JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 19–32 (1992)

GENERATION AND REARRANGEMENT OF SPIROCYCLOPROPANE-SUBSTITUTED 2-NORBORNYL CATIONS

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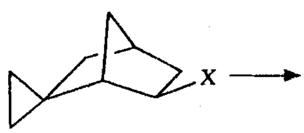
Access to spiro(bicyclo [2.2.1] heptane-2,1′-cycloprop-6-yl) derivatives was gained from the alkene spiro(bicyclo [2.2.1] hept-5-ene-2,1′-cyclopropane via separation of positional isomers. Spiro(bicyclo [2.2.1]-2,1′-cycloprop-*exo*-6-yl) *p*-toluenesulphonate (10) and spiro(bicyclo [2.2.1] heptane-2,1′-cycloprop-*exo*-6-yl) trifluoroacetate were found to solvolyse faster than the analogous *exo*-2-norbornyl esters, as predicted by theory. Ion-pair recombination, with the formation of tricyclo [4.2.1.$0^{3,7}$] non-3-yl *p*-toluenesulphonate, accounts for previous failures to assess the true reactivity of 10. An intervening bridged carbocation (3), labelled with deuterium, was shown to achieve equivalence of C-1 and C-6 prior to ring expansion. The rate of the formal Wagner–Meerwein rearrangement is estimated to be of the order of molecular vibrations, thus supporting the symmetrical bridged structure of 3. Methyl substitution at C-6 was found to direct nucleophilic attack exclusively to the tertiary carbon, and ring expansion preferentially to the secondary carbon. An equilibrating pair of 6(1)-methylspiro(bicyclo [2.2.1] heptane-2,1′-cycloprop-6-yl carbocations is thought to explain these observations most reasonably.

INTRODUCTION

Much effort over the past 40 years has been expended on studies of the 2-norbornyl cation.[1] The evidence supporting a symmetrically bridged structure of the 2-norbornyl cation in non-basic media,[2] in the solid state[3] and in the gas phase[4] is now overwhelming. The effect of substituents on the structure and reactivity of the 2-norbornyl cation has mostly been probed in solvolytic systems. Thus, electronegative substituents at C-6 were found to reduce (i) the rate of solvolysis of *exo*-2-norbornyl sulphonates,[5] (ii) the *exo*/*endo* rate ratio[5a] and (iii) the apparent rate of the Wagner–Meerwein rearrangements.[6] The data suggest a gradual change in mechanism from strong, to weak, to no participation (from k_Δ to k_C and k_S). The operation of electronic effects in 2-norbornyl systems has been viewed in different ways. Grob's success in correlating rates with σ_I led him to conclude that substituents at C-6 control solvolysis rates by the inductive effect only.[7] According to Grob, the substituent interacts with C-2 through the back lobe of the σ(C—R) orbital, without involving the C-6—C-1 bond. On the other hand, Schleyer and coworkers[8] interpret the effect of 6-R in terms of the (de)stabilizing interactions present in the bridged structure of the intermediate.

Although different principles are involved, these models are not readily distinguished by experiment. In each case, deactivating effects are predicted for all σ-withdrawing substituents at C-6, including methyl.[8b,9,10] Divergent results are anticipated, however, for spiroanellation of a cyclopropane ring at C-6. The inductive model predicts that the $-I$ effect of cyclopropyl[11] should reduce the rate of ionization of **1** relative to *exo*-2-norbornyl-X (cf. **2**). In contrast, theoretical studies suggest that the bridged ion **3** should be stabilized relative to the parent 2-norbornyl cation.[8b] The conductimetrically measured k_t for **1**-OTs (1/250 of *exo*-2-norbornyl tosylate in 80% EtOH at 70 °C) seems to support the inductive model.[10] We suspect that ion-pair recombination may have been a complicating



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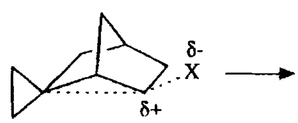

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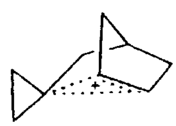

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0894–3230/92/010019–14$07.00

