The 7-Cycloheptatrienylmethyl/7-Norcaradienylmethyl Cation System[1]

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Reaction of 7-carbomethoxycycloheptatriene with either BCl_3 or BBr_3 gave a 1:1 complex in which the Lewis acid was complexed to the carbonyl oxygen. The low temperature p.m.r. and u.v. spectra of these zwitterions indicated that they existed almost entirely in the norcaradiene forms **10** and **14**, respectively. In contrast, reaction of *N,N*-dimethyl-1,3,5-cycloheptatriene-7-carboxamide with BCl_3 was found to result in the formation of a mixture of the cycloheptatriene **12** (65%) and norcaradiene **13** (35%). Comparison of the chemical shifts of the cyclopropyl proton resonances of **10** and **14** with model compounds showed that their positions were anomolous, the C_7 protons resonating at much higher and the C_1 and C_6 protons resonating at much lower field than expected and to account for this it is suggested that these norcaradienes are aromatic systems. Both **10** and **14** were thermally unstable and underwent an irreversible rearrangement to form the complex of methyl phenylacetate, the phenylmethylacylium cation and the appropriate counterion, $CH_3O\bar{B}Cl_3$ or $CH_3O\bar{B}Br_3$, respectively. The rate of these rearrangements and the product distribution was found to be dependent upon both the ratio of Lewis acid to ester used and the nature of the Lewis acid.

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La réaction du carbométhoxy-7 cycloheptatriène avec soit le BCl_3 soit le BBr_3 donne un complexe 1:1 dans lequel l'acide de Lewis est complexé à l'oxygène du carbonyle. Les spectres r.m.n. et u.v. à basse température de ces ions hermaphrodites indiquent qu'ils existent presque entièrement dans les formes respectives **10** et **14** du norcaradiène. Par opposition avec ces résultats, la réaction de la *N,N*-diméthylcycloheptatriène-1,3,5 carboxamide-7 avec BCl_3 conduit à la formation d'un mélange de cycloheptatriène **12** (65%) et de norcaradiène **13** (35%). La comparaison des déplacements chimiques des résonances des protons du cyclopropyle de **10** et **14** avec ceux de composés modèles montrent que leurs positions sont anormales; les protons C_7 présentent une résonance à des champs beaucoup plus haut et les protons en C_1 et C_6 présentent des résonances à des champs beaucoup plus bas que ceux attendus et pour tenir compte de ces résultats, on suggère que ces norcaradiènes sont des systèmes aromatiques. Les composés **10** et **14** sont thermiquement instables et subissent des réarrangements irréversibles pour former respectivement le complexe du phénylacétate de méthyle, le cation phénylméthylacylium et l'ion antagoniste approprié $CH_3O\bar{B}Cl_3$ ou $CH_3O\bar{B}Br_3$. On a trouvé que les vitesses de ces réarrangements et la distribution des produits dépendent à la fois du rapport d'acide de Lewis l'ester utilisé et de la nature de l'acide de Lewis. [Traduit par le journal]

Just as the monocyclic $(CH)_n{}^+$ cations, such as the cyclopropenium (1), cyclopentadienyl (2), and tropylium (3) cations, have been important in the development of the concept of aromaticity, so their monohomo counterparts, **1**, **2**, and **3**, have been of consequence in the evolution of the concepts of homoaromaticity (4). More recently, following the observation of a degenerate circumambulation of the cyclopropane around the periphery of the five-membered ring of **2** and its derivatives (5), cations **1**, **2**, and **3** have taken on a new significance in terms of the importance of orbital symmetry control of a molecular rearrangement. The degenerate rearrangement exhibited by **2**, which can be regarded as a 1,4 sigmatropic shift, takes place with a very high stereoselectivity in just that mode demanded by the dictates of orbital symmetry (6). The transition state for the rearrangement can be regarded as the cyclopentadienylmethyl cation **4**, in which, despite the overlap of the formally vacant p orbital on C_6 with the diene unit, a substantial fraction of the positive charge is localized on this carbon (5).

While comparable rearrangements of **1** and **3** have been considered from a theoretical viewpoint, as yet they have not been detected experimentally (7, 8). For example, with **3** and its

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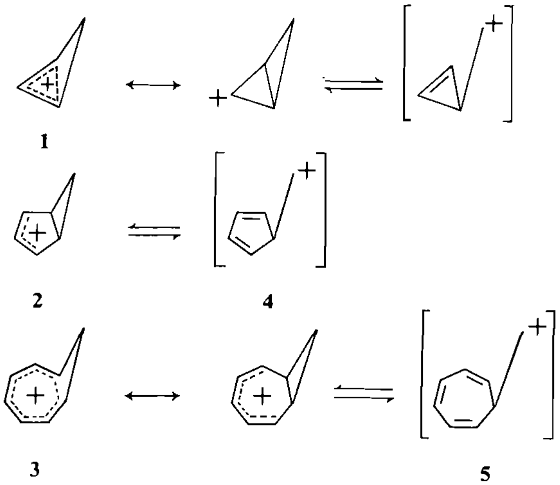
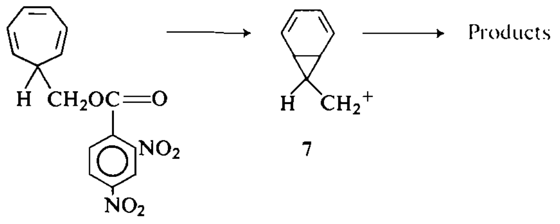


1 2 4 3 5

derivatives, competing reactions such as ring contraction or decomposition set in before the onset of any degenerate rearrangement. By analogy with the circumambulatory isomerization of **2**, a cycloheptatrienyl cation might well be expected to be involved in a degenerate rearrangement of **3**. However, as yet no consideration has been given to the importance of the structure and properties of a cation such as **5** in determining the possible occurrence of a degenerate isomerization of a homotropylium cation.

