nection with the solvolysis kinetics. Helpful discussions with Professor Göran Bergson and Dr. John Dirlam during the preparation of this manuscript are gratefully acknowledged.

Degenerate and Nondegenerate Isomerizations of 7-Norbornadienyl Cations[1]

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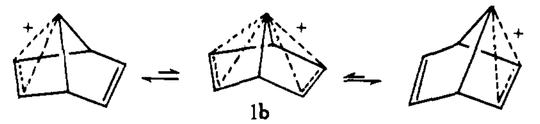
Abstract: Low-temperature nmr spectra for fluorosulfuric acid solutions of several substituted 7-norbornadienyl cations lead to assignments of unsymmetrically bridged ground states for the 7-methyl (**8**), 7-phenyl (**9**), 7-vinyl (**10**), and the three other possible methyl-substituted ions. The 7-methoxyl ion (**11**) is probably symmetrical. The activation free energy for degenerate bridge-flipping in the parent ion (**1**) is equal to or greater than 19.6 kcal/mol, for **8** it is 12.4 kcal/mol, and for **9** and **10** it is less than 5.2 and 8.2 kcal/mol, respectively. Ion **1** undergoes a degenerate isomerization which scrambles all but the "bonded" vinyl carbons. The mechanism involves a rapid equilibrium with the bicyclo[3.2.0]heptadienyl cation (**23**), the equilibrium constant at $-100°$ being $>1.2 \times 10^8$ in favor of **1**. The equilibrium constant between 2-methylbicyclo[3.2.0]heptadienyl cation (**21**) and 1-methyl-7-norbornadienyl cation (**14**) is only *ca.* 60 at $-100°$. Rate constants for the conversion of ions **1**, **9**, **10**, and **11** to the corresponding tropylium ions are reported as are the rate constants for formation of the 2-methyl-7-norbornadienyl ion (**12**) from **8**, and for decomposition of **12** and of the 5-methyl-7-norbornadienyl ion (**13**). Cation **13** may be prepared from the 7-methyl-7-quadricyclyl ion as well as from **21**, and it may be trapped to give the corresponding *syn*-7-methyl ether **24**. Ion **12** may be trapped to give the *anti*-methyl ether **25**. Mechanisms for the various degenerate and nondegenerate isomerizations are discussed.

The discovery of high solvolytic reactivity in the 7-norbornadienyl system led immediately to speculation about the structure of the apparently quite stable 7-norbornadienyl cation.[3,4] Of the several electron-delocalized possibilities envisioned in 1960,[3] the unsymmetrical one (**1a**) has since been chosen. The choice



1a **1b** **1a** (1)

is made principally on the basis of the nmr spectrum first reported by Story and Saunders.[5] This spectrum conclusively demonstrated the nonequivalence of the two vinyl functions. It also revealed a relatively substantial coupling between the downfield ("bonded") vinyl protons and the proton at C_7. Subsequent to the nmr result, the bridged nature of the ion was indicated chemically by the observation of stereospecific endo hydride attack at C_2.[6] Further support came from the strong analogies which may be drawn from several similar observations for the 7-norbornenyl cation[7] **2** (whose structure allows straightforward determination of the stereospecificity of nucleophilic attack at C_7 as well as at C_2) and from theoretical studies.[8]

In contrast to the demonstration of bridging *per se*, the stabilization that is actually afforded the 7-norbornadienyl ion by bridging has lacked experimental evaluation. The term "stabilization" may, of course, be defined in many ways, but it occurred to us that a good operational definition might derive from consideration of the energy difference between the unsymmetrical (bridged) form **1a** and the symmetrical (unbridged or symmetrically bridged) form **1b**. Couched in these terms, the problem becomes one of evaluating the activation energy for the degenerate reaction depicted in eq 1, since the transition state for this process, called bridge-flipping, would presumably be identical with the symmetrical form of the ion.[9] The techniques for generation and study of stable cations under conditions of long lifetime have attained a relatively high level of sophistication in recent years, and the bridge-flipping problem appeared quite amenable to investigation by nmr methods. Since an exchange of nonidentical vinyl functions is required, nmr line broadening and chemical tracer studies were suggested.

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(1) Preliminary communications: (a) M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6352 (1967); (b) *ibid.*, **89**, 6354 (1967); (c) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350 (1967); (d) *ibid.*, **90**, 7364 (1968).

(2) (a) National Institutes of Health Postdoctoral Fellow, 1966–1968; address inquiries to: Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pa. 15213; (b) National Science Foundation Postdoctoral Fellow, 1968; (c) deceased, Nov 23, 1969.

(3) S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.*, **82**, 2084 (1960).

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

(5) (a) P. R. Story and M. Saunders, *J. Amer. Chem. Soc.*, **82**, 6199 (1960); 84, 4876 (1962); (b) P. R. Story, L. C. Snyder, D. C. Douglass, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963). (c) The ^{13}C spectra of 1 and 2 have been reported recently: G. A. Olah and A. M. White, *ibid.*, **91**, 6883 (1969).

(6) P. R. Story, *ibid.*, **83**, 3347 (1961).

(7) See ref 4 for leading references; *cf.* also (a) H. Tanida and Y. Hata, *J. Org. Chem.*, 30, 977 (1965); (b) H. Tanida, T. Tsuji, and T. Iries, *J. Amer. Chem. Soc.*, 88, 864 (1966); (c) J. J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Commun.*, 1202 (1967).

(8) (a) M. Simonetta and S. Winstein, *J. Amer. Chem. Soc.*, **76**, 18 (1954); (b) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956); (c) R. J. Piccolini and S. Winstein, *Tetrahedron, Suppl.*, **19**, 423 (1963); (d) R. Hoffmann, *J. Amer. Chem. Soc.*, **86**, 1259 (1964); (e) H. O. Ohorodynk and D. P. Santry, *ibid.*, **91**, 4711 (1969).

(9) At least one calculation indicates that the only minimum on the potential surface for the bridge-flipping reaction is the bridged ion.[8d]

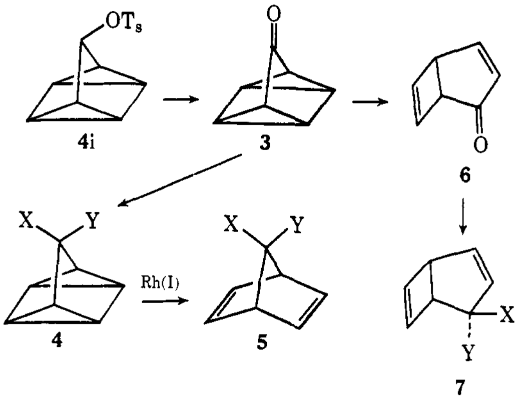
Detailed consideration of the bridge-flipping reaction leads to a prediction concerning the effect of substituents at C_7 on the activation barrier to the reaction. Bridging in **1** is thought to be accompanied by a substantial incorporation of s character in the "empty" orbital at C_7.[4,8b] A consequence of this reasoning is that the ground state of the ion will, in fact, bear most of the positive charge at the C_2 and C_3 positions, with only a small fraction of charge at C_7. In contrast, the symmetrical structure **1b**, with essentially trigonal hybridization at C_7, will bear a large proportion of the charge at this position. The prediction, then, is that charge-stabilizing substituents at C_7 will *selectively* stabilize the symmetrical form of the ion relative to the unsymmetrical form, since orbital overlap between substituent and C_7 will be large in the symmetrical geometry and small in the unsymmetrical geometry. Thus, charge-stabilizing substituents should cause a decrease in the activation barrier to bridge-flipping.

This paper reports a direct observation of the bridge-flipping phenomenon, a quantitative verification of the above prediction, and the establishment of a lower limit to the energy difference between **1a** and **1b**. Furthermore, our studies have resulted in the preparation of several new cations whose nmr spectra are of general interest, and our investigation of these cations over a wide temperature range has revealed several degenerate and nondegenerate isomerization reactions.

Results

Preparation of Cation Precursors. Several 7-norbornadienols were needed as precursors to cations desired for this study. Since the obvious route, oxidation of 7-norbornadienol to the corresponding ketone followed by Grignard addition, was precluded by the apparent thermodynamic instability of the ketone,[10] the approach adopted was that of using the quadricyclanone[11a] nucleus as "protection" for the integrity of the bridge position. Grignard addition followed by $[_{\sigma}2_s + {}_{\sigma}2_s]$ ring opening to the norbornadiene, utilizing transition metal catalysis,[12] afforded the desired compounds in routine order. The sequence is shown in Chart I and the details of all preparations are given in the Experimental Section. A key development turned out to be an improved synthesis of quadricyclanone (**3**) *via* the DMSO–$NaHCO_3$ oxidation of tosylate **4i**.[11b,13] High isolated yields and a clean separation of **3** from the crude reaction mixture were realized by employing a continuous extraction with pentane (≥ 12 hr) in the work-up.

Chart I



	X	Y
a,	H	OH
b,	D	OH
c,	CH_3	OH
d,	Ph	OH
e,	vinyl	OH
f,	OCH_3	OCH_3
g,	H	OAc
h,	H	OCH_3
i,	H	OTs
j,	D	OTs
k,	H	R

	X	Y
a,	H	OH
b,	OH	H
c,	D	OH
d,	OH	D
e,	CH_3	OH

The transition metal catalyzed isomerization of the quadricyclyl systems to the norbornadienyl systems was initially performed using glass which had been soaked in chromic acid (see Experimental Section). Results using this method were somewhat irreproducible.[14] More efficient and reproducible procedures were later developed using Rh(I) catalysts based on the reported prototypical conversion.[15] The preparation of norbornadienone dimethyl ketal (**5f**) was accomplished from quadricyclanone dimethyl ketal[11b] (**4f**) which was prepared using a standard procedure.[16] Bicyclo[3.2.0]-heptadienone (**6**) was prepared from **3** according to the procedure of Story[17] and converted to the exo and endo alcohols **7a–d**, also according to Story.[17] Addition of methyl Grignard to **6** gave largely one tertiary alcohol (>95%), assumed to have the endo configuration **7e**.

For the generation of deuterium-labeled 7-norbornadienyl cations from 7-substituted norbornadienes, precursors were prepared as shown in eq 2–4. *syn*-7-Acetoxynorbornadiene-*2-d* (**5g**) was prepared by solvolysis of the 7-quadricyclyl-*7-d* tosylate[18] (**4j**) in acetic acid. Solvolysis in formic acid gave slightly more rearranged material, but this finding was not pursued for fear of decomposition of the formate esters on the glpc columns. Alcohol **5b** was prepared by isomerization of **4b**.[15] The tetradeuterated 7-methoxynorbornadiene was prepared by exchange of the vinyl hydrogens using lithium cyclohexylamide-*N-d* in lithium cyclohexylamine-*N,N-d_2* by a modification of the standard Streitwieser procedure,[19] and was obtained with 77% deuterium incorporation. This enrichment was quite adequate for our present purposes.

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(10) *Cf.* S. Yankelevitch and B. Fuchs, *Tetrahedron Lett.*, 4945 (1967), and references therein.

(11) (a) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **86**, 1270 (1966); (b) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Lett.*, 2779 (1965), report a similar procedure with no details. We thank these authors for personal communication of unpublished material.

(12) (a) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **93**, 1123 (1971), and references therein; (b) F. D. Mango, *Tetrahedron Lett.*, 505 (1971).

(13) N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, **81**, 4113 (1959).

(14) Such irrascibility has been noted previously.[11b]

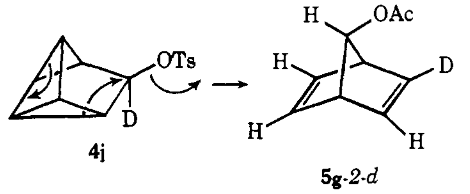
(15) *Cf.* H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967). The formation of **5b** in the present case was an adventitious occurrence presumably due to inadvertent exposure of **4b** to catalytic elements during reaction of **3** with LAD.

(16) W. T. Moreland, D. P. Cameron, R. G. Berry, and C. E. Maxwell, *ibid.*, 84, 2966 (1962).

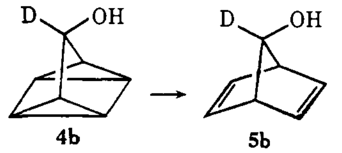
(17) P. R. Story and S. R. Fahrenholtz, *ibid.*, 87, 1623 (1965). We thank these authors for personal communication of unpublished results.

(18) (a) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963); (b) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964); **88**, 374 (1966).

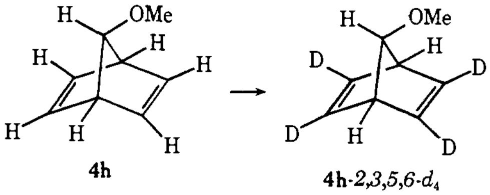
(19) A. Streitwieser, Jr., and W. C. Langworthy, *ibid.*, **85**, 1757 (1963); A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, 3, 73 (1965). We are grateful to Dr. C. Watts for assistance with this operation.



(2)



(3)



(4)

Generation and Observation of the Ions. All of the carbonium ions reported in this paper were generated in FSO_3H or FSO_3H-SO_2ClF media either by extraction of appropriate covalent precursors or by rearrangement of another ion. The specific extraction procedures are given in the Experimental Section. In general, the extraction was from pentane, methylene chloride, or perdeuteriomethylene chloride at −78° or below. It was noted that a 1:2 (v:v) solution of FSO_3H-SO_2ClF had a freezing point of *ca.* −140°, thus allowing generation of ions at *ca.* −130°. For ions which were very unstable with respect to rearrangement to other ions, generation was executed at *ca.* −130°, and the sample was then immediately stored at liquid nitrogen temperature until insertion into the precooled nmr probe.

