Metastable Norbornyl Cations

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Much effort over the past 30 years has been expended on studies of the 2-norbornyl cation.[1] The spectroscopic evidence supporting a bridged structure in nonbasic media[2-5] and in the solid state[5,6] is now overwhelming. The most advanced calculations (including electron correlation) indicate that the potential surface of the 2-norbornyl cation has a minimum corresponding to a bridged structure and no minimum corresponding to a classical ion.[7,8] These conclusions are not immediately applicable to nucleophilic media, where solvation is an important factor.[9] The magnitude of nonclassical stabilization and the origin of high exo/endo rate (product) ratios in solvolytic systems are debatable.[10] Nevertheless, a large body of kinetic and stereochemical data support the bridged-ion formulation.[11,12]

The $C_7H_{11}^+$ potential surface as a whole is even more fascinating than its global minimum, the 2-norbornyl cation (**4**). This account is concerned with metastable isomers of **4**, i.e. cations protected by potential barriers against immediate decay to **4**. Specifically, we address the 2-bicyclo[3.1.1]heptyl (**1**), 2-norbornyl (**3**) and 2-bicyclo[3.2.0]heptyl (**5**), 7-norbornyl (**7**) cations. The naming intends to cover both the localized (equilibrating) and bridged versions (**2** and **6**, respectively) of these ions. The classical structures contributing to **2** and **6** are nondegenerate; eventual bridging in **2** and **6** must be unsymmetrical. The investigation of such species serves to define the scope and limitations of two-electron, three-center bonding.

The barriers separating **2** and **6** from **4** differ substantially. The rearrangement of **2** involves only minor distortions of the carbon framework and occurs readily even in nucleophilic media (see below). In contrast, the transformation of **6** into **4** requires an interconversion of protonated cyclopropanes (**6** → **2**) or a 7,2-hydride shift (**7** → **3**) (Scheme I). This process is not observed in solvolytic systems. Antimony pentafluoride, however, ionizes 7-chloronorbornane to give **4**,[13] thus precluding the direct observation of **6** or **7** by NMR. Detection of the metastable norbornyl cations relies on indirect evidence such as product distribution, scrambling of labels, and configurational (in)stability. Although these methods have been used for decades, recent advances in instrumentation (NMR, GC, HPLC) greatly benefit their application.

2-Bicyclo[3.1.1]heptyl, 2-Norbornyl Cations

Several theoretical investigations of $C_7H_{11}^+$ included the 7-bridged ion **2**. Somewhat unexpectedly, **2** emerged as the most stable 2-norbornyl cation from MINDO/3 calculations (-3.5 kcal/mol relative to **3**).[14]

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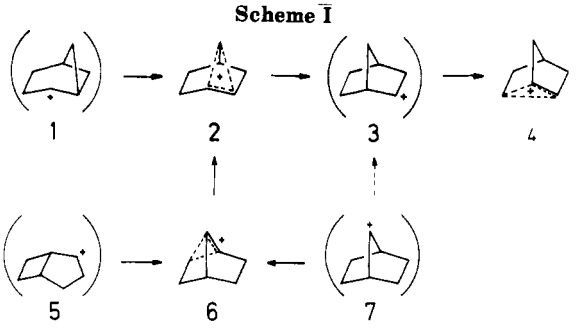
Scheme I



This result is due to inadequacies of the MINDO/3 method, which overestimates the heat of formation of norbornane by ca. 20 kcal/mol.[15] At the ab initio level, **2** is found well above **3**,[14,16,17] the energy difference depending on the (partial) inclusion of d functions.[17] Unfortunately, the most advanced calculations[7,8,18] disregard **2**.