Information about the cycloheptatrienylcarbinyl cation, available at the outset of this work, derived very largely from the results of a solvolytic study of **6** reported by Sargent *et al.* (9), and a number of others (10).[3] It was suggested by Sargent that the cation involved in this solvolysis was **7** rather than **5** and that no products derived from the homotropylium cation, which could have been formed by rearrangement of **5**, could be detected. Factors affecting the position of the equilibrium between cycloheptatriene and norcaradiene valence tautomers, such as **5** and **7**, have recently been considered by both Hoffmann (11) and Günther (12) and it was pointed out that a carbonium ion center attached to C_7 should very effectively stabilize the bicyclic form.

To examine the question of the structure of **5** and whether degenerate migrations of C_8 of a homotropylium cation can occur or not, we have attempted the preparation of some 7-cycloheptatrienylmethyl cations. As previously it had been shown to be possible to prepare derivatives of **4** by reaction of a 5-acylcyclopentadiene with strong Lewis acids (12), the extension of these techniques to cycloheptatriene derivatives has been investigated. We report here on the preparation of derivatives of **5** and **7**, on the role of the C_7 substituents in determining the equilibrium position, on the thermal rearrangement of these cations, and on the possible aromatic nature of **7**. Recently in a series of papers Betz and Daub (14) have reported the preparation of some differently substituted derivatives of these cations and in some respects our results parallel their findings.



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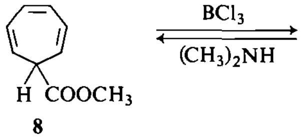
Results and Discussion

Treatment of a CD_2Cl_2 solution of 7-carbomethoxycycloheptatriene, **8**, with BCl_3 in CD_2Cl_2 at −60° resulted in the quantitative formation of a 1:1 complex of the ester and Lewis acid. The low temperature p.m.r. spectrum of the complex was independent of the ratio of the Lewis acid to ester used provided that there was at least a molar equivalent of the acid present. The complex was found to be stable at low temperatures and could be reacted with dimethylamine to regenerate **8** in high yield.



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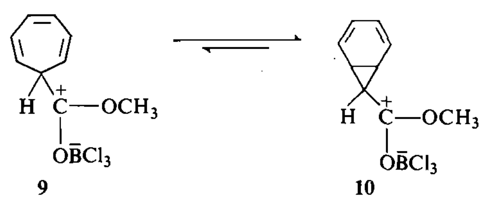

9 10

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[3] The acetolysis of (7-cycloheptatrienyl)methyl tosylate at 24° proceeds with a first-order rate constant of 5.2 ± 0.1 s^{-1}. The only product detected was styrene (>93% recovery). (Unpublished results of R. F. Childs and S. Winstein, University of California at Los Angeles, 1968.)

TABLE 1. Proton chemical shifts of cycloheptatrienes and zwitterions

Compound	Temperature (°C)	Proton chemical shifts*				
		H_1/H_6	H_2/H_5	H_3/H_4	H_7	Other
8	37	5.43	6.24	6.63	2.48	3.72
10	−40	3.41	6.14–6.54	6.14–6.54	1.60	4.14
14	−40	3.48	6.2–6.6	6.2–6.6	1.65	4.14
11	37	5.46	6.25	6.68	2.40	2.85, 2.95
12 + **13**	−40	4.81	6.35	6.52	3.20	3.43
15†	37	5.78	5.78	1.98–2.52	4.23	3.69
16†	−40	5.58	6.13	2.37	5.31	4.28

*In p.p.m. from TMS using $CHCl_3$ (taken as 7.30) as a secondary standard for the solutions of the zwitterions.
†Numbering schemes of cycloheptatriene maintained so as to facilitate comparison (ester grouping is then assumed to be attached to C_7).

The p.m.r. spectrum of the complex (Table 1 and Fig. 1) was completely consistent with the formation of a zwitterion in which the Lewis acid has reacted with the carbonyl oxygen of the ester. For example, the resonance attributable to the methoxy group is deshielded by the appropriate amount on reaction with BCl_3 and the signals due to the ring protons retain their plane of symmetry. It is also clear from the resonance position of the ring protons that the complex cannot be simply regarded as having the structure **9** but must be very largely in the norcaradiene form **10**. Thus the signals of the hydrogens in C_1, C_6, and C_7 all occur at considerably higher field than those of **8** and appear in similar regions to those encountered for other norcaradienes (14, 15).

