CENTENARY LECTURE

Nonclassical Ions and Homoaromaticity

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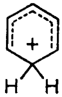
I am indeed honoured to be the Chemical Society's 1967 Centenary Lecturer and to participate in this Symposium on 'Some Aspects of Organic Reaction Mechanisms'.

1 Classical Carbonium Ions

While we will be dealing in the main with nonclassical ions, it may be helpful to begin with several examples of so-called classical carbonium ions. One example is the benzenonium ion (1), containing a 4π-electron 5-carbon system (4π5C). A typical transient carbonium ion is represented by (2), these being stabilized by α-methyl substitution and generally more so by α-phenyl substitution. In the case of the phenyl substituent, the effect of conjugative electron release by phenyl more than compensates for inductive electron removal. With two and three α-phenyl substituents, one comes to the well-known benzhydryl and triphenylmethyl cations (3) and (4), respectively. While these cations are sufficiently stable to be isolated as crystalline salts, they are still extremely reactive towards water as a nucleophile. Rough estimates of the first-order rate constants for collapse of these ions in aqueous solvents are 10^9 sec.$^{-1}$ for the benzhydryl cation and 10^5 sec.$^{-1}$ for the trityl cation.[1]



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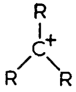

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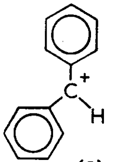

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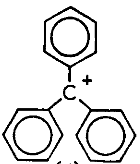

(4)

An extremely stable classical aromatic cation is the tropylium ion,[2] (5), representing a 6π7C system. From the work of Doering[2] and Eigen[3] one can estimate a value of 1 sec.$^{-1}$ for the first-order rate constant for collapse of

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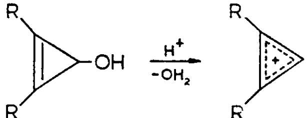
[1] A. Diaz and S. Winstein, unpublished work.

[2] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 352.

[3] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.

tropylium ion in water as solvent. Thus, as regards reactivity towards water, cations (3), (4), and (5) cover a range of 9 powers of 10. Cyclopropenyl cations,[4] *e.g.*, (7), are also extremely stable classical aromatic cations, these being available from acid treatment of the corresponding cyclopropenol (6).

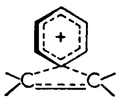
(5)



(6) (7)

2 Nonclassical Ions and Nonclassical Electron Delocalization

The classical cations mentioned above involve electron delocalization largely by way of familiar conjugation employing p π-orbital overlap. The illustrative nonclassical cations (8)—(13) involve nonclassical electron delocalization employing, at least in part, overlap of orbitals on carbon atoms between which there does not occur an additional σ-bond. Such orbital overlap is usually not π, but intermediate between σ and π.



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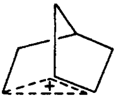

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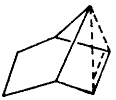

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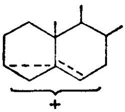

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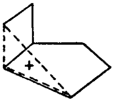

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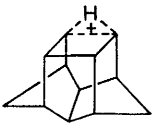

(13)

Cation (8) is the phenonium[5a] ion type, resulting from β-phenyl group participation in solvolysis. Nowadays, several representative phenonium ions have been directly viewed by n.m.r. in exceedingly non-nucleophilic media.[5b] Cations (10)—(12) contain the now familiar 2-electron 3-centre bonding arrangement (2π3C), the dotted lines representing partial bonds of bond order between 0 and 1. One of these, the norbornyl cation (10), was discussed in Sheffield at a Symposium on Stereochemistry by H. C. Brown. His paper has been published

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[4] R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, 1958, **80**, 5991; R. Breslow, H. Höver and H. W. Chang, *ibid.*, 1962, **84**, 3168; see, also, intervening papers.

[5] *a* D. J. Cram, *J. Amer. Chem. Soc.*, 1949, **71**, 3863; D. J. Cram and J. A. Thompson, *ibid.*, 1967, **89**, 6766, and intervening papers; *b* L. Eberson and S. Winstein, *J. Amer. Chem. Soc.*, 1965, **87**, 3506; G. A. Olah, E. Namanworth, M. B. Comisarow, and B. Ramsay, *ibid.*, 1967, **89**, 711, 5259.

in *Chem. in Britain,*[6] but there will not be time to comment on it in detail in my paper at this symposium. While the article in *Chem. in Britain* will undoubtedly prove to be of historical interest, I would recommend reading the actual older and more recent literature[7] for conclusive evidence that the secondary norborn-2-yl cation prefers a nonclassical structure. I plan to illustrate 2-electron 3-centre bonding more fully with the example of the norbornen-7-yl cation[8] (12), which has been studied, not only solvolytically, but also directly by n.m.r. Following this, I will hark back to the cholesteryl–*i*-cholesteryl ion (9), a homoallyl[9] ion, since it was this type of species which prompted the invention of the term 'homoconjugation'[9] and later on led us to the concept of homoaromaticity.[10] Then, a brief account of the now known homoaromatic species will be given, and, finally, we will go on to a description of current research on rearrangements of norbornadien-7-yl cations under conditions of long life.

3 Norbornen-7-yl and Norbornadien-7-yl Cations

The *anti*-norbornen-7-yl cation is best represented as in (12). In solvolytic work it arises by anchimerically assisted ionization of an *anti*-norbornen-7-yl derivative[8a,b] (14) or its tricyclic isomer[8c–e] (15) by the so-called π- and σ-routes, respectively. These ionizations are tremendously anchimerically accelerated, the acetolysis rate of *anti*-norbornen-7-yl toluene-*p*-sulphonate exceeding that of the saturated norborn-7-yl analogue (16) by a factor of 10^{11}. The hydrolysis rate of the tricyclic *p*-nitrobenzoate (15) in 90% aqueous acetone exceeds that of its bicyclic isomer (14) by a factor of 10^{12}, giving a rough value of 10^{16} for the factor by which the reactivity of (15) exceeds that of the *endo*-norbornyl analogue (17) without the cyclopropane ring.[8e]

Related to the norbornen-7-yl cation (12) is the norbornadien-7-yl species (19), first studied solvolytically by Winstein and Ordronneau.[11a] The reported 10^{14}

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[6] H. C. Brown, *Chem. in Britain*, 1966, **2**, 199.

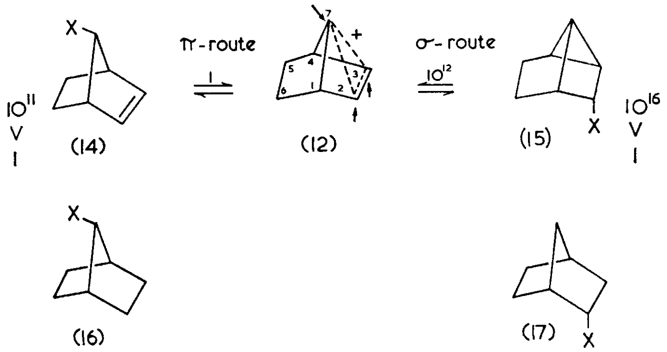
[7] *E.g.*, *a* S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, 1949, **71**, 2953; S. Winstein, *ibid.*, 1965, **87**, 381, and intervening papers; *b* E. J. Corey, J. Casanova, Jun., P. A. Vatakencherry, and R. Winter, *ibid.*, 1963, **85**, 169; S. G. Smith and J. P. Petrovitch, *Tetrahedron Letters*, 1964, 3363; *c* B. L. Murr, A. Nickon, T. D. Swartz and N. H. Werstiuk, *J. Amer. Chem. Soc.*, 1967, **89**, 1730; J. M. Jerkunica, S. Borcic and D. E. Sunko, *ibid.*, p. 1732; *d* E. J. Corey and R. S. Glass, *ibid.*, p. 2600; *e* W. J. le Nobel, B. L. Yates, and A. W. Scaplehorn, *ibid.*, p. 3751; *f* see also, P. G. Gassman and J. L. Marshall, *ibid.*, 1966, **88**, 2822; T. G. Traylor and C. L. Perrin, *ibid.*, p. 4934.

[8] *a* S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1955, **77**, 4183; S. Winstein and M. Shatavsky, *ibid.*, 1956, **78**, 592; *b* S. Winstein, A. L. Lewin, and K. C. Pande, *ibid.*, 1963, **85**, 2324; *c* M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, 1966, **88**, 3133, 3135; *d* J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Comm.*, 1967, 1202; *e* J. Lhomme, A. Diaz, and S. Winstein, unpublished work.

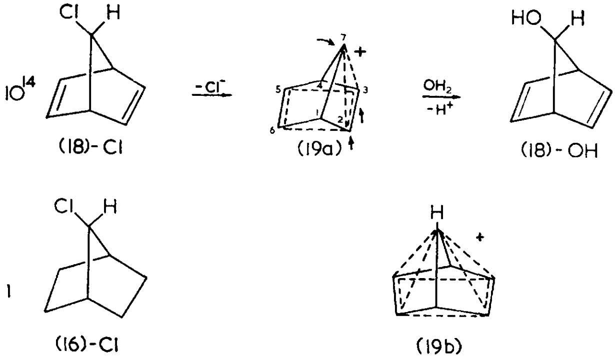
[9] *a* A. Winstein and R. Adams, *J. Amer. Chem. Soc.*, 1948, **70**, 838; *b* S. Winstein and A. H. Schlesinger, *ibid.*, p. 3528; *c* S. Winstein, H. M. Walborsky, and K. Schreiber, *ibid.*, 1950, **72**, 5795; *d* M. Simonetta and S. Winstein, *ibid.*, 1954, **76**, 18.

[10] *a* S. Winstein, *J. Amer. Chem. Soc.*, 1959, **81**, 6524; *b* S. Winstein and J. Sonnenberg, *ibid.*, 1961, **83**, 3244; *c* R. J. Piccolini and S. Winstein, *Tetrahedron*, 1963, **Suppl. 2**, 423; *d* S. Winstein, *Chem. Soc. Special Publ.* No. 21, 1967, 5.

[11] *a* S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.*, 1960, **82**, 2084; *b* R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, 1967, **89**, 6350; *c* M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, p. 6352; *d* M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, p. 6354.



factor by which the rate of solvolysis of norbornadien-7-yl chloride (18)-Cl exceeded that of the saturated norborn-7-yl analogue (16)-Cl set a world record for anchimeric acceleration.[11a] Of the possible nonclassical structures for the cation visualized by these authors, the unsymmetrical one represented by (19a) can be chosen on the basis of the n.m.r. spectrum first observed by Story and Saunders.[12] A symmetrical structure represented by (19b) was also considered,[11a] and this is clearly much less stable than (19a) (see below).



Ions (12) and (19a) react with nucleophiles at C-7 and C-2(C-3) with the C-7 :C-2 product ratio in kinetic control varying markedly with the nature of the nucleophile.[8,11] However, these reactions with nucleophiles such as H_2O, MeOH, Ph·CH_2·OH, MeO^-, Ph·CH_2O^-, CN^-, BH_4^-, and AlH_1^- are extremely highly stereospecific at both C-7 and C-2.[8,11]

Cation (12) may be generated by extraction of *anti*-norbornen-7-ol (14)-OH or the tricyclic ether (15)-OMe from CH_2Cl_2–CCl_4 into SO_2–SbF_5–FSO_3H at −50°.[8c] Similarly, cation (19a) is generated by extraction of norbornadien-7-ol

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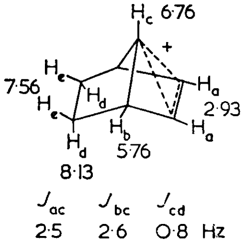
[12] *a* P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, 1962, **84**, 4876; *b* P. R. Story, *et al.*, *ibid.*, 1963, **85**, 3630.

(18)-OH into FSO_3H.[11b,c] The n.m.r. spectra of these ions (chemical shifts on the τ scale and coupling constants) are summarized in (20) and (21).