Early experimental evidence for endo-selective 2-norbornyl cations came from Meerwein's report that the Lewis acid catalyzed rearrangement of "pinene hydrochloride" (**8**) gave bornyl chloride (**14**).[19] Burrows and Eastman[20] showed that the rearrangements accompanying esterification of the 2-pinanols with acetic anhydride were stereospecific, **9** giving bornyl acetate (**15**) and **24** giving α-fenchyl acetate (**29**), though both also gave α-terpinyl acetate (**21**). The *p*-nitrobenzoates of the 2-pinanols were studied by Abraham[21] and by

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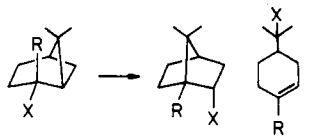
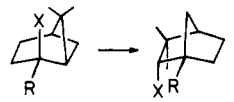
Scheme II



	R	X		
8	CH_3	Cl	14	
9	CH_3	OH		20
	CH_3	OAc	15	21
10	CH_3	OPNB	16	
11	CH_3	OCH_3	17	22
12	H	OH	18	23
13	H	OBs	19	



	R	X	
24	CH_3	OH	
	CH_3	OAc	29
25	CH_3	OPNB	30
26	CH_3	OCH_3	31
27	H	OH	
	H	OBs	32
28	H	NH_2	

Whittaker[22] who found that **10** rearranged to give bornyl *p*-nitrobenzoate (**16**) and **25** the corresponding fenchyl ester (**30**). Similarly, brosylation of the isomeric nopinols, **12** and **27**, led to the rearranged brosylates **19** and **32**, respectively.[23] It is clear from these results that the stereochemistry of the precursors is preserved in the ion pairs from which the rearranged esters originate. In the solvated ion stage, however, some stereospecificity is lost. Thus, the methanolysis of both **10** and **25** gave mixtures of **11**, **17**, **22**, **26**, and **31**.[22] The solvolysis of β-nopinyl brosylate (**13**),[24] the acid-catalyzed rearrangement of the nopinols (**12**, **27**)[25] and the nitrous acid deamination of α-nopinylamine (**28**)[25] all afforded exo/endo mixtures of 7,7- and 3,3-dimethyl-2-norbornanols (Scheme II).

The substrates employed in these studies are readily obtained from natural sources but suffer from several drawbacks. The *gem*-dimethyl group is supposed to affect the stereoselectivity of open 2-norbornyl cations. Fragmentation to give (nor) α-terpinyl products (**20–23**) and the analogous alkenes is a major, sometimes predominant reaction.[26] The intermediates responsible for fragmentation have not been established; their diversion to **20–23** can vitiate any conclusions based on the ratios and configurations of bicyclic products. Therefore, our studies were focused on nonfragmenting and stereochemically unbiased substrates.

The Parent Ion(s). The synthesis of bicyclo[3.1.1]heptan-2-one[27] provided access to a variety of

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Table I.
Exo to Endo Product Ratios from Norpinyl–Norbornyl Rearrangements

precursor, conditions	OR	40:38
33, 67% aq acetone, 120 °C	OH	1.8
(30% conversion)	(OPNB	0.15)
34, 3 M $LiClO_4$ in Et_2O, 70 °C	ODNB	0.50
35, HOAc, 20 °C	OAc	3.4
35, aq $HClO_4$ (pH 3.9), 20 °C	OH	2.0
35, 0.2 M NaOH, 20 °C	OH	1.6
35, 0.3 M NaOEt in EtOH, 20 °C	OEt	0.85
37, HOAc, 20 °C	OAc	1.3
37, HOAc, 50 °C	OAc	1.6
37, HOAc, 100 °C	OAc	2.2
37, 0.7 M H_2SO_4, 70% aq dioxane, 20 °C	OH	0.50
37, 0.1 M H_2SO_4, EtOH, 20 °C	OEt	0.41
39, aq $HClO_4$ (pH 3.8), 20 °C	OH	8.8

precursor, conditions	OR	47 + 49:45
41, aq $HClO_4$ (pH 3.8), 20 °C	OH	0.48
42, 0.2 M NaOH, 20 °C	OH	0.43
44, aq $HClO_4$ (pH 3.8), 20 °C	OH	0.97