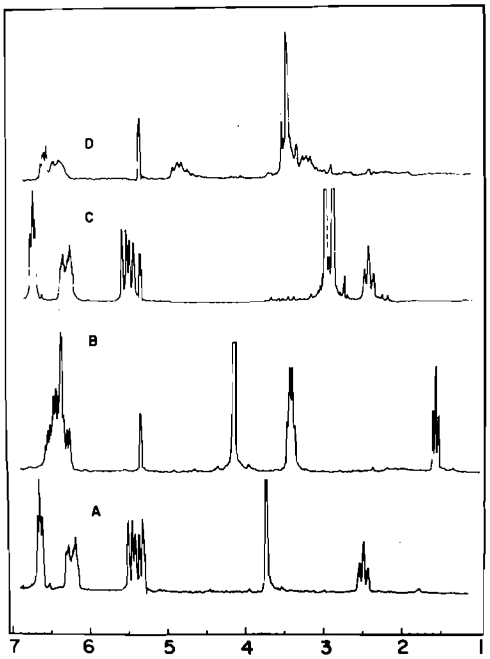
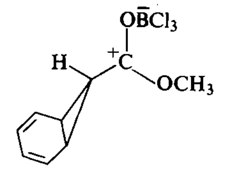


FIG. 1. Proton magnetic resonance spectra of cycloheptatrienes and their BCl_3 complexes in CD_2Cl_2. 7-Carbomethoxycycloheptatriene, **8**, spectrum *A*, and its BCl_3 complex **10**, spectrum *B*. *N*,*N*-Dimethylcycloheptatriene-7-carboxamide, **11**, spectrum *C*, and its BCl_3 complexes **12** and **13**, spectrum *D*. (Resonance at 5.3δ due to $CHDCl_2$.)

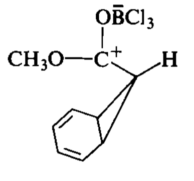
Ciganek (16) has shown the rate of interconversion of a substituted cycloheptatriene and norcaradiene to be slow enough at −110° to enable them to be observed as separate species by p.m.r. No additional p.m.r. signals could be detected when a CD_2Cl_2/CF_2ClH solution of the complex was cooled to −135°, indicating that the zwitterion exists predominantly in one form.

The low temperature u.v. spectrum of the complex in CH_2Cl_2 exhibited a single, fairly intense band at λ_{max} 284 (log ε 4.3). The position of this absorption is again indicative of the structure of the zwitterion being **10**, the absorption being at too long a wavelength to be attributable to a structure such as **9**.

Formally, two stereoisomers of **10** are possible in which the C_7 substituent can be either in the *exo* or *endo* position, **10***a*, and **10***b*, respectively. From the n.m.r. spectrum obtained, it is clear that only one of these two isomers is present. Comparison of the magnitude of the coupling constant between the protons on C_7 and C_1/C_6 ($J = 3.1$ Hz) with that reported for other cyclopropylcarbinyl cations, would indicate that the isomer formed is **10***a* (17). Stohrer and Daub have found a similar preference for the formation of the *exo* isomer and this has been attributed to unfavorable secondary interactions in the *endo* isomer, **10***b*, between the p orbital on C_7 and the diene molecular orbitals (18).

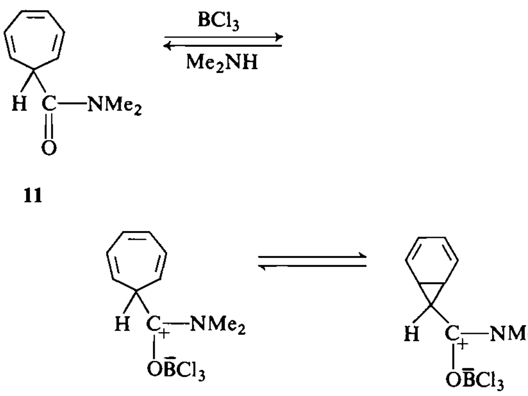


10a



10b

The dimethylamide **11** when reacted with BCl_3 in CD_2Cl_2, gave a zwitterion with a p.m.r. spectrum at −40° that indicated complexation had occurred with the carbonyl oxygen (19). However, the chemical shifts of the ring proton resonances (Table 1, Fig. 1) were now intermediate between those observed for **10** and **11**. It would appear that both **12** and **13** are being produced on reaction of **11** with BCl_3 and that these valence tautomers are interconverting sufficiently rapidly at −40° for their p.m.r. spectra to be averaged. The low solubility of these amide complexes prevented p.m.r. spectra from being obtained at sufficiently low temperatures to stop this interconversion. Reaction of **12** and **13** with dimethylamine regenerated **11** in high yield.

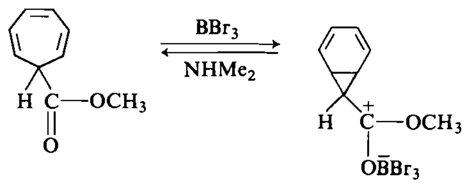


11

12 **13**

As a dimethylamino group is known to be more effective at stabilizing a positive charge than is a methoxy group (20), it would appear that the position of the equilibrium between the norcaradiene and cycloheptatriene forms of these zwitterions is dependent on the electron deficiency of C_8. The more electron deficient C_8 becomes, the greater is the amount of norcaradiene present.