(20)



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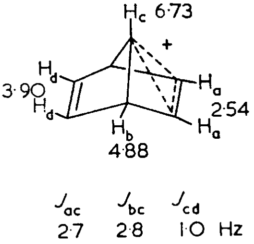
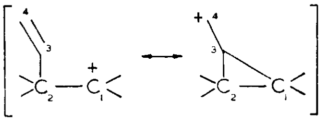


As regards chemical shifts and coupling constants, the norbornen-7-yl cation (12) and the norbornadien-7-yl cation (19a) are quite analogous. As regards the protons on the three-centre bonded carbon atoms, the H_c proton signal occurs at high field relative to that of the H_a protons in both ions. The features of the observed n.m.r. spectra are in good accord with a nonclassical structure allowing for the variation in charge distribution which results from hybridization changes at individual carbon atoms of a bridged ion. Actually, the bridging carbon atom in a bridged ion, *e.g.*, C-7 in (12), can be expected[10c] to have considerable tendency to rehybridize from sp^2 towards sp^3. Such rehybridization increases the C-7 Coulomb integral as well as C-7–C-2 and C-7–C-3 orbital overlap. This leads to net stabilization of the bridged ion, and these very features of rehybridization at C-7 tend to diminish the charge on this atom.[10c]

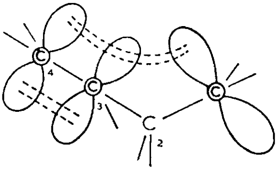
4 Homoconjugation and Homoaromaticity

It was the cholesteryl–*i*-cholesteryl cation (9) which prompted the invention of the terms 'homoallyl' and 'homoconjugation'.[9] The term homoallyl is made clearer with formulas (22a-c) which portray a carbonium ion with a β-olefinic group and show explicitly the overlapping atomic *p*-orbitals on the two olefinic carbon atoms C-3 and C-4 and the cationic carbon atom C-1. The idea behind the homoallyl designation is that a methylene group (C-2) is a poor insulator of conjugation if the proper rotational positions about the C-1–C-2 and C-2–C-3 bonds are assumed. With proper rotational positions, there is very appreciable 1,3-orbital overlap of a type intermediate between σ and π. Semiempirical molecular orbital calculations suggest substantial stabilization from electron delocalization.[9d,10c]

From the above point of view, one may say that a homoallyl cation is homoconjugatively stabilized. In conjugation there is electron delocalization over adjacent carbon atoms. Homoconjugation involves electron delocalization across intervening carbon atoms, a single intervening carbon atom in the case of cation (22).



(22a) (22b)



(22c)

While it is only a short jump from 'homoallyl' to 'homoaromatic' it took us several years to make this extrapolation.[10a] Just as for aromaticity, one criterion for homoaromaticity is increased stability or delocalization energy (DE) of a substrate due to cyclic electron delocalization, and another criterion is the ability of a substance to sustain an induced ring-current. The general idea of homoaromaticity and the nomenclature we have been employing are illustrated in Table 1 and Figure 1. As shown in Table 1, the HMO delocalization energy of the aromatic cyclopropenyl cation is considerably greater than that of an acyclic allyl cation. For a modified version of the cyclopropenyl cation involving interruption of the σ-backbone on one side so that the 1,3-resonance interval, namely β_1, is appreciable but less than β_0, the HMO delocalization energy is also greater than that of the allyl counterpart. Such a species may be termed homoaromatic. Interruption of the σ-backbone may involve removing the σ-bond entirely or interposition of one or more methylene groups. Analogous to the allyl–cyclopropenyl–homocyclopropenyl sequence is the heptatrienyl–tropylium–homotropylium sequence. In the case of the allyl anion, ring closure to the cyclopropenyl anion involves a decrease in the HMO delocalization energy. Thus, the cyclopropenyl anion may be termed antiaromatic in the terminology of Breslow[13a] and Dewar.[13b] Analogously, the monohomocyclopropenyl anion may be called antihomoaromatic. The monohomotropylium anion may be so designated, as well.

As indicated in Figure 1, the σ-skeleton of an aromatic species may be interrupted on one, two, or three sides, and thus one can conceive of bishomocyclopropenyl and trishomocyclopropenyl species as well as monohomo-. Also visualized in Figure 1 are a 1,3-bishomocyclopentadienide ion and a 1,2-bishomotropylium cation. It is important to note that designations such as mono-, bis-, and tri-homoaromatic are based on the number of sides where the σ-backbone is removed or lengthened and not on the number of methylene groups inserted on any particular side.

I will now present a partial survey or progress report on homoaromatic ions. First we shall review two-electron species, then six-electron systems and finally we shall consider nine- and ten-electron ions.

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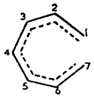
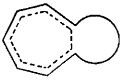
[13] *a* R. Breslow, *Chem. and Eng. News,* 1965, 90; *b* M. J. S. Dewar, *Adv. Chem. Phys.,* 1965 **8**, 65.

Table 1 *HMO Delocalization energies (β units) of some species*

No. of Electrons				
				 $\beta_1 = 0{\cdot}5\beta_0$
2	R^+	0·828	2·000 aromatic	1·372 homoaromatic
4	R^-	0·828	0·000 antiaromatic	0·372 antihomoaromatic
				 $\beta_1 = 0{\cdot}5\beta_0$
6	R^+	2·055	2·988	2·423 homoaromatic
8	R^-	2·055	2·098	1·938 antihomoaromatic

5 Mono- and Bis-homocyclopropenyl Cations

Considering homocyclopropenyl cations, we come first to ion (23) studied by Katz.[14] This pentamethylcyclobutenyl cation is an allylic species with an unusually important 1,3-interaction because the restraint of the four-membered ring makes for an unusually small 1,3-distance. The most important evidence for a serious 1,3-resonance integral in cation (23) is the u.v. spectrum. This shows an absorption band with λ_{max} 245 nm., intermediate between the values characteristic of allylic cations on the one hand and cyclopropenyl on the other. From the linear relation between the frequency of the long-wavelength u.v. absorption of a series of carbonium ions and the calculated HMO excitation energy an estimate of 0·33 β_0 is obtained for β_{13}. Thus, cation (23) may be appropriately called a monohomocyclopropenyl species.

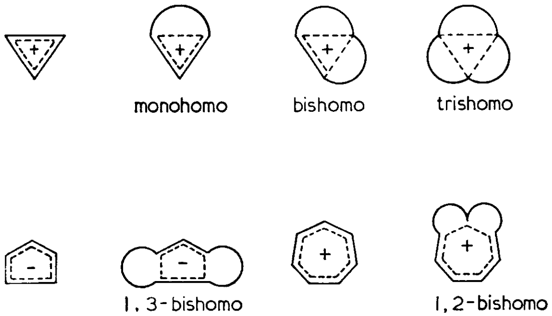


Figure 1 *Illustrative mono-, bis- and tris-homoaromatic species*

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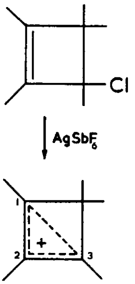
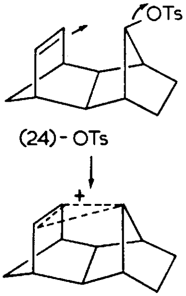
[14] T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, 1964, **86**, 1600.

Turning to possible examples of bishomocyclopropenyl species, we come to cation (12), discussed above, and (25), which we also investigated some years ago.[15] The latter cation is produced by ionization of (24)-OTs, this ester ionizing some 10^{11} times as rapidly as the saturated norborn-7-yl analogue as a result of tremendous anchimeric acceleration. According to our present terminology, both species (12) and (25) are bishomocyclopropenyl in type.



(23) λ_{max} 245 nm.

$\beta_{13} = 0{\cdot}33\,\beta_0$

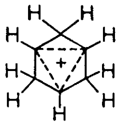


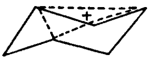
(24)-OTs

(25)

6 The Trishomocyclopropenyl Cation

The first recognized example of a trishomocyclopropenyl ion was the simple unsubstituted bicyclo[3,1,0]hex-3-yl cation (26).[10b,16] Atomic orbital overlap for the delocalized two-electron system is represented in (27). The evidence which led to the trishomocyclopropenyl formulation for the cationic intermediate from *cis*-bicyclo[3,1,0]hex-3-yl toluene-*p*-sulphonate (28)-OTs was the solvolytic behaviour of this substrate compared to that of the *trans*-epimer, (30)-OTs. For labelled substrates, 3-deuteriated alcohols and esters were originally employed, but more recently we have preferred to work with 6,6-dideuteriated specimens.[16c]





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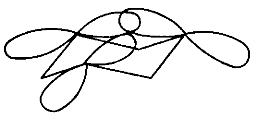

(27)

In acetolysis, the *cis*-toluene-*p*-sulphonate (28)-OTs displays a higher rate than does the *trans*-epimer. Also, it displays ion-pair return and a special salt effect. As product, it gives quantitatively the *cis*-acetate (28)-OAc with essentially complete retention of configuration (99%). The fraction of elimination product

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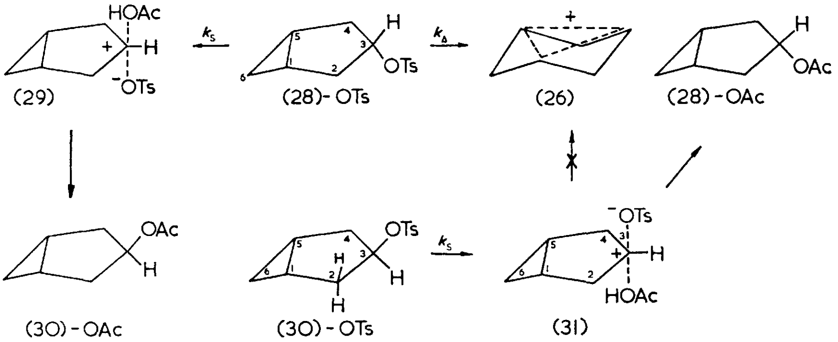
[15] S. Winstein and R. L. Hansen, *Tetrahedron Letters*, 1960, No. 25, 4.

[16] *a* S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, 1959, **81**, 6523; *b* S. Winstein and J. Sonnenberg, *ibid.*, 1961, **83**, 3235; *c* S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron*, 1966, **Suppl. 8 Part II**, 6211.

is negligible (0·3%), and no rearranged bicyclo[3,1,0]hex-2-yl or monocyclic products are observed. From dideuteriated (28)-OTs a product *cis*-acetate is observed with 1·35 ± 0·03 cyclopropane methylene protons, within experimental error of the value 1·33 predicted on the basis of the trishomocyclopropenyl intermediate.



In acetolysis of the *trans*-toluene-*p*-sulphonate (30)-OTs, no special salt effect is observed and a number of products is formed. Here, ionization without anchimeric assistance (k_S) leads to a classical cation (31). The latter may obviously collapse to inverted *cis*-acetate (28)-OAc. It may also set off a series of rearrangements *via* a 2 → 3 hydride shift leading to a bicyclo[3,1,0]hex-2-yl cation. The latter is related to a cyclohex-3-enyl cation by ring opening, which in turn can lead to an allylic cation by hydride shift. On this basis, one can understand the complex array of acetolysis products from *trans*-tosylate, three bicyclic acetates, two monocyclic acetates, a bicyclic olefin, and two monocyclic dienes.

As regards mechanism of solvolysis of *cis*-tosylate (28)-OTs, the essentially exclusive formation of *cis*-acetate with retention of configuration and complete equilibration of the label, the absence of elimination, the lack of rearrangement to bicyclo[3,1,0]hex-2-yl and monocyclic structures, and the special salt effect and ion-pair return phenomena provide a complete contrast with the behaviour of the *trans*-tosylate. All of the results are explicable on the basis of the trishomocyclopropenyl intermediate formed by anchimerically assisted ionization (k_Δ). Rate constant k_Δ evidently exceeds the rate constant for anchimerically unassisted solvolysis, k_S, by a factor of *ca.* 50 in acetolysis and by a somewhat smaller factor in aqueous acetone.

The most striking aspect of the solvolysis of *trans*-tosylate is the complete absence of equilibration of the deuterium label in the *cis*-acetate part of the product from (30)-$6D_2$-OTs (< 0·03 cyclopropane methylene proton). Evidently, leakage from the classical cation (31) to the nonclassical ion (26) competes unusually poorly with its other reactions.

7 Other Trishomocyclopropenyl Species

Since the first trishomocyclopropenyl cation was suggested, a number of other examples have been recognized. Evidence that alkyl-substituted examples (34) and (35) occur in acetolysis of neothujyl and neoisothujyl toluene-*p*-sulphonates has been published by Norin.[17] The very high relative reactivities of the 'cis' epimers and the unique nature of the products as regards stereochemistry and structure are in striking accord with the trishomocyclopropenyl formulation of the carbonium ions.

1-Methyl- and 1,5-dimethyl-bicyclo[3,1,0]hex-3-yl systems have been investigated by Yang-i Lin[18] at U.C.L.A. The high solvolytic reactivity of the *cis*-epimers relative to the *trans*, as well as the stereochemistry and deuterium scrambling in the product formation, are uniquely consistent with trishomocyclopropenyl type cations (32) and (33) in solvolysis of the *cis*-monomethyl- and dimethyl-bicyclo[3,1,0]hex-3-yl toluene-*p*-sulphonates.