2-norpinyl derivatives. 2-Norpinyl *p*-nitrobenzoate (**33**) was solvolyzed in aqueous acetone to give *exo*- and *endo*-2-norbornanol in a 1.8:1 ratio[28] (Table I). The *p*-nitrobenzoate recovered after 30% conversion contained 58% of **33**, 36.5% of **38**–OPNB, and 5.3% of **40**–OPNB.[28] The exo to endo ratio of the rearranged *p*-nitrobenzoates does not correctly reveal the stereochemistry of internal return as **40**–OPNB solvolyzes much faster than **38**–OPNB. Rearrangment of 2-norpinyl 3,5-dinitrobenzoate (**34**) under nonsolvolytic conditions (Et_2O, $LiClO_4$) gave a 2:1 ratio of **38**–ODNP and **40**–ODNP.[29] The decomposition of norpinane-2-diazonium ions (**35**) was studied in various solvents.[28,29] The exo to endo ratios of the 2-norbornyl products were found to decrease with increasing nucleophilicity of the medium (Table I). The deuterated diazonium ion [2-^{2}H]-**35** gave *endo*-norbornanol with deuterium exclusively at the bridgehead and *exo*-norbornanol with an even distribution of ^{2}H among positions 1 and 2.[29]

Obviously, **40** derives from the degenerate, exo-selective 2-norbornyl cation **4**. In norpinyl–norbornyl rearrangements, **4** appears to be preceded by an endo-selective intermediate that is captured in competition with its conversion into **4**. The open 2-norbornyl cation (**3**) is not an appropriate precursor to **38** as it should also give exo products and thus disturb the 1:1 ratio of 1-^{2}H and 2-^{2}H in **40**. The 7-bridged ion **2** reasonably represents the endo-selective intermediate provided that charge distribution and ring strain lead to predominant formation of **38**. Small amounts of 2-norpinyl products (**36**) have been obtained in all reactions of **33** and **35**, but their origin is difficult to assess. Increasing proportions of **36** with decreasing polarity of the solvent suggest that **36** arises in part, if not entirely, by k_s processes (Scheme III).

Another approach to **2** involves protonation of tricyclo[3.2.0.0^{2,7}]heptane (**37**).[30,31] The **40** to **38** ratios thus obtained were generally lower than those observed with **35** (tighter ion pairs?), but the solvent effect was the same[31] (Table I). Increasing **40** to **38** ratios with increasing temperature indicate that **2** and **4** are sepa-

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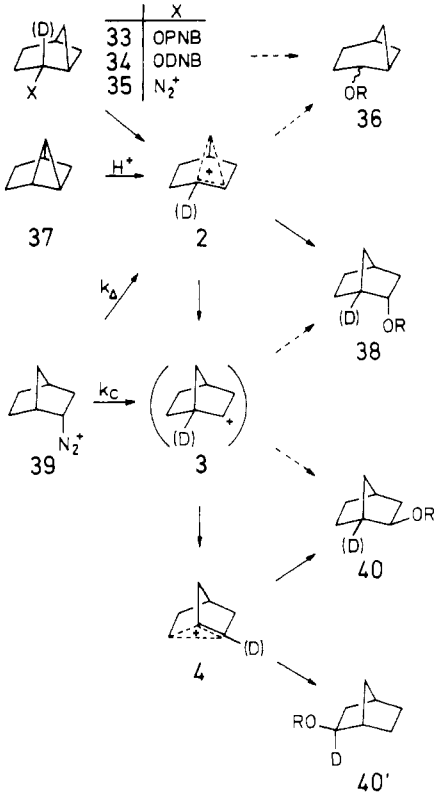
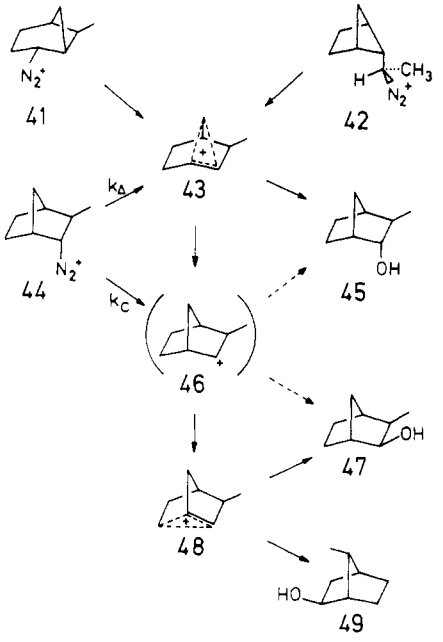
Scheme III



