

# Metastable Norbornyl Cations

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Much effort over the past 30 years has been expended on studies of the 2-norbornyl cation.<sup>1</sup> The spectroscopic evidence supporting a bridged structure in non-basic media<sup>2-5</sup> and in the solid state<sup>5,6</sup> 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.<sup>7,8</sup> These conclusions are not immediately applicable to nucleophilic media, where solvation is an important factor.<sup>9</sup> The magnitude of non-classical stabilization and the origin of high exo/endo rate (product) ratios in solvolytic systems are debatable.<sup>10</sup> Nevertheless, a large body of kinetic and stereochemical data support the bridged-ion formulation.<sup>11,12</sup>

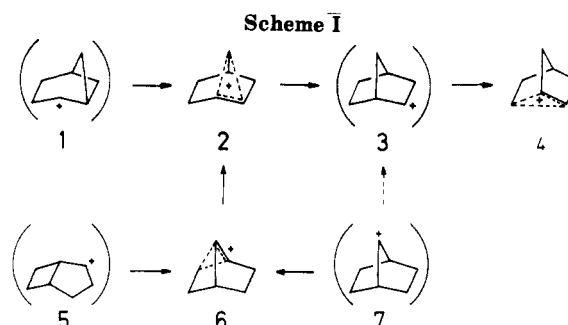
The  $C_7H_{11}^+$  potential surface as a whole is even more fascinating than its global minimum, the 2-norbornyl cation (4). This account is concerned with metastable isomers of 4, i.e. cations protected by potential barriers against immediate decay to 4. Specifically, we address the 2-bicyclo[3.1.1]heptyl (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 ( $6 \rightarrow 2$ ) or a 7,2-hydride shift ( $7 \rightarrow 3$ ) (Scheme I). This process is not observed in solvolytic systems. Antimony pentafluoride, however, ionizes 7-chloronorbornane to give 4,<sup>13</sup> 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).<sup>14</sup>

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This result is due to inadequacies of the MINDO/3 method, which overestimates the heat of formation of norbornane by ca. 20 kcal/mol.<sup>15</sup> At the ab initio level, 2 is found well above 3,<sup>14,16,17</sup> the energy difference depending on the (partial) inclusion of d functions.<sup>17</sup> Unfortunately, the most advanced calculations<sup>7,8,18</sup> 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).<sup>19</sup> Burrows and Eastman<sup>20</sup> showed that the rearrangements accompanying esterification of the 2-pinanol with acetic anhydride were stereospecific, 9 giving bornyl acetate (15) and 24 giving  $\alpha$ -fenchyl acetate (29), though both also gave  $\alpha$ -terpinyl acetate (21). The *p*-nitrobenzoates of the 2-pinanol were studied by Abraham<sup>21</sup> and by

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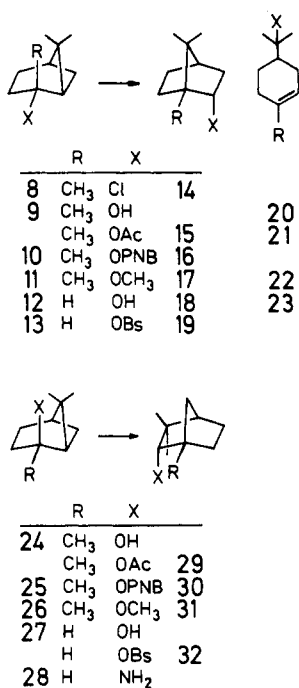
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Scheme II



Whittaker<sup>22</sup> 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.<sup>23</sup> 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**.<sup>22</sup> The solvolysis of  $\beta$ -nopinyl brosylate (**13**),<sup>24</sup> the acid-catalyzed rearrangement of the nopinols (**12**, **27**)<sup>25</sup> and the nitrous acid deamination of  $\alpha$ -nopinylamine (**28**)<sup>25</sup> 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)  $\alpha$ -terpinyl products (**20–23**) and the analogous alkenes is a major, sometimes predominant reaction.<sup>26</sup> 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<sup>27</sup> 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
<b>33</b> , 67% aq acetone, 120 °C (30% conversion)	OH (OPNB)	1.8 0.15
<b>34</b> , 3 M LiClO <sub>4</sub> in Et <sub>2</sub> O, 70 °C	ODNB	0.50
<b>35</b> , HOAc, 20 °C	OAc	3.4
<b>35</b> , aq HClO <sub>4</sub> (pH 3.9), 20 °C	OH	2.0
<b>35</b> , 0.2 M NaOH, 20 °C	OH	1.6
<b>35</b> , 0.3 M NaOEt in EtOH, 20 °C	OEt	0.85
<b>37</b> , HOAc, 20 °C	OAc	1.3
<b>37</b> , HOAc, 50 °C	OAc	1.6
<b>37</b> , HOAc, 100 °C	OAc	2.2
<b>37</b> , 0.7 M H <sub>2</sub> SO <sub>4</sub> , 70% aq dioxane, 20 °C	OH	0.50
<b>37</b> , 0.1 M H <sub>2</sub> SO <sub>4</sub> , EtOH, 20 °C	OEt	0.41
<b>39</b> , aq HClO <sub>4</sub> (pH 3.8), 20 °C	OH	8.8

