Stereoselectivity of 7-Methyl-7-norborn(en)yl Cations

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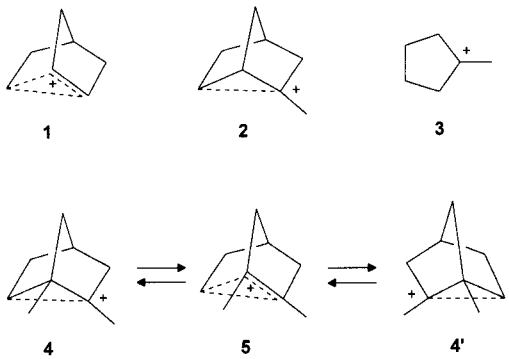
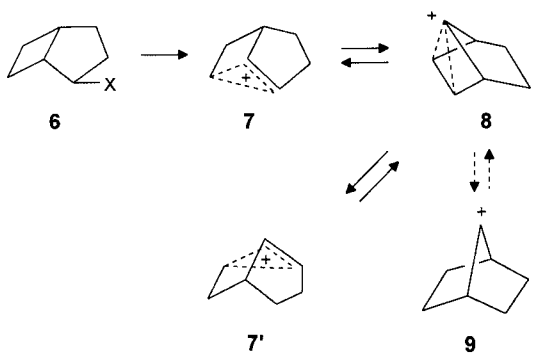
7-Methyl-7-norbornyl cations were generated, starting from 1-methylbicyclo[3.2.0]hept-2-yl substrates. While the *exo* diazonium ion (**26**) reacted exclusively with migration of the C-1–C-7 bond, competitive shifts of C-7 and C-5 were observed with the *endo* diazonium ion (**25**) and the *endo* brosylate (**24**). The stereorandom capture of 7-methyl-7-norbornyl cations was demonstrated by means of deuterium labels, thus supporting the classical structure **12** (C_{2v}). The inductive and hyperconjugative effects of the 7-Me group in **12** override the σ delocalization that is characteristic of the analogous secondary cation (**7**, C_1). 1,2-Dimethylbicyclo[3.2.0]hept-2-yl cations (**34**), labeled with deuterium, were shown to give 1,7-dimethyl-7-norbornanol (**35**) without undergoing a degenerate shift of C-5. A variety of 1-methylbicyclo[3.2.0]hept-6-en-2-yl substrates were found to display a similar pattern of rearrangements as their saturated analogs. However, the 7-methyl-7-norbornenyl cation (**48**) thus generated accepts nucleophiles stereoselectively, i.e., the delocalization of π electrons to C-7 is not affected by methyl substitution.

Bonding in secondary and tertiary 2-norbornyl cations is markedly different[1]. Strong evidence supports the symmetrically bridged structure **1** of the 2-norbornyl cation in nonbasic media[2], in the solid state[3], and in the gas phase[4]. The positive charge of the 2-methyl-2-norbornyl cation (**2**), on the other hand, appears to be largely localized at C-2. However, ^{13}C chemical shifts (δ_C+ = 271 for **2**, 336 for **3**)[5] and ESCA spectra ($\Delta E_b(C^+-C)$ = 3.7 eV for **2**, 4.2 eV for **3**)[6] point to more delocalization in **2** than in the 1-methyl-1-cyclopentyl cation (**3**). The chiral 1,2-dimethyl-2-norbornyl cation (**4**) has been trapped by nucleophiles, competitively with racemization by way of **5** ($k_{rac} \approx 10\ k_s$)[7]. Whereas averaged NMR spectra were obtained in nonbasic solutions, the degenerate rearrangement (**4** ⇌ **4'**) was "frozen out" in solid SbF_5 matrices below 100 K[8]. As compared to the 1,2-dimethyl-1-cyclopentyl cation, **4** rearranges more readily, is less deshielded (δ_C+ = 250)[8], and shows smaller isotopic perturbation[9]. Ab initio computational studies[10a], as well as the X-ray structure of a related cation[10b,c], also support the notion that **4** is partially delocalized.



The *exo*:*endo* rate and product ratios of **2** and **4** are comparable, or even superior, to those of **1**[11]. The degree of bridging appears not to affect the stereoselectivity – a much debated and yet unsolved problem in the "nonclassical ion controversy"[12]. Since the inherent *exo* selectivity of the norbornane skeleton is a complicating factor, a more straightforward case would be desirable. In the present paper, the 7-norbornyl cation is examined for the effect of a methyl substituent on σ delocalization, and the π-delocalized 2-norbornen-7-yl cation is included for comparison.

Reactions of the 7-norbornyl cation with nucleophiles are highly stereospecific[13], particularly if the ion is generated by rearrangement of bicyclo[3.2.0]hept-*exo*-2-yl precursors **6**[14]. From such studies, the bridged chiral (C_1) cation **7** emerged as the most stable species although **7** interconverts readily with its enantiomer **7'** by way of the transition state **8** (C_s) ("same side bridge flipping"). *Anti* → *syn* leakage, mediated by **9** (C_{2v}), was not observed in nucleophilic solvents. Recently, the IR spectrum of **7** was recorded after ionizing **6**-Cl in a cryogenic SbF_5 matrix[15]. According to high-level ab initio calculations, the relative energies of **7**, **8**, and **9** are 0.0, 2.9, and 5.2 kcal/mol, respectively[16].



In order to explore the effect of a methyl substituent, 1-methylbicyclo[3.2.0]hept-2-yl precursors (**10**) are preferable to 7-methyl-7-norbornyl substrates. The use of **10** ensures

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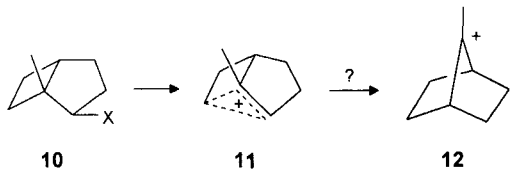
that the bridged structure **11** is passed en route to the symmetrical (C_{2v}) species **12**. Thus the relative stability of **11** and **12** is most readily assessed.