Scheme IV



	47+49/45
41	0.48
42	0.43
44	0.97

rated by an activation barrier.[31]

The 7-bridged ion **2** may also intervene in the decompostion of norbornane-*endo*-2-diazonium ions (**39**). The nitrous acid deamination of optically active *endo*-2-norbornylamine in water gave 10.2% of *endo*-2-norbornanol with 100% ee and 89.8% of racemic *exo*-2-norbornanol.[32] These results are incompatible with **3** as the precursor of **38**–OH (see above). The high exo to endo product ratio is attributed to k_c,k_Δ competition in the extrusion of nitrogen from **39**. As a rule, k_Δ processes provide low-energy reaction paths. The present case is an exception because the formation of **2** from **39** is associated with an increase in strain energy. This argument also explains why **2** is not accessible from *endo*-2-norbornyl sulfonates. The compressed energy scale in deaminations[33] often enhances the energetically more demanding processes, as compared to the solvolysis of sulfonates or halides.

exo-6-Methyl-2-norpinyl, *exo*-3-Methyl-2-norbornyl Cations

In contrast to the low yield (10.2%) of *endo*-2-norbornanol (**38**–OH) obtained from *endo*-2-norbornanediazonium ions (**39**),[32] *exo*-3-methyl-*endo*-2-norbornanediazonium ions (**44**) afforded 43–47% of the analogous alcohol **45**.[34-36] Apparently, the major effect of substituting an *exo*-3-methyl for hydrogen in **39** is to increase the k_Δ to k_c ratio. On the other hand, the decomposition of *exo*-6-methylnorpinane-*endo*-2-diazonium ions (**41**), proceeding entirely by way of the 7-bridged ion **43**, also led to remarkably low exo to endo ratios (Table I).[36] Here, the *exo*-3-methyl substituent appears to raise the barrier of the **43** → **48** interconversion as compared to the unsubstituted case (**2** → **4**) (Scheme IV).

Both effects are probably steric in origin. Repulsive interactions of *exo*-3-CH_3 with 7-H would distort the norbornane skeleton in such a way as to improve p (C-2)–σ (C-1–C-7) overlap. Exo to endo ratios from *endo*-3-methylnorbornane-*endo*-2-diazonium ions (>500)[35] and from 3,3-dimethylnorbornane-*endo*-2-diazonium ions (3.4)[37] support our hypothesis. Moreover, judging from product distributions, the decomposition of 1-(*endo*-5-bicyclo[2.1.1]hexyl)ethanediazonium ions (**42**) proceeds largely by way of **43**.[36] The ring expansion of **42** enforces exactly that distortion of the 2-norbornyl cation (C-2 "up", C-3 "down"), which is held responsible for the enhanced formation and stability of **43**. As expected, the exo isomer of **42** gave virtually no endo alcohol **45**.[36]

2-Methyl-2-norpinyl, 1-Methyl-2-norbornyl Cations

The type of methyl substitution narrows the energy gap between 2-norpinyl cations (now tertiary, **52**) and 2-norbornyl cations (remaining secondary, **58**). The positive charge of the 7-bridged ion **54** is therefore expected to be more evenly distributed than in previous examples. In fact, 2-methyl-2-norpinyl substrates (**50**, **51**) yielded comparable quantities of 2-methyl-2-norpinyl (**53**) and 1-methyl-*endo*-2-norbornyl products (**57**).[38] The **57** to **53** ratio and the conversion of **54** into the 2-methyl-2-norbornyl cation (**60**) decreased with increasing nucleophilicity of the solvent but did not

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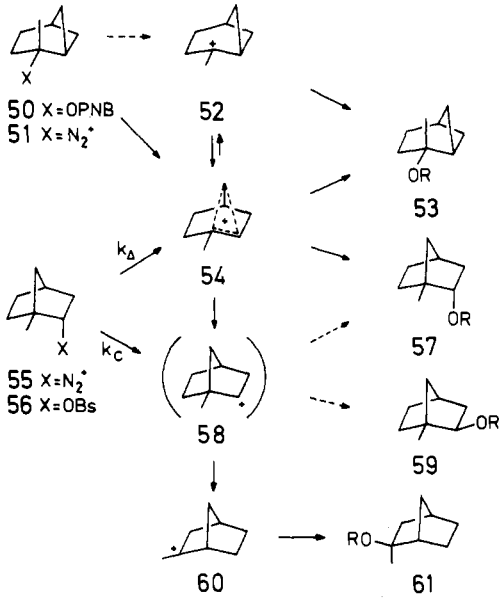
Table II.
Product Distributions from 2-Methyl-2-norpinyl and 1-Methyl-2-norbornyl Substrates