precursor, conditions	OR	47 + 49:45
<b>41</b> , aq HClO <sub>4</sub> (pH 3.8), 20 °C	OH	0.48
<b>42</b> , 0.2 M NaOH, 20 °C	OH	0.43
<b>44</b> , aq HClO <sub>4</sub> (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<sup>28</sup> (Table I). The *p*-nitrobenzoate recovered after 30% conversion contained 58% of **33**, 36.5% of **38**-OPNB, and 5.3% of **40**-OPNB.<sup>28</sup> 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. Rearrangement of 2-norpinyl 3,5-dinitrobenzoate (**34**) under nonsolvolytic conditions (Et<sub>2</sub>O, LiClO<sub>4</sub>) gave a 2:1 ratio of **38**-ODNP and **40**-ODNP.<sup>29</sup> The decomposition of norpinane-2-diazonium ions (**35**) was studied in various solvents.<sup>28,29</sup> 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-<sup>2</sup>H]-**35** gave *endo*-norbornanol with deuterium exclusively at the bridgehead and *exo*-norbornanol with an even distribution of <sup>2</sup>H among positions 1 and 2.<sup>29</sup>

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-<sup>2</sup>H and 2-<sup>2</sup>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*<sub>2</sub> processes (Scheme III).

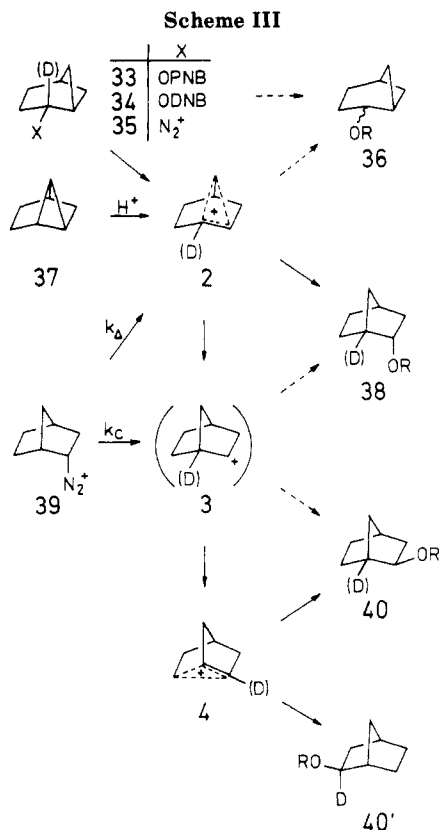
Another approach to **2** involves protonation of tricyclo[3.2.0.0<sup>2,7</sup>]heptane (**37**).<sup>30,31</sup> The **40** to **38** ratios thus obtained were generally lower than those observed with **35** (tighter ion pairs?), but the solvent effect was the same<sup>31</sup> (Table I). Increasing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

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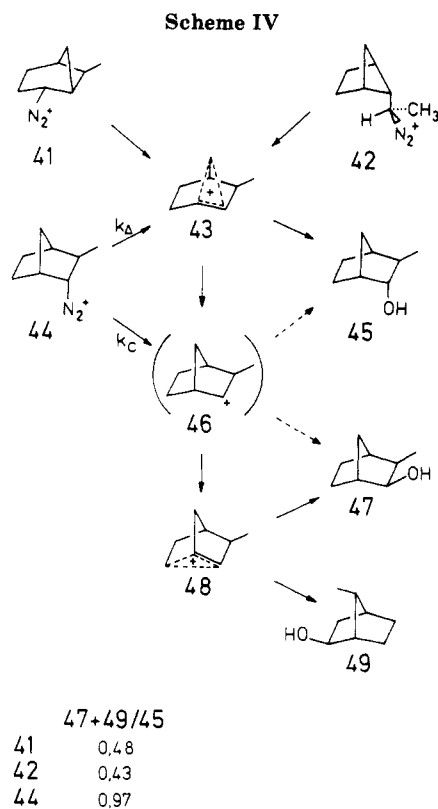


