catalyzed benzidine rearrangements, sometimes to a very small degree and sometimes to an extent far larger than rearrangement itself.[4] The mechanism of disproportionation is quite unknown,[4-6,10,11] and so is the way in which disproportionation and rearrangement may be linked together. Nevertheless, a large number of examples of disproportionation are known and the kinetic boundaries of the reaction have been established.[6,11] The second reaction which accompanies acid-catalyzed benzidine rearrangements is reductive scission, and this has been a much more fugitive and perplexing feature of the overall benzidine rearrangement problem. It is this feature with which we are now concerned.

Disproportionation of hydrazoaromatics leads to a 1:2 mole ratio of azoaromatic and scission amine (eq 1). Reductive scission leads to **3** and is detected when the ratio **3**:**2** obtained from a hydrazoaromatic is more than eq 1 will accommodate.

$$\underset{\mathbf{1}}{2\mathrm{ArNHNHAr}} \longrightarrow \underset{\mathbf{2}}{\mathrm{ArN{=}NAr}} + \underset{\mathbf{3}}{2\mathrm{ArNH_2}} \qquad (1)$$

This was first noticed by Carlin and Wich in their very careful analysis of the products of reaction of *p*-hydrazotoluene with acid,[12] in which it was found that the ratio of the amounts of *p*-toluidine and *p*-azotoluene was a little larger than attainable by eq 1. Carlin and Wich concluded that some of their *p*-hydrazotoluene had undergone reductive scission, and assumed that solvent ethanol was the reducing agent. They did not, however, search for the oxidation product, acetaldehyde, because of the very small amount that would have been formed. Hammond and Clovis[13] confirmed the finding[12] that a small excess of *p*-toluidine was formed, and were also unsuccessful in accounting for the reaction, although they concluded that a transient oxidizing agent of unknown structure was probably associated with the high yield of *p*-toluidine. At the same time the reducing agent responsible for the excess of *p*-toluidine was not designated.