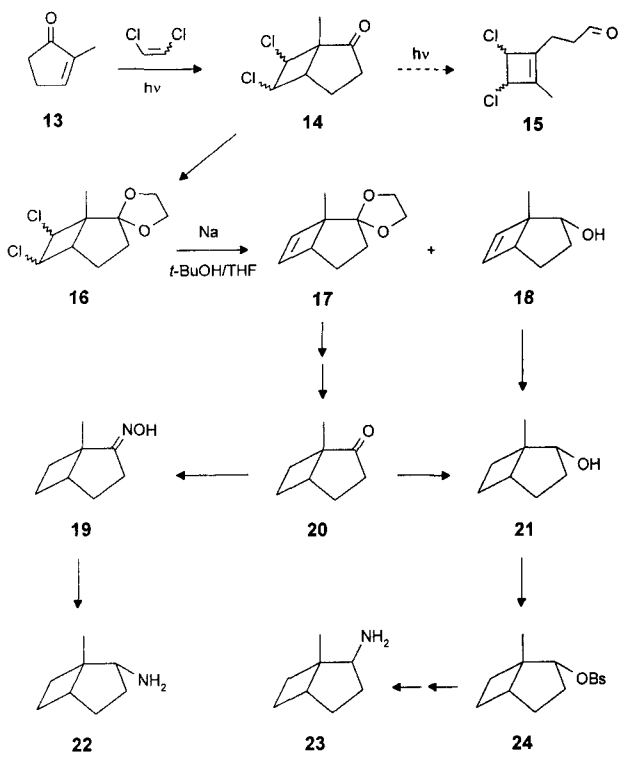


10 **11** **12**

1-Methylbicyclo[3.2.0]hept-2-yl Substrates

The synthesis of 1-methylbicyclo[3.2.0]heptan-2-one (**20**) has been described[17], with photochemical [2 + 2] addition of 1,2-dichloroethene to 2-methylcyclopent-2-en-1-one (**13**) as the first step (Scheme 1). From the reaction mixture, we isolated all four isomers of **14** (see the Experimental Section) and two isomers of **15**, the latter arising from **14** by α cleavage. In our hands, the *exo*-6,*endo*-7 isomer of **14** was not ketalized to give **16**. Hence the subsequent dehalogenation with sodium[17] afforded, in addition to the unsaturated ketal **17**, 1-methylbicyclo[3.2.0]hept-6-en-*endo*-2-ol (**18**) as a minor product (ca. 20%). Hydrogenation of **18** led to 1-methylbicyclo[3.2.0]heptan-*endo*-2-ol (**21**), thus confirming the assignment. Hydrogenation and hydrolysis of **17** provided **20**, which was converted into the oxime **19**. Reduction of **19** with sodium in ethanol gave 1-methylbicyclo[3.2.0]heptan-*endo*-2-amine (**22**) and the analogous *exo* isomer **23** in a 10:1 ratio. PGC of the mixture enhanced the purity of **22** to 99.8%. Useful amounts of **23** were obtained by a stereoselective route involving **21** and the analogous brosylate **24**. Inverting displacement of **24** with azide, followed by $LiAlH_4$ reduction, afforded **23** (≥99% *exo*).

Scheme 1



Nitrous acid deamination of **23**, proceeding by way of the *exo* diazonium ion **26**, gave 7-methyl-7-norbornanol (**31**) as the only product. The orientation of the leaving group in **26** invites participation of the C-1–C-7 bond (dihedral angle Θ ≈ 177°) with immediate formation of **11** and/or **12** (Scheme 2). The *endo* amine **22** gave rise to a more complex product mixture, containing 1-methylbicyclo[3.2.0]heptan-*exo*-2-ol (**27**) and the epimeric 2-methylbicyclo[3.2.0]heptan-2-ols (**29**, **30**) as well as **31** (Table 1). In the *endo* diazonium ion **25**, the C-5–C1 bond (Θ ≈ 154°) is much more suited to participation than the C-7–C-1 bond (Θ ≈ 57°) (all angles refer to the favored *endo* or boat conformation of bicyclo[3.2.0]heptane[18]). However, the alignment is far from perfect, and rearrangement to the 2-methylbicyclo[3.2.0]hept-2-yl cation (**28**) does not release ring strain. Thus inverting solvolytic displacement (k_s), producing **27**, and unassisted dissociation (k_c), leading eventually to **31**, are competitive. The solvolysis of the *endo* brosylate **24** proceeds similarly although the contributions of the competing processes are influenced by the leaving group. The predominance of **30** over **29** is known from earlier work in which **30**-OPNB served to generate **28**[14].

Scheme 2

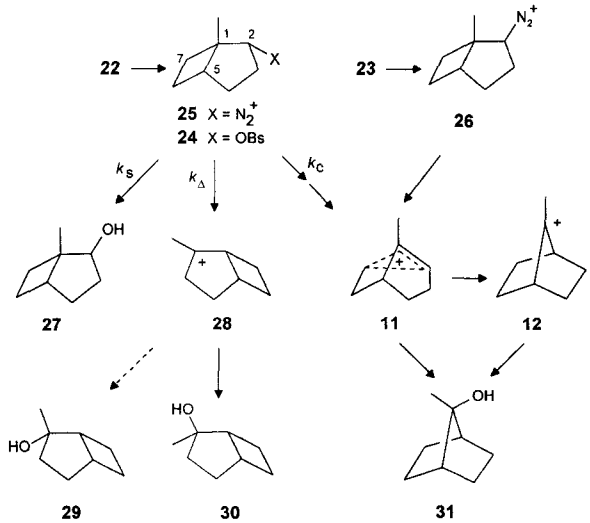


Table 1. Product distributions (%) obtained from 1-methylbicyclo-[3.2.0]hept-2-yl substrates

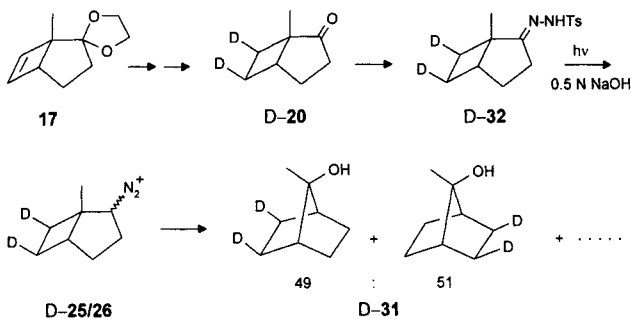
Substrate	Conditions	27	29	30	31
23	H_2O, H^+, $NaNO_2$, pH 3.8	–	–	–	100
22	H_2O, H^+, $NaNO_2$, pH 3.8	2.1	1.2	27.6	68.1
24	Dioxane/H_2O, 7:3, 80 °C	5.4	n.d.[a]	16.9	77.7
32	0.5 N NaOH, hν	0.5	n.d.[a]	23.6	75.9

[a] n.d. = Not determined.

The product distribution obtained on photolysis of the tosylhydrazone **32** in 0.5 N NaOH approached that obtained from nitrous acid deamination of **22**, i.e., the diazo compound initially formed from **32** reacts predominantly by way of the *endo* diazonium ion **25**. In order to explore

the origin of **31**, the deuterated tosylhydrazone D-**32** was prepared, starting with Pd-catalyzed addition of deuterium to **17**. The ^{1}H- and ^{2}H-NMR spectra of D-**20** indicated *exo* deuteration (Scheme 3).

Scheme 3



Photolysis of D-**32** afforded D-**31** with nearly equal distributions of deuterium between the *exo*-2,3 and *exo*-5,6 positions. The lack of stereoselectivity points to intervention of the symmetrical ion **12**. There is no evidence for the intermediacy of **11**, which would direct the attacking nucleophile *anti* to D. The small deviation of the observed ratio (49:51) from 50:50 is within experimental error and opposite to what would be expected from a contribution of **11**. If **11** and **12** are equilibrating species, ΔG° of **11** exceeds that of **12** by more than 10 kJ/mol. As compared with the parent species **7/8/9**, the relative stability of the bridged and open ions is reversed in the methyl analogs **11/12**. It should be emphasized that **12** is less stable than a typical tertiary carbocation, such as **3**, owing to the small bond angle at C-7 (**31**-OTs solvolyzes more slowly than 1-methylcyclopentyl tosylate by a factor of 10^5-10^6)[19]. Therefore, the 7-norbornyl case can be regarded as a rigorous test for the "swamping" of σ delocalization by the inductive and hyperconjugative effects of a methyl group.