rated by an activation barrier.<sup>31</sup>

The 7-bridged ion **2** may also intervene in the decomposition 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.<sup>32</sup> These results are incompatible with **3** as the precursor of **38-OH** (see above). The high *exo* to *endo* product ratio is attributed to  $k_c, k_\Delta$  competition in the extrusion of nitrogen from **39**. As a rule,  $k_\Delta$  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<sup>33</sup> 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-norbornane-diazonium ions (**39**),<sup>32</sup> *exo*-3-methyl-*endo*-2-norbornanediazonium ions (**44**) afforded 43–47% of the analogous alcohol **45**.<sup>34–36</sup> Apparently, the major effect of substituting an *exo*-3-methyl for hydrogen in **39** is to increase the  $k_\Delta$  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).<sup>36</sup> 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<sub>3</sub> 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)<sup>35</sup> and from 3,3-dimethylnorbornane-*endo*-2-diazonium ions (**3.4**)<sup>37</sup> 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**.<sup>36</sup> 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**.<sup>36</sup>

#### **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**).<sup>38</sup> 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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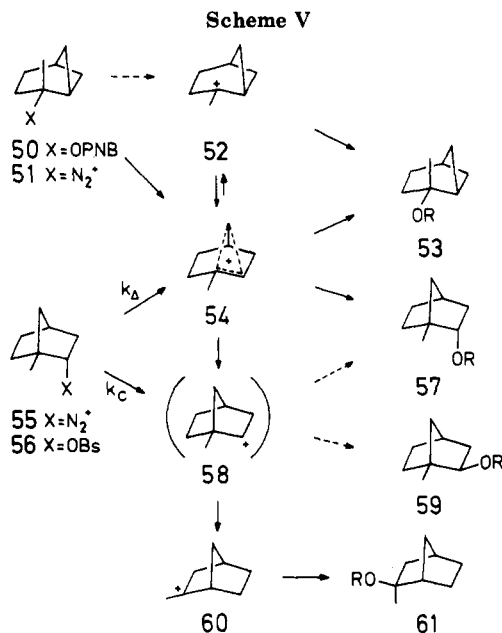
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**Table II.**  
Product Distributions from 2-Methyl-2-norpinyl and 1-Methyl-2-norbornyl Substrates

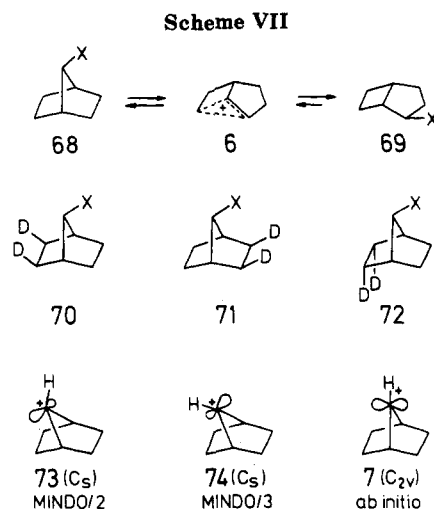
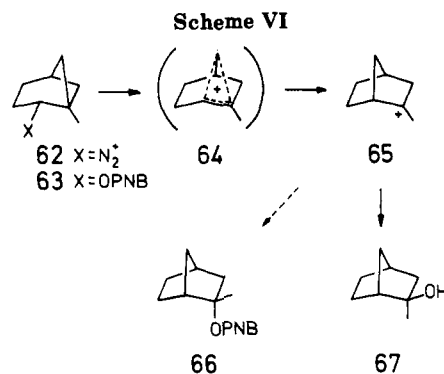
precursor, conditions	OR	53	57	59	61
50, HOAc, NaOAc, 20 °C	OAc	28	42		30
50, 67% aq acetone, CaCO <sub>3</sub> , reflux	OH	53.6	37.2	0.1	9.2
50, MeOH, lutidine, reflux	OCH <sub>3</sub>	73.9	20.4		5.7
51, aq HClO <sub>4</sub> (pH 3.8), 20 °C	OH	49	41		10
55, HOAc, 20 °C	OAc	7.5	15.4	6.8	70.3
55, aq HClO <sub>4</sub> (pH 3.8), 20 °C	OH	19.6	17.2	1.2	62.0
56, 67% aq acetone, CaCO <sub>3</sub> , reflux	OH	0.26	0.22	11.3	88.2



depend on the leaving group (OPNB vs. N<sub>2</sub><sup>+</sup>) (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.<sup>39</sup>

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.<sup>40</sup> 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).<sup>40</sup> These observations indicate that equilibration of 52 and 54 competes with nucleophilic capture. The bridged ion 54



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).<sup>41</sup> The bridged structure 64 now assumes the role of a transition state or high-energy intermediary, 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.<sup>41</sup> In the absence of bridging, internal return from ion pairs may lead to *endo* esters,<sup>42</sup> 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.<sup>43</sup> 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.