precursor, conditions	OR	53	57	59	61
50, HOAc, NaOAc, 20 °C	OAc	28	42		30
50, 67% aq acetone, $CaCO_3$, reflux	OH	53.6	37.2	0.1	9.2
50, MeOH, lutidine, reflux	OCH_3	73.9	20.4		5.7
51, aq $HClO_4$ (pH 3.8), 20 °C	OH	49	41		10
55, HOAc, 20 °C	OAc	7.5	15.4	6.8	70.3
55, aq $HClO_4$ (pH 3.8), 20 °C	OH	19.6	17.2	1.2	62.0
56, 67% aq acetone, $CaCO_3$, reflux	OH	0.26	0.22	11.3	88.2

Scheme V



depend on the leaving group (OPNB vs. N_2^+) (Table II). The virtual absence of 1-methyl-*exo*-2-norbornyl products (**59**) indicates that **58** is not a capturable intermediate on the reaction path from **54** to **60** (Scheme V). Methyl turns out to be a good choice as a "balancing" substituent; stronger charge-stabilizing groups (Ph, OMe) frustrate the norpinyl–norbornyl rearrangement almost completely.[39]

1-Methylnorbornane-*endo*-2-diazonium ions (**55**) gave enhanced yields of **59** and **61** (which we attribute to k_s and k_c processes, respectively), but the **57** to **53** ratios were similar to those observed with **50** and **51**.[40] Solvolyses of 1-methyl-*endo*-2-norbornyl brosylate (**56**) proceeded largely by k_c and k_s routes, but small quantities of **53** and **57** in the appropriate ratio indicate the onset of C-7 participation.

The experiments described so far do not reveal whether **53** and **57** originate from a single intermediate, **54**, or from two intermediates, **52** and **54**. In order to gain further insight we labeled 1-methylnorbornane-*endo*-2-diazonium ions (**55**) at C-3 (complete deuteration). The intervention of **52** should distribute the label among positions 6 and 7 of **53** and—if **52** reverts to **54**—among positions 3 and 7 of **57**. Some scrambling of the label was indeed observed, but the distribution was uneven (61:39 in **53**; 69:31 in **57**).[40] These observations indicate that equilibration of **52** and **54** competes with nucelophilic capture. The bridged ion **54**

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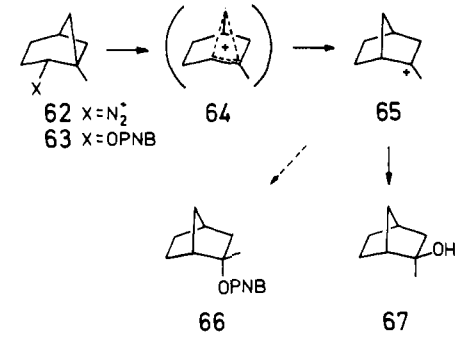
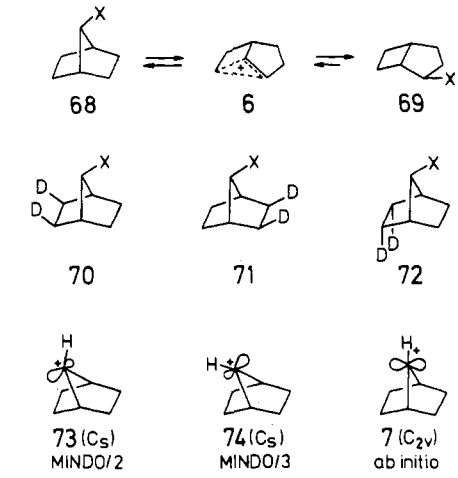
Scheme VI



Scheme VII



gives rise to both **53** and **57** (although not in the ratio suggested by the figures of Table II), and **52** must be slightly above **54** in energy.