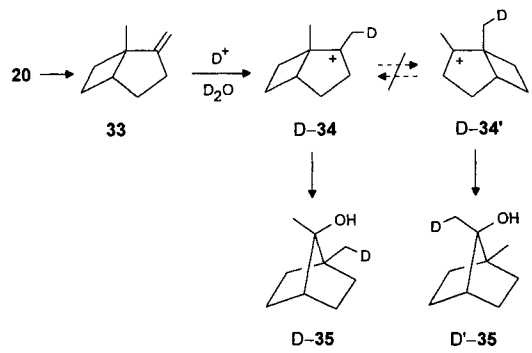
1,2-Dimethylbicyclo[3.2.0]hept-2-yl Substrates

1-Methyl-2-methylenebicyclo[3.2.0]heptane (**33**) was obtained from the ketone **20** by means of a Wittig reaction. Treatment of **33** with aqueous acid afforded 1,7-dimethyl-7-norbornanol (**35**). The analogous transformation of 2-methylenebicyclo[3.2.0]heptane into 1-methyl-7-norbornanol has been reported previously[20]. Exocyclic protonation of **33** is thought to generate the 1,2-dimethylbicyclo[3.2.0]hept-2-yl cation (**34**), rearrangement of which eventually leads to **35**. In the presence of D^+/D_2O, deuterium was incorporated exclusively into the 1-methyl group of **35**, i.e., the C-5–C-1 bond does not migrate prior to ring expansion (Scheme 4). Since our findings exclude reacemization at the bicyclo[3.2.0]heptyl stage (**34** ⇌ **34'**), the stereoselectivity of the 1,7-dimethyl-7-norbornyl cation could be probed by means of nonracemic substrates. So far, our efforts to this end have not been successful.

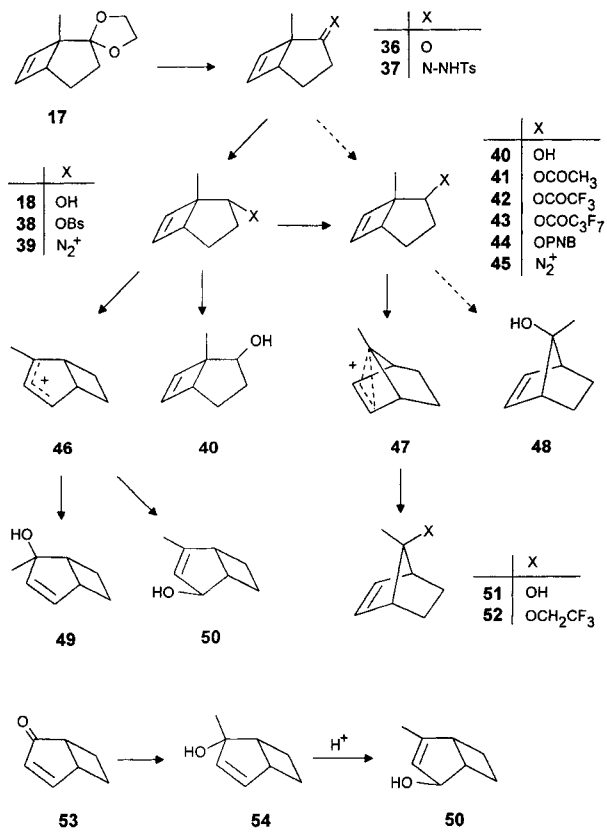
1-Methylbicyclo[3.2.0]hept-6-en-2-yl Substrates

Hydrolysis of the ketal **17** afforded 1-methylbicyclo-[3.2.0]hept-6-en-2-one (**36**)[21], from which the tosylhydrazone **37** was prepared. Reduction of **36** with $LiAlH_4$ gave selectively 1-methylbicyclo[3.2.0]hept-6-en-*endo*-2-ol (**18**) which was converted into the brosylate **38**. Inverting displacement of **38** with tetrabutylammonium acetate provided the *exo* acetate **41** from which the *exo* alcohol **40** was obtained (Scheme 5). Attempted brosylation or tosylation failed to give sulfonates of **40**. However, **40** was readily converted into the trifluoroacetate **42**, heptafluorobutyrate **43**, and *p*-nitrobenzoate **44**.

Scheme 4



Scheme 5



Photolysis of **37** in 0.2 N NaOH, generating a mixture of the epimeric diazonium ions **39** and **45**, was found to proceed preferentially with migration of the C-1–C-7 bond to give *syn*-7-methylbicyclo[2.2.1]hept-2-en-*anti*-7-ol (**51**). Some participation of the C-1–C-5 bond was also ob-

served, generating the 2-methylbicyclo[3.2.0]hept-2-enylium ion (**46**) from which the allylic alcohols **49** and **50** were derived (Table 2). For comparison, a sample of **50** was prepared by addition of methyl lithium to bicyclo[3.2.0]hept-3-en-2-one (**53**), followed by acid-catalyzed isomerization of **54**. Neither step of this reaction sequence gave significant amounts of the tertiary *exo* alcohol **49**. Hydrogenation, leading to **30**, served to identify **49** in the product mixture obtained from **37**.

Solvolysis of the *endo* brosylate **38** in aqueous dioxane produced **40** and **51** as the major products, along with a small amount of **50** (Table 2). As compared with the analogous diazonium ion, **38** shows enhanced inverting displacement (k_s) and less participation of the C-1−C-5 bond, as expected for a less efficient leaving group. The k_s pathway was minimized by performing the solvolysis in formic acid. In the *exo* series, sulfonates of **40** are too reactive for isolation whereas the carboxylates **42**, **43**, and **44** suffer from (competitive) deacylation. Thus methanolysis of the trifluoroacetate **42** gave exclusively the *alcohol* **40**. Increasing C−O heterolysis in more polar media led to rearrangement with formation of **51**; in 2,2,2-trifluoroethanol (TFE) the trifluoroethyl ether **52** was the only product. Variation of the leaving group also confirms that **40** arises by deacylation (**43** vs. **42** in aqueous dioxane; **44** vs. **42** in formic acid).

Table 2. Product distributions (%) obtained from 1-methylbicyclo-[3.2.0]hept-6-en-2-yl substrates

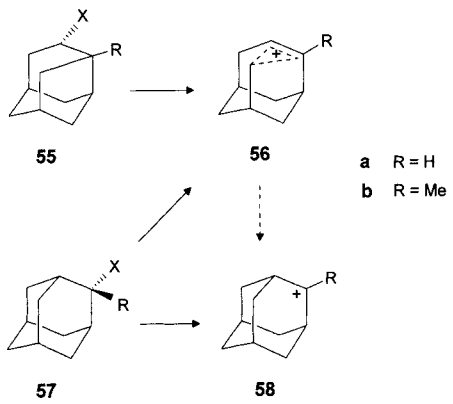
Substrate	Conditions	40	48	49	50	51
37	0.2 N NaOH, hv	2.0	1.1	6.9	18.5	71.5
38	dioxane/water (7:3), 80 °C	40.5	–	–	3.0	56.5
38	formic acid, 70 °C[a]	3.0	1.0	–	–	96.0
42	dioxane/MeOH (7:3), 80 °C	100	–	–	–	–
42	dioxane/water (7:3), 80 °C	93.5	–	–	–	6.5
42	dioxane/water (3:7), 80 °C	65.0	–	–	–	35.0
42	formic acid, 70 °C[a]	22.2	–	–	–	77.8
42	TFE, 70 °C	–	–	–	–	100[b]
43	dioxane/water (3:7), 80 °C	9.9	–	–	–	90.1
44	formic acid, 70 °C[a]	75.2	–	–	–	24.8

[a] Products were analyzed after alkaline hydrolysis of the formates. – [b] Product is **52**.