As summarized in Table 2, kinetic product control from the methyl substituted cations (32) and (33) favours *tertiary* rather than *secondary* product. However each type of product is formed stereospecifically in the *cis*-configuration. With 6,6-dideuteriated monomethyl substituted *cis*-toluene-*p*-sulphonate, the *tertiary* solvolysis product contains two cyclopropane methylene protons, while the secondary product contains one, in exact accord with expectations from the trishomocyclopropenyl cation (32) (Table 3). On the other hand, the secondary product from the dideuteriated *trans*-toluene-*p*-sulphonate shows $< 0{\cdot}02$ cyclopropane methylene protons. Again, as with the unsubstituted *trans*-bicyclo[3,1,0]hex-3-yl toluene-*p*-sulphonate, there is no leakage to the nonclassical ion during solvolysis of the *trans*-toluene-*p*-sulphonate.

There is a somewhat more complicated example of a bicyclo[3,1,0]hex-3-yl nonclassical ion which is very instructive. This ion is generated by anchimerically assisted ionization of a substrate molecule (36)-OTs containing two cyclopropane rings and the tosylate group in the all-*cis* configuration.[19] Either one or both of the cyclopropane rings could conceivably become involved with the developing carbonium ion centre in ionization. Thus, one might conceive of either a three-centre trishomocyclopropenyl type of ion (37) or other ions such as the five-centre pentahomocyclopentadienyl cation (38). HMO calculations give a clear prediction in favour of the three centre cation and this is borne out by the experimental results starting with the deuterium-labelled toluene-*p*-sulphonate. The results show clearly that only one of the cyclopropane groups in (36)-OTs participates in ionization with formation of a specific three-centre trishomocyclopropenyl cation and this maintains its integrity until destroyed by nucleophilic attack.[19]

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[17] T. Norin, *Tetrahedron Letters*, 1964, 37.

[18] Y. Lin, Thesis, UCLA, 1967.

[19] S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Amer. Chem. Soc.*, 1964, **86**, 1867; P. Bruck, unpublished work.

Table 2 *Relative rates and products in solvolysis of some bicyclo*[3,1,0]*hex-3-yl systems*

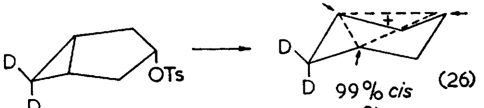
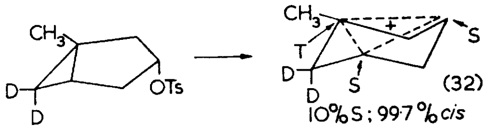
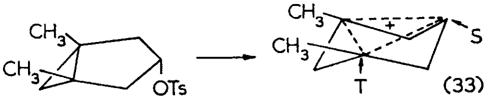
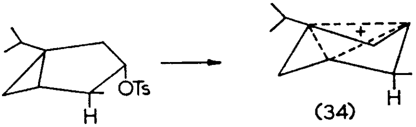
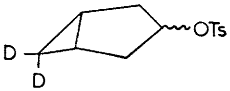
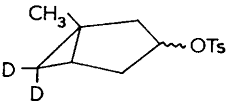
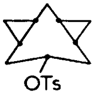
	Rel. Rate of cis ROTs	cis/trans *Rate Ratio*
 (28)-6D_2-OTs → (26) 99% *cis* 1% *trans*	1·0	40
 → (32) 10% S ; 99·7% *cis* 90% T ; 99·9% *cis*	5·1	97
 → (33) 3% S 97% T ; 99·9% *cis*	7·0	119
 → (34)	6·4	324
 → (35)	9·5	922

Table 3 *Deuterium scrambling in bicyclo*[3,1,0]*hex-3-yl systems*

System	*Cyclopropane methylene protons in* cis-*solvolysis product from:* cis-ROTs	trans-ROTs
	1·35	< 0·03
	T 2·03 S 1·00	S < 0·02


OTs

(36) - OTs

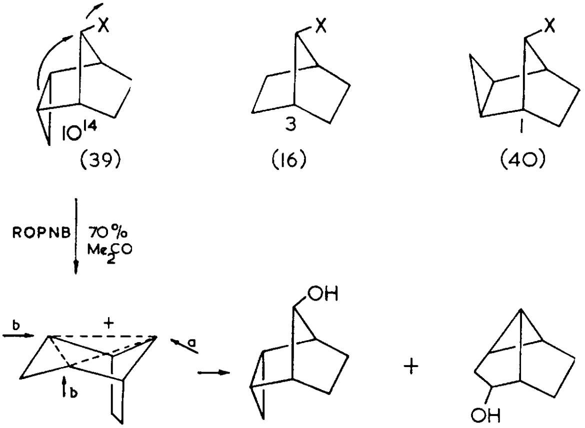

(37)


OTs

(36) - OTs


(38)

A very striking example of a trishomocyclopropenyl cation is the intermediate (41) in the very recently reported hydrolysis of (39)-*p*-nitrobenzoate, with an *endo*-fused cyclopropane group in an *anti*-norborn-7-yl system.[20] The isomeric ester (40) displays an unaccelerated rate, 'face-participation' by the cyclopropane group being poor. On the other hand, 'edge-participation' by the cyclopropane group in (39) is excellent, (39) being 10^{14} times as reactive as the isomeric analogue (40). Thus, solvolysis of (39) equals the world record for anchimeric acceleration. Consistent with the nonclassical trishomocyclopropenyl structure (41) for the intermediate cation is the high stereospecificity in the formation of the alcoholic products (39)-OH and (42)-OH.



Very recently, hydrolysis of the related system (43) with two cyclopropane groups has been described by Coates and Kirkpatrick.[21] This system is also

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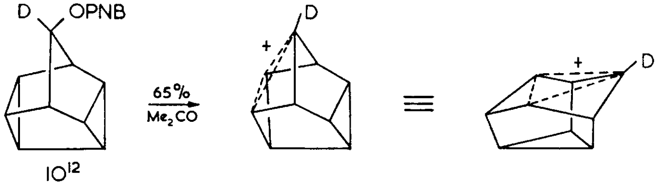
[20] *a* H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, 1967, **89**, 1953; *b* M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, p. 1954.

[21] R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, 1968, **90**, 4162.

extremely reactive, and deuterium labelling shows the intermediate to be the three-fold-degenerate ion (44). 'Bridge-flipping' does not occur in this species during solvolysis.



(43) (44)

8 Homotropylium Cations

Turning to six-electron homoaromatic systems, let us consider first the $C_8H_9^+$ ion as a possible monohomotropylium ion. This ion may be generated by protonation of cyclo-octatetraene (C_8H_8) in concentrated sulphuric acid.[22a,23a] Alternatively, it may be isolated as a solid salt,[22a] $C_8H_9^+SbCl_6^-$, by treatment of the hydrocarbon with HCl and $SbCl_5$. In this connection, it will be instructive to consider also the protonation of the cyclo-octatetraene transition-metal carbonyl complexes,[23a,24] $C_8H_8{\cdot}Mo(CO)_3$ and $C_8H_8{\cdot}Fe(CO)_3$. The different electronic requirements of transition-metal atoms in their complexes exert a corresponding control on the resulting structure and thus constitute a powerful tool in the study of homoaromaticity.[23a]

The observed n.m.r. spectra of the three cations from protonation of C_8H_8 and its two complexes in H_2SO_4 are summarized in formulae (45)—(47). For $C_8H_9^+$, the spectrum displays a 5:2:1:1 proton pattern, and especially striking is the large chemical shift (5·8 p.p.m.) between 'inside' and 'outside' H_b and H_a methylene protons. The n.m.r. spectrum of $C_8H_9Mo(CO)_3^+$ with a 5:2:1:1 proton pattern and a large chemical shift between H_b and H_a (3·5 p.p.m.), bears a striking resemblance to that of the parent $C_8H_9^+$ ion. In contrast, the n.m.r. spectrum of $C_8H_9FeCO_3^+$ displays a 1:4:2:2 proton pattern and the methylene H_b and H_a protons display nearly the same chemical shift.

The striking similarity between the n.m.r. spectra of the free ion and its $Mo(CO)_3$ complex and the contrast with that of the $Fe(CO)_3$ complex give one considerable insight into the electronic structure of each of the species. It seems evident that the $Fe(CO)_3$ complex may be represented to a fair approximation by the classical structure (47) which was preferred by Wilkinson[24b] and which is in accord with the $4\pi5C$ preference of the Fe atom. For the $Mo(CO)_3$ complex, the 6π electronic preference of Mo limits the choice of structure to cyclo-

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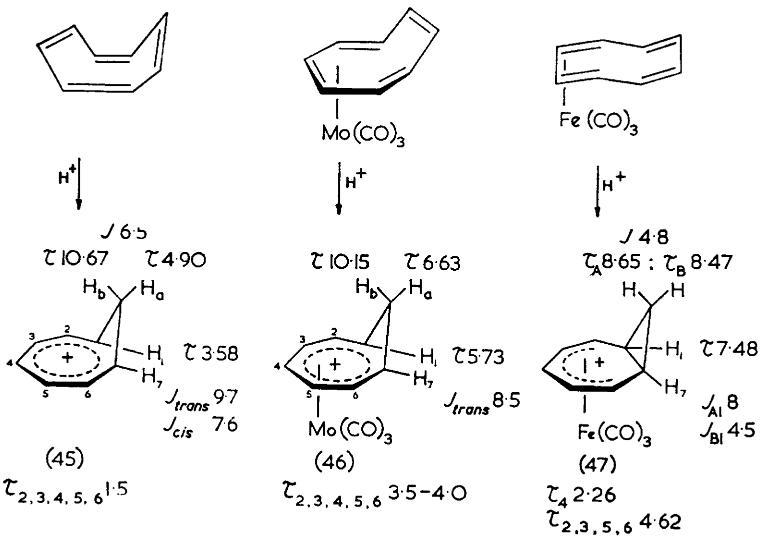
[22] *a* J. L. Rosenberg, J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, 1962, **84**, 2842; *b* C. E. Keller and R. Pettit, *ibid.*, 1966, **88**, 604; *c* J. D. Holmes and R. Pettit, *ibid.*, 1963, **85**, 2531.

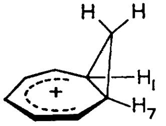
[23] *a* S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1965, **87**, 3267; *b* S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, 1966, **88**, 2047.

[24] *a* G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1961, **83**, 2966; *b* A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4821.

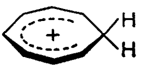
octatrienyl (49) or homotropylium (46). Only the latter is able to account for the large observed chemical shift between the 'inside' and 'outside' H_b and H_a protons. This assignment is strengthened by the analogy between the $Mo(CO)_3$ complex and the free ion. As regards the free $C_8H_9^+$ ion, the planar cyclooctatrienyl structure (49) may be excluded because this would have magnetically equivalent H_a and H_b methylene protons. For a classical structure (48) with a relatively fully formed cyclopropane ring we would expect the n.m.r. signal for $H_{1,7}$ to be at τ *ca.* 7 or above, a *gem* $J_{a,b}$ of 4·5—5 c./sec., and a *cis* $J_{a,1}$ (*ca.* 8 c./sec.) larger than the *trans* $J_{b,1}$ (*ca.* 4—5 c./sec.), by analogy with known cyclopropyl substituted carbonium ions and other cyclopropane derivatives. Such a structure is excluded by the extensive deshielding of the $H_{1,7}$ protons (τ 3·6) and the pattern of the available coupling constants, *trans* ($J_{b,1}$ 10 c./sec.) being larger than *cis* ($J_{a,1}$ 7·5 c./sec.). On the other hand, we should note that the n.m.r. spectrum of the $Fe(CO)_3$ complex is just what would be expected for a structure of this type with the cyclopropane electrons excluded from the delocalized electronic system.