1-Methyl-2-norpinyl, 2-Methyl-2-norbornyl Cations

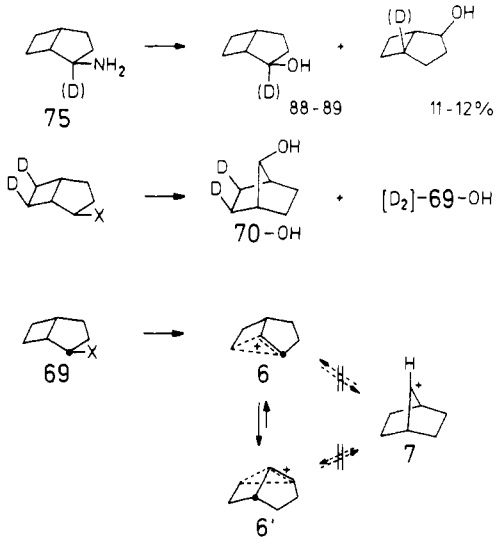
In contrast to the preceding paragraph, the methyl group is now positioned to enhance the energy gap between the open norpinyl and norbornyl cations. As expected, the only rearranged alcohol obtained from 1-methylnorpinane-2-diazonium ion (**62**) or 1-methyl-2-norpinanol *p*-nitrobenzoate (**63**) was *endo*-2-methyl-*exo*-2-norbornanol (**67**).[41] The bridged structure **64** now assumes the role of a transition state or high-energy intermediate, collapsing immediately to the stable tertiary cation **65**. The *p*-nitrobenzoate recovered after 20–50% conversion of **63** was found to contain up to 3.5% of the rearranged endo ester **66**.[41] In the absence of bridging, internal return from ion pairs may lead to endo esters,[42] but no endo attack is seen in the deaminative or solvolytic formation of alcohols.

2-Bicyclo[3.2.0]heptyl, 7-Norbornyl Cations

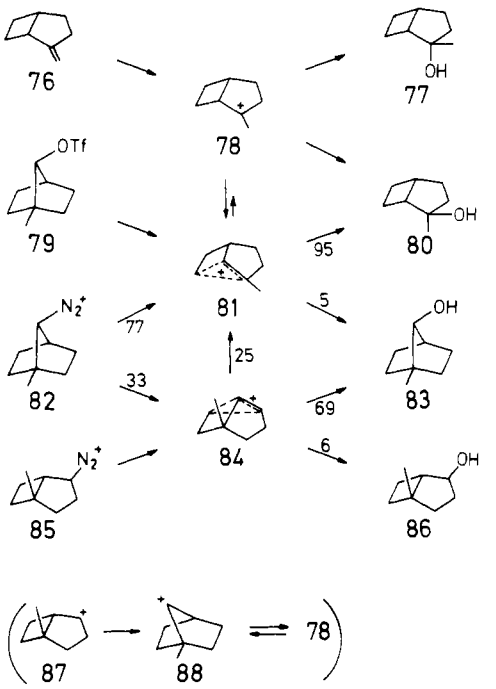
In 1958 Winstein et al.[43] observed that acetolysis of either 7-norbornyl brosylate (**68**–OBs) or *exo*-2-bicyclo[3.2.0]heptyl brosylate (**69**–OBs) led to similar product distributions (**68**–OAc:**69**–OAc ≃ 95:5). The bridged ion **6** was proposed as a common intermediate. Subsequent studies focused on 7-norbornyl substrates.

(41) Monstadt, G., unpublished results (Diplomarbeit, Ruhr-Universität Bochum, 1984).
(42) For a review, see: Collins, C. J. *Chem. Soc. Rev.* **1975**, *4*, 251.
(43) Winstein, S.; Gadient, F.; Stafford, E. T.; Klinedinst, P. E. *J. Am. Chem. Soc.* **1958**, *80*, 5895.