Whenever carbocations are generated from 1-methylbicyclo[3.2.0]hept-6-en-2-yl substrates, *syn*-7-methylnorbornen-*anti*-7-ol (**51**) is formed exclusively or in large excess over the epimer **48**, as expected for the bridged intermediate **47**. The π delocalization of the parent 7-norbornenyl cation is not "swamped" by the methyl effect in **47**, in contrast to σ delocalization in the 7-norbornyl series. Similar conclusions had been drawn from the NMR spectra of **47**[22] and from solvolyses of **51**-OTs[17]. The earlier data are complemented by the present approach to **47**, which parallels our route to 7-norbornyl cations.

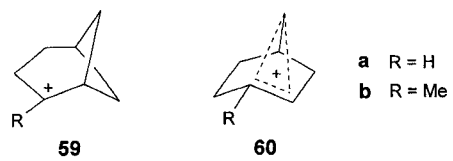
Concluding Remarks

As we have seen, the 7-norbornyl system provides an exceptionally clear example of a σ delocalized secondary cation **7** (C_1) as opposed to a "classical" tertiary cation **12** (C_{2v}). An analogous situation, with regard to strain and symmetry, ensues in the 2-adamantyl series. Full stereoselectivity is observed if the 2-adamantyl cation (**56a**) is generated from 4-protoadamantyl precursors (**55a**)[23] while 2-adamantyl substrates (**57a**) show substantial "leakage"[24].



Stereorandom reactions of the 2-methyl-2-adamantyl cation (**58b**), on the other hand, have been demonstrated only with 2-methyl-2-adamantyl precursors (**57b**)[25], the approach from **55b** not being practical. Thus the methyl effect on **56/58** is less rigorously defined than that on the 7-norbornyl cation.

Deviating behavior has been reported for the 2-norpinyl cation, where the bridged structure **60** is more stable than the open ion **59** for both the secondary (R = H) and tertiary (R = Me) species[26]. In the 2-norpinyl case, ring strain and methyl stabilization are compensating (**59b** experiences the full methyl effect but is more strained than **60b**). For 7-norbornyl and 2-adamantyl cations, on the other hand, both factors are reinforcing to favor classical tertiary cations.



Experimental Section

^{1}H NMR: Bruker WP 80 and Bruker AM 400; δ = 0 for tetramethylsilane as internal standard, δ = 7.26 for chloroform. – ^{13}C NMR (100.6 MHz) and ^{2}H NMR (61.4 MHz): Bruker AM 400. – ^{19}F NMR (75.4 MHz): Bruker WP 80. – IR: Perkin-Elmer 881. – MS: Varian MAT CH 5 (70 eV). – Gas chromatography (GC): Siemens Sichromat 1, equipped with glass capillary columns. – High pressure liquid chromatography (HPLC): Constametric I and II (LDC) with refractometric or UV detection. – Low pressure liquid chromatography (LPLC): Glass columns, 30 × 3 cm, 4.5 bar, refractometer detection. – Melting points: Kofler hot plate (Reichert), not corrected.

6,7-Dichloro-1-methylbicyclo[3.2.0]heptan-2-one (**14**): A solution of 2-methylcyclopent-2-en-1-one (**13**) (8.75 g, 91 mmol) and hydroquinone (50 mg) in freshly distilled 1,2-dichloroethene (*E*/*Z* mixture) was irradiated for 50 h (250 W medium-pressure mercury arc, pyrex). The progress of the reaction was monitored by GC. At 95% conversion, distillation of the mixture afforded 9.66 g (61%) of the

crude product, b.p. 56–60°C (0.1 Torr). Six compounds were detected by GC (20 m OV 17, 150°C), in the order of elution: I (39%), II (6%), III (27%), IV (10%), V (4%), and VI (4%). LPLC (silica gel, hexane/ether, 3:2) gave fractions A (I + II + III), B (IV), C (V), and D (V + VI).

The components of fraction A were separated by HPLC (Polygosil 60-10 CN, pentane/ether, 99:1); compound VI was isolated from fraction D after oxidation of V with Jones reagent. Taking into account the spectra of 6,7-dichlorobicyclo[3.2.0]hetan-2-ones[27], the following tentative assignments were made on the basis of ^{1}H NMR ($CDCl_3$): *exo*-6,*endo*-7-Cl-**14** (I): δ = 1.25 (s, 3H), 1.97 (dtd, *J* = 14.5/9.0/6.0 Hz, 1H), 2.08 (dt, *J* = 14.5/9.0 Hz, 1H), 2.44 (dt, *J* = 18.8/9.0 Hz, 1H), 2.54 (dt, *J* = 18.8/9.0 Hz, 1H), 2.77 (dd, *J* = 6.0/5.8 Hz, 1H), 4.00 (dd, *J* = 6.8/5.8 Hz, 1H), 4.12 (d, *J* = 6.8 Hz, 1H). – *cis*-**15** (II): δ = 1.72 (m, 3H), 2.3–2.9 (m, 4H), 4.58 (m, 2H), 9.78 (m, 1H), *endo*-6,*exo*-7-Cl-**14** (III): δ = 1.23 (s, 3H), 2.08 (dtd, *J* = 14.5, 10.0 and 7.8 Hz, 1H), 2.32 (dddd, *J* = 14.5, 10.0, 6.0 and 4.0 Hz, 1H), 2.44 (ddd, *J* = 18.2, 10.0 and 6.0 Hz, 1H), 2.66 (ddd, *J* = 18.2, 10.0 and 7.8 Hz, 1H), 2.97 (ddd, *J* = 10.0, 8.7 and 1.0 Hz, 1H), 4.21 (dd, *J* = 7.2 and 1.0 Hz, 1H), 4.63 (dd, *J* = 8.7 and 7.2 Hz, 1H). – *exo*-6,*exo*-7-Cl-**14** (IV): δ = 1.25 (s, 3H), 2.00 (m, 1H), 2.04 (m, 1H), 2.50 (ddd, *J* = 20.0, 10.0 and 4.5 Hz, 1H), 2.60 (ddd, *J* = 20.0, 10.0 and 9.5 Hz, 1H), 2.94 (td, *J* = 6.0 and 1.0 Hz, 1H), 4.28 (t, *J* = 6.0 Hz, 1H), 4.50 (dd, *J* = 6.0 and 1.0 Hz, 1H). – *trans*-**15** (V): δ = 1.77 (m, 3H), 2.2–2.8 (m, 4H), 4.88 (m, 2H), 9.77 (m, 1H). – *endo*-6,*endo*-7-Cl-**14**: δ = 1.28 (s, 3H), 1.98 (dddd, *J* = 14.2, 10.0, 9.5 and ca. 8 Hz, 1H), 2.30 (ddd, *J* = 14.2, 10.0, 3.2 and ca. 2 Hz, 1H), 2.42 (ddd, *J* = 18.8, 9.5 and 3.2 Hz, 1H), 2.75 (dt, *J* = 18.8 and 10.0 Hz, 1H), 3.0 (tt, *J* ≈ 8 and 2 Hz, 1H), 4.47 (dd, *J* = 8.0 and 1.8 Hz, 1H), 5.03 (t, *J* = 8.0 Hz, 1H).