(45) (46) (47)



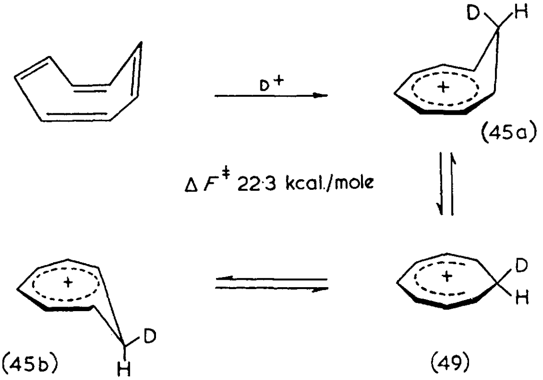
(48)



(49)

The available data are compelling in favour of nonclassical homotropylium structures for the free $C_8H_9^+$ ion and its $Mo(CO)_3$ complex. These involve 1,7-orbital overlap of a type intermediate between σ and π and the species may be called homoaromatic. Ring currents associated with these structures account in the main for the large chemical shift between the 'inside' and 'outside' methylene protons.[23b]

The large chemical shift between inside and outside methylene protons in the monohomotropylium ion makes it possible to measure the rate of ring inversion in this species. This in turn leads to a value for the free-energy difference between the classical cyclo-octatrienyl cation (49) and the preferred homoaromatic one.[23b] The rate measurement depends on the fact that there is considerable stereospecificity in the protonation of C_8H_8 in D_2SO_4 at lower temperatures (−15°), *ca.* 80% of the incoming deuterium being 'inside'.[23b] As observation of the solution of C_8H_8 in D_2SO_4 is continued, the intensities of the inside and outside proton signals approach the value corresponding to half a proton in each position, thus permitting the evaluation of a first-order rate constant for the (45a) → (45b) isomerization. This is $9{\cdot}8 \times 10^{-4}$ sec.$^{-1}$ at *ca.* 37° and $6{\cdot}1 \times 10^{-4}$ sec.$^{-1}$ at *ca.* 32°, corresponding to a $\Delta F^{\ddagger}$ of 22·3 kcal/mole. If the equilibration is visualized as proceeding by ring inversion through a planar form, that of the classical cyclo-octatrienyl cation (49), then the free energy of (49) is shown to be 22·3 kcal./mole higher than that of the homoaromatic monohomotropylium ion.[23b]



Further insight into the electronic structure of the homotropylium ion is provided by its u.v. spectrum.[23b] The two λ_{max} values, 232·5 nm. (log ϵ 4·52) and 313 nm. (log ϵ 3·48) are at somewhat higher wavelengths than those for tropylium ion,[25] 217 nm. (log ϵ 4·61) and 273·5 nm. (log ϵ 3·63). However, it is very illuminating that the λ_{max} for u.v. absorption of the homotropylium ion

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[25] H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, 1957, **79**, 4557.

resembles more closely the value for tropylium ion, with an HMO excitation energy (E_T) of 1·692β, than the value to be expected for a classical planar cyclooctatrienyl species (49) with negligible 1,7-interaction. The HMO excitation energy for such an ion is 0·765β, and Deno[26] has reported λ_{max} at 470 nm. for an actual heptatrienyl cation which could be taken as a model for (49).

An estimate can be made of the value of the 1,7-resonance integral (β_{17}) in the homotropylium ion from the position of the long-wavelength u.v. absorption maximum at 313 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 homotropylium fit such a correlation its HMO excitation energy must be approximately 1·45 β_0 which corresponds to β_{17} = 0·73 β_0. With this β_{17}, the HMO treatment leads to a bond order of 0·56 for the 1,7-bond and values of 0·69, 0·62, and 0·65 for the π-electron 1,2-, 2,3-, and 3,4-bond orders, respectively. These values are to be compared with a π-bond order of 0·64 for the bonds in tropylium ion.

A tropylium-like electronic description of the monohomotropylium ion with a relatively even electron distribution around the C-1–C-7 carbon atom framework, together with a ring current model using a tropylium-like 1·6 Å ring radius and a six-electron induced ring current, accounts very well for the general features of the n.m.r. spectrum of (45). Thus, the chemical shift of protons H_{2-6} in (45) is very similar to the value for H_{1-7} in tropylium ion. Such a model also accounts very well for the chemical shift between 'inside' and 'outside' C-8 protons.[23b]

More direct evidence regarding the aromatic ring current in monohomotropylium ion comes from the volume diamagnetic susceptibility of this species measured by Dauben.[27] As shown in Table 4, the χ_M value for benzene shows an exaltation, Λ, of 13·7 compared to the nonaromatic calculated value, while tropylium ion shows a Λ of 16·0.[27b] It is striking that the Λ for monohomotropylium ion is larger than that of tropylium ion. If the usual exaltation (Λ = 5·2) associated with a cyclopropane ring is subtracted from that of monohomotropylium ion (Λ =20), the resultant Λ, namely 15, is only slightly less than the tropylium exaltation.

Homotropylium ions with 'inside' and 'outside' 8-chloro-substituents have been reported recently by Huisgen[28] and his co-workers. These ions have a chemical shift (Δ) between inside and outside H_b and H_a protons identical to that for the unsubstituted homotropylium ion. Further, the rate of equilibration of the epimer 8-chloro-ions[28] is essentially the same as for the unsubstituted analogue (45).

It is interesting to enquire how far one may proceed with substituents in the monohomotropylium ion without converting the structure into a classical one. Judging by the chemical shift (Δ) between inside and outside H_b and H_a protons

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[26] N. C. Deno, *et al.*, *J. Amer. Chem. Soc.*, 1965, **87**, 2153.

[27] *a* H. J. Dauben, jun., J. D. Wilson, and J. L. Laity, *J. Amer. Chem. Soc.*, 1968, **90**, 811; *b* J. Laity, unpublished work; *c* H. J. Dauben, J. Laity, and S. Winstein, unpublished work.

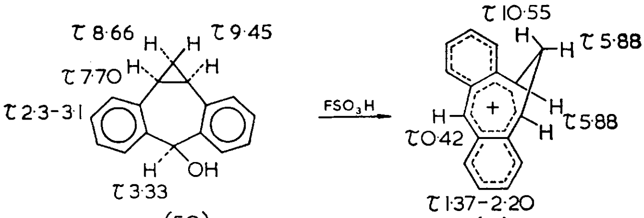
[28] G. Boche, W. Hechtl, H. Huber, and R. Huisgen, *J. Amer. Chem. Soc.*, 1967, **89**, 3344.

and other features of the n.m.r. spectra, 1-methyl-, 1-phenyl-, and 2-hydroxy-monohomotropylium ions are still decidedly homoaromatic.[22b,c] Still more instructive is the 1-hydroxymonohomotropylium ion from protonation of cyclo-octatrienone.[29] Even this species is decidedly homoaromatic. As in the case of the unsubstituted homotropylium ion, diamagnetic susceptibilities confirm the homoaromatic character of the 1-methyl-, 1-phenyl-, and 1-hydroxy-homotropylium species (Table 4).[27c]

It seemed to us that a homo-counterpart of the 2,3,6,7-dibenzotropylium ion would be instructive from the viewpoint of homoaromaticity since the two benzene rings dampen considerably the gain in ΔE_π due to cyclic electron delocalization attending formation of a tropylium species. Such a dibenzo-homotropylium ion (51) has in fact been prepared[30] from the covalent alcohol precursor (50). The n.m.r. spectrum of the ion, especially the high Δ value at the methylene group, shows this species to be homoaromatic. Very recently, a monobenzohomotropylium ion has also been reported.[31]

9 A Bishomocyclopentadienide Anion

Continuing the six-electron homoaromatic theme, but switching to homocyclopentadienide ions, we shall now consider a 1,3-bishomocyclopentadienide species, namely (54). The possibility that this ion is an intermediate in some base-catalysed deuterium exchanges was suggested by the work of Brown and Occolowitz[32a] on the relative rates of deuterium exchange of the bicyclic diene (52) and monoene (53). In dimethyl sulphoxide (DMSO) containing $KOBu^t$, diene (52) is more reactive in exchange than monoene (53) by a factor of $10^{4 \cdot 5}$. This increased reactivity of the diene relative to the monoene was ascribed to the presence of the additional olefinic group in (52). Exchange involved only the allylic protons in the bicyclic diene and monoene, and no formation of isomeric hydrocarbons from the diene was observed.



(50) (51)

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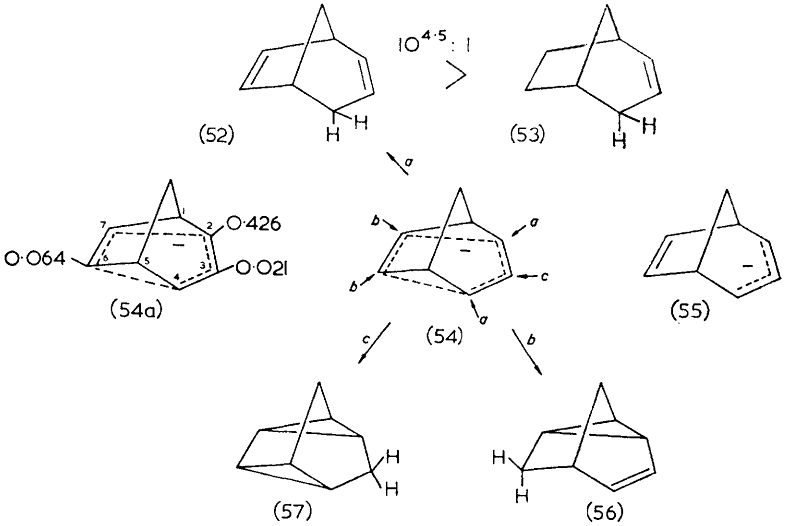
[29] M. Brookhart, M. Ogliaruso, and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 1965.
[30] R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 6348.
[31] W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, 1968, **90**, 814.
[32] *a* J. M. Brown and J. L. Occolowitz, *Chem. Comm.*, 1965, 376; *b* J. M. Brown, *ibid.*, 1967, 639.

Table 4 *Some 'inside-outside' proton Δ values and volume diamagnetic susceptibilities*

			Homotropylium ions					
	C_6H_6	$C_7H_7^+$	Unsub.	8-Cl	1-Me	1-Ph	2-OH	1-OH
Δ (p.p.m.)	—	—	5·8	5·7	5·0	*ca.* 5	3·1	3·1
χ_M (obs.)	54·8	56 ± 1	72 ± 2	—	83 ± 2	120 ± 2	—	75 ± 5
χ_M (calc.)	41·1	40·0	52·0	—	63·3	100·5	—	57·4
Λ	13·7	16	20	—	20	19·5	—	18

HMO Calculations do in fact predict a bonding interaction between allylic anion and olefinic systems in carbanion (55). This interaction is quite appreciable even for (β_{27}/β_0) equal to 0·3, and it is specifically allowed for by the 1,3-bishomocyclopentadienide description.[10d] The charge distribution in such an ion depends, of course, on the molecular geometry and the relative importance of the different atomic orbital overlaps. Illustrated in (54a) are the HMO calculated charge densities for (β_{27}/β_0) equal to 0·3. Charge is greatest at C-2 and C-4, considerably smaller at C-6 and C-7, and least at C-3.

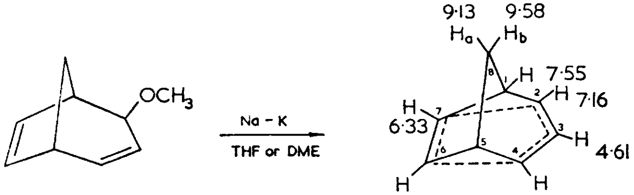


(52) (53) (54a) (54) (55) (57) (56)

One may visualize proton donation at the different carbanionic centres of a bishomocyclopentadienide ion (54), reaction at C-2 or C-4 (*a*) leading to bicyclic diene (52), C-6 or C-7 (*b*) giving tricyclic olefin (56), and C-3 (*c*) leading to tetracyclic hydrocarbon (57). One may in fact anticipate the possibility of base-catalysed equilibration of the bicyclic, tricyclic, and tetracyclic hydrocarbons.

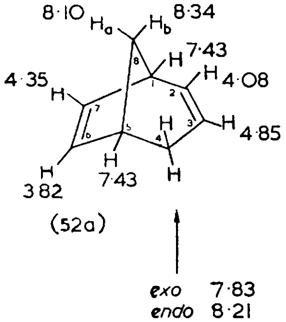
Such equilibration of the three hydrocarbons is in fact observed[33a] using Streitwieser's catalyst–solvent system, $CsNHC_6H_{11}$ in $C_6H_{11}NH_2$, which gives much greater equilibration (and exchange) rates than does the $KOBu^t$–DMSO system. These equilibration studies in $C_6H_{11}NH_2$ have shown the relative reactivities of the three hydrocarbons to be in the sequence, bicyclic > tricyclic ≫ tetracyclic. On the other hand, thermodynamic stabilities of the three hydrocarbons are in the sequence, tricyclic > bicyclic > tetracyclic.[33a]

The bicyclo-octadienyl anion (54) is sufficiently stable to permit preparation of the potassium salt and observation of its n.m.r. spectrum in tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME).[32b,33b] On shaking in THF or DME with Na–K alloy at *ca.* 0°, the allylic ether (52)-OCH_3 reacts quite rapidly to generate the bicyclo-octadienide salt. The resulting orange carbanion solutions are only very faintly contaminated, *e.g.*, with diene (52), and are stable for many hours. One of the signals in the n.m.r. spectrum of (54) is obscured by a solvent signal in ordinary THF or DME, but this difficulty is largely avoided in perdeuteriotetrahydrofuran. The chemical shifts on the τ-scale for the various protons in the anion (54) are shown in (54b) and these are compared with the corresponding values in the parent diene in (52a).