Confirmation that the complex derived from **8** existed almost entirely in the norcaradiene form **10** was obtained by reaction of **8** with BBr_3. The zwitterion so obtained, which was stable at low temperatures and could be reacted with dimethylamine to give back **8**, exhibited a p.m.r spectrum that was directly comparable to that of **10**, suggesting that its structure can be regarded as **14**. Complexation of the oxygen atom of a carbonyl group with BBr_3 results in the accumulation of a larger fraction of the positive charge on the carbon atom of the group than similar BCl_3 complexes (13, 21). Thus replacement of the BCl_3 in the complexes derived from **8** by BBr_3 would be expected to result in an increase in the amount of norcaradiene present and unless the equilibrium mixture of **9** and **10** was almost completely in favor of **10** with BCl_3, a net upfield shift of C_1/C_6 and C_7 protons would occur. As no such change was observed (Table 1) it is clear that the complexes of **8** with both BCl_3 and BBr_3 must exist almost completely in the norcaradiene forms **10** and **14**, respectively.



8 **14**

To evaluate the position of the equilibrium between **12** and **13**, it is necessary to know the resonance positions of the signals of some of the protons in unaveraged spectra of **12** and **13**. An estimate for the position of the C_7 and C_1/C_6 proton resonances of **12** can be obtained by adding to the values found for the corresponding protons of the uncomplexed cycloheptatriene, the appropriate changes in chemical shifts observed on complexation of the model compound **15**.[4] As the zwitterion formed from reaction of **8** with BCl_3 has been shown to be in the norcaradiene form, the resonance positions of the C_1/C_6 and C_7 protons of **13** were taken to be those observed for **10**. On this basis the amount of norcaradiene **13** present in the equilibrium mixture of **12** and **13** was found to be 35%.

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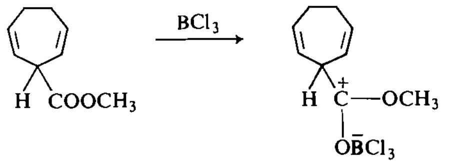
[4] Compound **15** was prepared by the addition of 4-phenyl-1,2,4-triazoline-3,5-dione to 7-carbomethoxycycloheptatriene, reduction of the so formed adduct with H_2/Pd and subsequent hydrolysis, oxidation, nitrogen elimination, and esterification. Experimental details will be given in a forthcoming full paper.

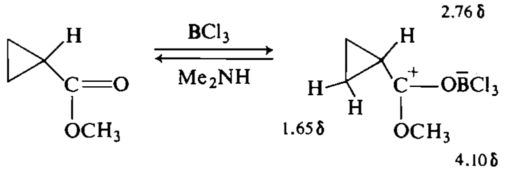


15 **16**

The Structure of Norcaradienes 10 and 14

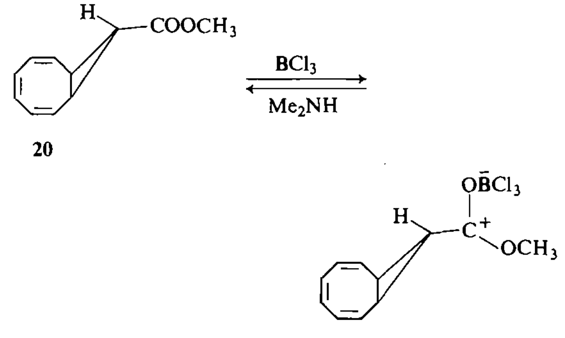
It is instructive to compare the position of the C_7 and C_1/C_6 proton resonances of **10** and **14** with that generally encountered for the comparable protons of cyclopropylcarbinyl cations. Frequently, the ring proton resonances of a protonated cyclopropyl ketone or carboxylic ester are observed as overlapping multiplets; however, typically the range over which the α-proton resonates is at lower field than that of the β-protons. For example the α-proton signal is usually found in the range 1.9 to 3.4 p.p.m. whereas the β-proton signal is found between 1.75 and 2.40 p.p.m. (25). This is quite the reverse of the situation encountered with the cyclopropyl proton resonances of **10** and **14**, in which the signal attributable to the α-proton is found to be more than 1.8 p.p.m. upfield from that of the β-protons. To ensure that these seemingly anomolous positions of the proton resonances of **10** (and **14**) cannot be attributed to the use of a boron halide rather than proton to induce the positive charge, complexes of some model cyclopropylcarbonyl compounds were prepared.

Reaction of the cyclopropyl ester **17** with BCl_3 in CD_2Cl_2 gave the zwitterion **18**. The p.m.r. spectrum of **18** exhibited a single, sharp, three proton resonance at 4.10 δ, a four proton signal at 1.65 δ, and a single proton resonance at 2.76 δ which is similar to that encountered for comparable protonated species and is quite different from that of **10** (17).