1-Methylspiro[bicyclo[3.2.0]hept-6-ene-2,2'-[1,3]dioxolane (**17**) *and 1-Methylbicyclo[3.2.0]hept-6-en-endo-2-ol* (**18**): According to the reported procedure[17], crude **14** (9.66 g, 49 mmol) was converted into the ketal **16** (7.09 g, 43%). While three isomers of **14** reacted readily, a large fraction of *exo*-6,*endo*-7-Cl-**14** was recovered (HPLC). A solution of the mixture (7.88 g, 23 mmol) in tetrahydrofuran (150 ml) was treated with sodium (13.3 g, 0.58 mol) and 2-methylpropan-2-ol (30.0 g, 0.41 mol), as described by Gassman[17]. PGC (1.6 m SE 30, 160°C) or LPLC (silica gel, hexane/ether, 1:1) of the distilled product (2.9 g, 52%) provided **17**[17] (ca. 70%) and **18** (ca. 20%). ^{1}H NMR ($CDCl_3$) of **18**: δ = 1.28 (s, 3H), 1.36 (m, 3H), 1.8 (m, 1H), 1.9 (m, 1H), 2.63 (dd, *J* = 4.5 and 3.5 Hz, 1H), 3.58 (dd, *J* = 10 and 6.5 Hz, 1H), 6.04 (d, *J* = 3 Hz, 1H), 6.06 (d, *J* = 3 Hz, 1H). – $C_9H_{12}O$ (124.2): calcd. C 77.37, H 9.74; found C 77.35, H 9.69. Most probably, **18** arises by dehalogenation and reduction of unketalized *exo*-6,*endo*-7-Cl-**14**.

1-Methylbicyclo[3.2.0]heptan-2-one (**20**) *and p-Toluenesulfonylhydrazone* (**32**): A solution of **17** (1.1 g, 6.4 mmol) in ethanol (25 ml) was hydrogenated (10% Pd-C, 2 bar, 2 h), and the product was hydrolyzed (5% H_2SO_4, 2 h) to give 0.75 g (93%) of **20**[17]; ^{1}H NMR ($CDCl_3$): δ = 1.12 (s, 3H), 1.68 (m, 1H), 1.77 (dddd, *J* = 13.5, 9.3, 2.8 and 1.5 Hz, 1H), 1.85–2.0 (m, 3H), 2.23 (m, 1H), 2.31 (dddd, *J* = 18.5, 9.3, 2.8 and 0.6 Hz, 1H), 2.60 (m, 1H), 2.73 (dddd, *J* = 18.5, 10.5, 9.3 and 0.6 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 19.67 (CH_3), 21.39 (CH_2), 26.07 (CH_2), 29.14 (CH_2), 36.74 (CH_2), 41.21 (CH), 48.52 (C), 224.24 (C=O).

For the preparation of D-**20**, deuterium was used in the first step of this procedure. ^{2}H NMR ($CHCl_3$): δ = 1.88 (51.5%), 2.28 (48.5%). In the ^{1}H-NMR spectrum of D-**20**, the multiplet at δ = 1.85–2.0 was narrowed and reduced to 2H; the signal at δ = 2.23 was absent. In the ^{13}C-NMR spectrum of D-**20**, triplets (*J* = 21 Hz) appeared at δ = 21.04 and 28.64. These data indicate that the deuterium is located in the *exo*-6 and *exo*-7-positions of D-**20**.

To a refluxing solution of *p*-toluenesulfonohydrazide (0.56 g, 3.0 mmol) in methanol (3 ml) was added **20** (0.35 g, 2.7 mmol). After the mixture was heated at reflux for 2 h, it was kept at –20°C for 12 h. The precipitate was filtered off and recrystallized from methanol to give 552 mg (70%) of **32**, m.p. 155°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3200, 3050 cm^{-1} (NH), 1600 (C=N), 1330, 1170 (SO_2). – ^{1}H NMR (CD_3COCD_3): δ = 1.12 (s, 3H), 1.7–1.95 (m, 6H), 2.15–2.3 (m, 1H), 2.40 (s, 3H), 2.5–2.8 (m, 2H), 7.33 and 7.77 (AA'BB', 4H); NH is not observed, due to exchange. – $C_{15}H_{20}N_2O_2S$ (292.4): calcd. C 61.62, H 6.89, N 9.58; found C 61.55, H 6.94, N 9.70. – The same procedure was applied to D-**20**, in order to obtain D-**32**.

Solutions of **32** or D-**32** (0.20 g, 0.68 mmol) in 0.5 N NaOH (40 ml) were photolyzed (120-W medium pressure mercury arc, pyrex vessel) for 3 h. The reaction mixture was extracted with diethyl ether (3 × 30 ml).The combined extracts were washed with a saturated aqueous solution of NaCl, dried (Na_2SO_4), and concentrated by distillation (Vigreux column). **27**[17] (0.5%), **30**[20] (23.6%), and **31**[28] (75.9%) were detected by GC (151 m Carbowax, 120°C). The major products **30** (oil) and **31** (m.p. 96°C, ref.[28] 97–98°C) were isolated by HPLC (Polygosil 60-5, pentane/ether, 1:1); their NMR spectra were in agreement with reported data. ^{2}H NMR ($CHCl_3$) of D-**31**: δ = 1.64 (49 ± 1%), 1.93 (51 ± 1%). These signals are assigned to *exo,anti*(*exo*-5,6) and *exo,syn*(*exo*-2,3)-D, respectively, by comparison with the ^{1}H-NMR spectrum of **31** ($CDCl_3$): δ = 1.15–1.28 (m, 4H), 1.34 (s, 3H), 1.46 (br. s, 1H), 1.61–1.67 (m, 4H), 1.91–1.97 (m, 2H), and the ^{2}H-NMR spectra of deuterated 7-norbornanols[14].

1-Methylbicyclo[3.2.0]heptan-endo-2-amine (**22**): To a solution of hydroxylammonium chloride (1.37 g, 20 mmol) in water (20 ml) was added **20** (1.64 g, 13.2 mmol). The mixture was neutralized with sodium carbonate, heated at reflux for 4 h, and partitioned between water and diethyl ether. The combined ether solutions were dried ($MgSO_4$) and evaporated in vacuo to give 0.90 g (49%) of the oxime **19**; ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 3H), 1.1–3.0 (m, 9H), 6.5 (br. s, 1H). To a solution of crude **19** (0.50 g, 3.6 mmol) in anhydrous ethanol (80 ml) were added strips of sodium (ca. 10 g, 0.43 mol). As soon as the metal had dissolved, the mixture was cooled, diluted with water (50 ml), saturated with NaCl, and extracted with diethyl ether (5 × 40 ml). The combined ether solutions were extracted with 2 N HCl. The aqueous phase was made alkaline with NaOH and extracted with diethyl ether. The extracts were dried (K_2CO_3) and concentrated by distillation (Vigreux column) to give 0.24 g (53%) of crude amine (**22**:**23** = 9:1). Pure (≥99.8%) **22** was obtained by PGC (2.3 m Carbowax + KOH, 140°C). – ^{1}H NMR (C_6D_6): δ = 0.6 (br. s, 2H), 1.05 (s, 3H), 1.15–2.2 (m, 9H), 2.55 (dd, *J* = 11 and 6 Hz, 1H). – $C_8H_{15}N$ (125.2): calcd. C 76.74, H 12.08, N 11.19; found C 76.81, H 12.09, N 11.18.