(52) - OCH_3

(54b)



(52a)

In the n.m.r. spectrum of the anion (54) the signal for vinylic protons $H_{2,4}$ appears as a triplet at τ7·16, shifted upfield by 3·1 p.p.m. relative to H_2 in diene (52). The signal for $H_{6,7}$ appears as a singlet at τ6·33, upfield by an average of

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[33] *a* J. M. Nicholson, E. Dart, A. Streitwieser, and S. Winstein, unpublished work; *b* S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, 1967, **89**, 3656.

2·3 p.p.m. relative to H_6 and H_7 in the diene. On the other hand, the signal for H_3 appears as a triplet at $\tau 4{\cdot}62$, actually slightly downfield (*ca.* 0·2 p.p.m.) from H_3 in (52). For the bridgehead protons $H_{1,5}$ in the anion, the signal appears as a skewed triplet at $\tau 7{\cdot}55$, nearly the same position as in (52) ($\tau 7{\cdot}43$). The signals for the H_8 protons appear as a multiplet at $\tau 9{\cdot}12$ for H_{8a} and a doublet at $\tau 9{\cdot}58$ for H_{8b}, an average of 1·1 p.p.m. upfield relative to the values for $H_{8a,8b}$ in the diene.

All the features of the n.m.r. spectrum of the anion are very much in accord with a delocalized bishomocyclopentadienide structure (54) with an appreciable aromatic ring current. Very striking is the relatively large upfield shift of the $H_{6,7}$ signal on going from diene to anion, in contrast with the negligible effect on the bridgehead 1,5 protons. The upfield shift of the $H_{6,7}$ signal by an amount *ca.* 2/3 as large as for $H_{2,4}$ indicates the substantial delocalization of negative charge to C-6 and C-7. The chemical shifts of the $H_{2,4}$, $H_{6,7}$ and H_3 protons relative to the values in (52) namely 3·1, 2·3, and $-0{\cdot}2$ p.p.m., respectively, are in just the C-2,4 > C-6,7 > C-3 order for the predicted charge distribution in the anion. The slight negative shift for H_3 relative to H_3 in the diene can be ascribed to the fact that the appreciable deshielding due to the aromatic ring current more than offsets the shielding effect of the negative charge at C-3, the very atom expected to bear the least negative charge. The substantial shielding of the H_8 protons in (54) relative to (52) by 1·1 p.p.m. may also be ascribed at least partly to a ring-current effect.

Quenching of the carbanion solutions in CH_3OH or CH_3OD produces essentially quantitatively the diene (52) containing $< 0{\cdot}5\%$ of tricyclic (56) or tetracyclic (57). The data show that kinetic control in the protonation of (54) favours C-2 and C-4 very strongly. As regards possible stereospecificity of the protonation, the n.m.r. spectrum of the diene recovered from the CH_3OD quench shows the presence of both *exo*- and *endo*-4-D in comparable amounts. Thus, no appreciable stereospecificity is evident in the protonation.[33b]

Whereas the 6,7-olefinic group in the bicyclo-octadienyl anion (54) stabilizes it by making it a six-electron bishomoaromatic species, the situation in the corresponding cation should be different. Here, the 6,7-olefinic group makes the cation a four-electron antihomoaromatic bishomocyclopentadienyl species. Therefore, it is of some interest to see the effect of the second olefinic group in solvolysis of the bicyclo-octenyl and bicyclo-octadienyl *p*-nitrobenzoates. As might be expected, the second olefinic group in the *exo*- and *endo*-bicyclo-octadienyl *p*-nitrobenzoates (52)-X-OPNB and (52)-E-OPNB is markedly rate retarding,[34] alkyl–oxygen ionization in these esters being 0·0043 and 0·0041 times as rapid as it is in the monoenyl analogue (53)-OPNB. The retardation is probably even larger than can be ascribed to the rate-retarding inductive effect of the second olefinic group, in line with the antihomoaromatic designation for the first intermediate cation formed in solvolysis of the dienyl *p*-nitrobenzoates. The products of such solvolysis are very largely the *exo*- and *endo*-bicyclic allylic

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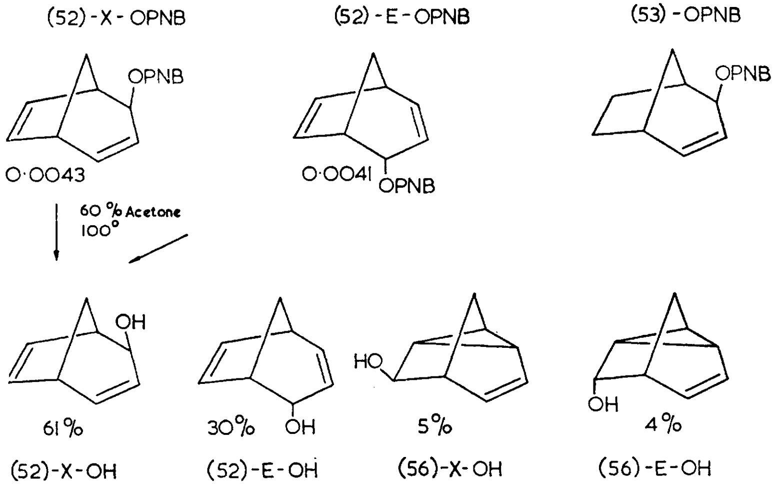
[34] M. Sakai, A. Diaz, and S. Winstein, unpublished work.

alcohols, together with small proportions of tricyclic alcohols.[34] The exact mechanistic account of the mode of formation of these tricyclic alcohols is not yet clear.



10 Monohomocyclo-octatetraene Anion Radical. A Nine-electron Homoaromatic

Instead of entering an antibonding olefinic molecular orbital, an additional electron supplied to tub cyclo-octatetraene prefers to go into a nonbonding molecular orbital of a planar cyclo-octatetraene.[35] The HMO delocalization energy of cyclo-octatetraene anion radical is so large that aromatization is induced by donation of an electron to cyclo-octatetraene. Similarly, donation of two electrons to cyclo-octatetraene produces the aromatic 10 π-electron-containing cyclo-octatetraene dianon.[36] Treatment of cyclo-octatetraene monomethylene adduct (58) (monohomocyclo-octatetraene) with a small amount of potassium in glyme at low temperature gives an anion radical whose e.s.r. spectrum can be observed.[37,38] Compared to cyclo-octatetraene anion radical with a nine-line e.s.r. spectrum due to spin coupling of the odd electron with eight equivalent protons (a_H = 3·209 gauss), the monohomocyclo-octatetraene anion radical displays a relatively complex e.s.r. spectrum appropriate for a species with the symmetry of (59). The interpretation of the spectrum is further substantiated with the aid of the dideuterio-analogue of (59), prepared from (58) containing two deuterium atoms on C-9.

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[35] T. J. Katz and H. L. Strauss, *J. Chem. Phys.*, 1960, **32**, 1873.

[36] *a* T. J. Katz, *J. Amer. Chem. Soc.*, 1960, **82**, 3784; *b* C. A. Coulson, *Tetrahedron*, 1961, **12**, 193.

[37] *a* R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Amer. Chem. Soc.*, 1966, **88**, 4729; *b* G. Moshuk, G. Petrowski, and S. Winstein, *ibid.*, 1968, **90**, 2179.

[38] *a* T. J. Katz and C. Talcott, *J. Amer. Chem. Soc.*, 1966, **88**, 4732; *b* F. J. Smentowski, R. M. Owens, and B. D. Faubion, *ibid.*, 1968, **90**, 1537.

As regards the structure of the anion radical species from monohomocyclo-octatetraene, it is clear that the classical structure (60) with a fully formed cyclopropane ring must be rejected. Such a structure would not accommodate the large a_H value observed for one of the C-9 protons. The C-9 protons are γ to the nearest radical centre in (60), and any observed a_H values for γ-protons are always very small. The planar classical structure (61), with negligible 1,8 interaction, must also be rejected since the two C-9 protons are equivalent in this structure and would have equal a_H values. On the other hand, the non-classical monohomocyclo-octatetraene anion radical structure (59) accommodates all features of the e.s.r. spectrum. Setting a_D equal to $2a_H/13$, spectra of both the protonated and deuteriated anion radical species can be well simulated as regards line positions and intensities with the set of a_H values shown for (59). The specific assignment of a_H values for the protons on C-1—C-8 is based on calculated spin densities at C-1—C-8 of the nonclassical anion radical (59). With either Hückel or the more sophisticated McLachlan[39] spin densities one predicts the sequence of a_H values as $a_{1,8} > a_{3,6} > a_{4,5} > a_{2,7}$. Calculations to simulate these observed a_H values with the aid of the McConnell relation,[40] $a_H = Q\rho$, support the nonclassical structure with appreciable 1,8 overlap and resonance integrals.[37]

In the monohomocyclo-octatetraene anion radical (59) the cyclopropane electrons are obviously included in the delocalized electronic system. An interesting and instructive contrast is provided by the anion radical prepared from the *trans*-fused monomethylene adduct of cyclo-octatetraene,[37b] namely (62).

Brief treatment of (62) in DME with a potassium mirror at −90° produces an anion radical whose e.s.r. spectrum can be recorded at −90°. This is very different from that of (59). It consists of more than 60 well resolved lines spread over 37·7 gauss, and it can be simulated excellently with hyperfine splitting constants (a_H) of 8·11, 5·61, 4·22, and 0·46 gauss, each for two protons. Evidently, the a_H value for the two remaining protons must be essentially zero ($< |0{\cdot}10|$ gauss). The assignment of the a_H value of 0·46 gauss to the C-9 protons is clear from the spectrum of the anion radical prepared from the 9,9-dideuterio-(62). In this spectrum the 0·46 gauss splitting is no longer observed. The anion radical from (62) showed no tendency to rearrange to (59) on long observation (6 hr.) at −90°. Raising the temperature to −60° caused the spectrum of the anion radical from (62) to disappear, with no evidence at any point of an isomerization to (59).[37b]

All the features of the spectrum of the anion radical from (62) are in line with a classical structure (63), the *trans*-fused analogue of (60), containing an essentially fully closed cyclopropane ring and a hexatriene anion radical system. Such a structure is supported by the small and equal a_H values for the two C-9 protons (0·46 gauss) and the fact that the pattern of remaining a_H values is appropriate for a hexatriene anion radical system. The assignment of the a_H values to the different protons is based on calculated spin densities at C-2 to C-7 of a hexatriene

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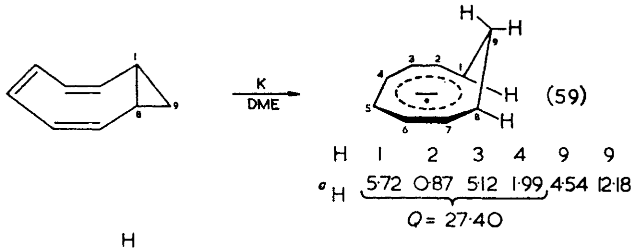
[39] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.
[40] H. M. McConnell, *J. Chem. Phys.*, 1956, **23**, 632, 764.