Scheme VIII



Scheme IX



The solvolytic rates of **68**–OTs conform to the Foote–Schleyer correlation and exclude significant k_s contributions.[44] The products from the deuterated precursors **70** (X = OTs, OBs, OTf) were predominantly the anti isomers **70**–OR, but ca. 10% of the syn isomers **71**–OR was also present.[45-47] The γ-isotope effects in **70**–OTf (1.024) and **72**–OTf (1.011) were found to be small[47] (Scheme VII). These data indicate little, if any, anchimeric assistance in the ionization of **68**. Neither bridged nor open ions can account for the entirety of the stereochemical results.

Quantum mechanical calculations give different structures for the 7-norbornyl cation. MINDO/2[48] and MINDO/3[16,49] produce bent (C_s) geometries while ab initio (STO-3G) procedures[16] prefer the more symmetrical (C_{2v}) structure **7**. In the absence of full-geometry optimization the relative energy of **6** could not be assessed.

The unsatisfactory status of the problem and its obvious similarity to the 2-norpinyl, 2-norbornyl case prompted our own studies.[50] We felt that the reluctant ionization of **68** might be a complicating factor and made extensive use of 2-bicyclo[3.2.0]heptyl substrates (**69**). Winstein[43,51] and Svensson[52] were the only previous authors who considered **69**, but they did not exploit the chirality of **69** and **6** as a mechanistic probe.

The Parent Ion(s). The nitrous acid deamination of *exo*-2-bicyclo[3.2.0]heptanamine (**75**) gave an unexceptional 92:8 ratio of 7-norbornanol (**68**–OH) and *exo*-2-bicyclo[3.2.0]heptanol (**69**–OH). Optically active **75** afforded **69**–OH with 22% racemization. In the deamination of [2-^{2}H]-**75**, 12% of the deuterium was relocated to the 5-position of **69**–OH (Scheme VIII). The 7-norbornanol obtained from the deamination of [*exo*-6,7-$^2H_2$]-**75**, or by acid-catalyzed rearrangement of the analogous alcohol, was exclusively the anti isomer (**70**–OH). The anti → syn leakage associated with the solvolyses of 7-norbornyl sulfonates[45-47] is not observed with 2-bicyclo[3.2.0]heptyl precursors. 7-Norbornyl cations of C_{2v} symmetry (**7**) do not intervene in the reactions of **69**. The partial exchange of C-2 with C-5 in **6** proceeds without exchange of C-3,4 with C-6,7 and is referred to as "same-side bridge-flipping", **6** ⇄ **6'** (Scheme VIII). These conclusions have been fully substantiated by the analogous behavior of 6- and 7-methylbicyclo[3.2.0]hept-2-yl substrates.[50]

Table III.
Kinetically Controlled Product Distributions from 2-Methylbicyclo[3.2.0]hept-2-yl, 1-Methyl-7-norbornyl, and 5-Methylbicyclo[3.2.0]hept-2-yl Substrates

precursor, conditions	80	77	83	86
76, 70% aq dioxane, 0.3 N H_2SO_4	91.1	3.8	5.1	
80–OPNB, 50% aq acetone, reflux	96.6	1.7	1.7	
79, 70% aq acetone, reflux	91.6	3.3	5.1	
82, aq $HClO_4$ (pH 3.5), 20 °C	78.9	0.6	18.4	2.1
85, aq $HClO_4$ (pH 3.5), 20 °C	24.0	0.1	69.0	5.8

2-Methylbicyclo[3.2.0]hept-2-yl, 1-Methyl-7-norbornyl Cations

2-Methylenebicyclo[3.2.0]heptane (**76**) and the 2-methylbicyclo[3.2.0]heptan-2-ols (**77**, **80**) gave 1-methyl-7-norbornanol (**83**) on treatment with acid[53] (Scheme IX). The rearrangement of optically active **76** proceeded without loss of enantiomeric purity.[50] On the other hand, *endo*-2-methylbicyclo[3.2.0]heptan-*exo*-2-ol (**80**) was the predominant product of kinetically controlled reactions of **76**, 1-methyl-7-norbornyl triflate (**79**), and the *p*-nitrobenzoate of **80** (Table III). The high yield of **80** reflects the stabilization of charge at the methyl-substituted carbon. The formation of some endo alcohol **77** suggests the open tertiary cation **78** as an intermediate, in addition to the bridged ion **81**, which is the most likely source of optically active **83**. In contrast to the bicyclo[3.2.0]heptyl substrates, 1-

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methyl-7-norbornyl triflate (**79**) gave **83** with 5–10% racemization. The analogy with anti → syn leakage of the parent series is obvious, confirming the notion that such processes are associated with the ionization of 7-norbornyl derivatives (k_Δ/k_c competition is a tentative explanation).