To a solution of **22** (30 mg, 0.24 mmol) in water (30 ml), adjusted to pH 3 (glass electrode) with 0.1 N $HClO_4$, was added sodium nitrate (67 mg, 1.0 mmol). The mixture was stirred for 12 h while pH 3.8 was maintained by occasional addition of 0.1 N $HClO_4$. The deamination products were distributed between water and diethyl ether. The combined ether solutions were washed with aqueous $NaHCO_3$, dried ($MgSO_4$), treated with $LiAlH_4$ (50 mg), concentrated by distillation, and analyzed by GC (151 m Carbowax, 100°C): **27**[17] (2.1%), **29**[20] (1.2%), **30**[20] (27.6%), and **31**[28] (68.1%).

1-Methylbicyclo[3.2.0]heptan-endo-2-ol (**21**) *and p-Bromobenzenesulfonate* (**24**): Reduction of **20** (0.50 g, 3.8 mmol) with $LiAlH_4$

(155 mg, 4.2 mmol) in diethyl ether (40 ml) afforded 0.46 g (90%) of **21**[17]; ^{1}H NMR ($CDCl_3$): δ = 1.15 (s, 3H), 1.2–2.3 (m, 10H), 3.65 (dd, *J* = 10 and 8 Hz, 1H). To a solution of **21** (0.33 g, 2.6 mmol) in anhydrous pyridine (10 ml) was added at −20°C *p*-bromobenzenesulfonyl chloride (735 mg, 2.9 mmol). After the mixture was stirred for 24 h at room temp., it was diluted with diethyl ether. The solution was washed with 2 N HCl and with aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by HPLC (Polygosil 60-5, hexane/ether, 7:e) to give 0.74 g (82%) of **24**, m.p. 76°C. – ^{1}H NMR ($CDCl_3$): δ = 1.08 (s, 3H), 1.2–1.75 (m, 4H), 1.8–2.3 (m, 5H), 4.35 (dd, *J* = 9 and 7 Hz, 1H), 7.7 (m, 4H). – $C_{14}H_{17}BrO_3S$ (345.2): calcd. C 48.70, H 4.96; found C 48.65, H 5.00.

To a solution of **24** (5 mg, 0.014 mmol) in dioxane/water (7:3, 0.5 ml) was added 2,6-dimethylpyridine (15 mg, 0.14 mmol). After the mixture was stirred at 80°C for 6 h, it was diluted with diethyl ether, washed with saturated aqueous NaCl, dried ($MgSO_4$), and analyzed by GC (151 m Carbowax, 120°C): **27** (5.4%), **30** (16.9%), and **31** (77.7%). Virtually the same product distribution was obtained after 24 h.

Bicyclo[3.2.0]heptan-exo-2-amine (**23**): To a solution of **24** (1.7 g, 4.9 mmol) in dimethyl sulfoxide (25 ml) was added sodium azide (0.64 g, 9.8 mmol). The mixture was heated at 80°C for 24 h, diluted with water (50 ml), and extracted with diethyl ether (3 × 40 ml). The combined extracts were washed with water, dried with $MgSO_4$, and concentrated by distillation to give 0.59 g (80%) of crude bicyclo[3.2.0]hept-*exo*-2-yl azide; IR (film): $\tilde{\nu}$ = 2096 cm^{-1} (N_3). To a solution of the azide (0.50 g, 3.3 mmol) in diethyl ether (20 ml) was added $LiAlH_4$ (0.44 g, 11.6 mmol). After the mixture was stirred at room temp. for 16 h, 10% aqueous NaOH (1.6 g) was added dropwise. Stirring for 1 h produced a flaky precipitate which was filtered off. The solution was dried ($MgSO_4$), and gaseous HCl was introduced slowly. The precipitate was filtered off and recrystallized from ethyl acetate/ethanol to give 0.30 g (56%) of **23** · HCl, m.p. 295°C (dec.). – $C_8H_{16}ClN$ (161.7): calcd. C 59.43, H 9.98, N 8.66; found C 59.46, H 9.94, N 8.63.

In order to obtain **23**, an aqueous solution of **23** · HCl was made alkaline with NaOH and extracted with diethyl ether. The extracts were dried (K_2CO_3) and concentrated by distillation; the residue was purified by PGC (2.2 m Carbowax + KOH, 140°C). ^{1}H NMR (C_6D_6): δ = 0.55 (br. s, 2H), 1.05 (s, 3H), 1.2–2.3 (m, 9H), 2.72 (d, *J* = 2 Hz, 1H). – The nitrous acid deamination of **23**, following the procedure described for **22**, afforded **31** as the only product (GC: 151 m Carbowax, 120°C).

1-Methyl-2-methylenebicyclo[3.2.0]heptane (**33**): To methyltriphenylphosphonium bromide (23.8 g, 67 mmol), suspended in anhydrous diethyl ether (170 ml), was added sodium amide (2.5 g, 64 mmol). With vigorous stirring, the mixture was heated at reflux for 24 h and then cooled to room temp. A solution of **20** (3.8 g, 30 mmol) in diethyl ether (30 ml) was added dropwise during 1 h. The mixture was heated at reflux for 2 h. Solids were filtered off; the filtrate was concentrated and the residue distilled at 500 Torr to give 3.2 g (87%) of **33**, b.p. 120°C/500 Torr. – IR (film): $\tilde{\nu}$ = 1648 cm^{-1} (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 3H), 1.3–2.0 (m, 9H), 4.60 (m, 1H), 4.75 (m, 1H). – C_9H_{14} (122.2): calcd. C 88.45, H 11.55; found C 88.46, H 11.53.

A solution of **33** (37 mg, 0.3 mmol) in 0.75 N D_2SO_4/D_2O (1 ml) was stirred at 40°C for 48 h. After the mixture was saturated with K_2CO_3, the organic phase was separated and dried (K_2CO_3). 1,7-Dimethyl-7-norbornanol (**35**), the only product detected by GC, was purified by HPLC (polygosil 60-5, pentane/ether, 1:1), m.p. 124°C. – ^{2}H NMR ($CHCl_3$) of D-**35**: δ = 0.87 (t, *J* = 2 Hz).