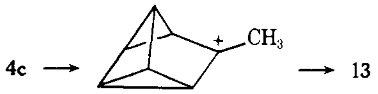
Chemical shifts for the 7-norbornadienyl ions observed are given in Table I.[5,20] Table II[21-23] lists most of the known 7-norbornenyl cations for comparison. In general, chemical shifts were recorded at temperatures between −50 and −70° and are referenced to internal $CHDCl_2$ assumed to absorb at τ 4.70. Except for those cases where specific isomerizations of the ions occur, no significant temperature dependence of the chemical shifts was noted. In selected cases, quenching of the cation solution in methanol–bicarbonate at −78° yielded methyl ethers whose structures were entirely consistent with the structures assigned to their precursor cations (*vide infra*).

Complete proton decoupling experiments for cations **1** and **2** have been discussed previously.[5,21a] While the remaining ions in Tables I and II have not been analyzed by double resonance experiments, the following qualitative observations are worth noting.

(1) The appearance of the downfield vinyl hydrogen resonance falls into one of two categories. The first category is characterized by a quartet with a 7.5–8.5-Hz spacing between outer lines and a 1–2-Hz spacing between inner lines. The second category is characterized by a decidedly different pattern, namely a triplet of lines, with 4–5-Hz spacings. Ions which fall in the first category are **1** (with deuterium at C_7), **8**, **9**, **10**, **13**, **14**, **2**, **15**, and **18**. Ions **11**, **19**, and **20** fall in the latter category as does the 7-*p*-anisyl-7-norbornenyl ion and all 7-substituted norbornenes and norbornadienes which are substituted so as to preclude the "W" coupling between anti-7-H and vinyl hydrogens.[24]

(2) The signals due to the aromatic protons in cations **9** and **18**, τ 2.48 and 2.25, respectively, are very narrow (on the order of 0.15 ppm at half-height) relative to other known benzylic-type ions.[25] This point is an important clue regarding the geometry of these ions (see Discussion). Also of interest are the chemical shifts of the terminal vinyl protons in **10**. Though these were not determined by a fitting routine, they must fall in the 0.25-ppm range defined by the four strong signals which are observed. In comparison, the terminal protons on the 1,1,2-trimethylallyl ion[26] present a simple first-order pattern and are separated by 0.55 ppm. They are also at considerably lower field (τ 1.73–2.28) than are the terminal vinyl protons in **10**.

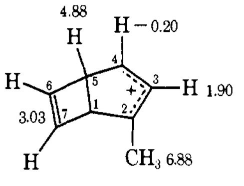
Attempted generation of 7-quadricyclyl cations from several of their quadricyclyl precursors **4** was met with limited success. It was possible to generate the 7-hydroxy and 7-methoxy ions, and to study their subsequent rearrangements;[27] however, the 7-methyl-7-quadricyclyl ion rearranges too rapidly to be observed (eq 5).[28] The rearrangement product is assigned



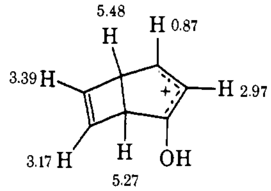
(5)

structure **13** on the basis of its spectrum, the analogy to the rearrangement of the parent system,[18] and the spectrum of the quenching product.

Ions were also generated from the bicyclo[3.2.0]heptadienyl systems **6** and **7**. As was the case with **4c**, the only cation observed after ionization of **7a**, **7b**, or the methyl ether of **7a**[29] at −125° was a rearrangement product (*vide infra*). It was possible, however, to observe the methyl ion **21** and the hydroxy ion **22**, and



21



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(20) R. K. Lustgarten, M. Brookhart, and S. Winstein, *Tetrahedron Lett.*, 141 (1971).

(21) (a) M. Brookhart, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3135 (1966); (b) H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966).

(22) R. K. Lustgarten, M. Brookhart, S. Winstein, P. G. Gassman, D. S. Patton, H. G. Richey, Jr., and J. D. Nichols, *Tetrahedron Lett.*, 1699 (1970).

(23) H. G. Richey, Jr., J. D. Nichols, P. G. Gassman, A. F. Fentiman, Jr., S. Winstein, M. Brookhart, and R. K. Lustgarten, *J. Amer. Chem. Soc.*, **92**, 3784 (1970).

(24) P. Laszlo and P. v. R. Schleyer, *ibid.*, **86**, 1171 (1964), and references therein.

(25) (a) G. A. Olah, *ibid.*, **86**, 932 (1964); (b) D. G. Farnum, *ibid.*, **86**, 934 (1964); **89**, 2970 (1967); (c) D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969); (d) L. J. Oosterhoff, *et al.*, *Rec. Trav. Chim. Pays-Bas*, **89**, 1230 (1971).

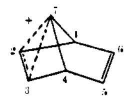
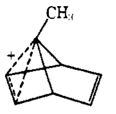
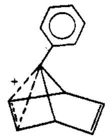
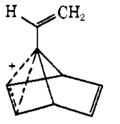
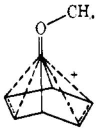
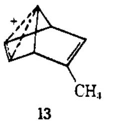
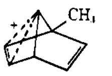
(26) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **90**, 6082 (1968); **82**, 6362 (1960).

(27) This work has been reported separately: M. Brookhart, R. K. Lustgarten, D. Harris, and S. Winstein, *Tetrahedron Lett.*, 943 (1971).

(28) Dr. D. L. Harris has now studied the 5-phenyl-7-norbornadienyl cation and its rearrangements by generation from 7-phenyl-7-quadricyclanol (personal communication).

(29) Prepared from the alcohol with MeI and Ag_2O in conjunction with another project.

Table I.[a] Nmr Spectra of 7-Norbornadienyl Cations in FSO_3H-SO_2ClF Medium (τ Values)

	Vinyl protons H_2, H_3	Vinyl protons H_5, H_6	Bridgehead H_1, H_4	Bridge H_7	Other resonances
 1[b]	2.54	3.90	4.88	6.73	
 8[c]	2.45	3.87	4.98		8.36 (3 H)
 9	2.85[d]		4.40		2.48 (5 H)[e]
 10	2.99		4.74		3.99 4.08 (3 H)[f] 4.16 4.24
 11	2.92		5.24[g] 5.49		5.46 (3 H)
 12	3.19 (1 H)	3.88	5.11	6.58	7.44 (3 H)
 13	2.64	4.35 (1 H)	5.12	6.85	8.18 (3 H)
 14[h]	2.60	3.97	5.12 (1 H)	6.95	8.22 (3 H)

[a] These spectra were all recorded on the same (60 MHz) instrument under comparable conditions unless noted otherwise. The spectra were recorded at −50 to −70°. [b] First reported in ref 5. The present data are in agreement with those of ref 5. [c] The resonances are sharp below −45°. Above −45°, the vinyl bands broaden and coalesce at −14°; see text. [d] All four vinyl protons appear as a sharp triplet and remain unbroadened (except for some viscosity broadening of all the signals) down to −140°. These data are for a 100-MHz spectrum. See text. [e] The aromatic signal appears as a narrow band with a width at half-height of *ca.* 0.15 ppm at −68°. [f] The three nonequivalent allylic hydrogens appear to present a strongly coupled ABC spin system. [g] The bridgehead protons are nonequivalent due to restricted rotation around the C–O bond; *cf.* ref 20. [h] Spectrum recorded at −130°.

the chemical shifts of these are recorded below. Like the ketone **6**,[17] **22** displays a separate resonance for each proton, and since a detailed analysis of the spectrum was not undertaken, the shift assignments for **22** are not certain. Ion **21** is unstable at −105° with respect to rearrangement, but the protonated ketone **22** is stable for several days at ambient room temperature.

As regards the generation of 7-norbornenyl ions, it is interesting to note that **18** is formed from either the syn or anti precursor alcohols.[30] This is in marked contrast to the situation with the parent systems in which the syn alcohol gives an unidentified ion or ions,[21b,31] and is presumably due to the fact that the transition state for ionization of the precursors to **18** has a substantial amount of benzylic resonance stabilization.[32]

Finally, it is worth noting specifically that the cation generated from **5g**-*2-d* has an integrated signal ratio of 2:1 for the τ 2.54 and 3.90 signals (Table I), respectively, as expected. This observation represents the first direct demonstration that the 7-norbornadienyl

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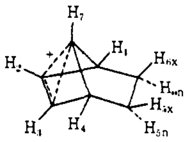
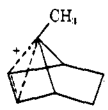
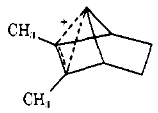
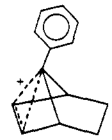
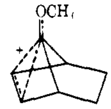
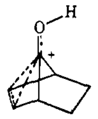
(30) We thank Professor P. Gassman for samples of these alcohols.

(31) *Cf.* footnote 7 of ref 22.

(32) The same conclusion has been deduced fom solvolytic rate data: P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968); P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545 (1969); **92**, 2549 (1970).

Table II. 7-Norbornenyl Ions (τ Values)

	Vinyl protons H_2, H_3	Bridgehead H_1, H_4	$H_{5x,6x}$	$H_{5n,6n}$	Bridge H_7	Other resonances
 **2**[a,b]	2.93	5.76	7.56	8.13	6.76	
 **15**[b,c]	2.82	5.93	7.60	8.18		8.13 (3 H)
 **16**[c]	3.53 (1 H)	5.92	Not determined		6.58	7.58 (3 H)
 **17**[c]		6.18	7.90	8.29	6.50	7.82 (6 H)
 **18**[d]	2.56	5.28	7.45	8.03		2.25 (5 H)[e]
 **19**[f]	3.18	6.17 6.42	7.77	8.22		5.33 (3 H)
 **20**[g]	3.23	6.35	7.70	8.28		−2.75 (hydroxyl)

[a] Reference 21a. [b] Reference 21b. [c] Reference 22. [d] This cation may be prepared readily from either the syn or anti epimers of the precursor tertiary alcohol. The shifts recorded in this work agree well with those recorded at Penn State; see ref 23. [e] Width at half-height is *ca.* 0.15 ppm. [f] Reference 20. [g] First reported in ref 21b. The data here are for a FSO_3H–SO_2–SbF_5 solution in which the H on oxygen can be observed.

ion is formed from 7-norbornadienyl precursors with stereospecific interaction of the anti-olefinic function.

Five-Carbon Scrambling in 1 and Related Results. In accord with those results previously published by Story, *et al.*,[5] we found that warming FSO_3H solutions of **1**, *e. g.*, to 45°, caused decomposition with no evident broadening of the resonances. Formation of tropylium ion accompanied decomposition, and this is discussed below. Further experimentation showed that spectra of **1** could be obtained at still higher temperatures by inserting a fresh sample in the preheated, pretuned probe, allowing a moment for temperature equilibration and then scanning. In this way, spectra were recorded at temperatures as high as 77°, even though $t_{1/2}$ for destruction of the ion was *ca.* 7 min at 65°. At temperatures ranging between 67 and 77°, line broadening characteristic of an exchange between magnetic environments[33] was observed. Astonishingly, the interchanging positions were not the two sets of vinyl hydrogens, as would be expected for a bridge-flipping reaction (eq 1), but rather all the positions other than the downfield or "bridged" vinyl function. Samples of the spectra obtained are shown in Figure 1. We have labeled this exchange phenomenon the "five-carbon scrambling process" in order to distinguish it from another (seven-carbon) degenerate isomerization which was subsequently uncovered. From the observed line broadenings, first-order rate constants for loss of a proton from a given site could be computed using the slow exchange approximation.[33] These

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[33] (a) C. S. Johnson, Jr., *Advan. Magn. Resonance*, 1, 33 (1967); (b) G. Binsch, *Top. Stereochem.*, 3, 97 (1967); (c) J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Elmsford, N. Y., 1965, p 481 ff; (d) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

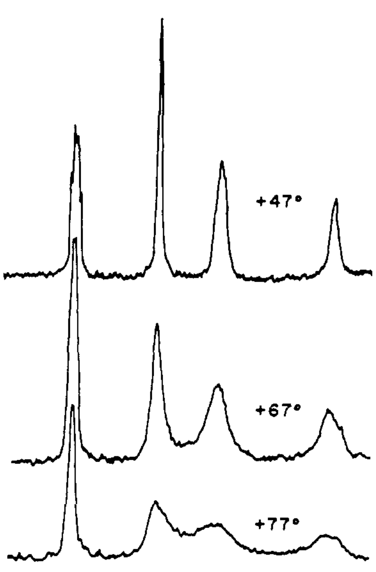


Figure 1. High-temperature spectra of the 7-norbornadienyl ion.

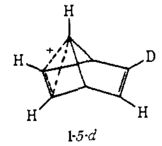
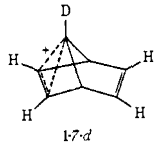
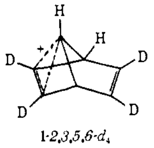
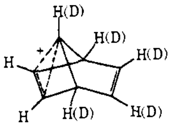
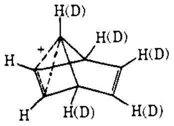
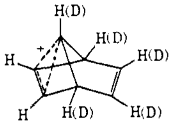
are given in Table III along with the calculated average lifetime of a proton at a given site.

Table III. Exchange of Protons from Different Sites in the 7-Norbornadienyl Cation (60 MHz)

Resonance signal, τ	T,[a] °C	$\delta\nu$,[b] Hz	$k = \pi(\delta\nu)$,[c] sec^{-1}	$\tau = 1/k$, sec
3.90	67	7	22	0.045
($H_{5,6}$)	71	9	28	0.036
	77	17	54	0.019
4.88	67	12	38	0.026
($H_{1,4}$)	71	17	54	0.019
	77	34	107	0.009
6.73	67	14	44	0.023
(H_7)	71	17	54	0.019
	77	35	110	0.009

[a] Absolute temperatures are in error by ±4°, but relative values are within ±1°. [b] Width at half-height minus width at half-height at 47°. The value for the τ 3.54 signal ("bound" vinyl function) is *ca.* −3 Hz at each temperature owing to averaging of couplings. [c] First-order rate constant for exchange of proton from given site; *cf.* ref 33d.