1-Methyl-7-norbornyl triflate (**79**) rearranged exclusively with migration of C-2(6) to generate **81**, rather than the less stable bridged ion **84**. 1-Methylnorbornane-7-diazonium ions (**82**) showed less discrimination, giving rise to some 5-methylbicyclo[3.2.0]heptan-*exo*-2-ol (**86**), the product of C-3(5) migration, and to a larger fraction of **83** (Table III). The product patterns suggest the formation of some **84** from **82**, but not from **79** (Scheme IX).

5-Methylbicyclo[3.2.0]hept-2-yl, 1-Methyl-7-norbornyl Cations

For further insights into the partitioning of the postulated intermediates we studied the decomposition of 5-methylbicyclo[3.2.0]heptane-*exo*-2-diazonium ions (**85**). With the aid of the product distribution obtained from **85**, partitioning factors may be derived for **81**, **82**, and **84**, which reproduce the data of Table III within experimental error (Scheme IX). The remote methyl group in **84** does not affect the charge distribution significantly; the **83** to **86** ratio (11.5) attributed to **84** is similar to the **68**–OH to **69**–OH ratio (13) of the parent ion **6**. Owing to the stabilization of **81**, the exothermic **84** → **81** transformation occurs more readily (25%) than the degenerate bridge flipping of **6** (11–12%).

Attempts to rationalize the product distributions in terms of open ions lead to serious discrepancies. Only a bent 1-methyl-7-norbornyl cation (**88**), rapidly equilibrating with **78**, could account for the stereochemical results and for the similar **80** to **83** ratios obtained from **76** and **79**. Product **86** must then originate from an open 5-methyl-2-bicyclo[3.2.0]heptyl cation (**87**), which rearranges irreversibly to **88** ⇄ **78** (no **86** is formed from **76** or **79**). It follows that the **80** to **83** ratios from all substrates should be identical. This is clearly not the case (Table III). As pointed out above, the bridged ions **81** and **84** provide an internally consistent interpretation of all data. Structure **88** may be viewed as the transition state of the **84** → **81** bridge flipping.

Conclusion

A vast amount of experimental evidence supports the intermediacy of the bridged ions **2** and **6**. Bridging in these ions must be highly unsymmetrical, as indicated by the predominant formation of norbornanols, and yet exerts a remarkable degree of stereochemical control. The conversion of **2** into the degenerate, exo-selective 2-norbornyl cation (**4**) and bridge flipping in **6** are closely related reorganizations. Quantitative differences in the formation and capture of **2** and **6** may be rationalized in terms of a smaller contribution of 2-norpinyl (**1**) to **2** than of 2-bicyclo[3.2.0]heptyl (**5**) to **6**. The faster rearrangement of **2** to **4**, as compared to bridge flipping in **6**, also indicates that the open 2-norbornyl cation (**3**) is closer in energy to **2** than the open 7-norbornyl cation (**7**) is to **6**.

Crude estimates of the energies of the open cations conform to these views. The heats of formation (MM1) of bicyclo[3.1.1]heptane (5.98 kcal/mol) and bicyclo[3.2.0]heptane (4.46 kcal/mol)[54] are similar, and we see no reason why the carbocations **1** and **5** should differ substantially. The 7-norbornyl cation (**7**, C_{2v}), however, is much higher in energy (7.5 kcal/mol by STO-3G[16]) than the classical 2-norbornyl cation (**3**). The smaller energy gap between **5** and **7** explains the enhanced contribution of **5** to the overall structure of **6**, as compared to **1** and **2**. We hope that this paper will stimulate more elaborate theoretical investigations of **2** and **6**. Extension of these principles to other bicyclic cations should help to evaluate the thermodynamic and geometrical prerequisites of "graded bridging".[11]

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