(58)



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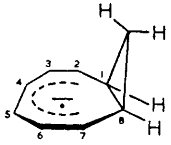

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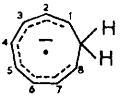

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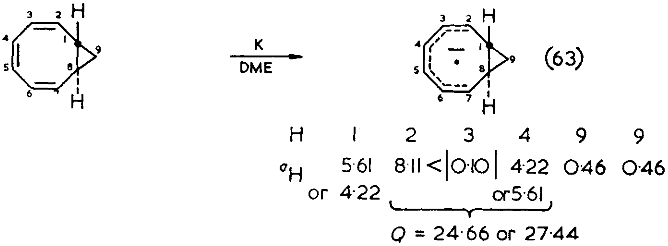
(62)



(63)

π-system. With either Hückel or more sophisticated McLachlan[39] calculated spin densities one predicts the same sequence of a_H values for C-2 to C-7 and simulates the values quite well with the McConnell relation.[40] A remaining ambiguity in the a_H assignments is whether the 5·61 and 4·22 values belong to C-1,8 and C-4,5, respectively, or *vice versa.*

Not only can the pattern of a_H values for C-2 to C-7 in (63) be simulated by calculations for a hexatriene π-system, but it is experimentally quite similar to that for a known hexatriene anion radical, generated from cycloheptatriene by Levy and Myers.[41] A strong argument in favour of structure (63) may be based on the observed Q value. Thus, the sum of a_H values, 24·66 or 27·44, for C-2 to C-7 is a reasonable value for Q. On the other hand, the sum of a_H values, 35·88, for C-1 to C-8 is well out of the range of known Q values. This strongly supports structure (63) with the C-1—C-8 cyclopropane electrons excluded from the delocalized π-electron system. The observed a_H value of 5·61 or 4·22 gauss for C-1,8 is also appropriate for protons β to the hexatriene anion radical system in (63).

The inclusion of the C-1—C-8 cyclopropane electrons in the delocalized electronic system in anion radical (59) and their exclusion in (63) is very signifi-

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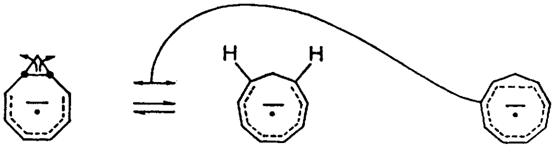
[41] D. H. Levy and R. J. Myers, *J. Chem. Phys.*, 1964, **41**, 1062.

cant. The difference between the two cases may be understood with the aid of an orbital symmetry argument of the type employed by Woodward and Hoffman[42] for electrocyclic reactions. Examining the highest occupied molecular orbital in an octatetraene anion radical, the conversion of a cyclononatetraene anion radical (61) into a bicyclic hexatriene anion radical (60) and the reverse reaction are predicted to be disrotatory. The opening of the anion radical from *cis*-(58) leads to the anion radical of the all-*cis*-cyclononatetraene and geometry is favourable for a compromised delocalized electronic system intermediate in character between the bicyclic hexatriene and monocyclic cyclononatraene anion radical extremes. *trans*-(62) has the C-2—C-7 hexatriene system in a nearly planar arrangement. Thus, the situation is more favourable for conjugation in the triene portion of the hydrocarbon or in a triene anion radical system than it is in the tub-like *cis*-(58). The disrotatory opening of anion radical (63) is towards a very uncomfortable *trans*-*cis*-*cis*-*cis*-cyclononatetraene anion radical (64). Models of the *trans*-*cis*-*cis*-*cis*-tetraene (65) show the relative orientation of olefinic groups to be unfavourable for conjugation in the hydrocarbon and in the corresponding anion radical. It is also very unfavourable for a C-1—C-8 interaction in the latter. It is thus clearly more advantageous for (63) to remain a relatively favourable hexatriene type anion radical than to open partially or fully.

The occurrence of nonclassical electron delocalization in any particular system depends on stereoelectronic and quantum mechanical factors. This is illustrated by the pair of anion radicals just discussed, namely, classical (63) and nonclassical (59). Another illustration was provided above by the $C_8H_9^+$ species from protonation of cyclo-octatetraene. Thus, the free $C_8H_9^+$ and its 6 π-metal carbonyl complex, $C_8H_9^+Mo(CO)_3$, are nonclassical homotropylium species, while the 4π-iron complex, $C_8H_9^+Fe(CO)_3$, is a classical one.



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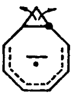

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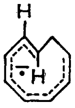

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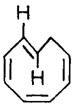

(65)

11 Monohomocyclo-octatetraene Dianion. A Ten-electron Homoaromatic

Allowing a dilute solution of monohomocyclo-octatetraene (58) in THF or DME to stand at −80° over a mirror of an excess of potassium gives rise to a

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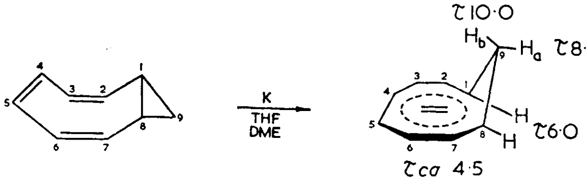
[42] *a* R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395; *b* R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1968, **1**, 17.

solution of a potassium salt.[43a] Only dilute solutions of this material may be obtained since precipitation of the salt occurs if the concentration is too high. If care is taken to obtain relatively complete reduction of the anion radical, satisfactory n.m.r. spectra may be obtained for the salt species at −60°. The n.m.r. spectrum of the salt solution, compared with that of the original hydrocarbon, is appropriate for the dianion species (66).

In both THF and DME as solvents, the n.m.r. spectrum of the parent hydrocarbon (58) contains a six-vinyl-proton multiplet centred at τ 4·1, a three proton complex multiplet centred at τ 8·8 for the two tertiary cyclopropane C-1,8 protons plus one of the cyclopropane C-9 methylene protons, and a one-proton multiplet at τ 10·0 for the other C-9 proton. For the dianion species in perdeuteriotetrahydrofuran, the n.m.r. spectrum contains a complex multiplet for six protons centred at τ *ca.* 4·5 and multiplets for two protons at τ 6·0 and one proton at τ 10·0. The τ 6·0 signal overlaps one of the solvent signals (τ 6·40), so that the relative area of this signal is obtained by a difficult dissection and is therefore only approximate. In perdeuterio-1,2-dimethoxyethane the six-proton multiplet is centred at τ *ca.* 4·8, and the two-proton signal at τ 6·1 is better separated from the nearby solvent peak at τ 6·58. Also visible is a one-proton signal centred at τ 8·0 which was hidden in THF by the THF solvent peak at τ 8·25. Finally, the remaining one-proton signal occurs at τ 10·0. The n.m.r. spectrum of the dianion from the 9,9-dideuteriated (58) is similar, except that no signal appears in the τ 6·8—10·5 range.

(58)



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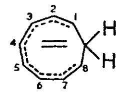
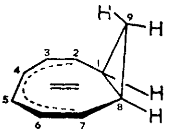
(68)





(67)

As regards assignments for the different signals in the dianion, the signal at τ 4·5 is assigned to the six C-2—C-7 protons, somewhat upfield from the vinyl proton signal in the parent hydrocarbon. The signal at τ 6·0 is assigned to the two C-1,8 protons, considerably downfield from the position of the tertiary cyclopropane protons in (58). The signal at τ 8·0 is assigned to the 'outside' C-9 proton, this being deshielded as compared to the same proton in (58), while the signal at τ 10·0 is assigned to the 'inside' C-9 proton.

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[43] *a* M. Ogliaruso, R. Rieke, and S. Winstein, *J. Amer. Chem. Soc.*, 1966, **88**, 4731; *b* M. Ogliaruso and S. Winstein, *ibid.*, 1967, **89**, 5290.

As in the case of the anion radical (59), the available evidence strongly supports a homoaromatic structure (66) for the product from donation of two electrons to the monohomocyclo-octatetraene. A classical planar structure (68) with negligible 1,8-interaction is ruled out by the nonequivalence of the two C-9 protons, as well as the relatively low chemical shift of the C-2—C-7 protons. A classical structure (67) with a fully formed cyclopropane ring may also be rejected, since the 1,8 protons and also the 2—7 protons are too deshielded. Further, it is not easy to account for the chemical shift between the 'inside' and 'outside' C-9 protons on the basis of (67). On the other hand, all the features of the n.m.r. spectrum are well accounted for by a homoaromatic structure (66) with considerable 1,8 interaction and an appreciable ring current. On this basis, the intermediate value of the chemical shift of the C-1,8 protons is easily understandable. Further, the ring current in (66) helps explain the chemical shift between the 'inside' and 'outside' C-9 protons, and also the low τ value for the C-2—C-7 'vinyl' protons. From the known relationship between the charge which a carbon atom bears and the chemical shift of a proton attached to it, one might expect the change from parent hydrocarbon to a dianion, with a double negative charge distributed over eight carbon atoms, to cause a shielding of the C-2—C-7 protons by *ca.* 2·5 p.p.m. from this cause alone. The observed net effect is only *ca.* 0·4—0·7 p.p.m. (THF or DME); since charge density and ring current are very probably the two most important influences on the C-2—C-7 proton chemical shifts, deshielding due to the aromatic ring current must be quite substantial.

Reactions of the aromatic 10 π-electron cyclo-octatetraene dianion as a nucleophile[36a,44] are both interesting and useful. Similar interest attaches to the chemistry of the homoaromatic counterpart of cyclo-octatetraene dianion, namely monohomocyclo-octatetraene dianion (66). However, only a little information is available regarding the chemistry of (66), specifically its behaviour on protonation with methanol.[43b] This gives only one main product, namely, bicyclo[6,1,0]octa-2,4-diene (70), obtained in over 85% yield by preparative v.p.c.

When the dianion from 9,9-dideuterio-(58) is quenched with MeOH the final product is pure 9,9-dideuterio-(70). When CH_3OD is employed in the quench of dianion (66) the bicyclo-octadiene product contains two deuterium atoms as judged by the mass spectrum, and the n.m.r. spectrum shows that these are located at least very largely as in 2,3-dideuterio-(70). As regards possible stereospecificity of the protonations at C-2 and C-3, we do not as yet have any precise information.

Mechanistic considerations suggest that the first protonation of (66) occurs at C-2 and gives rise to the bicyclic anion (69) which then reacts at C-3 in the second protonation.[43b]

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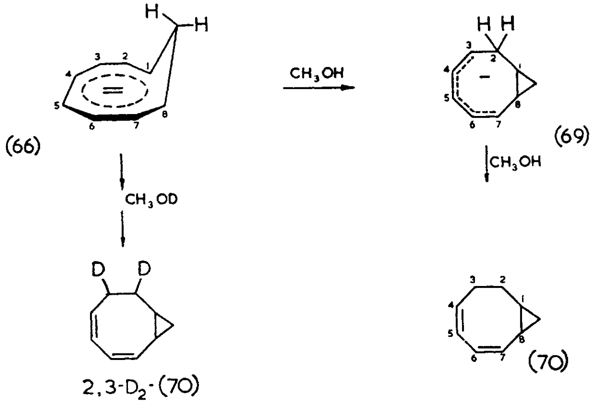
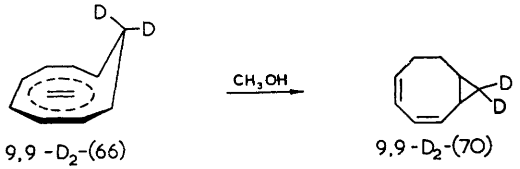
[44] *a* T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 1964, **86**, 4876, 5194; *b* W. R. Roth, *Annalen*, 1964, **671**, 25; *c* D. A. Bak and K. Conrow, *J. Org. Chem.*, 1966, **31**, 3958.





12 Five-Carbon Degenerate Rearrangement and Bridge Flipping of the Norbornadien-7-yl Cation

As indicated earlier, it is now possible, in extremely non-nucleophilic media, to observe directly by n.m.r. many of the nonclassical carbonium-ion intermediates previously proposed to explain unusual rates, products, and stereochemistry in solvolytic work. It is thus possible to study directly the behaviour of these species under conditions of long life. Such studies are uncovering fascinating new carbonium-ion rearrangements which will be illustrated with current work on norbornadien-7-yl cations.[11]

Extraction of norbornadien-7-ol from pentane or CH_2Cl_2 into FSO_3H at $-78°$ gives an FSO_3H solution of cation[11b] (19). Warming the solution to $+45°$ caused no noticeable broadening of the proton signals for the 'bound' and 'unbound' vinyl groups, thus showing that there is a substantial barrier to bridge flipping, *i.e.*, (19a) = (19c), *via* symmetrical (19b) as a transition state (or intermediate).[11c] On the other hand, extended Hückel calculations predict a relatively low value for this barrier (8 kcal.; 0·35 ev).[45]

Cation (19) decomposes at 45° as evidenced by the development of some broad, undetailed n.m.r. signals, as well as a sharp signal at τ 0·76 for tropylium ion formed in *ca.* 25% yield. Despite very rapid decomposition, the n.m.r. spectrum of (19) could be recorded at 77°. At this temperature the τ 2·54 signal for the 'bound' vinyl protons was still sharp with the coupling pattern somewhat

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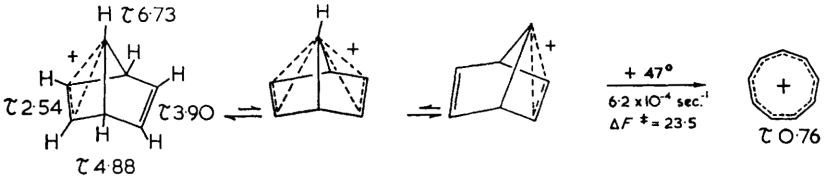
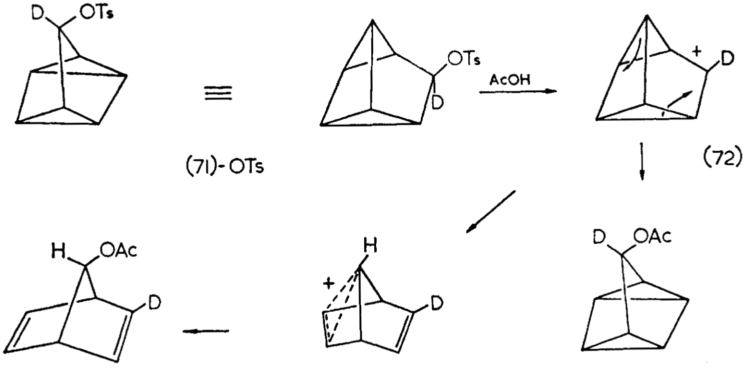
[45] R. Hoffmann, *J. Amer. Chem. Soc.*, 1964, **86**, 1259.