Table IV. Rates and Free Energies of Activation of Degenerate Isomerizations of the 7-Norbornadienyl Cation

Cation	 1-5-*d*	 1-7-*d*	 1-2,3,5,6-*d*$_4$
Product			
Temp, °C	−47	−55	−50
10^4k, sec^{-1}	$3^{a,b}$	$1.7^{a,c}$	$2^{a,b}$
$\Delta F^{\ddagger}$, kcal/mol	16.7	16.4	16.7

[a] Evaluated graphically using $\ln[(H_\infty - H_0)/(H_\infty - H_t)] = kt$, with H_∞ equal to the equilibrium amount of protium. [b] In the unbound vinyl group. [c] At C_7.

Table V. Rate Data for "Five-Carbon Scrambling" and Related Processes

Reactant ion	Product ion	Temp, °C	k, sec^{-1}	$\Delta F^{\ddagger}$, kcal/mol
1	**23**	−50	3×10^{-4}	16.6
14	**21**	−75	2.2×10^{-3} [a]	13.8
13	**21**	−75	$\sim 1 \times 10^{-4}$ [a]	~15.2
23	**1**	−120	$> 1 \times 10^{-2}$ [b]	<10.2
21	**14**	−105	2.5×10^{-4}	12.4
21	**13**	−105	2.0×10^{-4}	12.5
8	**12**	−17	4×10^{-4}	18.9
12	**26**	32	$< 9.5 \times 10^{-4}$ [c]	>22.1
13	**27**	−42	$< 9 \times 10^{-4}$ [d]	>16.6

[a] Estimated on the basis of 4% of **14** in equilibrium with **13**, and the assumption that **21** partitions to **13** and **14** in the same ratio at −75° as at −105°. [b] Low limit based on the inability to observe **23** within 2 min after generation at −120°. See text. [c] This is the rate constant for decomposition of **12**. [d] This is the rate constant for decomposition of **13**.

In order to sudy this degenerate isomerization of **1** on a more conventional time scale, the ion was generated from each of the labeled precursors, **5b**, **5g**-*2-d*, and **4h**-*2,3,5,6-d*$_4$.[34] Indeed, warming of each of these ions caused scrambling of the label between the five positions C_1, C_4, C_5, C_6, and C_7, and the equilibrium distribution of deuterium was statistical.[35] It was found that the scrambling process could be conveniently monitored at temperatures around −50°. The results are summarized in Table IV and in the first entry of Table V. Careful examination of the spectra yielded another important observation. The signal growth patterns revealed that deuterium is incorporated sequentially at adjacent positions. Thus, in the case of **1**-*5-d* and **1**-*2,3,5,6-d*$_4$, the label is first incorporated into the bridgehead, then into the bridge position. With **1**-*7-d*, deuterium appears first at the bridgehead, then in the unbound vinyl group. These observations indicate that the isomerization occurs by a stepwise circumambulatory motion of the five-carbon framework of **1** with respect to the two-carbon bridge which comprises the bound vinyl function. Such a process requires that the lifetime of the unbound vinyl protons be twice that of the bridge and bridgehead protons since each step of the circumambulation will move both the bridgehead and bridge carbons to adjacent sites, but only one of the two vinyl positions will move to a bridgehead position. Indeed, inspection of the data in Table III shows that the C_7 and bridgehead signals are broadened to twice the extent of the unbound vinyl protons.

In general, the rate data obtained by nmr monitoring are insufficiently precise to allow accurate determination of temperature coefficients over a small temperature range. However, the rate data of Tables III and IV represent rate measurements for the same reaction over two widely separated temperature ranges, and from these data, $\Delta H^{\ddagger}$ for the process may be estimated at 14.5 ± 2.0 kcal/mol.

At this point, it occurred to us that a reasonable mechanism for this isomerization involved equilibra-

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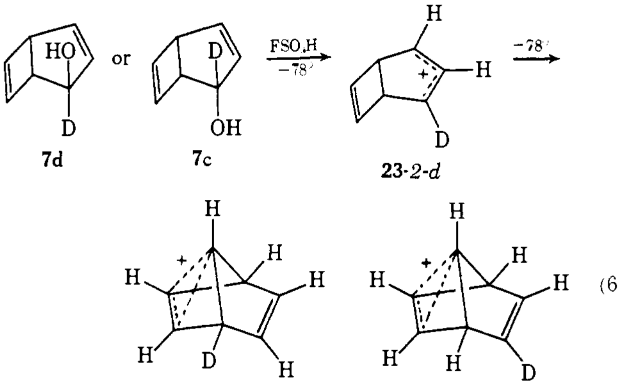
(34) The spectrum produced by ionization of **5g** showed a signal for protonated acetic acid at *ca.* τ 7.25; that produced from **5h** showed protonated methanol at τ 5.82.

(35) For example, the ion generated from **5g**-*2-d* showed relative peak intensities of 2.0:1.6:1.6:0.8 for the τ 2.54, 3.90, 4.88, and 6.73 signals, respectively, at equilibrium.

tion with the bicyclo[3.2.0]heptadienyl cation (**23**). Accordingly, alcohols **7a** and **7b** were extracted into FSO_3H at −78°, and the resulting spectra were observed at −78°. In either case the nmr spectrum of **1** and only **1** was observed. Most importantly, when **7c** and **7d** were used as precursors, the integrated signal intensities for the bound vinyl, unbound vinyl, bridgehead, and bridge protons, respectively, were 2.0: 1.5:1.5:1.0. In other words, 50% of the deuterium label appeared at a bridgehead position, and 50% appeared in the unbound vinyl group. This result is in exact accord with a mechanism wherein the first formed cation, **23**-*2-d*, ring expands to **1** with either carbon of the cyclobutene vinyl function undergoing a 1,2 shift as the migrating vinyl group becomes the bound vinyl function (eq 6). Subsequent experimentation showed that even when **7a** and **7b** were extracted into FSO_3H–SO_2ClF at −130° and the resulting solution was observed within 2 min at −120°, only **1** was present in solution. From this result it may be estimated that the rate constant for conversion of **23** to **1** at −120° is greater than 1×10^{-2} sec^{-1}. The information currently available concerning the equilibrium between **23** and **1** is summarized in Table VI.



7d **7c** **23**-*2-d*

(6)

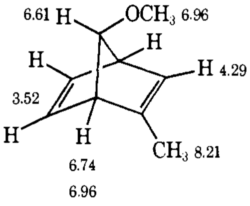
Table VI. Equilibria between Bicycloheptadienyl Cations

Equilibrium	Temp, °C	K
23 ⇌ **1**	−100	>1.2 × 10$^{8\,a}$
21 ⇌ **14**	−100	60^a
14 ⇌ **13**	−75	24^b
	−100	38^a
21 ⇌ **13**	−100	~2300^a

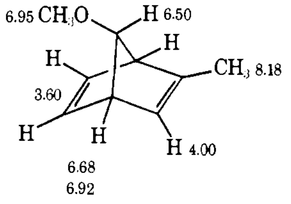
^{a} Computed using activation free energies for forward and reverse reactions (Table V). ^{b} Measured directly.

As mentioned in the previous section, and in marked contrast to the results with **7a** and **7b**, the tertiary alcohol **7e** gave ion **21** when extracted into FSO_3H–SO_2ClF at −130°. At −105°, however, this cation does undergo (quantitatively) the ring expansion to the [2.2.1] system. The ring expansion occurs to give the methyl-substituted cations **13** and **14** in a 45:55 ratio (eq 7). The identities of **13** and **14** are determined from their nmr spectra, from the fact that **13** may also be prepared from **4c**, and from the fact that **13** could be quenched with CH_3OH–$NaHCO_3$ at −78° to give a methyl ether (representing at least 95% of the isolable quench product) whose nmr spectrum is most compatible with structure **24**. This compound is differentiated from its epimer (*i.e.*, **25**) by virtue of the fact that the single propylenic vinyl proton in 24 appears as a broad singlet, and the two equivalent olefinic hydrogens appear characteristically, as a distinct triplet (J = 2 Hz). Ether **25** shows a distinct sextet (J = 2 Hz) for the lone vinyl hydrogen whereas the triplet representing the two equivalent olefinic hydrogens is broadened and barely resolved. The broadened appearance of these signals is attributed to coupling with the anti hydrogen at C_7.[24]

$$\mathbf{21} \xrightarrow[k\,=\,4.5\,\times\,10^{-4}\ \text{sec}^{-1}]{-105^\circ} \underset{45\%}{\mathbf{13}} + \underset{55\%}{\mathbf{14}} \qquad (7)$$



24



25

Warming of the solution containing **13** and **14** caused isomerization of the latter ion to the former.[36] The rate for this process was measured at −75° (Table V). The rearrangement apparently proceeds to give equilibrium concentrations of **14** (4%) and **13** (96%).[37] Further warming of the solution produced only decomposition with no noticeable appearance of signals which might be attributable to a discrete cationic intermediate. The rate of disappearance of **13** was measured at −42° (eq 8).

$$\mathbf{13} \xrightarrow[k\,\sim\,9\,\times\,10^{-4}\ \text{sec}^{-1}]{-42^\circ} \text{dec} \qquad (8)$$

Warming of a solution of the 7-methyl-7-norbornadienyl ion (**8**) caused rearrangement to the 2-methyl ion **12**. The rate was measured at −17° (Table V). The reaction proceeds in *ca.* 60% yield with development of about 40% decomposition products characterized by broad nondiscrete signals. Further warming of the solution to 32° results in decomposition of **12** with no apparent discrete species remaining. The rate constant was estimated from the data (eq 9). As was the case for **13**, **12** could be quenched with CH_3OH–$NaHCO_3$ at −78° to give the anti methyl ether **25** whose assignment is based on its nmr spectrum as discussed above.

$$\mathbf{12} \xrightarrow[k\,\sim\,9.5\,\times\,10^{-4}]{32^\circ} \text{dec} \qquad (9)$$

On the assumption that the mechanism outlined above to account for the five-carbon deuterium scrambling in the parent ion is the same one operating during the isomerizations of the methylated ions **21**, **13**, and **14**, the collected rate data may be tabulated as in Table V. Rate limits to hypothetical processes based on the observed rates of decomposition of ions **13** and **14** are also given in Table V. (Ions **26** and **27** in Table

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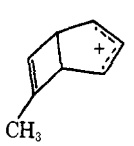
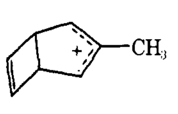
(36) This observation further substantiates the isomeric relation between **13** and **14** and, hence, the structural assignment to **14**, since the structures **8**, **12**, and **13** are established by the combination of quenching experiments and independent modes of generation.

(37) The resonances of **13** and **14** are nearly overlapping except for the shifts of the unbound vinyl hydrogens. At equilibrium, integration of the τ 3.97 signal indicated 4% of **14** remaining.



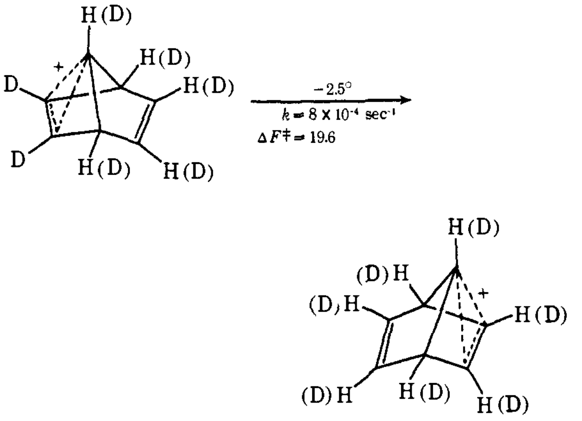
26



27

V have never been observed.) The equilibrium constants which may be estimated from the data in Table V are given in Table VI.

The Bridge-Flipping Reaction. Returning to the original line of inquiry, it will be recognized that the five-carbon scrambling process described in the previous section leaves the labeled cations **1**-*5-d*, **1**-*7-d*, and **1**-*2,3,5,6-d*$_4$ with deuterium equally distributed with respect to the five-carbon locus, but not statistically distributed to all seven positions. The ratio of protium concentrations in the bound vinyl and unbound vinyl functions is decidedly greater than unity. Therefore, the potential for observing a bridge-flipping reaction still existed, since this isomerization would cause scrambling of label to the "bound" vinyl positions (and lead to total statistical scrambling in the ion). The fact that there was no indication of such a process from the line broadening observed as 77° by no means precluded the possibility of observing it using conventional label scrambling. Accordingly, the solutions which were used to obtain the data reported in Table IV were warmed further. At 0°, the anticipated scrambling was indeed observed. Using the sample derived from **1**-*2,3,5,6-d*$_4$, a rate was measured at −2.5° (eq 10). This scrambling—called "seven-carbon scrambling"—may not be due to a bridge-flip mechanism (*cf.* Discussion) but its rate represents, at least, a lower limit to the rate of bridge-flipping, and is entered in Table VII as such.



(10)

The 7-methyl ion **8** was examined next for bridge-flipping, and here the result was explicit and unequivocal. As the temperature is raised above −45°, the vinyl signals of **8** begin to broaden. They eventually coalesce at −14°. Furthermore, the bandwidth of the bridgehead protons actually narrows and sharpens to a symmetrical pentuplet at −14° and the methyl signal remains sharp. The narrowing of the bridgehead signal is due to the averaging of couplings to the two nonequivalent vinyl signals. Only the signals for the two vinyl functions are averaged, and hence this is a true bridge-flip reaction. The rate at the coalescence temperature was estimated using the appropriate expression[33] and the value is the second entry in Table VII. The nondegenerate rearrangement of **8** to **12**, described in the previous subsection, is considerably slower than the bridge-flipping of **8**, and hence does not interfere with measurement of the latter.