1,7-Dimethylbicyclo[2.2.1]heptan-7-ol (**35**): To a solution of 1-methylbicyclo[2.2.1]heptan-7-one[20] (0.30 g, 2.4 mmol) in diethyl ether (20 ml) was added dropwise at 0°C methyl lithium (1.35 M in diethyl ether; 4.6 ml, 6.2 mmol). After the mixture was stirred for 1 h, it was partitioned between water and diethyl ether. The combined ether solutions were dried ($MgSO_4$) and concentrated in vacuo to give 0.30 g (89%) of **35**, m.p. 124°C. ^{1}H NMR ($CDCl_3$): δ = 0.87 (s, 3H), 1.18 (s, 3H), 1.20–1.43 (m, 6H), 1.55–1.70 (m, 2H), 1.75 (t, *J* = 4.5 Hz, 1H), 1.89 (m, 1H). – $C_9H_{16}O$ (140.2): calcd. C 77.09, H 11.50; found C 77.10, H 11.61.

1-Methylbicyclo[3.2.0]hept-6-en-2-one (**36**) *and p-Toluenesulfonylhydrazone* (**37**): Hydrolysis of **17**, as described for **20**[17], afforded 95% of **36**[21]. – ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 3H), 1.72 (m, 2H), 2.18 (ddd, *J* = 18.8, 7.5 and 1.8 Hz, 1H), 2.98 (ddd, *J* = 18.8, 11.8 and 9.5 Hz, 1H), 3.08 (br. d, *J* = 7 Hz, 1H), 6.05 (d, *J* = 2.5 Hz, 1H), 6.28 (d, *J* = 2.5 Hz, 1H). – To a refluxing solution of *p*-toluenesulfonohydrazide (1.32 g, 7.1 mmol) in methanol (7 ml) was added **36** (0.79 g, 6.5 mmol). Heating at reflux was continued for 1 h. On cooling to room temperature, a precipitate formed which was filtered off and recrystallized from ethanol to give 1.2 g (64%) of **37**, m.p. 145°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3210, 3052 cm^{-1} (NH), 1649 (C=C), 1596 (C=N), 1326, 1186 (SO_2). – ^{1}H NMR ($CDCl_3$): δ = 1.25 (s, 3H), 1.65 (m, 2H), 2.40 (m + s, 5H), 2.90 (dd, *J* = 5 and 3 Hz, 1H), 5.92 (d, *J* = 3 Hz, 1H), 5.98 (d, *J* = 3 Hz, 1H), 7.25 and 7.80 (AA'BB', 4H). – $C_{15}H_{18}N_2O_2S$ (290.4): calcd. C 62.04, H 6.25, N 9.65; found C 62.13, H 6.20, N 9.65.

A solution of **37** (0.23 g, 0.79 mmol) in 0.2 N NaOH (30 ml) was irradiated for 3 h and processed as described for **32**. The products (Table 2) were analyzed by GC (60 m Marlophen, 100°C) and identified by comparison with authentic samples of **40** (see below), **48**[29], **50** (see below), and **51**[29]. **49** was identified by hydrogenation (2 bar, 5% Pd-C, diethyl ether) to give **30**[20].

1-Methylbicyclo[3.2.0]hept-6-en-endo-2-yl p-Bromobenzenesulfonate (**38**): Following the procedure for the preparation of **21**[17], reduction of **36** with $LiAlH_4$ afforded 92% of **18**, which was identical in every respect with the compound described above. – To a solution of **18** (4.97 g, 40 mmol) in anhydrous pyridine (50 ml) was added in small portions at 0°C *p*-bromobenzenesulfonyl chloride (10.5 g, 41 mmol). After the mixture was stirred at room temp. for 2 h, it was poured into ice-water (250 ml) and extracted with diethyl ether (3 × 150 ml). The combined extracts were washed with 1 N H_2SO_4, aqueous $NaHCO_3$, and water. The solution was dried ($MgSO_4$) and evaporated in vacuo to give 10.0 g (72%) of **38**, m.p. 82°C. – ^{1}H NMR($CDCl_3$): δ = 1.15 (s, 3H), 1.33 (m, 2H), 1.85 (m, 2H), 2.62 (dd, *J* = 5 and 3 Hz, 1H), 4.30 (dd, *J* = 9 and 7 Hz, 1H), 6.0 (br. s, 2H), 7.7 (m, 4H). – $C_{14}H_{15}BrO_3S$ (343.2): calcd. C 48.99, H 4.41; found C 49.03, H 4.33.

Solvolyses of **38** in dioxane/water (7:3, 80°C, 24 h) were performed as described for **24**. – To a solution of **38** (20.0 mg, 0.058 mmol) in formic acid (1 ml) was added sodium formate (19.7 mg, 0.29 mmol). The mixture was stirred at 70°C for 24 h. It was then cooled to room temp., made alkaline by careful addition of 2 N NaOH, and heated at 50°C for 2 h, in order to hydrolyze alkyl formates. After the solution was cooled to room temp., the products were extracted with diethyl ether. The extracts were dried (Na_2SO_4), concentrated by distillation, and analyzed by GC (60 m Marlophen, 100°C); results are recorded in Table 2.

1-Methylbicyclo[3.2.0]hept-6-en-exo-2-ol (**40**) *and Esters* (**41**–**44**): A solution of tetra-*n*-butylammonium acetate (7.0 g, 23 mmol) in benzene (90 ml) was dehydrated by azeotropic distillation of 8–10 ml. **38** (6.0 g, 17.5 mmol) was added, and the mixture was heated at reflux for 3 h. The benzene solution was extracted with

water, dried ($MgSO_4$), and concentrated by distillation (Vigreux column). The residue was distilled at reduced pressure to give 2.7 g (93%) of 1-methylbicyclo[3.2.0]hept-6-en-*exo*-2-yl acetate (**41**), b.p. 81°C (18 Torr). – IR (film): $\tilde{\nu}$ = 1740 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.20 (s, 3H), 1.4–2.35 (m, 4H), 2.03 (s, 3H), 2.83 (br. d, *J* = 5 Hz, 1H), 4.98 (d, *J* = 4 Hz, 1H), 5.87 (d, *J* = 3 Hz, 1H), 6.00 (dd, *J* = 3 and 0.8 Hz, 1H). – $C_{10}H_{14}O_2$ (166.2): calcd. C 72.62, H 8.49; found C 72.13, H 8.36.

To a suspension of $LiAlH_4$ (1.2 g, 31.7 mmol) in diethyl ether (50 ml) was added a solution of **41** (2.0 g, 12 mmol) in diethyl ether (20 ml). The mixture was stirred at room temp. for 2 h. Conventional workup afforded 1.46 g (98%) of **40**, m.p. 29°C. – ^1H NMR ($CDCl_3$): δ = 1.16 (br. s, 1H), 1.29 (s, 3H), 1.44 (dd, *J* = 13 and 7 Hz, 1H), 1.71 (dd, *J* = 13 and 7 Hz, 1H), 1.81 (tt, *J* = 13 and 7 Hz, 1H), 2.18 (tdd, *J* = 13, 7 and 4 Hz, 1H), 2.78 (d, *J* = 7 Hz, 1H), 3.83 (d, *J* = 4 Hz, 1H), 5.87 (d, *J* = 3 Hz, 1H), 5.99 (dd, *J* = 3 and 1 Hz, 1H). – $C_8H_{12}O$ (124.2): calcd. C 77.37, H 9.74; found C 77.41, H 9.74.