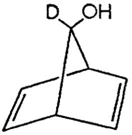
(19a) (19b) (19c) (5)

collapsed. However, the τ 3·90, 4·88, and 6·73 signals for 'unbound' vinyl, bridgehead, and bridge protons were broadened, indicating the onset of an interesting degenerate rearrangement.[11b]

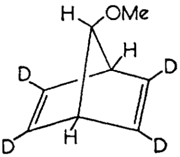
To study this rearrangement on a conventional rather than n.m.r. time-scale, labelled norbornadien-7-yl precursors were employed. These were: (18A)-OAc with a *syn* vinyl deuterium obtained from acetolysis of 7-deuterioquadricyclyl OTs, (71)-OTs, *via* the Richey–Story rearrangement;[46] (18B)-OH with a 7-deuterium obtained from 7-deuterioquadricyclanol; and (18C)-OMe with 77% of 4 vinyl deuterium atoms obtained by base-catalysed exchange of norbornadien-7-yl methyl ether with $LiNDC_6H_{11}$ in $C_6H_{11}ND_2$.



(71)-OTs (72) (18A) - OAc (19A) (71) - OAc



(18B) - OH



(18C) - OMe

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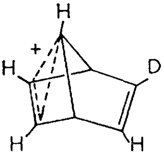
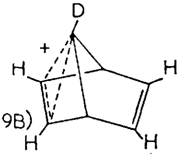
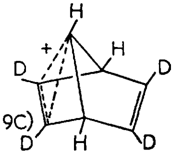
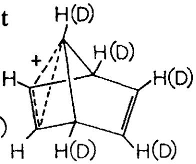
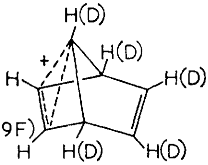
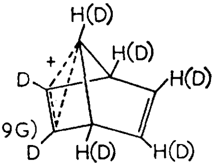
[46] *a* H. G. Richey and N. C. Buckley, *J. Amer. Chem. Soc.*, 1963, **85**, 3057; *b* P. R. Story and S. R. Fahrenholtz, *ibid.*, 1964, **86**, 527; 1966, **88**, 374.

In FSO_3H at −73°, (18A)-OAc displayed the four-signal spectrum of (19) with the intensity of the unbound vinyl signal only half as great as that for the bound vinyl; see (19A) in Table 5.[11b] When the cation solution was warmed to −47°, a scrambling of the deuterium label was observed with a rate constant of 3×10^{-4} sec.$^{-1}$ (Table 5). However, the vinyl proton peak intensities did not approach the 1:1 ratio expected for a bridge-flip phenomenon. Rather, the peak intensities approached a 2:1·6:1·6:0·8 ratio for the bound vinyl, unbound vinyl, bridgehead, and bridge protons, respectively, as in (19E). In other words, deuterium was scrambled to all positions *except* the bound vinyl! The same phenomenon was demonstrated with cations (19B) and (19C) from (18B)-OH and (18C)-OMe, respectively (Table 5). At −60° initially, both of these cations exhibited the same relative peak intensities as their precursors, but on warming to *ca.* −50°, these intensities approached the ratios expected for a five-carbon scrambling reaction; see (19F) and (19G) in Table 5.[11b]

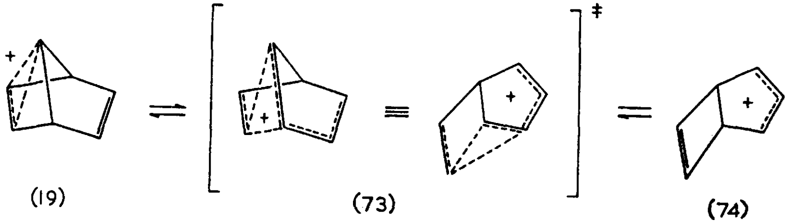
Table 5 *Rates and free energies of activation of degenerate isomerizations of the norbornadien-7-yl cation*

Cation	 (19A)	 (19B)	 (19C)
Product	 (19E)	 (19F)	 (19G)
Temp.	−47°	−55°	−50°
$10^4\ k$ (sec.$^{-1}$)	3^a	$1{\cdot}7^b$	2^a
$\Delta F^{\ddagger}$ (kcal./mole)	16·7	16·4	16·7

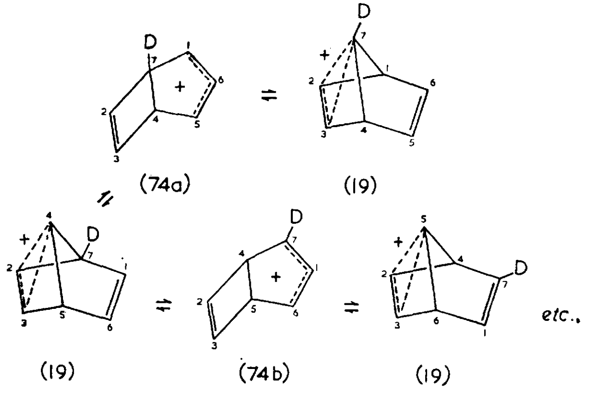
[a,b] Evaluated graphically using $\ln[(H_\infty - H_0)/(H_\infty - H_t)] = kt$, with H_∞ equal to the equilibrium amount of protium: (*a*) in the unbound vinyl group; (*b*) at C-7.

Examination of the n.m.r. signal intensities during scrambling of (19A), (19B), and (19C) revealed that deuterium is incorporated sequentially at the different positions. Thus, in the case of (19A) and (19C), deuterium is first incorporated into the bridgehead, then into the bridge position. With (19B), deuterium appears first at the bridgehead, then in the unbound vinyl group. Thus, the isomerization may be said to occur by a stepwise circumambulatory motion of five carbons of the framework of (19) with respect to the two which comprise the bound vinyl function.

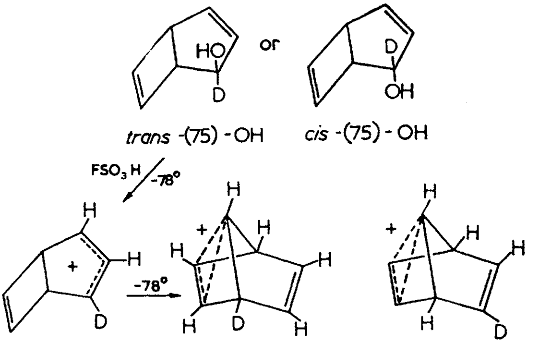
The simplest specific mechanism which we can conceive for the five-carbon degenerate rearrangement involves the ring contraction of (19) to a bicyclo-[3,2,0]heptadienyl cation (74) by means of a 1,2-shift of a bound vinyl carbon atom from C-1 or C-4 to C-7 *via* a transition state such as (73), followed immediately by a ring expansion which leaves the same vinyl function bound to C-7.



This is pictured by (19) ⇌ (74a) ⇌ (19) ⇌ (74b) ⇌ (19), *etc.*, which shows the bound vinyl group working its way around the five-membered ring defined by the five other carbon atoms in (19). This mechanism is supported by the behaviour of the *cis*- and *trans*-bicyclo[3,2,0]heptadienols, *cis*-(75)-OH and *trans*-(75)-OH in FSO_3H.[11b]



When either *cis*-(75)-OH or *trans*-(75)-OH was extracted into FSO_3H at −78°, and the carbonium-ion solution was observed at −78° within 120 sec., the n.m.r. spectrum of (19) was obtained with no trace of a signal for a [3,2,0]-cation (74). Most importantly, the α-deuterio-*cis*- and -*trans*-[3,2,0]-alcohols both gave (19) with 2·0:1·5:1·5:1·0 ratios of signal intensities for bound vinyl, unbound vinyl, bridgehead, and bridge protons, respectively. In other words, 50% of the deuterium label appears at a bridgehead, and 50% in the unbound vinyl group. This result is in exact accord with a mechanism wherein the first formed [3,2,0]-cation ring-expands to the [2,2,1]-ion with either carbon of the cyclobutene vinyl function undergoing a 1,2-shift as the migrating vinyl group becomes the bound vinyl of (19). The evidence is thus strongly in favour of the ring contraction–ring expansion mechanism^{11b} for the degenerate five-carbon scrambling of (19).

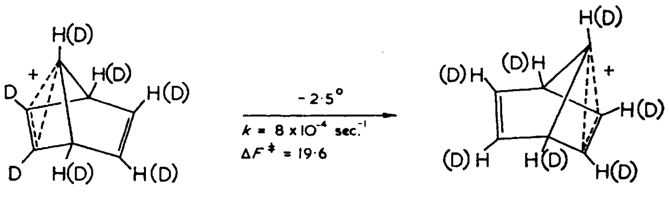


(74) (19)

As regards the equilibrium between the [3,2,0]-ion and the [2,2,1]-ion (19), the latter is strongly favoured. A minimum figure for the rate constant for (74)→(19) is 10^{-2} sec.$^{-1}$ at $-78°$, and the rate constant for (19)→(74) at this temperature may be estimated as $1{\cdot}5 \times 10^{-6}$ sec.$^{-1}$ from the available data. Thus, a minimum figure for the equilibrium constant for (74)$\rightleftharpoons$(19) is 7000 at $-78°$.

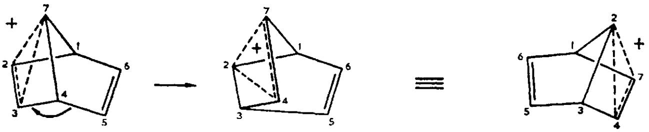
Returning to the phenomenon of 'bridge-flipping', it was possible to study^{11c} the equilibration of bound and unbound vinyl groups in (19) by observing the labelled cation (19G) derived from the precursor (18C)-OMe as a result of degenerate five-carbon scrambling. Cation (19G) has a deuterium atom at each bound vinyl position but only 2/5 of a deuterium atom at each unbound vinyl position. At *ca.* 0° protium incorporation into the bound vinyl positions is indeed observed, the bound and unbound vinyl signals approaching equal intensities as in (19H). At $-2{\cdot}5°$, $k = 8 \times 10^{-4}$ sec.$^{-1}$ and thus $\Delta F^{\ddagger}$ is 19·6 kcal./mole, some 3 kcal. greater than $\Delta F^{\ddagger}$ for five-carbon scrambling.