Table VII. Rate Constants for Bridge-Flipping Reactions

Ion	Temp, °C	k, sec^{-1}	$\Delta F^{\ddagger}$, kcal/mol
1	−2.5	$\leq 8 \times 10^{-4}$ [a]	≥ 19.6
8	−14	1.89×10^{2}	12.4
9	−140	$>7 \times 10^{3}$ [b,c]	<5.2
10	−76	$>3.7 \times 10^{3}$ [b]	<8.2
11[d]	−100	$>8.3 \times 10^{1}$ [b]	<8.4
12	32	$<9.5 \times 10^{-4}$ [e]	>22.1
13	−42	$<9 + 10^{-4}$ [e]	>16.6

[a] The process measured may be bridge-flipping, or may be due to some other mechanism which superposes a seven-carbon scrambling on the more rapid five-carbon scrambling; see text. [b] Limit established by equivalence of the four vinyl hydrogens in the spectrum; see text. [c] 100-MHz spectrum. [d] This ion is thought to have a symmetrical ground state; *cf.* ref 20. [e] This is the rate constant for decomposition of the ion, quoted as an upper limit to the nondegenerate bridge-flip.

The 7-phenyl (**9**), 7-vinyl (**10**), and 7-methoxyl (**11**) ions each show magnetic equivalence of the four vinyl hydrogens (*cf.* Table I), and this circumstance remains unaltered at the lowest temperature at which each ion was observed. Cation **9** was chosen as a test case for which 100-MHz nmr spectra were recorded at as low a temperature as was possible (−140°, FSO$_3$H (0.09 ml)–SO$_2$ClF (0.25 ml)–SO$_2$F$_2$ (0.30 ml) medium).[38] No indication of nonequivalence of the vinyl hydrogens was recorded. The third, fourth, and fifth entries of Table VII result from these observations. These lower limits are computed by application of the fast exchange approximation (eq 11),[33c,d]

$$k = \pi \nu_{AB}^{2}/2\delta\nu \qquad (11)$$

where ν_{AB} is the chemical shift difference between the bridged and unbridged vinyl hydrogens in the "frozen" ions, and $\delta\nu$ is the observed broadening of the averaged (observed) resonance. The assumption was made that a broadening of 4 Hz would have been observed ($\delta\nu = 4$), and that ν_{AB} is 1.38, 1.62, and 0.24 ppm for **9**, **10**, and **11**, respectively. These values were estimated as follows. First, it was noted that addition of a double bond to **2** (to give **1**) or to **15** (to give **8**) causes a deshielding of the "bonded" olefinic protons by the same amount, *ca.* 0.38 ppm. On the assumption that the same shift will occur in going from the corresponding 7-norbornenyl ions to **9**, **10**, and **11**, the models **18** and **19** were used to estimate the shift of the "bonded" olefinic protons in **9** and **11**. Combination of the estimated value with the observed (average) shift for all four olefinic protons yields the estimated value for the "nonbonded" or upfield olefinic proton shift.[39] Since the 7-vinyl-7-norbornenyl cation is unknown, it was assumed that the "bonded" olefinic proton shift for **10** is the same as for **9**. The last two entries in Table VII represent limits established by the observed rates of decomposition for ions **12** and **13**.

Tropylium Ion Formation. Table VIII lists the rates of formation of several tropylium ions. The re-

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(38) At this temperature viscosity effects cause broadening of all signals to about twice their widths at −125°.

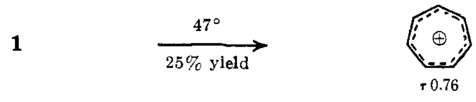
(39) This approach obviates the problem of estimating the anisotropic deshielding effect of the C$_7$ substituent on the syn or "nonbonded" olefinic protons.

Table VIII. Tropylium Ion Formation from 7-Norbornadienyl Cations

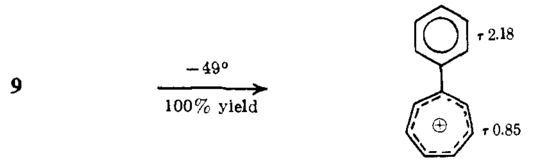
Ion	Product	Temp, °C	k, sec^{-1}	$\Delta F^{\ddagger}$, kcal/mol
1	**28**	47	6.2×10^{-4}	23.5
9	**29**	−49	1.6×10^{-3}	15.9
10	**30**	−42	3.1×10^{-4}	17.1
11	**31**	43	1.15×10^{-4}	24.2
12	Methyltropylium	32	$<9.5 \times 10^{-4}$ [a]	>22.1
13	Methyltropylium	−42	$<9 \times 10^{-4}$ [a]	>16.6

[a] This is the rate constant for decomposition of the ion, quoted as an upper limit to the rate of tropylium ion formation since methyltropylium should be stable at this temperature.

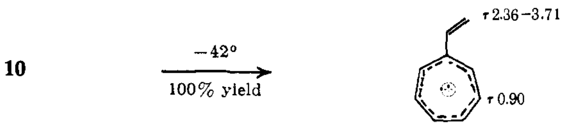
action was observed for ions **1**, **9**, **10**, and **11** in yields as shown in eq 12–15. The assignments of structure to the tropylium ions follow from the characteristic sharp, downfield signal representing six hydrogens, and/or comparison of the spectral data with reported values.[40] Further possible reaction or decomposition of the tropylium ions was not studied. As indicated by data given above, neither of the methylated ions **12** and **13** gave any detectable formation of the methyltropylium ion at a rate competitive with their decompositions (Table VIII). From the observation that at least **28** and **31** are stable at *ca.* 45°, it is expected that the methyltropylium ion would be stable at temperatures well above those at which **12** and **13** were observed to decompose.



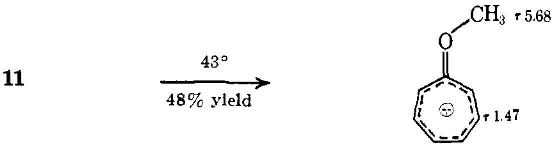
28 (12)



29 (13)



30 (14)



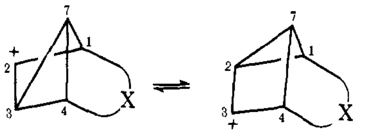
31 (15)

Miscellaneous Observations. Another degenerate reaction which was observed in this work was methoxyl rotation in ions **11**, **19**, and the saturated homolog. This process could be studied by virtue of the fact that the syn and anti bridgehead protons of each ion are magnetically nonequivalent. Since the data have been discussed in detail previously,[20] they will not be presented here.

Regarding the stabilities of the 7-norbornenyl ions, some qualitative observations may be recorded. Ion **15** decomposes or isomerizes to unknown product(s) at 9° with a measured first-order rate constant of *ca.* 3.1×10^{-4} sec^{-1}. Ion **18** rearranges to an unknown species at 8° with a rate constant of *ca.* 1.1×10^{-3} sec^{-1}. In each of these two cases, the reaction proceeds with development of complicated and complex nmr signals, but not with the broad, nondiscrete absorptions and blackened appearance usually characteristic of gross decomposition. However, these reactions were not investigated further. Ion **2** has a half-life of *ca.* 20 min at 0° (FSO_3H–SO_2–SbF_5 medium). Ions **16** and **17** are respectively very much less stable than and substantially more stable than **2** and **15**. Cation **16** has a half-life of *ca.* 5 min at −50° while **17** decomposes with a first-order rate constant of *ca.* 2×10^{-4} sec^{-1} at 49°.[22] Ion **20** has a half-life of *ca.* 15 min at −25° while **19** was stable for at least several minutes at ambient room temperature.

Discussion

The combined chemical, theoretical, and detailed nmr data which have been gathered for ions **1** and **2** make the case for unsymmetrical bridging in these ions almost incontrovertible. The nmr spectra of ions **1** and **2** have been discussed and compared in detail.[4,5,21a,41] In the present instance, we will concentrate on comparisons involving substituted ions. The only serious structural rival to the bridged model for both **1** and **2** has been the set of classical, equilibrating tricyclic ions (windshield-wiper degeneracy) **32**.[42] While this formulation (eq 16) is highly unlikely on the basis of solvolytic data, it is not necessarily ruled out by the nmr shift data *per se.*[42a] The H_7 chemical shifts are within the range of those encountered for β hydrogens on stable cyclopropylcarbinyl cations,[43] and the $H_{2,3}$ shift could conceivably represent the time-averaged signal for an α-cyclopropyl hydrogen and the hydrogen directly attached to the carbinyl carbon.



(16)

32a, X = CH_2CH_2
b, X = CH═CH

However, consideration of the nmr spectra of **12** and **16** strongly suggests that the windshield-wiper formulation is incorrect. If eq 16 *were* correct, then the equilibrium for the monomethyl ions **12** and **16** would surely be shifted in favor of the (classical)

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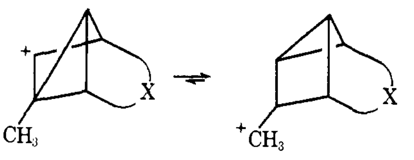
(40) Tropylium ion: (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960); (b) B. P. Dailey, A. Gawer, and W. C. Neikam, *Discuss. Faraday Soc.*, **34**, 18 (1962). Phenyltropylium ion: (c) H. J. Dauben, R. B. Medz, and W. R. Gresham, personal communication; (d) R. B. Medz, Ph.D. Thesis, University of Washington, 1964. Hydroxytropylium ion: (e) *cf.* ref 41.

(41) M. Brookhart, Ph.D. Thesis, University of California at Los Angeles, 1968.

(42) (a) H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.*, **85**, 2324 (1963); (b) H. C. Brown, "Non-Classical Intermediates," Organic Reaction Mechanisms Conference, Brookhaven, N. Y., Sept 5–8, 1962; (c) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 159 (1964); (d) *Chem. Eng. News*, **45**, **88** (Oct. 5, 1964). (e) The fact that the vinyl hydrogen signals for 1 and 2 are sharp at −75° requires that the hypothetical "windshield-wiper degeneracy" have a rate constant of *ca.* 10^5 sec^{-1} at this temperature.

(43) C. U. Pittman and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 5123 (1965).



(17)

33

tertiary ions (eq 17) and the nmr spectrum would be that of **33**, essentially a tertiary cyclopropylcarbinyl cation. The cyclopropyl α and β hydrogens of such an ion may be expected to absorb at *ca.* τ 7–8,[43] yet the corresponding absorptions in **12** and **16** are τ 3.19 and 3.53, respectively, for the unique vinyl proton. This places them *ca.* 3 ppm downfield from H_7 (τ 6.58 and 6.58 in **12** and **16**, respectively). It is also to be noted that the methyl shifts in **12** and **16** are τ 7.44 and 7.58, respectively, which places them at higher field than might have been expected for **33** (*e. g.*, dimethylcyclopropylcarbinyl cation has methyls at τ 6.86 and 7.40).[43] Though there is a small deshielding of H_7 as methyl groups are added to the "bound" vinyl function, the relative constancy of the H_7 shift in ions **1–2**, **12–14**, and **16–17** is another indication of the failure of methyl substituents at other positions to alter drastically the charge distributions of **1** and **2**. Clearly the data are only compatible with a bridged formulation for **12** and **16**. Obviously, the π-electron distribution in the three-centered cations **1** and **2** is insufficiently sensitive to 2-methyl substitution for **12** and **16** to be formulated in terms of equilibrating tricyclic structures.

All of the four possible methyl-substituted 7-norbornadienyl cations have now been observed. The chemical shift of the methyl group in this series serves as a probe for relative charge distribution, just as hydrogen does in the parent ions. The methyl group in **12** is substantially deshielded relative to the one in **8**. Again, this supports the general structural argument which states that the C_7–CH_3 bond is largely tetrahedrally hybridized, and that much of the positive charge in the ion resides at C_2 and C_3. The shift of the methyl group in **13** appears hardly affected by the positive charge (compare with **24** and **25**) and the same may be said for **14**. The same arguments apply to **15**, **16**, and **17**, where again the shift of methyl at C_7 is at substantially higher field than the shifts for the methyls on the ("bound") vinyl function. Thus, consideration of the methyl shift affords yet one more indication of the bridged nature of **1** and **2**.

The spectra of **9** and **10** show four equivalent vinyl hydrogens at low temperatures. Nevertheless, we feel that both of these ions are unsymmetrically bridged in the ground state. This conclusion follows from the observed chemical shifts for the protons on the phenyl and vinyl moieties, and from the appearance of these signals. First of all, concerning **9** and **18**, the shifts of the aromatic protons (2.48 and 2.25, respectively) are at substantially high field relative to typical α-phenyl carbonium ions. Examples of the latter are cumyl, τ 1.20–2.03,[25a] and benzhydryl, τ 1.54–2.02.[25a] Even the phenyltropylium ion, with positive charge substantially delocalized in the seven-membered ring, has a lower shift (τ 2.18) for the phenyl hydrogens. The relatively high chemical shift for the aryl hydrogens in **9** and **18** indicates that there is very little positive charge delocalized into the rings, as would be anticipated from our model of the bridged ion.

Perhaps an even more important clue concerning the structures of **9** and **18** comes from the pattern of the aromatic resonance. The clue is that there is no pattern! That is to say, the five hydrogens appear as a narrow signal (Tables I and II). By contrast, carbonium ions in which an α-phenyl group tolerates considerable positive charge have relatively large shift differences between different protons. For example, the cumyl and benzhydryl cations[25a] have their ortho and meta proton shifts separated by 0.83 and 0.48 ppm, respectively. On this basis, the phenyl rings in **9** and **18**[23] bear very little positive charge. This finding strongly supports the conclusion that **9** and **18**[23] are bridged in the ground state with extensive rehybridization at C_7 which precludes any significant π–π overlap between C_7 and the phenyl ring. The same conclusion follows for **10**. First of all, it may be reasoned by analogy that if phenyl is not a sufficiently charge stabilizing group to cause benzylic resonance to outweigh the stabilization afforded by bridging, then vinyl will not be either, since benzylic and allylic cations probably have similar delocalization energies.[44] More importantly, the positions of the three nonequivalent vinyl hydrogens in **10** are at substantially higher field than might be expected for an allyl cation[26] and the pattern displayed is more like that of a three-substituted propene. Even in the highly stabilized vinyltropylium ion **30**, the vinyl hydrogens are all deshielded and more widely split than those in **10**.