To a solution of **40** (1.0 g, 8.1 mmol) in anhydrous pyridine (15 ml) was added at 0°C trifluoroacetic anhydride (2.38 g, 11.3 mmol). The mixture was stirred at room temp. for 16 h and then diluted with diethyl ether (60 ml). After the solution was washed with 10% aqueous HCl and aqueous $NaHCO_3$, it was dried ($MgSO_4$), concentrated by distillation, and filtered through silica to give 1.5 g (84%) of 1-methylbicyclo[3.2.0]hept-6-en-*exo*-2-yl trifluoroacetate (**42**). A sample of **42** was purified by PGC (1.6 m DC 200, 100°C). – ^1H NMR ($CDCl_3$): δ = 1.23 (s, 3H), 1.55 (dd, *J* = 13 and 7 Hz, 1H), 1.77 (tt, *J* = 13 and 6.5 Hz, 1H), 1.87 (dd, *J* = 14.5 and 6.5 Hz, 1H), 2.35 (dddd, *J* = 14.5, 13, 7 and 4 Hz, 1H), 2.91 (d, *J* = 6.5 Hz, 1H), 5.18 (d, *J* = 4 Hz, 1H), 5.92 (d, *J* = 2.8 Hz, 1H), 5.99 (dd, *J* = 2.8 and 1 Hz, 1H). – ^{19}F NMR ($CDCl_3$): δ = –76.44 (s). – $C_{10}H_{11}F_3O_2$ (220.2): calcd. C 54.55, H 5.04; found C 54.66, H 4.99.

Analogous treatment of **40** (0.10 g, 0.81 mmol) with heptafluorobutyric anhydride (0.36 g, 0.88 mmol) afforded 205 mg (80%) of 1-methylbicyclo[3.2.0]hept-6-en-*exo*-2-yl heptafluorobutyrate (**43**). – IR ($CDCl_3$): $\tilde{\nu}$ = 1770 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 1.23 (s, 3H), 1.45–2.0 (m, 3H), 2.3 (m, 1H), 2.90 (d, *J* = 6.4 Hz, 1H), 5.18 (d, *J* = 4 Hz, 1H), 5.91 (d, *J* = 3 Hz, 1H), 6.00 (dd, *J* = 3 and 1 Hz, 1H). – ^{19}F NMR ($CDCl_3$): δ = –81.91 (t, *J* = 7.5 Hz, 3 F), –120.25 (q, *J* = 7.5 Hz, 2 F), –127.98 (s, 2 F). – $C_{12}H_{11}F_7O_2$ (320.2): calcd. C 45.01, H 3.46; found C 45.18, H 3.65.

Following the procedure for the preparation of **38**, 0.18 g (1.45 mmol) of **40** was reacted with *p*-nitrobenzoyl chloride (0.27 g, 1.45 mmol) to give 0.30 g (76%) of 1-methylbicyclo[3.2.0]hept-6-en-*exo*-2-yl *p*-nitrobenzoate (**44**), m.p. 93°C. – IR (KBr): $\tilde{\nu}$ = 1711 cm^{-1} (C=O), 1528, 1349 (NO_2). – ^1H NMR ($CDCl_3$): δ = 1.28 (s, 3H), 1.4–2.1 (m, 3H), 2.35 (m, 1H), 2.95 (d, *J* = 7 Hz, 1H), 5.28 (d, *J* = 4 Hz, 1H), 5.95 (d, *J* = 3 Hz, 1H), 6.06 (dd, *J* = 3 and 1 Hz, 1H), 8.22 (m, 4H). – $C_{15}H_{15}NO_4$ (273.3): calcd. C 65.92, H 5.53, N 5.13; found C 65.85, H 5.61, N 5.20.

Solvolyses of **42**–**44** in dioxane/water (24 h) and formic acid (24 h) were performed as described for **24** and **38**, respectively. Conditions and results are recorded in Table 2. – To a solution of **42** (0.40 g, 1.82 mmol) in 2,2,2-trifluoroethanol (5 ml) was added 2,6-dimethylpyridine (0.39 g, 3.64 mmol). The mixture was heated at 70°C for 24 h, cooled to room temp., and extracted with pentane. The extracts were dried (Na_2SO_4) and concentrated by distillation. A single product, *syn*-7-methyl-*anti*-7-(2',2',2'-trifluoroethoxy)-bicyclo[2.2.1]hept-2-ene (**52**), was detected by GC and isolated by PGC (1.6 m DC 200, 100°C; 0.30 g, 80%). For comparison, **52** was preapred by reacting **51**[29] with 2,2,2-trifluoroethanol and a catalytic amount of trifluoroacetic acid (room temp., 24 h, 92%). – ^1H NMR ($CDCl_3$): δ = 0.92 (dd, *J* = 10 and 4 Hz, 2H), 1.25 (s, 3H), 1.93 (dd, *J* = 10 and 2 Hz, 2H), 2.52 (m, 2H), 3.65 (q, *J* = 9 Hz, 2H), 5.98 (t, *J* = 2 Hz, 2H). – ^{19}F NMR ($CDCl_3$): δ = –75.64 (t, *J* = 9 Hz). – $C_{10}H_{13}F_3O$ (206.2): calcd. C 58.25, H 6.36; found C 58.18, H 6.28.

4-Methylbicyclo[3.2.0]hept-3-en-exo-2-ol (**50**): To a solution of bicyclo[3.2.0]hept-3-en-2-one (**53**)[30] (1.0 g, 9.3 mmol) in diethyl ether (40 ml) was added at 0°C 1.35 N methyl lithium in diethyl ether (7.77 ml, 10.5 mmol). After the mixture was stirred for 1 h, it was partitioned between water (20 ml) and diethyl ether (70 ml). The ether solution was washed with water (4 × 15 ml), dried (Na_2SO_4), and concentrated by distillation. The residue (1.05 g, 91%) was largely (96%, GC) *exo*-2-methylbicyclo[3.2.0]hept-3-en-*endo*-2-ol (**54**); ^1H NMR ($CDCl_3$): δ = 1.25 (s, 3H), 1.53 (m, 2H), 1.68 (br. s, 1H), 2.03 (m, 2H), 2.70 (m, 1H), 3.13 (m, 1H), 5.57 (d, *J* = 6 Hz, 1H), 5.75 (dd, *J* = 6 and 2 Hz, 1H).

To a mixture of acetone and aqueous 0.2 N $HClO_4$ (2:1) was added **54** (1.0 g, 8.1 mmol). The solution was stirred at room temp. for 30 min, diluted with water (30 ml) and extracted with diethyl ether. The extracts were washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated in vacuo. HPLC (Polygosil 60-5-CN, pentane/ether, 8:2) of the residue (0.95 g, 95%) provided **50** with 99% purity (GC). – ^1H NMR ($CDCl_3$): δ = 1.25 (br. s, 1H), 1.50 (m, 2H), 1.77 (d, *J* = 1 Hz, 3H), 2.15–2.21 (m, 2H), 2.70 (dt, *J* = 9.5 and 7 Hz, 1H), 3.15 (m, 1H), 4.35 (br. s, 1H), 5.57 (br. q, *J* = 1 Hz, 1H). – $C_8H_{12}O$ (124.2): calcd. C 77.37, H 9.74; found C 77.15, H 9.62.

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