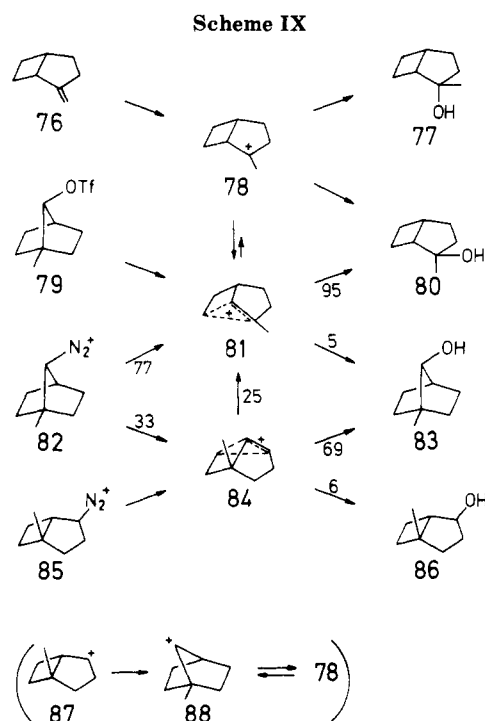
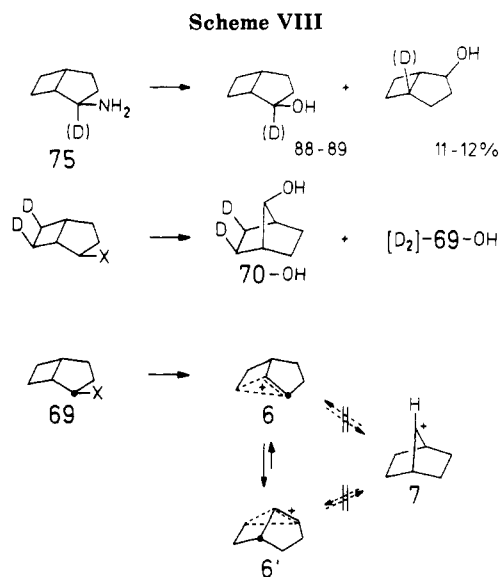
(41) Monstadt, G., unpublished results (Diplomarbeit, Ruhr-Universität Bochum, 1984).

(42) For a review, see: Collins, C. J. *Chem. Soc. Rev.* 1975, 4, 251.

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The solvolytic rates of 68-OTs conform to the Foote-Schleyer correlation and exclude significant  $k_s$  contributions.<sup>44</sup> 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.<sup>45-47</sup> The  $\gamma$ -isotope effects in 70-OTf (1.024) and 72-OTf (1.011) were found to be small<sup>47</sup> (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<sup>48</sup> and MINDO/3<sup>16,49</sup> produce bent ( $C_s$ ) geometries while ab initio (STO-3G) procedures<sup>16</sup> 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.<sup>50</sup> 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<sup>43,51</sup> and Svensson<sup>52</sup> 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-<sup>2</sup>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-<sup>2</sup>H<sub>2</sub>]-75, or by acid-catalyzed rearrangement of

**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 <sub>2</sub> SO <sub>4</sub>	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 <sub>4</sub> (pH 3.5), 20 °C	78.9	0.6	18.4	2.1
85, aq HClO <sub>4</sub> (pH 3.5), 20 °C	24.0	0.1	69.0	5.8

the analogous alcohol, was exclusively the anti isomer (70-OH). The anti  $\rightarrow$  syn leakage associated with the solvolyses of 7-norbornyl sulfonates<sup>45-47</sup> 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",  $6 \rightleftharpoons 6'$  (Scheme VIII). These conclusions have been fully substantiated by the analogous behavior of 6- and 7-methylbicyclo[3.2.0]hept-2-yl substrates.<sup>50</sup>

### 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<sup>53</sup> (Scheme IX). The rearrangement of optically active 76 proceeded without loss of enantiomeric purity.<sup>50</sup> 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  $\rightarrow$  syn leakage of the parent series is obvious, confirming the notion that such processes are associated with the ionization of 7-norbornyl derivatives ( $k_{\Delta}/k_c$  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  $\rightarrow$  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  $\rightleftharpoons$  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  $\rightarrow$  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)<sup>54</sup> 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<sup>16</sup>) 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".<sup>11</sup>

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