As regards the structure of the methoxyl ions **11** and **19** (and **20** by analogy), we believe that the bridging interaction is minimal and that **11** has a symmetrical ground state with full π–π overlap between C_7 and oxygen. The arguments that lead to this conclusion are based on the observed methoxyl rotation (or inversion) and have been summarized in detail elsewhere.[20]

For 7-norbornenyl ions, the dividing line distinguishing those with significant bridging from those with insignificant or zero bridging appear to fall between 7-phenyl and 7-anisyl.[23]

Since the ground-state geometries are intimately related to the conclusions to be drawn from the data in Table VII, the bridge-flipping reaction will now be discussed. All of the previous lines of reasoning which led to the assignment of an unsymmetrically bridged ground state for the 7-norbornadienyl ion culminate quite dramatically in the data of Table VII. Because of mechanistic uncertainties, it cannot be stated unequivocally that bridge-flipping in **1** has $\Delta F^{\ddagger} = 19.6$ kcal/mol. However, it is at least certain that this value is a minimum $\Delta F^{\ddagger}$ for the isomerization. Thus, the symmetrical form of **1** is less stable than the bridged form by at least 19.6 kcal/mol.[45] This energy difference is clearly and strikingly diminished when the hydrogen at C_7 is replaced by methyl. There is a further diminution when methyl is replaced by phenyl, and the barrier is probably inverted when phenyl is replaced by methoxyl.[20] Thus, the original prediction is verified: the symmetrical form of the ion becomes more stable relative to the ground state when increasingly charge-stabilizing substituents are placed at the

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[44] *Cf.* D. Bethel and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, p 67.

[45] An extended Hückel calculation had predicted a barrier of 8 kcal/mol.[8d]

bridge position because of the far greater overlap between the substituent and C$_7$ in the symmetrical form.

Bridge-flipping for ions **12** and **13** would represent the nondegenerate conversion of one to the other. Presumably, the reaction is exothermic in the **13** → **12** direction. The barriers to bridge-flipping are not expected to be much different than that for **1** itself. The lower limits to $\Delta F^{\ddagger}$ established by the observed rates of decomposition of **12** and **13** (Table VII) are thus entirely reasonable.[46]

The reason that 19.6 kcal/mol must be taken as a lower limit for bridge-flipping in **1** is that the seven-carbon scrambling reaction described in the Results section may be explained by mechanisms other than bridge-flipping. The seven-carbon scrambling reaction is superposed on the much more rapid five-carbon scrambling process. This means that the seven-carbon scrambling is accommodated by any mechanism which transfers a bound vinyl carbon to *any other site* in the ion. Mechanisms which may be considered in addition to bridge-flipping will be described below, but first we will discuss the five-carbon scrambling phenomenon.

The five-carbon scrambling, described by the data of Tables III and IV (Figure 1), and the other results described in the preceding section are best interpreted in terms of a rapid equilibrium between the ion **1** and ion **23**. The precise mechanism envisioned for the reaction involves the shift of a bound vinyl carbon from C$_1$ or C$_4$ of **1** to C$_7$ (eq 18). The reaction proceeds through transition state **34** such that the partial bonding which exists between C$_2$ and C$_7$ in the ground state of **1** is solidified to a full σ bond, while the bond between C$_2$ and C$_1$ is completely broken. This is a simple 1,2 shift in the classical sense, but presumably facilitated by the elements of 1,3-orbital overlap which exist in the ground state of **1**. Ring expansion of **23** back to **1** is the microscopic reverse. Since either of the two equivalent cyclobutenyl vinyl carbons in **23** will undergo the expansion, a series of ring contractions of **1** and ring expansions of **23** comprises, in essence, a net perambulatory motion of the "bound" vinyl function about a locus described by the other five carbons of cation **1**. The movement of the "bound" bridge may be envisioned as occurring in an inchworm, ratchet-like fashion. This is illustrated in Chart II. This mechanism accounts for all of the observed facts. It maintains the identity of the "bound" vinyl carbons as required by the line broadening and labeling data. It accommodates the sequencing of the label incorporations to adjacent positions of the five-carbon locus (as opposed to a random scrambling). It correctly predicts that half of the label in **7c** or **7d** will be incorporated at C$_1$ and half at C$_5$ when **1** is generated irreversibly at −120°.

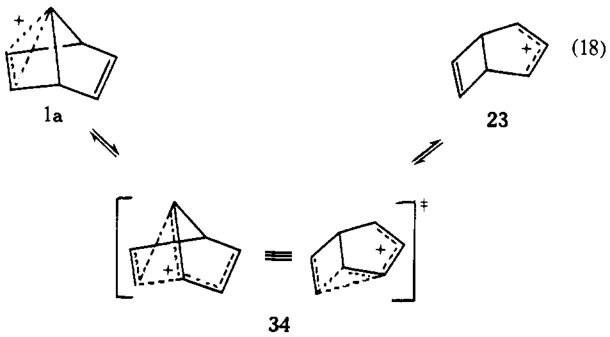
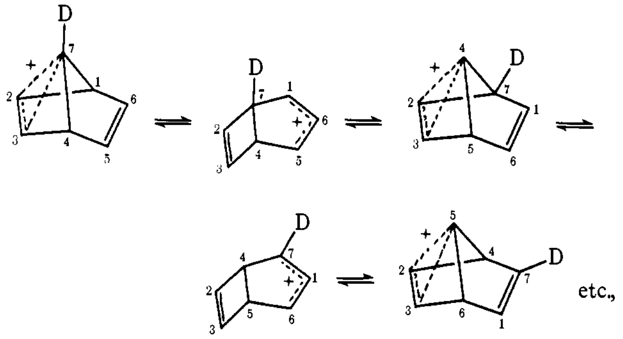
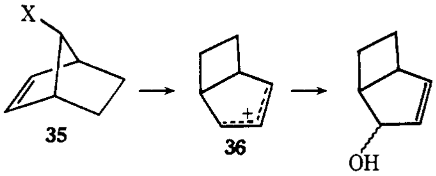
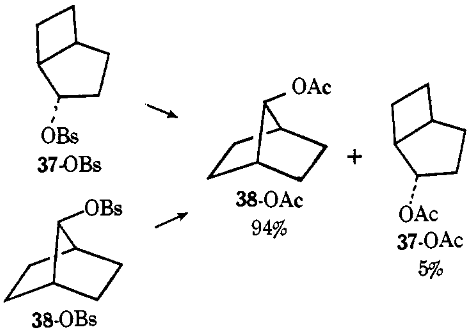


Chart II



It is worth noting that neither ring contraction of **1**[4] nor ring expansion of **23**[47] occurs under solvolytic conditions where the lifetime of the ions is very short. Nevertheless, there is no lack of solvolytic analogy. For example, syn-7-norbornenyl derivatives (**35**) hydrolyze to give a ring contracted 2-bicyclo[3.2.0]heptenol presumably through the intermediate bicyclo[3.2.0]heptenyl cation (**36**).[48] Either *trans*-2-bicyclo[3.2.0] brosylate (**37**) or 7-norbornyl brosylate (**38**) give the same mixture of acetates in acetolysis.[49] The anti-7-norbornenyl system is formed during acetolysis of a *trans*-2-bicyclo[3.2.0]-5-heptenyl tosylate.[50] Driving force due to strain and electronic factors is considerable in all of these systems and rearrangement is competitive with solvent capture. In contrast, because homoallylic and allylic resonance in **1** and **23**, respectively, is large, the barriers to interconversion are sufficiently high that they may only be measured in a solvent of very low nucleophilicity where carbonium





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[46] The difference in rates for decomposition of these two ions may have nothing to do with their relative thermodynamic stabilities, but rather may reflect a kinetic reactivity differential. For example, 13 may be much more susceptibile to electrophilic attack by acid at the "unbridged" vinyl function than is 12. Alternatively, either or both of the ions may undergo discrete unimolecular isomerization to other species which are unstable under the reaction conditions.

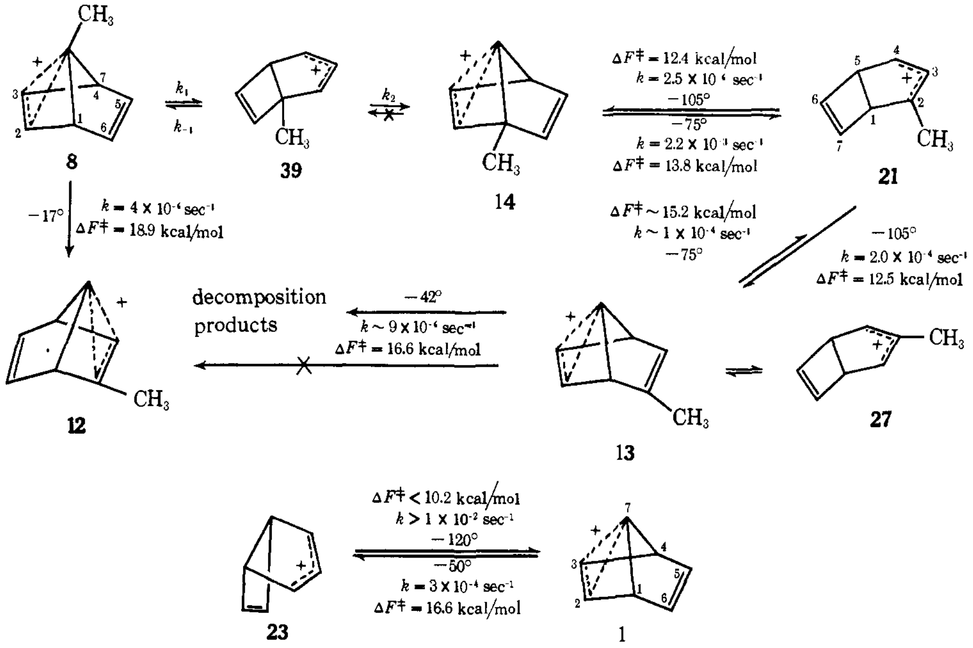
(47) P. R. Story and J. A. Cooke, *Chem. Commun.*, **18**, 1080 (1968).

(48) S. Winstein and E. Stafford, *J. Amer. Chem. Soc.*, **79**, 505 (1957).

(49) (a) S. Winstein, F. Gadient, E. Stafford, and P. E. Klinedinst, *ibid.*, **80**, 5895 (1958); (b) F. B. Miles, *ibid.*, **90**, 1265 (1968); (c) P. Gassman, *et al.*, *ibid.*, **90**, 6238 (1968); (d) B. Funke and S. Winstein, *Tetrahedron Lett.*, 1477 (1971).

(50) S. C. Lewis and G. H. Whitham, *J. Chem. Soc. C*, 274 (1967).

Chart III

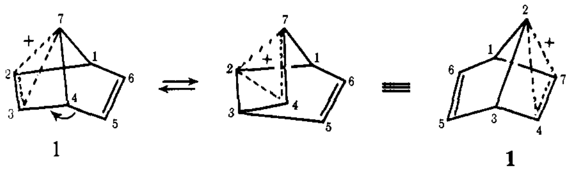


ion lifetime is relatively long. From the data in Table V, the minimum figure for the equilibrium constant between **1** and **23** may be estimated to be greater than 1.2×10^8 at $-100°$, and this is given in Table VI.

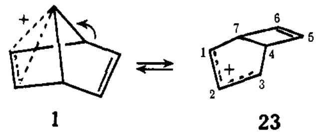
It is evident that **1** is substantially stabilized relative to **23**, but it is not clear how much of the stabilization is due to the difference in strain energy and how much to a resonance energy difference. Simple calculations indicate that the resonance energies of the two systems are comparable.[8b] The standard free energy difference between the bicyclo[2.2.1]heptane and bicyclo[3.2.0]heptane systems is probably on the order of 14 kcal/mol.[49a] Though this does not necessarily relate to the unsaturated homologs, a substantial strain energy difference may quite reasonably be expected for the latter. If the difference between resonance energies is a small factor in determining the equilibrium between **1** and **23**, it apparently assumes a substantially greater significance for the equilibrium between **14** and **21**. Making the reasonable assumptions that the methyl group at the bridgehead position in **14** imposes only negligible perturbation of the delocalization energy of **1**, and that the methyl group does not alter the relative strain energies of the two systems, one notes that it has an enormous effect in stabilizing **21**. Inspection of Table VI shows that it causes the equilibrium to shift in favor of the [3.2.0] ion by more than six powers of ten at $-100°$. This effect is obviously associated with the much greater influence of the methyl group in the terminal allylic position of **21** than at the saturated quaternary bridgehead of **14**. The stabilization effect of the methyl group is exhibited to a smaller degree for the third equilibrium in Table VI. Cation **13** is favored over **14**, presumably because of the greater stability of the trisubstituted double bond in **13**. The last entry in Table VI is determined by the preceding two. It reflects both the large stabilizing effect of the methyl group in **21** and the smaller effect in **13**.

The individual reaction rate components of the equilibria just discussed are entirely in accord with the five-carbon scrambling mechanism given above for the parent (degenerate) system. Thus, the ring contractions of **13** and **14** to **21** are both accelerated relative to the **1** → **23** contraction (see Chart III), because of the methyl stabilization in **21**. It is not known whether **13** ring-contracts the "other way" to give the unobserved ion **27**. It seems unlikely, however, that this reaction would compete significantly with the conversion to **21**, since the substituent will have a much greater stabilizing effect on the terminal allylic position. For the same reason, it also seems unlikely that "other way" ring contraction of **14** to the unobserved isomer **39** would compete with conversion to **21**. It is probable that if **39** had been formed, it, in turn, would have ring-expanded, at least in part, to **8**. Cation **8** was not observed.