The value of 19·6 kcal./mole is actually a lower limit to the free-energy difference between the symmetrical and unsymmetrical structures of the



(19G) (19H)

norbornadien-7-yl cation. This is because bridge flipping is not the only possible mechanism for exchange of vinyl groups. For example, another plausible mechanism involves 1,2-shifts of an unbound vinyl carbon atom from C-1 to C-2, or C-4 to C-3. Such shifts move the bound vinyl group around so as to scramble C-1, C-2, C-3, C-4, and C-7. Coupled with the more rapid degenerate five-carbon rearrangement, all seven carbon atoms become scrambled.[11b,c]



13 The 7- and 2-Methyl-norbornadien-7-yl Cations[11c]

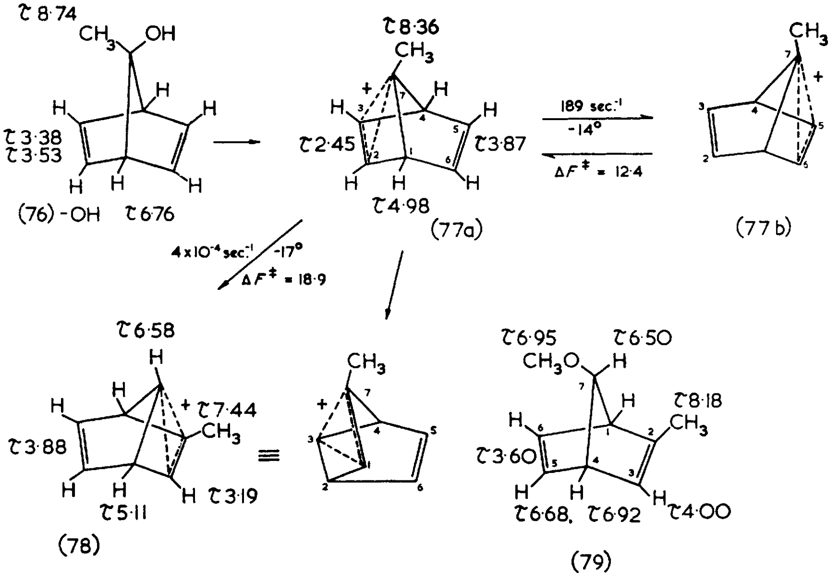
One would expect a 7-methyl substituent to lower the barrier to bridge flipping, so we proceeded to examine the 7-methyl cation (77). As the precursor for this ion we employed alcohol (76)-OH. Extraction of (76)-OH from CD_2Cl_2 into FSO_3H at −78° yielded an FSO_3H solution of (77) whose n.m.r. spectrum below −45° corresponds to an unsymmetrical structure. This spectrum consists of a two-proton bound vinyl quartet at τ 2·45, a broad two-proton unbound vinyl singlet at τ 3·87, a two-proton bridgehead multiplet at τ 4·98, and a methyl singlet at τ 8·36.

As the temperature is raised, the vinyl signals of (77) begin to broaden and eventually coalesce at −14°, while the bridgehead signal sharpens to a quintuplet and the methyl peak remains sharp. The fact that the bridgehead signal actually sharpens indicates that only the magnetic environments of the vinyl protons are being averaged, so this must occur by bridge-flipping, namely (77a)$\rightleftharpoons$(77b). At the coalescence temperature, the first-order rate constant for bridge-flip is 189 sec.$^{-1}$ and $\Delta F^{\ddagger}$ is 12·4 kcal./mole.

Above *ca.* −5°, (77) rearranges quite rapidly to a more stable species, the 2-methyl ion (78). This is formed at −17° in *ca.* 60% yield with a rate constant of 4×10^{-4} sec.$^{-1}$ ($\Delta F^{\ddagger} = 18{\cdot}9$ kcal./mole). As regards conceivable mechanisms of the (77)→(78) rearrangement, the simplest is by way of a C-1→C-2 shift of the unbound vinyl carbon C-6 in (77), producing (78) directly. Upon further heating of (78), decomposition occurs with no detectable formation of methyl tropylium ion.

The 2-methyl ion (78) was identified by its n.m.r. spectrum and the results of quenching it in MeOH. In the n.m.r. spectrum of (78), signals appear at τ 3·19, 3·88, 5·11, 6·58, and 7·44 for bound vinyl, unbound vinyl, bridgehead, bridge, and methyl protons, respectively. From quenching the FSO_3H solution of (78) in MeOH there was isolated the corresponding *anti* methyl ether with a correct analysis and an appropriate n.m.r. spectrum summarized in (79) (solvent CS_2).

The chemical shifts of the C-7, C-2, and C-3 protons in (19), and in the *anti*-norbornen-7-yl ion as well, were previously explained on the basis that C-7,



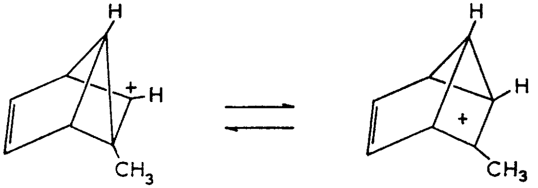
where considerable rehybridization from trigonal towards sp^3 is expected[10c] bears very little of the positive charge, while C-2 and C-3 carry most of it. This interpretation is strongly supported by the n.m.r. spectra of (77) and (78). Thus, in the n.m.r. spectrum of the 7-methyl cation (77), the chemical shifts at C-2 and C-3 (and C-5 and C-6, also) are nearly the same as for (19) and the 7-CH_3 chemical shift is nearly as high as in covalent (76)-OH. Thus, a 7-CH_3 group, on a carbon atom bearing very little positive charge, interacts very little with the cationic electronic system and perturbs the charge distribution negligibly. As expected, however, the 2-CH_3 group in (78) does interact very appreciably with the cationic electronic system. Thus, in the n.m.r. spectrum of (78), the chemical shift of the 2-CH_3 group is shifted downfield by 0·92 p.p.m. and that of the 3-proton is shifted upfield by 0·74 p.p.m. relative to the values in (77). One would expect (78) to be the most stable of the monomethyl norbornadienyl cations and this is in line with the observed substantial equilibrium constant for (77)$\rightleftharpoons$(78).

The large barrier to bridge flipping in (19) ($\Delta F^{\ddagger} \geqslant$ 19·6 kcal./mole) discloses the enormous gain in stability when C-7 in symmetrical (19b) is at least partially rehybridized and the geometry is distorted to that of unsymmetrical (19) where the interaction of C-7 is entirely with one of the two available olefinic groups. While a 7-methyl group has little effect on unsymmetrical (19), it would be expected to have a strongly stabilizing effect on symmetrical (19b), where olefinic electron involvement is much less, and much more positive charge resides at C-7. On this basis one can understand the substantial reduction in the bridge-flipping barrier in (77) relative to (19) by an amount equal to or greater than 7·2 kcal./mole.

The n.m.r. spectrum of (78) is of interest in connection with Brown's and

Deno's formulation[47a,b] of (19), and the norbornen-7-yl cation as well, as a pair of rapidly equilibrating tricyclic ions. On such a basis, the equilibrating tricyclic 2-methyl cation, (80a)⇌(80b), would surely be nearly exclusively tertiary (80b) and the n.m.r. spectrum would be that of (80b). Spectra of a number of cyclopropylcarbinyl cations are now recorded[48] and these show signals for the cyclopropane α- and β-protons at similar and very high field (τ *ca.* 7). Contrary to this, the chemical shift of the C-3 proton in the 2-methyl cation (78) (τ 3·19) is at lower field than the C-7 proton by 3·4 p.p.m., and also at lower field than the cyclopropane α-proton in known cyclopropylcarbinyl cations by at least 3 p.p.m. Thus, we can add a strong n.m.r. argument to those based on chemistry and stereochemistry[8] against the equilibrating tricyclic ion formation.

(80a)



(80b)

14 The 7-Phenyl-norbornadien-7-yl Cation[11d]

Since one would expect an even greater diminution of the bridge-flipping barrier due to a 7-phenyl substituent, we proceeded to investigate the 7-phenyl cation (82). The precursor to this ion was the 7-phenyl-norbornadien-7-ol (81)-OH (n.m.r. spectrum in CCl_4). The n.m.r. spectrum of the 7-phenyl cation (82) in FSO_3H at −70° exhibits a sharp four-proton triplet at τ 2·85 for four equivalent vinyl protons, a two-proton quintuplet at τ 4·40 for the bridgehead protons, and a five-proton broad singlet centred at τ 2·48 for the aromatic protons. Of considerable interest is the relative width of the aromatic proton signal, being only *ca.* 9 cps at half height. When the acid solution is diluted with SO_2, spectra may be recorded as low as −100° without viscosity broadening. Even at this temperature (82) still exhibits a vinyl triplet broadened less than 3 c./sec.

When the temperature of the FSO_3H solution is raised, cation (82) undergoes a clean rearrangement to phenyltropylium ion (83). The first-order rate constant for appearance of phenyltropylium ion at −49° is $1{\cdot}6 \times 10^{-3}$ sec.$^{-1}$, corresponding to a $\Delta F^{\ddagger}$ of 15·9 kcal./mole. Ion (83) was identified by its n.m.r. spectrum which exhibits a six-proton multiplet at τ 0·85 and a five-proton multiplet centred at τ 2·18. The n.m.r. spectrum was identical to that of authentic phenyltropylium fluoroborate.

The equivalence of the four vinyl protons in the 7-phenyl cation, taken alone without considering other features of the n.m.r. spectra, indicates that this

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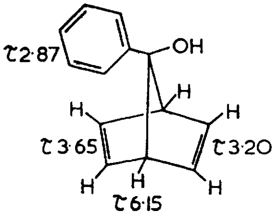
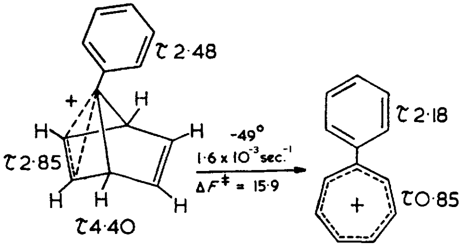
[47] *a* H. C. Brown and M. Bell, *J. Amer. Chem. Soc.*, 1963, **85**, 2324; *b* N. C. Deno, *Progr. Phys. Org. Chem.*, 1964, **2**, 159.

[48] *E.g.*, C. U. Pittman and G. A. Olah, *J. Amer. Chem. Soc.*, 1965, **87**, 5123.



(81)-OH



(82)

(83)

cation is either symmetrical, or it is unsymmetrical and yet bridge-flipping rapidly even at $-100°$. In the latter case, assuming that the chemical shifts of the two sets of vinyls would differ by at least 40 c./sec., the rate of bridge-flip must be greater than 840 sec.$^{-1}$, which leads to a maximum $\Delta F^{\ddagger}$ of 7·6 kcal./mole.

The chemical shifts of the vinyl protons in (82) provide essentially no assistance in deciding between the symmetrical and rapidly equilibrating unsymmetrical formulations. This is because the observed chemical shift of τ 2·85 in (82) is not so very different from the average chemical shift of bound and unbound vinyl protons in (19) (τ 3·22) and (77) (τ 3·16), nor are they unreasonable values for a symmetrical ion.

In the case of the 7-phenyl cation (82), an important clue is the chemical shift and signal pattern for the aromatic protons. The spread in chemical shift for the various *o*-, *m*-, and *p*-protons is very small, the whole half-band width being 9 c./sec. On the other hand, a substantial spread in chemical shift values of the benzene ring protons is observed in carbonium ions where an α-phenyl group is tolerating considerable positive charge.[49] Examples of such cations are cumyl and benzhydryl, where the difference between *meta* and *ortho* chemical shift values is 0·83 and 0·48 p.p.m., respectively. Not only is the signal pattern for the aromatic protons in (82) quite narrow, but their chemical shift is at quite high field compared to typical α-phenyl carbonium ions. In fact, the phenyl proton signal even in the extreme case of the phenyl tropylium ion (83) comes at definitely lower field and has much more of a spread pattern than in cation (82). It is thus evident that the phenyl group in (82) tolerates very little positive charge. Since it would undoubtedly bear a great deal of charge in the symmetrical ion, we have a strong argument that (82) is unsymmetrical and similar to (19) and (77). On this basis, (19), (77), and (82) are all three unsymmetrical norbornadienyl cations with flipping barriers of $\geqslant$ 19·6, 12·4, and $<$ 7·6 kcal./mole, respectively, in just the sequence expected for 7-H, 7-CH_3 and 7-C_6H_5 substituents.[11c,d]

The new work on norbornadienyl cations described above serves to illustrate the fact that the study of carbonium ions under conditions of long life presents

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[49] *E.g.*, D. G. Farnum, *J. Amer. Chem. Soc.*, 1964, **86**, 934.

us with a whole host of exciting new observations and new problems in organic reaction mechanisms.

It is interesting to enquire which of the rearrangements of the norbornadien-7-yl and bicyclo[3,2,0]heptadienyl ions mentioned above are able to compete in solvolysis in typical solvolysing solvents where carbonium-ion lifetime is very short. The answer is that ring contraction, bridge-flipping, and other rearrangements of the norbornadien-7-yl cations, and ring expansion of the bicyclo-[3,2,0]heptadienyl cation do not compete visibly in typical solvolytic work. Solvent capture of the cation in question is much more rapid than are these various rearrangements. On the other hand, the Richey–Story rearrangement[46] of the quadricyclyl ion (72) to norbornadienyl ion (19) does compete with product formation quite well in AcOH[46] and even better in HCOOH[11b].

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