17 **18**

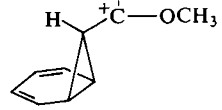
As the cyclopropane of **10** bears vinyl substituents, perhaps a better model for the expected chemical shifts of the protons is provided by the zwitterion **19**. This complex, which was readily formed by reaction **20** (22) with BCl_3 in CD_2Cl_2, was stable at temperatures below 0° and gave back **20** on reaction with dimethylamine. The p.m.r. spectrum of the complex was consistent with its structure being that shown for **19**. The cyclopropyl proton resonances of **19** occurred as an overlapping multiplet in the range 2.56 to 2.83 δ and individual α- and β-proton resonances could not be assigned. However, it is apparent that the vinyl groups on the β-carbons do deshield the β-protons to some extent.



20 **19**

While neither **18** nor **19** is a perfect model for **10**, they do suggest that the position of the cyclopropyl proton resonances of **10** cannot be adequately described by the effect of the adjacent positively charged group. Clearly the six-membered ring of **10** must be influencing the cyclopropyl protons in some different way to the effect of the eight-membered ring of **19**. The complexes **10** and **19** differ in two respects. Firstly the geometry of these two systems is expected to be different, the six-membered ring of **10** being almost flat (23) while the eight-membered ring of **19** would be expected to exist preferentially in a tub conformation with the cyclopropane ring being in a pseudo-equatorial position. Secondly, **10** and **19** differ in the number of π electrons in the unsaturated ring.

A major consequence of the first factor is that the cyclopropyl protons of **10** could be affected by the diamagnetic anisotropy of the carbon–carbon double bonds (24). However using the



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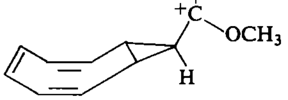
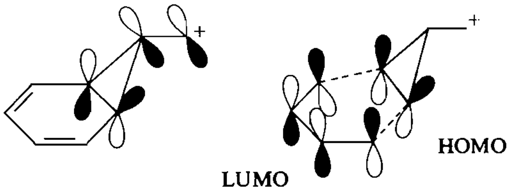


19

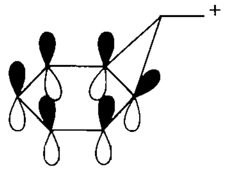
values of either Tillieu (25) or Pople (26) for the long range shielding of a double bond, the effect on the C_7 proton is found to be very small. With the data of Tillieu, the C_7 proton was found to be shielded by less than 0.1 p.p.m. and with that of Pople a deshielding of 0.1 p.p.m. was estimated. In either case the effect is very much smaller than the observed *ca.* 1 p.p.m. upfield shift of the resonance of this proton as compared to the corresponding proton of **19**. Similarly, the downfield position of the C_1/C_6 proton signals cannot be accounted for on this basis.

Both Hoffmann (11) and Günther (12) have suggested a way in which an electron withdrawing substituent on C_7 of a cycloheptatriene can affect the equilibrium between this and its norcaradiene valence tautomer. In essence, the lowest unoccupied molecular orbital of a π electron withdrawing substituent, and a carbonium ion is such a group 'par excellence', can interact with the antisymmetric, highest occupied Walsh molecular orbital of the cyclopropane ring of a norcaradiene, resulting in electron transfer from the three membered ring to its substituent. The net effect is that the C_1/C_6 antibonding component is weakened and this bond should become stronger.



The remaining symmetric Walsh orbital of the cyclopropane, which is bonding between C_1 and C_6 and contains two electrons, has the correct symmetry to interact with the lowest unoccupied orbital of the diene component of the norcaradiene (27). Moreover, the symmetry of the highest occupied molecular orbital of the diene is the same as the antisymmetric Walsh orbital from which electron transfer to the C_7 substituent has occurred. Such interactions should lead to a net stabilization of the norcaradiene structure.

It is of importance to note that this involvement of the diene with the cyclopropane results in an aromatic system. Viewed from the Hückel–Möbius viewpoint, in these norcaradienes there are formally six electrons contained in a Hückel array of atomic p orbitals (8, 28). One result of this should be that in a magnetic field, a diamagnetic ring current should be induced which would shield the *endo* C_7 proton and deshield the C_1 and C_6 bridgehead protons, *just as is observed with both 10 and 14* (4).



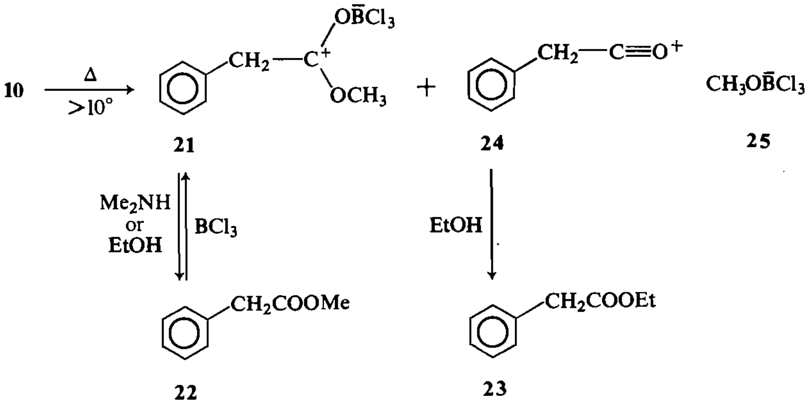
Hückel array: 6π electrons, aromatic.