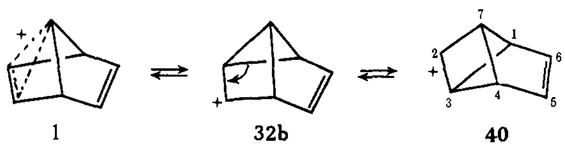
Returning to the problem of seven-carbon scrambling in **1**, we list below (eq 19–21) three mechanisms



(19)



(20)



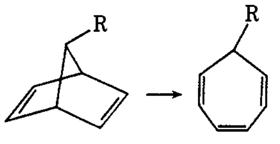
(21)

which, in addition to eq 1, would account for the seven-carbon scrambling in **1** when superposed on the five-carbon scrambling of eq 18. All of these mechanisms may be written as if occurring through simple 1,2 shifts. In eq 19, an " unbound" vinyl carbon shifts to a "bound" vinyl carbon. The result is a one-step degenerate isomerization. Equation 20 represents the equilibrium between **1** and **23** as occurring *via* a series of "wrong way" ring contractions and expansions.[51] Equations 19 and 20 both represent five-carbon scrambling reactions in which the integrity of the "unbound" vinyl function is maintained. Equation 21 is a mechanism homologous with that postulated[52] for a three-carbon scrambling process in the hexamethylbicyclo[2.1.1]hexenyl cation. It specifically scrambles only the "bound" vinyl carbons with the bridge position. Formally, it may be considered as a ring expansion of the classical cyclopropylcarbinyl ion **31b** to the cyclobutyl ion **40**. Since **40** is symmetrical, positions 3 and 7 are equivalent, and ring contraction to **1** has the net effect of scrambling C_2, C_3, and C_7, sequentially.[53–55]

Since all of the mechanisms (eq 19–21) involve scrambling of "bound" vinyl carbons to other positions in **1**, concurrence with eq 18 will lead to seven-carbon scrambling. In fact, the scrambling will be completely random, thus precluding the possibility of differentiation by a multiple labeling experiment. Equation 19 may be energetically favorable to eq 20, since the former involves a migration to a more positively charged terminus than does the latter. The closest analogy to eq 19 may be the degenerate isomerization of the nortricyclyl cation,[56] which occurs during solvolysis of the 5-norbornenyl system. The closest analogy to eq 20 may be the isomerization, under solvolytic conditions, of the syn-7-norbornenyl system (*vide supra*). Despite these analogies, there is no clear basis on which to choose from eq 19–21, and the rate of the observed seven-carbon scrambling in **1** must remain as an upper limit to the rate for bridge-flipping (eq 1).

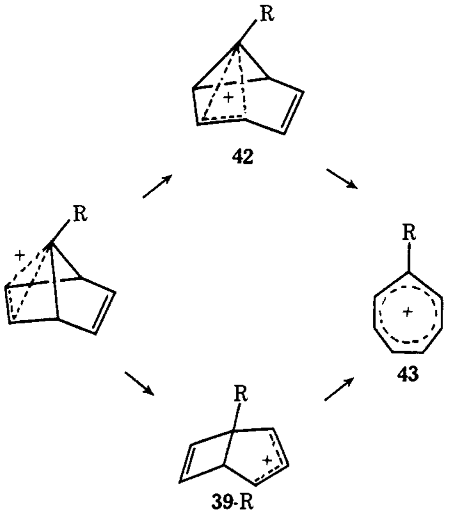
The nondegenerate rearrangement of **8** to **12** ($\Delta F^{\ddagger}$ = 18.9 kcal/mol) might, in principle, involve any of the mechanisms of eq 18 and 19–21. Equation 19 would afford **12** in one step from **8**; eq 21 would require two steps. It is impossible to distinguish between these possibilities at present. Equation 20 is ruled out in this case, because it would require that **21** ring-expand directly to **12**, a reaction which does not occur (Chart III). In order to invoke eq 18 in this case, one must hypothesize that five-carbon scrambling proceeds through the sequence **8** → **39** → **14** → **21** → **13**, followed by bridge-flipping of the latter to give **12** as shown in Chart III. Since the **8** → **12** transformation at −17° proceeded in *ca.* 60% yield, *ca.* 40% of **8** decomposing to give broad, nondescript absorptions, it is possible that 40% of **8** does proceed to **13** by this route with subsequent very rapid decomposition of **13**. This possibility is plausible on energetic grounds, since the methyl group in **8** might cause the barrier to ring contraction of **1** (16.6 kcal/mol) to be raised just enough such that the process becomes competitive with the direct conversion of **8** to **12**. The ring-expansive partitioning of **39** between **14** and **8** will probably not be a prohibitive factor, though, clearly, it is of interest to prepare **39** independently and to examine its chemistry. Whatever the mechanism involved in the partial decomposition of **8**, it is evident that the discrete conversion of **8** to **12** occurs by a mechanism other than sequential five-carbon scrambling.[53]

The nondegenerate (and irreversible) formation of tropylium ions (eq 12–15 and Table VIII) is reminiscent of the thermally induced isomerization of norbornadienes **5k** to tropilidenes **41k** (eq 22).[57] However, differences between the two cases are immediately apparent. First of all, activation energies are much lower in the present case (*ca.* 50 kcal/mol for norbornadiene, *ca.* 24 kcal/mol for **1**). Second, substituent effects on the two reactions show dissimilar trends. In eq 22, phenyl and methoxy substituents lower the $\Delta F^{\ddagger}$ by *ca.* 20 kcal/mol each.[57] Table VIII shows that phenyl lowers $\Delta F^{\ddagger}$ but methoxy causes it to be raised again. Actually, there is no reason to suspect that the isomerizations of the neutral and cationic species are related in more than a formal sense.



5k **41k** (22)

Possible mechanisms for the tropylium ion formation are given below. In eq 23 the net effect is cleavage of the C_4–C_7 σ bond and insertion of C_7 into the C_1–C_2 bond. Bond realignment is probably a totally continuous process, but the transition state **42** may have the character of a nonplanar cyclopropyl cation, weakly bonded to elements of the incipient π-electron system. In eq 24, ring contraction occurs as in eq 18 and the intermediate **39-R** (and/or other bicyclo[3.2.0]heptadienyl ions formed *via* five-carbon scrambling) ring-opens to give the tropylium ion.



42 (23)

43

39-R (24)

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(51) It is emphasized that the expansions are also "wrong way," in order to avoid confusion about microscopic reversibility when considering a superposition of eq 18 and 20.

(52) H. Hogeveen and H. C. Volger, *Rec. Trav. Chim. Pays-Bas*, 87, 385 (1968).

(53) Since eq 19 places a "bound" vinyl carbon at the bridgehead position and eq 21 does not, these two may in principle be distinguished by utilizing a suitably labeled precursor.

(54) It is possible that the 7-norbornenyl cation undergoes a degenerate isomerization by any or all of the mechanisms in eq 18–21. At present, there is no evidence to suggest that this occurs.

(55) A referee has suggested an additional mechanistic possibility which involves degenerate isomerization of **23** *via* a 1,2 shift of the central bond such that the vinyl and allyl functions are interchanged.

(56) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, 77, 3034 (1955).

(57) R. K. Lustgarten and H. G. Richey, Jr., *Tetrahedron Lett.*, 4655 (1966), and references therein.

Both of these mechanisms have the advantage of utilizing the partial bond already existing in ions **1**, **9**, and **10** (but not in **11**). Equation 23 has the formal advantage of encompassing the appropriate orbital-symmetry-favored disrotatory mode of cyclopropyl cation ring opening, whereas the second mechanism has the disadvantage of requiring the restrictive conrotatory opening of **39-R**.[58] On this basis, the first mechanism would be favored over the second. However, it is entirely possible that a symmetry disallowed process may be the lowest energy potential surface, and the problem remains entirely open.[59] Furthermore, it is far from clear why **12** and **13** decompose without giving any methyltropylium ion[46] and, for that matter, why **9**, **10**, and **11** give the tropylium formation without any detectable product which might be ascribed to the other rearrangements detected for **1**, **8**, and **14**. The last two entries of Table VIII are the rates of decomposition of **12** and **13**, respectively. These serve as estimated upper limits to methyltropylium ion formation. The higher activation energy for eq 15 relative to eq 12–14 (*cf.* Table VIII) may well be associated with the lack of an unsymmetrical ground-state bridging interaction in **11**.[20]

Experimental Section

Nuclear Magnetic Resonance Spectra. Standard room-temperature spectra were recorded on the Varian A-60 spectrometer in thin-walled nmr tubes supplied by Varian Associates. All chemical shifts are reported in parts per million relative to internal tetramethylsilane (TMS) at τ 10.00, unless noted otherwise. Chemical shifts reported for strong acid solutions are relative to internal methylene chloride (CH_2Cl_2) assumed to absorb at τ 4.70. Low-temperature spectra were recorded at 60 or 100 MHz on Varian A-60 or HA-100 spectrometers equipped with variable-temperature probes. Spectra could be recorded between room temperature and *ca.* −140°. The probe was always precooled before insertion of sample tubes. The probe temperature was measured by utilizing the precalibrated temperature dependence of a methanol sample.[60] The reproducibility of the temperature readings was within ±2°. When tubes remained in the probe for extended periods (*e.g.*, 2–3 hr), the temperature was controlled to ±4°. High-temperature spectra were also recorded on the variable-temperature Varian A-60 spectrometer. The temperature was measured using the precalibrated temperature dependence of ethylene glycol.[60]

In general, the rearrangement rates reported in this paper were monitored by electronic integration of appropriate signals of the reactants and products. The fluorosulfuric acid (FSO_3H) or CH_2Cl_2 signals were used as internal standards for determination of per cent yields. The probe temperature was measured before and after a given run. Rate constants were realized from graphical evaluation of the simple first-order expression, and are probably good to ±10%.

Gas Chromatography. Gas chromatography (glpc) was used in this work primarily for purifying small quantities of material (10–300 mg) and for checking the purity of compounds synthesized. All work was done on an Aerograph Model A-90 unit equipped with 0.25-in. coiled columns. The columns employed in this work are listed here and will be referred to by letter: (A) 3 m × 0.25 in. 10% XF-1150 on nonacid washed Chromosorb W, 60–80 mesh; (B) 2 m × 0.25 in. 20% XF-1150 on nonacid washed Chromosorb W, 80–100 mesh; (C) 2 m × 0.25 in. 10% XF-1150 on nonacid washed Chromosorb W, 80–100 mesh; (D) 4 m × 0.25 in. 25% DC-550 on nonacid washed Chromosorb W, 60–80 mesh; (E) 1.3 m × 0.25 in. 20% Carbowax 4000 on nonacid washed Chromosorb W, 60–80 mesh.

Melting Points. Melting points are uncorrected and were recorded with a Fisher-Johns melting point block.

Microanalyses. Microanalyses were performed by Miss Heather King, University of California at Los Angeles.

Reagents. FSO_3H was obtained commercially from Allied Chemical Co. It was purified by distillation through an all-glass, greaseless apparatus. In a typical procedure, 85 ml of FSO_3H was distilled through an 8-in. glass bead column. The first 20 ml was discarded (quenched by slow addition to ice) and the middle cut (45 ml) was collected. This pure, very mobile liquid was sealed in glass ampoules (previously flushed with argon) in approximately 1-ml quantities. A fresh vial of acid was opened for each experiment.

Sulfuryl Chloride Fluoride (SO_2ClF). This material was obtained from Allied Chemical in 2-lb lecture cylinders and was used directly without prior purification.

Generation of Carbonium Ions in Strong Acid Media. The general techniques of carbonium ion observation continually evolved through the course of this work, and no attempt will be made to detail all of the procedures used. Basic to all the techniques was the addition of the precursor alcohol, ether, or acetate to the acid medium (FSO_3H or FSO_3H–SO_2ClF) as a dilute solution in a solvent such as CH_2Cl_2, CD_2Cl_2, or pentane. The additions were carried out at low temperatures directly in the nmr tube so as to effectively use small quantities of material. One of the most satisfactory techniques is outlined below.

A clean, dry nmr tube was continuously flushed with argon using a capillary tube bent at a 90° angle. To the tube was added 0.15 ml of FSO_3H. The tube was cooled to −78° (Dry Ice–acetone bath), *ca.* 0.30 ml of SO_2ClF was condensed onto the FSO_3H *via* a capillary inlet, and the two components were mixed with a long, beaded melting-point capillary. The precursor alcohol (15–60 mg) was dissolved in 0.20 ml of CD_2Cl_2 and this solution was cooled to −78°. In cases where the alcohol precipitated from solution, higher temperatures were employed. This cold CD_2Cl_2 solution was added through a small funnel to the cooled acid solution and the two solutions were rapidly mixed. Samples prepared by this technique were generally stored at liquid nitrogen temperatures until examined by nmr.

The principal variation on this technique was the use of neat FSO_3H as the acid medium. In this case, CD_2Cl_2 separates as a second (upper) layer. The FSO_3H–SO_2ClF medium is generally superior, because generations can be done at lower temperatures, and viscosity broadening of nmr signals is minimal.

For cation generations below *ca.* −80°, the FSO_3H (freezing point −87°) must be diluted with SO_2ClF (or some other suitable diluent). Such generations were accomplished by using a test tube filled with 2-methylbutane as the cooling bath. This tube was supported in a vacuum-jacketed Pyrex cylinder which was itself secured on a dewar flask containing liquid nitrogen. The nitrogen was vaporized with the aid of a tiny heating coil so that a steady stream of cold gas passed around the test tube. By adjusting the voltage across the heater, the temperature of the 2-methylbutane could be controlled to ±3°.

Quenching of Strong Acid Solutions of Carbonium Ions. The most satisfactory procedure was the following. A 2-ml syringe was jacketed with a piece of large glass tubing fitted onto the syringe by means of an inverted one-holed rubber stopper which was placed over the head of the syringe. The syringe was fitted with a fine bore needle which had been pinched partially shut at the end so that liquid forced through the needle was emitted in a very fine stream. The plunger of the syringe was removed, and the jacket around the barrel was filled with powdered Dry Ice. The acid solution of the ion at −78° was poured from the nmr tube into the syringe, the plunger was inserted and the acid solution was forced into a rapidly stirred quenching solution which had been cooled to −78°. The quenching solution was a small volume of dry methanol (*ca.* 20 ml) containing either excess sodium methoxide or sodium bicarbonate. After quenching, water was added to the methanol solution and it was extracted three times with ether. The combined ether layers were washed with saturated sodium chloride solution and dried over anhydrous potassium carbonate. The solution was filtered and concentrated, and the product was isolated by glpc.