We would suggest then that the norcaradienes **10** and **14** can be regarded as homoaromatic molecules and that to some degree such cyclic delocalization is required to account for their p.m.r. spectra. It is interesting that Sargent *et al.* (9) in their initial communication recognized that formulating the cyclopropylcarbinyl portion of these cations in the usual way imparted partial benzenoid character to the norcaradiene six-membered ring.

Thermal Rearrangement of Zwitterions

While the norcaradiene complexes were stable at low temperatures, on heating they underwent a ring contraction to give benzenoid compounds. Thus **10** at temperatures above 0° gave three products, one of which was identified as the methyl phenylacetate complex **21** by its p.m.r. spectrum (resonances at 4.19, 4.62, and 7.4 δ) and by the recovery of **22** when the solution containing the rearranged product was reacted with dimethylamine. Reaction of **22** with BCl_3 in CD_2Cl_2 gave **21**, with a p.m.r. spectrum identical to that obtained by the rearrangement of **10**.

The p.m.r. spectrum of the rearrangement products of **10** contained resonances over and above those attributable to **21** (Table 2). In particular, signals at 3.87, 4.16 δ and part of the multiplet of aromatic protons remained to be accounted for. Reaction of a solution of the rearranged products with ethanol gave rise to two esters which were isolated and characterized as **22** and the ethyl ester **23**. On this basis and by comparison with the results obtained with the BBr_3 complexes (*vide infra*), it is suggested that the additional products formed on the rearrangement of **10** are the acylium cation **24** and its counterion **25**. The methyl resonance of **25** occurs in a very similar region to that of the BCl_3 complex of methanol (3.95 δ). Comparable



anions to **25** involving BF_3 have been described (29).

While the formation of acylium cations from protonated carboxylic acid derivatives is well known (30), in this case **24** is not being formed directly from **21**. On heating a solution of **21**, prepared by reacting **22** with BCl_3, at 50° for 1 h, no formation of **24** and **25** could be detected by p.m.r. Thus **21**, **24**, and **25** must be primary products of the rearrangement of **10**.

The rate of rearrangement of **10** and the distribution of products was found to be dependent on the ratio of the Lewis acid to ester used. Increase in the ratio of BCl_3 to **8** resulted both in an increase in the rate of rearrangement of **10** and also an increase in the amount of the acylium cation **24**, formed (Tables 3 and 4).

TABLE 3. Rate constants for rearrangement of norcaradiene complexes*

Complex	Ester to Lewis acid ratio	k (s^{-1})	Temperature (°C)
10	1:1.1	4.6×10^{-5}	0
10	1:10	$>2.8 \times 10^{-4}$	0
14	1:2	2.7×10^{-4}	−43

*Rate constants obtained by following the reaction by p.m.r.

TABLE 4. Products of rearrangement of **10**

Ester to Lewis acid ratio	Temperature (°C)	Products*	
		%**21**	%**24**
1:0.9	20	93	7
1:2	20	77	23
1:8	20	42	58

*Product composition determined by integration of p.m.r. spectra.

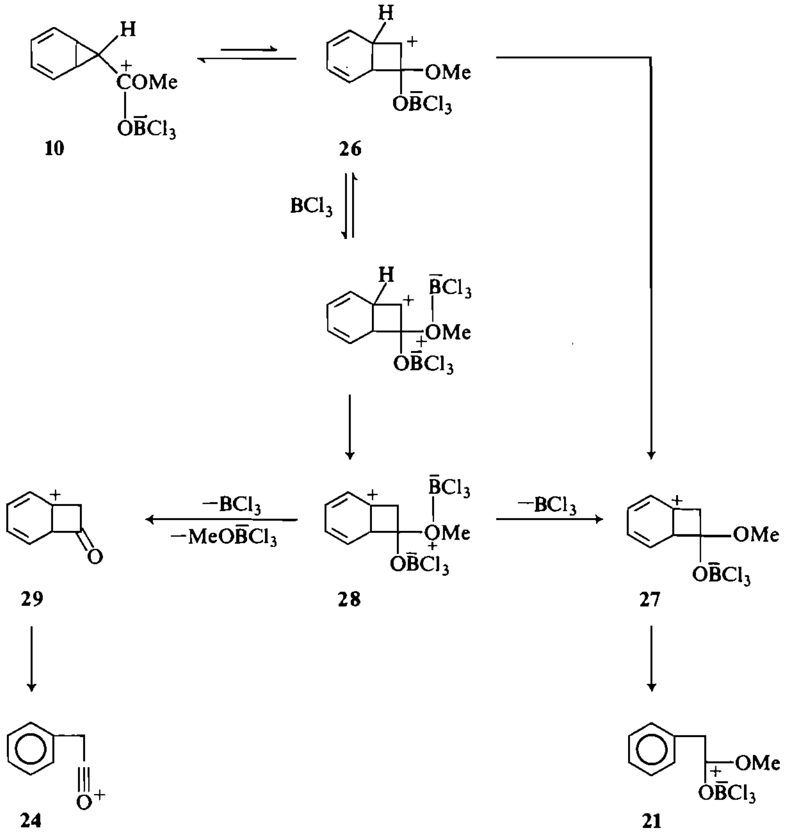
A possible reaction sequence which can account for these observations is shown in Scheme 1. In its simplest form the cyclobutyl cation **26**, which can be considered to be in equilibrium with **10** (31), undergoes a 1,2 hydride shift to give **27**. This hydride shift could well be the slow step in the rearrangement for two reasons. Firstly, the free energy difference between **26** and **27** might not be all that great in that the hexadienyl cation in **27** is forced to be twisted by the fused cyclobutane ring. Secondly, the rigidity of the system makes it difficult for the appropriate geometry for this hydride shift to be attained (32). Comparable cyclobutyl cations have been suggested to be involved in the ring contraction reactions of certain homotropylium cations (33).

TABLE 2. Proton chemical shift data of norcaradiene rearrangement products

Product	Chemical shift*		
	ArH	CH_2	OCH_3
21	7.2–7.6	4.71	4.30
30	7.2–7.6	4.75	4.48
24 + **25**	7.2–7.6	4.16	3.87
24 + $CH_3O\bar{B}Br_3$	7.2–7.6	4.27	3.96

*In p.p.m. from TMS using $CHCl_3$ as internal standard.

In the cyclobutyl cation **26**, the positive charge has been formally removed from the oxygen atoms and further reaction of the ether oxygen with additional BCl_3 could take place. The extra positive charge so induced in the system could result in an enhancement of the rate of the 1,2 hydride shift to give **28**, which could then give the acylium ion **24** or complex **21** as indicated. Comparable ring openings of



SCHEME 1

cyclobutanone cations such as **29** have been reported (34).

The BBr_3 complex **14** rearranged in an analogous manner to that described for **10** to give the BBr_3 complex of methylphenylacetate, **30**, **24** and $MeO\bar{B}Br_3$, however in this case, **30** was slowly converted into **24** and its counterion under the isomerization conditions. The formation of the acylium cation on rearrangement of **14** was confirmed by examination of its i.r. spectrum when an absorption at 2270 cm^{-1} was found. Acylium cations typically exhibit a carbonyl absorption in this region, the phenylmethylacylium cation with a SbF_6^- counterion being reported to absorb at 2279 cm^{-1} (30). The temperature at which this rearrangement of **14** occurred was found to be much lower than that required for **10**. With a two-fold excess of BBr_3, **14** rearranged at −43° with a half-life of 40 min. The amide complex mixture of **12** and **13** did not rearrange until heated to above +20°, the BCl_3 adduct of *N*,*N*-dimethylphenylacetamide being the major product. Clearly, both the amount of norcaradiene present in these tautomeric mixtures and also the ease of their rearrangement to aromatic systems are directly related to the ability of the C_8 substituents to stabilize the positive charge.

The existence of these complexes almost entirely in the norcaradiene form does not necessarily preclude the migration of C_8 around the periphery of the system. This could either occur in the norcaradiene form in a comparable manner to that found by Berson *et al.* for related systems (35) or by intervention of a homotropylium cation species as outlined at the start of this paper. However, at the temperatures at which the thermal ring contraction reaction occurred, no line broadening could be detected in the p.m.r. spectra of either **10** or **14**, indicating that no degenerate rearrangement was occurring at those temperatures with a sufficiently high rate to cause averaging of the p.m.r. signals.

Based on the characteristics of the analogous migrations observed with derivatives of **4** (13), one way to lower the energy barrier for the degenerate rearrangement of these norcaradienyl/cycloheptatrienyl methyl cations would be to decrease the ability of the C_8 substituents to stabilize positive charge. However, as has been shown, this would also result in an increase in the rate of the collapse of these cations to benzenoid systems. Indeed, in the limit, it is known that the rearrangement of the unsubstituted ion **7** to styrene under acetolysis conditions is sufficiently rapid to completely exclude either collapse of **7** with solvent to give cycloheptatriene derivatives or formation of the homotropylium ion and its subsequent products.[3] We are then in a dilemma, as changes made with these systems intended to enhance the rate of the degenerate migration, also increase the rate of their collapse to benzene derivatives and it would appear that we are unlikely to be able to devise a system in which the degenerate rearrangement can compete with this facile ring contraction. Taking this further, it would also seem that the production of a cycloheptatrienylmethyl cation as the first step of a degenerate rearrangement of a homotropylium cation would lead irreversibly to a benzenoid cation and not to the regeneration of the homotropylium cation. Perhaps, indeed, the often encountered ring contraction reactions of homotropylium cations involve just such a pathway.

Experimental

Proton magnetic resonance spectra were recorded on a Varian HA-100 spectrometer fitted with a variable temperature probe controlled by a Varian V-6040 temperature controller. The probe temperature was measured with a copper–constantan thermocouple and Leeds and Northrup 8692 potentiometer. The thermocouple was mounted at the appropriate depth in a nonrotating sample tube. Chemical shifts are referred to TMS or $CHCl_3$ (taken as 7.30 δ) for the zwitterions. Vapor phase chromatographic separations were performed with either an Aerograph A-90P3 instrument (preparative) using a 10 ft × $\frac{1}{4}$ in. column with 15% carbowax on chromosorb W, or with a Varian-Aerograph 204-1B instrument (analytical) using a 10 ft × $\frac{1}{8}$ in. column with 5% carbowax on chromosorb W. Ultraviolet spectra were measured with a Carry 14 spectrometer.