Quench of the 2-Methyl-7-norbornadienyl Cation (12). The 7-methyl-7-norbornadienyl cation (**8**) was generated by extraction of the precursor **5c** from CH_2Cl_2 into 0.6 ml of FSO_3H. The sample (144 mg) used to generate this ion was contaminated with 10% 7-

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(58) The photochemically activated, and presumably sequential formation from **28**, of **23** and **1**, respectively, has been reported: R. F. Childs and V. Toguchi, *Chem. Commun.*, 695 (1970); *cf.* also, E. E. van Tamelen, *et al.*, *J. Amer. Chem. Soc.*, **90**, 1372 (1968); K. E. Hine and R. F. Childs, *ibid.*, **93**, 2323 (1971).

(59) Note that the **39-R** → **43** conversion is isoelectronic with the formally disallowed Dewar benzene → benzene conversion.

(60) Varian Instruction Manual for V-6057 Temperature System, Publication No. 87-100-110, Varian Associates, Palo Alto, Calif.

methyl-7-quadricyclanol and *ca.* 10% CCl_4. The acid solution of the cation was warmed to 0° for 20 min to induce rearrangement to **12**, a reaction which occurs in 60% yield. The solution was cooled back down to −78° and quenched into a rapidly stirred solution of 5.5 ml of dry methanol and 1.9 g of sodium bicarbonate. After work-up, the ether was reduced to a small volume, and the quench product was isolated by glpc (column C, 13 psi, 70°). The trace showed a minor component (10%, retention time 12.0 min) and a major component (90%, retention time 15.5 min). Approximately half of the ether solution was subjected to glpc and the major component was collected to yield 20 mg of a clear oil. Taking into account the impurity of the starting sample, the yield of the rearrangement reaction, and the fraction of the sample purified by glpc, a crude yield may be estimated as *ca.* 50%. The nmr of the pure oil fit perfectly for the expected 2-methyl-*anti*-7-methoxynorbornadiene (**25**) showing a two-proton vinyl multiplet at τ 3.60, a one-proton vinyl multiplet at 4.00, bridgehead and bridge proton multiplets at 6.50, 6.68, and 6.92, a methoxyl singlet at 6.95 (overlapping the 6.92 multiplet), and a methyl doublet at 8.18 (J = 1.8 Hz).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88; mol wt, 136.0881. Found: C, 79.05; H, 9.09; mol wt (high resolution mass spectrum), 136.08878.

Quench of the 5-Methyl-7-norbornadienyl Cation (13). The cation **13** was prepared in the usual way by extraction of 104 mg of the quadricyclic alcohol **4c** into 0.25 ml of FSO_3H and 0.50 ml of SO_2ClF at −125°. The resulting solution was very dark. It was immediately quenched as described above into a rapidly stirred MeOH (20 ml)–$NaHCO_3$ (5 g) mixture at −78°. The worked-up ether solution was reduced to a small volume and examined by glpc (column C, 8 psi, 75°). Two volatile products were observed in the ratio of 95:5 with retention times of 8 min (minor component) and 10 min (major component). The major component was collected to yield 15 mg of 2-methyl-*syn*-7-methoxynorbornadiene (**24**). The 100-MHz nmr spectrum (CS_2) showed bands at τ 3.52 (2 H, triplet, J = 2 Hz), 4.29 (1 H, broad singlet), 6.61 (1 H, singlet), 6.74 (1 H, singlet), 6.96 (4 H, singlet), and 8.21 (3 H, doublet, J = 2 Hz). The high resolution mass spectrum gave a value of 136.08812 (calcd for $C_9H_{12}O$, 136.08881). The minor component was not identified but may be 1-methyl-*syn*-7-methoxynorbornadiene (see Results and Discussion sections).

7-*tert*-Butoxynorbornadiene. This material was purchased from Frinton Laboratories, Inc., and was used without further purification in preparing 7-acetoxynorbornadiene.

7-Acetoxynorbornadiene (5g). This compound was prepared in a manner similar to the published procedure,[61] bp 77° (25 mm) (lit.[61] 65° (8 mm)). The nmr spectrum (CS_2, external TMS in $CDCl_3$) exhibited triplets at τ 3.28 (2 H) and 3.46 (2 H), multiplets at 5.48 (1 H) and 6.40 (2 H), and a methyl singlet at 8.08 (3 H).

7-Norbornadienol (5a). This compound was prepared in good yield *via* a methyl Grignard reaction with **5g** as reported by Story.[61] The crude alcohol was distilled before use, bp 67° (29 mm) (lit.[61] 79° (57 mm)). The nmr spectrum (CCl_4) showed multiplets at τ 3.48 (4 H) and 6.26 (1 H), a sextet at 6.64 (2 H), and a singlet at 6.90 (1 H).

7-Quadricyclyl Acetate (4g). Synthesis of this compound has been previously reported;[18a,62] however, a somewhat simplified procedure has been developed and is recorded here. The irradiation apparatus used in this preparation consisted of a cylindrical reaction vessel which was fitted with a water condenser and a water-cooled inner quartz immersion tube. A Hanovia 450-W L679A lamp, placed in the inner tube, was the photon source. The effective volume of the apparatus was *ca.* 250 ml. Solutions were stirred magnetically.

In a typical experiment, 9.12 g of pure **5a** was dissolved in 250 ml of spectral grade hexane and irradiated for 71 hr. Polymer was cleaned from the walls of the quartz immersion tube with chromic acid at 19, 50, and 58 hr. The reaction was monitored by nmr, using ratios of the α-proton peaks at τ 5.48 for **5g** and 4.50 for **4g**. When the reaction was *ca.* 98% complete, the solution was filtered and spin evaporated to a volume of *ca.* 35 ml. The flask was placed in the freezer and **4g** crystallized in *ca.* 5 hr. The crystals were collected and washed with cold hexane to yield 7.09 g of white solid. The mother liquors were combined and reduced to a volume of *ca.* 15 ml. A seed crystal was added and a second crop of crystals (0.26 g) was recovered. The total yield was 81%. The nmr spectrum (CCl_4) showed a triplet at τ 4.50 (1 H, J = 1.7 Hz), a singlet at 8.00 (3 H), and a complex multiplet at 8.65–8.10 (6 H).

7-Quadricyclanol (4a). This compound has also been previously prepared by saponification of quadricyclyl acetate;[18a,62] however, the following procedure is somewhat simpler and gives **4a** in higher yields. To a rapidly stirred mixture of lithium aluminum hydride (2.31 g, 61 mmol) in 250 ml of dry ether was added dropwise over 25 min a solution of 4.93 g (33 mmol) of **4g** in 100 ml of ether. The reaction mixture was allowed to stir at room temperature for an additional 20 min. The mixture was then cooled to 0° and quenched with 150 ml of saturated sodium potassium tartrate solution. After extraction with two 100-ml portions of ether, the combined extracts were dried over anhydrous potassium carbonate. The ether was slowly removed by rotary evaporation to yield 3.40 g (33 mmol) of a clear oil. The nmr showed this oil to be essentially pure **4a**, yield *ca.* 96%. This material was used without further purification in the conversion to **4i**. The nmr (CCl_4, external TMS in $CDCl_3$) showed a triplet at τ 5.09 (1 H, J = 1.8 Hz), a singlet at 6.32 (1 H), and complex multiplets at 8.17 (2 H) and 8.47 (4 H).

7-Quadricyclyl Tosylate (4i). This compound, previously reported by Story,[18b] was prepared in 80% yield by treating **4a** with *p*-toluenesulfonyl chloride in pyridine. The tosylate was crystallized from pentane to yield white needles, mp 68.0–68.5°. Nmr ($CDCl_3$) showed an AB quartet (J = 8 Hz) at τ 2.12 and 2.63 (4 H), a triplet (J = 1.7 Hz) at 4.53 (1 H), a singlet at 7.57 (3 H), and multiplets at 8.23 (2 H) and 8.50 (4 H).

Quadricyclanone (3). Quadricyclanone has previously been prepared in 14% yield by *tert*-butyl hypochlorite oxidation of **4a**[11a] and, more recently, in 39% yield by Kornblum oxidation of **4i**.[11b] The following modified procedure of the Kornblum oxidation[13] gives **3** in 80% yield from **4i**. A 3.36-g sample of **4i** was added to a rapidly stirred mixture of 15 g of sodium bicarbonate in 150 ml of dimethyl sulfoxide (<0.02% water) under argon at 80°. The mixture was stirred for 18 min during which time the temperature was raised to 91°. The reaction was then cooled in an ice bath, and 600 ml of a dilute potassium carbonate solution was added. The solution was continuously extracted overnight with pentane. The high solubility of **3** in water made continuous extraction necessary. The pentane solution was reduced to 100 ml and allowed to cool in the freezer. Spots of brown oil precipitated in the flask along with white needles. The pentane was decanted, and the residue was dried in a stream of argon. The brown oil was sufficiently tactile that most of the white needles (0.642 g) could be mechanically removed from the flask with no contamination. The residue was taken up in pentane, combined with the mother liquor, and reduced to 40 ml. Upon cooling, more crystals were obtained. These were collected and recrystallized from pentane to yield 0.363 g of off-white crystals. The mother liquors and residue were combined, reduced to an oil, and taken up in a small amount of acetone. An additional 86 mg of **3** was collected by glpc (column B, 120°) to give a combined yield of 81%. Nmr (CCl_4) showed a doublet (J = 3.9 Hz) with additional fine structure at τ 7.80 (4 H) and a triplet (J = 3.9 Hz) with additional fine structure at τ 8.98 (2 H).

7-Methyl-7-quadricyclanol (4c). A Grignard reagent was prepared by adding 0.768 g of methyl iodide to 25 ml of dry ether containing 0.146 g of magnesium. To this solution was added dropwise with stirring 0.312 g of **3** in 20 ml of ether over a period of 25 min. The solution was refluxed for 20 min and quenched with saturated ammonium chloride solution. The resulting solution was extracted twice with ether; the ether extracts were combined and washed once with water and twice with saturated sodium chloride solution. The ether layer was dried over anhydrous potassium carbonate, filtered, and spin evaporated to yield 0.287 g (80%) of a pale yellow oil. Nmr analysis of this oil showed it to be 98% **4c** and *ca.* 1–2% of **5c**. The nmr (CCl_4, external TMS in $CDCl_3$) consisted of an OH singlet at τ 7.50 (1 H), a sharp methyl singlet at 8.36 overlapping a multiplet at *ca.* 8.28 (7 H, total), and a skewed triplet (J = 4 Hz) with additional fine structure at 8.79 (2 H). This sample was used without further purification for conversion to **5c**.

Isomerization of 7-Quadricyclyl Derivatives to 7-Norbornadienyl Derivatives. All of the 7-substituted norbornadienols reported here were prepared by isomerization of the corresponding 7-substituted quadricyclanols. Methods used for these isomerizations evolved through the course of the work. Initially the ring openings were accomplished cleanly by using nmr tubes which had been previously soaked in a chromic acid bath for 1 day, rinsed twice with water, and dried in a stream of air. Carbon tetrachloride solutions of quadricyclic alcohol were sealed in the tubes under 100

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(61) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(62) R. K. Lustgarten, Ph.D. Thesis, Pennsylvania State University, 1966.

mm of argon. The tubes usually had to be warmed in a 50 or 75° bath to effect a convenient reaction time. The rates were generally nonreproducible and conditions ranging from 10 hr at 50° to 40 hr at 75° were employed. Occasionally a tube "went dead" before completion of the reaction, and the solution was transferred to another tube. Lemal has remarked on the irreproducibility and the apparently catalytic nature of the openings of various quadcyclic ketals to the diene ketals.[11b]

A technique used later in the work and found to be more reliable and reproducible than that just given is based on the report of Hogeveen[15] of Rh(I)-catalyzed isomerization of quadricyclane to norbornadiene. Typically, a small sample of alcohol (*ca.* 150 mg) was treated with 3–5 mg of μ-dichloro-tetraethylenerhodium(I) in CCl_4. The isomerizations were monitored by nmr and usually found to be complete in *ca.* 5–10 hr. Work-up consisted of filtration and evaporation of solvent. Yields were *ca.* 90–100%.

7-Methyl-7-norbornadienol (5c). This compound was prepared by isomerization of a carbon tetrachloride solution of **4c** in an acid-washed nmr tube (see above). In a typical isomerization, 107 mg of **4c** was placed in 0.5 ml of carbon tetrachloride and sealed under argon in a chromic acid washed nmr tube. The nmr showed *ca.* 30% isomerization after 1 day. The tube was then placed in a 50° bath, and after 22 hr there was *ca.* 95% isomerization with no side products evident. Pure alcohol was collected as a clear oil by glpc (column D).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.42; H, 8.34.

The nmr showed triplets at τ 3.38 (2 H) and 3.53 (2 H), a singlet at 6.49 (1 H), a quintet at 6.76 (2 H), and a singlet at 8.74 (3 H).

In another experiment, 3 mg of μ-dichloro-tetraethylenedirhodium(I) was added to 175 mg of quadricyclic alcohol in 0.75 ml of CCl_4. This reaction was stirred and monitored by nmr. After 4 hr, the reaction was 90% completed and, after 10 hr, it was 100% completed. The mixture was filtered and CCl_4 was removed at reduced pressure to yield **5c**.