CD_2Cl_2, BCl_3, and BBr_3 were purified by distillation, stored over P_2O_5 and further distilled immediately before use. All manipulations were carried out on a vacuum line. $CHCl_3$ was washed with H_2O, H_2SO_4, 0.1 *N* $NaHCO_3$, and H_2O, dried over P_2O_5 and distilled twice. CF_2ClH was doubly distilled before use.

*7-Carbomethoxycycloheptatriene (**8**)*

7-cyanocycloheptatriene (10 g) was refluxed under N_2 in MeOH (150 ml) containing concentrated H_2SO_4 (30 g) for 30 h. The bulk of the solvent was removed *in vacuo* and the residue poured into H_2O (400 ml). The solution was extracted with petroleum ether (30–60°) (3 × 100 ml), the extract dried over $MgSO_4$, and the solvent removed *in vacuo* to give the crude ester. Distillation gave 9.0 g (80%) of **8** (b.p. 60° at 0.5 mm) containing a small amount of methyl phenylacetate (~2%). Pure material was obtained by preparative v.p.c. at a temperature below 130°.

*N,N-Dimethyl-1,3,5-cycloheptatriene-7-carboxamide (**11**)*

An excess of gaseous dimethylamine was added to a 10% solution of 7-chlorocarbonylcycloheptatriene in anhydrous ether. The dimethylamine hydrochloride formed was filtered off and the filtrate concentrated *in vacuo* to give a brown oil. This was chromatographed on neutral alumina eluting with ether to give a colorless solid. Recrystallization from pentane gave **11** as colorless crystals (m.p. 64.5°) which slowly became colored on standing. Nuclear magnetic resonance spectral data are given in Table 1.

*9-Carbomethoxybicyclo[6.1.0]nona-2,4,6-triene (**20**)*

Compound **20**, prepared by ester exchange of the corresponding ethyl ester, had properties identical to those previously reported (22).

Preparation of Complexes, General Procedure

All manipulations were carried out under high vacuum conditions. The starting organic compound (*ca.* 30 mg) was weighed into a small reaction vessel which contained a magnetic stirrer, was fitted with a sealed on n.m.r. tube, and could be attached to a vacuum line through a suitable high vacuum stopcock. The reactor was cooled and CD_2Cl_2 (1 ml) was transferred from a reservoir where it had been stored over P_2O_5. The organic material was dissolved and then a weighed amount of the appropriate Lewis acid was slowly distilled in while the solution was being stirred and maintained at −78°. On completion of the addition, the reactor was separated from the vacuum line and the appropriate amount of the solution transferred to the n.m.r. tube which was then sealed. During this transfer the apparatus was kept at −78°.

For the u.v. determinations, a similar technique was used except that a larger reaction vessel with an attached 0.2 cm u.v. cell was employed.

Infrared spectra of **24** and its counterion were obtained as Nujol mulls of the residue left after evaporation of the solvent *in vacuo*.

Quenching of Complexes

An excess of gaseous $(CH_3)_2NH$ was passed into the CD_2Cl_2 solution of the zwitterions at −78°. The resulting mixture was treated with water and the organic material was extracted three times with ether. The combined ether extracts were dried over $MgSO_4$ and the solvent removed *in vacuo* prior to analysis by g.l.p.c. and n.m.r. Hexamethylbenzene was used as an internal standard in some of the reactions in order to quantitatively measure the recovery of the starting compounds. The results of these quenches are shown in Table 5.

*Reaction of the Rearrangement Products of **10** with EtOH*

Ethanol (2 ml) was slowly added to a CD_2Cl_2 solution

TABLE 5. Products obtained on quenching zwitterions

Complex(es)	Quenching agent	Product (%recovery)*
10	Me_2NH	**8** (100%)
21 (58%) + **24** (42%)	Me_2NH	**22** (70%)
21 (60%) + **24** (40%)	EtOH	**22** (58%) + **23** (42%)
24 + $MeO\bar{B}Br_3$	EtOH	**22** (13%) + **23** (87%)
12 + **13**	Me_2NH	**11**†
19	Me_2NH	**20**†
16	Me_2NH	2-methoxycarbonyl-1,3-cycloheptatriene†

*Yield determined by comparison with internal hexamethylbenzene.
†No other products detected by p.m.r.

of the rearrangement products of **10** at −78°. Water (10 ml) was added, the mixture extracted with ether (3 × 5 ml), and the extract dried over $MgSO_4$. Evaporation of the ether gave an oil which was analyzed by both p.m.r. and also analytical g.l.p.c. using authentic samples of **22** and **23** for comparison purposes. The two esters, **22** and **23** in the quenched material were separated by preparative g.l.p.c. and the p.m.r. spectra of the isolated compounds were identical in all respects to that of the authentic samples.

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