7,7-Dimethoxyquadricyclane (4f). This compound, which was previously reported by Lemal,[11b] was prepared from **3** in a procedure similar to one described by Moreland, *et al.*[63] To a 121-mg sample of **3** was added 11 ml of a solution prepared by dissolving 38 mg of *p*-toluenesulfonic acid monohydrate in 30 ml of dry CH_2Cl_2 and 37 ml of dry methanol. The reaction was refluxed, and it developed a light violet color after 30 min. After 4 hr, the deep violet solution was cooled, poured into pentane, and extracted three times with dilute potassium carbonate and finally with water. The pentane was dried over anhydrous potassium carbonate, filtered, and evaporated. The nmr of the remaining oil was that of pure quadricyclic ketal. The compound was collected by glpc (column B, 105°) affording 71 mg (41%) of pure **4f**. The nmr (CCl_4), ext TMS in $CHCl_3$) displayed a singlet at τ 6.64 (6 H), a skewed doublet ($J \simeq 4$ Hz) at 8.37 (4 H), and a skewed triplet ($J \simeq 4$ Hz) at 8.70 (2 H).

7,7-Dimethoxynorbornadiene (5f). This compound was prepared from **4f** by isomerization in carbon tetrachloride in an acid-washed nmr tube as described above. The compound was collected by glpc (column B, 105°) to give a clear oil. The nmr (CD_2Cl_2, internal CH_2Cl_2) showed a triplet at τ 3.39 (4 H), a quintet at τ 6.40 (2 H), and a singlet at τ 6.94 (6 H).

7-Phenyl-7-quadricyclanol (4d). This compound was prepared in good yield by the addition of phenyl Grignard to **3** as previously reported.[64] Analysis (nmr) of the crude product showed it to contain the tertiary alcohol plus some small amounts of aromatic hydrocarbon impurity, later identified as biphenyl. The biphenyl could be removed by two recrystallizations from pentane. **4d** was obtained as white crystals, mp 65.0–65.8°.

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.75; H, 6.54.

7-Phenyl-7-norbornadienol (5d). Crude **4d** from the above preparation was isomerized in carbon tetrachloride in an acid-washed nmr tube as described above. This material was then chromatographed on basic alumina, activity 3, eluting with mixtures of petroleum ether and benzene. A small amount of biphenyl, identified by nmr, was first eluted followed by pure **5d**. The nmr (CCl_4) was identical with that previously reported,[64] showing a broad singlet at τ 2.87 (5 H), vinyl triplets at 3.20 (2 H) and 3.65 (2 H), a quintet at 6.15 (2 H), and a singlet at 6.33 (1 H).

7-Vinyl-7-quadricyclanol (4e). To a solution of 980 ml (9.24 mmol) of **3** in 5 ml of ether was added, over a 45-min period, 12 ml of a 1.7 *M* solution of vinylmagnesium chloride (20 mmol) in THF (Penninsular Chemical Research, Inc.). During the addition, the reaction mixture was maintained under a nitrogen atmosphere. After addition, the mixture was refluxed gently for 30 min. Water and saturated potassium sodium tartrate solution were added to the mixture. The phases were separated, and the aqueous layer was extracted with ether. The combined extracts were washed with saturated sodium chloride solution and dried over anhydrous potassium carbonate. The solvent was removed by evaporation at reduced pressure to give 1.084 g (8.10 mmol, 88%) of crude product. The material could not be crystallized from petroleum ether solution. Short path distillation at 55–60° (*ca.* 80 Torr), in a small sublimer, gave a colorless oil. The nmr spectrum (CS_2) showed bands at τ 8.76 (2 H, triplet, J = 3.5 Hz), 8.31 (4 H, triplet, J = 3.5 Hz), 4.65 (1 H), 4.94 (1 H), 3.66 (1 H), and an OH singlet at 7.0; ir 3600 (m, OH), 1160 (s, CO), 1640 (w, olefin), 990, 915 cm^{-1} (sh, terminal vinyl function); high resolution mass spectrum 134.07294 (calcd for $C_9H_{10}O$, 134.07316). The vinyl AMX system was analyzed to yield the following coupling constants: J_{cis} = 10.2 Hz, J_{trans} = 17.2 Hz, and J_{gem} = 2.7 Hz.

7-Vinyl-7-norbornadienol (5e). This alcohol was prepared by Rh(I) isomerization of **4e** as described above. It was purified sufficiently for the purpose of preparing a carbonium ion solution by short-path distillation in a small sublimer. bath temperature 55–60° (20–40 Torr). The nmr (CS_2) showed bands at τ 6.61 (2 H, quintet, $J \simeq 2$ Hz), 3.24 (2 H, triplet), 3.45 (2 H, triplet), 4.57 (1 H), 4.92 (1 H), 3.87 (1 H), and a broad absorption at 6.5; high resolution mass spectrum 134.07307 (calcd for $C_9H_{10}O$, 134.07316). The 7-vinyl AMX spin system was analyzed to give J_{cis} = 10.6 Hz, J_{trans} = 17.4 Hz, and J_{gem} = 2.6 Hz.

syn-**7-Acetoxynorbornadiene-**2-*d* (**5g**-2-*d*).[18b] To a solution of 11.2 ml of glacial acetic acid containing 0.5 ml of acetic anhydride and 449 mg (5.5 mmol) of sodium acetate was added 880 mg (3.34 mmol) of **4j**. The resulting solution was allowed to stand at 75° for 44.25 hr. It was then poured into a mixture of petroleum ether and water. The aqueous phase was extracted with petroleum ether, and the combined organic layers were washed with saturated sodium bicarbonate solution and dried over anhydrous potassium carbonate. The solution was concentrated, and the two product acetates were collected by glpc on column A operated at 128° and 25 psi. Under these conditions **5g** eluted after 11.25 min and **4g** after 20.0 min. The nmr spectrum of **5g**-2-*d* showed an integrated ratio of 2.0:1.1 for the anti and syn vinyl hydrogens, repectively.[18b]

7-Norbornadienol-7-*d* (**5b**). This alcohol was unexpectedly formed as a product of an apparently anomalous lithium aluminum deuteride–ether reduction of **3**, since in many other runs **3** was routinely reduced to **4a** or **4b** with $LiAlH_4$ or $LiAlD_4$, respectively. It is presumed that the present anomaly was caused by contamination with a transition metal impurity.[14] Formation of **5b** was accompanied by formation of dilabeled *anti*-7-norbornenol, formed by further reduction of **5b**.[65] **5b** was isolated by preparative glpc. There is no reason to believe that **5b** could not be prepared by controlled isomerization of **2b** as described above for **4c** or **4d**.

7-Methoxynorbornadiene-2,3,5,6-d_4 (**5h**-2,3,5,6-d_4). Preparations of exchange solutions and handling of materials were performed under a dry nitrogen atmosphere. To 300 ml of **5h** was added 0.5 ml of cyclohexylamine-*N,N*-d_2 and 5.0 ml of a 0.1–0.2 *M* solution of lithium cyclohexylamide-*N*-*d* in cyclohexylamine-*N,N*-d_2.[19] (This solution was prepared and calibrated by Dr. Chris Watts.) The solution was warmed in a sealed tube at 50° for 2.0 hr. It was quenched by addition to a mixture of 50 ml of ether and 10 ml of water. The organic layer was washed with 5% HCl solution until the wash was acid, then with saturated bicarbonate solution, and finally with saturated sodium chloride solution. After drying (anhydrous potassium carbonate) the solution was concentrated to *ca.* 1 ml volume, and the product (*ca.* 260 mg) was collected by glpc on column A. The neat material was allowed to stand over 10 mg of Linde Type 4A molecular sieves and then exchanged again according to the above procedure with 0.4 ml of deuterated amine and 4.5 ml of the deuterated amide–amine solution at 50° for 115 min. The nmr spectrum of the product showed 77% deuteration of all vinyl positions.

Bicyclo[3.2.0]heptadienone (6). This compound has previously been reported by Story.[17] In this work the following procedure

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(63) W. T. Moreland, D. P. Cameron, R. G. Berry, and C. E. Maxwell, *J. Amer. Chem. Soc.*, **84**, 2966 (1962).

(64) A. F. Breazeale, Ph.D. Thesis, University of Washington, 1964.

(65) B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965).

was used. A 0.522-g sample of alumina (Woelm acid-washed grade 1 activated at 230° for 2 hr under vacuum) was stirred with 35 ml of petroleum ether (dried over a portion of above alumina) for 16 hr at room temperature. The alumina was then filtered and washed two times with ether (*ca.* 30 ml) and the clear ether solution set aside. The alumina was then washed two times with 20 ml of CH_2Cl_2 and this solution set aside. A third wash was done with two 15-ml portions of methanol and one 15-ml portion of ether to yield a yellow solution. Each solution was reduced on the steam bath and analyzed by glpc. The ether solution contained only ketone. The CH_2Cl_2 solution contained only ketone but in relatively small quantities, while the methanol solution contained only traces of ketone along with other unidentified compounds. The ketone was collected by glpc (column D, 135°) to yield 191 mg of clear oil (181 mg from ether solution, 10 mg from CH_2Cl_2 solution). The nmr (CCl_4) of the ketone agreed with the published one[17] showing one proton resonances at τ 2.48, 3.51, 3.70, 4.05, 6.12, and 6.66.

endo- **and** *exo-***Bicyclo[3.2.0]heptadienol (7a and 7b).** These alcohols were prepared according to Story and Fahrenholtz[17] by lithium aluminum hydride reduction of **6**. The reaction mixture was worked up by quenching with potassium sodium tartrate solution. The alcohols were collected by glpc (column E, 133°, 20 psi). **7a** had a retention time of 22.5 min and **7b**, 27 min. The ratio of **7a** to **7b** (peak areas) was 59 ± 2:41 ± 2, and by direct weighing of isolated alcohols the ratio was 58:42.

The nmr spectrum (CD_2Cl_2) of **7a** (endo) showed resonances at τ 3.37 (1 H, doublet, J = 3 Hz), 3.90 (2 H, multiplet), 4.39 (1 H, doublet, J = 6 Hz), 5.24 (1 H, doublet, J = 10 Hz) (unresolved multiplets), 6.40 (2 H, multiplet), and 7.84 (1 H, singlet, OH). The exo epimer **7b** exhibited bands at τ 3.50 (1 H, doublet, J = 2.5 Hz), 3.80 (2 H, multiplet), 4.20 (1 H, doublet, J = 7 Hz), 5.50 (unresolved multiplet), 6.19 (1 H, multiplet), 6.87 (1 H, quartet, J = 1.5, 3 Hz), and 8.00 (1 H, singlet, OH).

endo- **and** *exo-***Bicyclo[3.2.0]heptadienol-*2-d* (7c and 7d).** These alcohols were prepared exactly as **7a** and **7b** except lithium aluminum chloride was used as the reducing agent. High resolution mass spectra (calcd for C_7H_6DO, 108.05596) gave 108.05609 for **7c** and 108.0560 for **7d**.

2-Methyl-*endo*-bicyclo[3.2.0]heptadienol (7e). To a solution of 218 mg (2.06 mmol) of ketone **6** in 20 ml of dry ether was added dropwise 1.8 ml (2.9 mmol) of 1.6 M solution of methyllithium in ether (Foote Mineral Co.). During the addition, which lasted 5 min, the reaction mixture was cooled in an ice–water bath. After stirring the mixture for an additional 0.5 hr, it was quenched with a small quantity of water. Sodium sulfate was added, and the mixture was extracted with ether. The precipitated material was then dissolved in an excess of water and the aqueous phase was extracted well with more ether. The combined ether layers were dried over anhydrous potassium carbonate, filtered through anhydrous sodium sulfate, and concentrated. The product was purified by short-path distillation in a small sublimer. The nmr spectrum (CD_2Cl_2, internal CH_2Cl_2) showed bands at τ 3.40 (1 H, doublet, J = 2.5 Hz), 3.85 (1 H, doublet, J = 2.5 Hz), 4.08 (1 H, doublet of doublets, J = 2.5, 5.5 Hz), 4.53 (1 H, doublet, J = 5.5 Hz), 6.45 (1 H, multiplet), 6.75 (1 H, multiplet), 8.16 (1 H, singlet, OH), and 8.70 (3 H, singlet); high resolution mass spectrum 122.07283 (calcd for $C_8H_{10}O$, 122.07316).

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Carbon-to-Metal Chlorine Exchange. IV. Mercuric Salt Promoted Acetolysis of *exo*-Norbornyl Chloride[1]

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Abstract: Mercuric salts enhance the rate of acetolysis of *exo*-norbornyl chloride, I-Cl. Rate constants have been measured for solvolysis, k_t, exchange of radiolabeled chlorine between mercuric chloride and I-Cl, k_e, and loss of optical activity, k_α. Relative solvolytic rate constants for mercuric acetate, chloromercuric acetate, and mercuric chloride promoted reactions at 75° are 1820, 89, and 1, respectively. Since the rate enhancements are much greater than expected for normal salt effects, the mercuric salts must be intimately involved in the ionization process. For the mercuric chloride promoted reaction, $k_\alpha/k_t = 9.6$ indicating that some 90% of the ion pairs return to covalent I-Cl in the poorly dissociating acetic acid solvent. The ratio $k_{rac}/k_e = (k_\alpha - k_t)/k_e = 2.0$ for mercuric chloride can be interpreted in terms of one or more ion-pair intermediates $I^+HgCl_3^-$ of differing structure. In a manner similar to $HgCl_2$, $Hg(OAc)_2$ facilitates C–Cl bond heterolysis, and carries the solvent anion, OAc^-, into intimate contact with the incipient carbonium ion, which makes the chloromercuric diacetate anion a unique "leaving group."

Mercuric salt promoted reactions of alkyl halides have been known for some time. Mercuric halides have been studied most extensively, but some early work with mercuric nitrate and mercuric perchlorate has been reported.

Satchell[4–6] studied the racemization of optically active 1-phenylethyl chloride in the presence of high concentrations of mercuric halides in the aprotic solvents nitrobenzene and acetone. The rate of loss of optical activity could be fit by eq 1 up to 0.8 M mercuric salt.

$$\text{obsd } k_\alpha = k_I[\text{HgHal}_2] + k_{II}[\text{HgHal}_2]^2 \qquad (1)$$

The first-order term is explained as simple electrophilic

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