Received 16 July 1991
Revised 9 October 1991

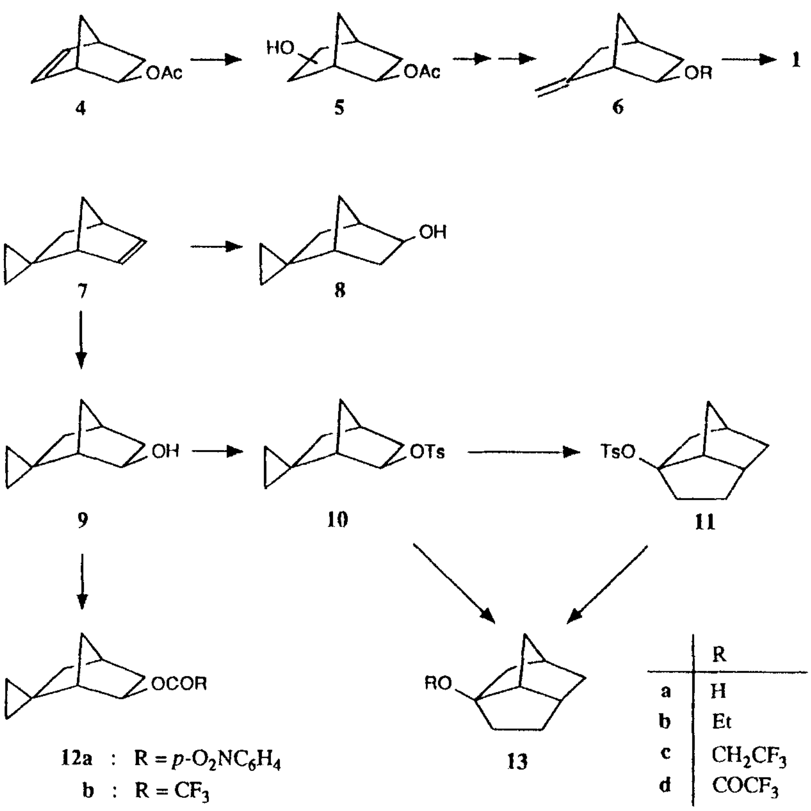
factor in these studies. As a result of the present reinvestigation we report that **1**-OTs and **1**-$OCOCF_3$ solvolyse in fact faster than the analogous 2-norbornyl derivatives. We have also introduced a deuterium label to probe the degeneracy of the intervening carbocation(s).

RESULTS

Esters of spiro(bicyclo[2.2.1]heptane-2,1′-cyclopropane)-*exo*-6-ol (9). Rates of solvolysis

Syntheses of **1** require at some stage the separation of 2,5- and 2,6 positional isomers. Fischer *et al.*[12] separated the hydroxy acetates **5** by liquid chromatography (LC). The cyclopropane ring was then attached to the site of the hydroxy group in three steps, via **6**.[10] We found it more convenient to start from **7**, the [4 + 2]cycloadduct of cyclopentadiene to methylenecyclopropane.[13] Hydroboration of **7** afforded the isomeric *exo* alcohols **8** and **9** (55 : 45, 67% yield), which were separated by high-performance LC (HPLC) (Scheme 1). Tosylation of **9** at −20 to 0 °C provided the analogous tosylate **10**, while tosylation at ambient temperature proceeded with rearrangement to give **11**. Crystalline **10** was found to rearrange slowly on standing, even in a refrigerator. Ion-pair recombination, yielding **11**, is also a major pathway in the solvolysis of **10** in 80% EtOH, additional products being **13a** and **13b** (16 : 84). Rate constants at 15–22 °C were estimated from the decrease in **10** against an internal standard, measured by HPLC (Table 1). Solvolysis of **10** is negligible under these conditions but proceeds at 70 °C at a rate similar to that previously reported for **10**.[10] The true solvolysis rate of **10** is now seen to exceed that of *exo*-2-norbornyl tosylate by a factor of 8 (25 °C).

The limited stability of **10** and the complications caused by ion-pair recombination prompted us to study less reactive esters of **9**. The *p*-nitrobenzoate **12a** was readily prepared but was found to solvolyse in 2,2,2-trifluoroethanol (TFE) with exclusive formation of **9**, i.e. by acyl—*O* cleavage. In contrast, the trifluoroacetate **12b** was well behaved, giving rise to **13c** and **13d** (89 : 11). The rearranged trifluoroacetate **13d** was not converted to **13c** at 70 °C. Rate constants for the solvolysis of **12b** in TFE at 60–70 °C were estimated by gas chromatography (GC) (Table 1). For comparison, the



Scheme 1

Table 1. Rate constants for solvolyses of **10–12** and of 2-norbornyl (Nb) reference compounds

Solvent	Substrate	Temperature (°C)	$k \times 10^4$ (s^{-1})	ΔH^* ($kcal\,mol^{-1}$)[a]	ΔS^* ($cal\,mol^{-1}\,K^{-1}$)[a]
80% Ethanol–water	**10**	15·0	5·56 ± 0·22	20·8	−1·1
		18·0	8·42 ± 0·40		
		21·5	12·5 ± 0·8		
		25·0[b]	19·3		
	exo-2-Nb-OTs[c]	25·1	2·37	22·0	−1·2
	11	62·4	1·78 ± 0·02	24·6	−2·5
		71·9	4·75 ± 0·02		
		80·4	12·43 ± 0·05		
97% Trifluoroethanol–water	**12b**	64·2	0·75 ± 0·02		
		67·9	1·02 ± 0·01		
		68·5	1·07 ± 0·01		
		70·0[b]	1·21		
	exo-2-Nb-OCOCF$_3$	101·5	0·42 ± 0·01	24·4	−11·2
		107·6	0·72 ± 0·02		
		111·4	1·04 ± 0·03		
		114·3	1·26 ± 0·02		
		70·0[b]	0·019		

[a] 1 cal = 4·184 J.
[b] Extrapolated from other temperatures.
[c] From Ref. 5.

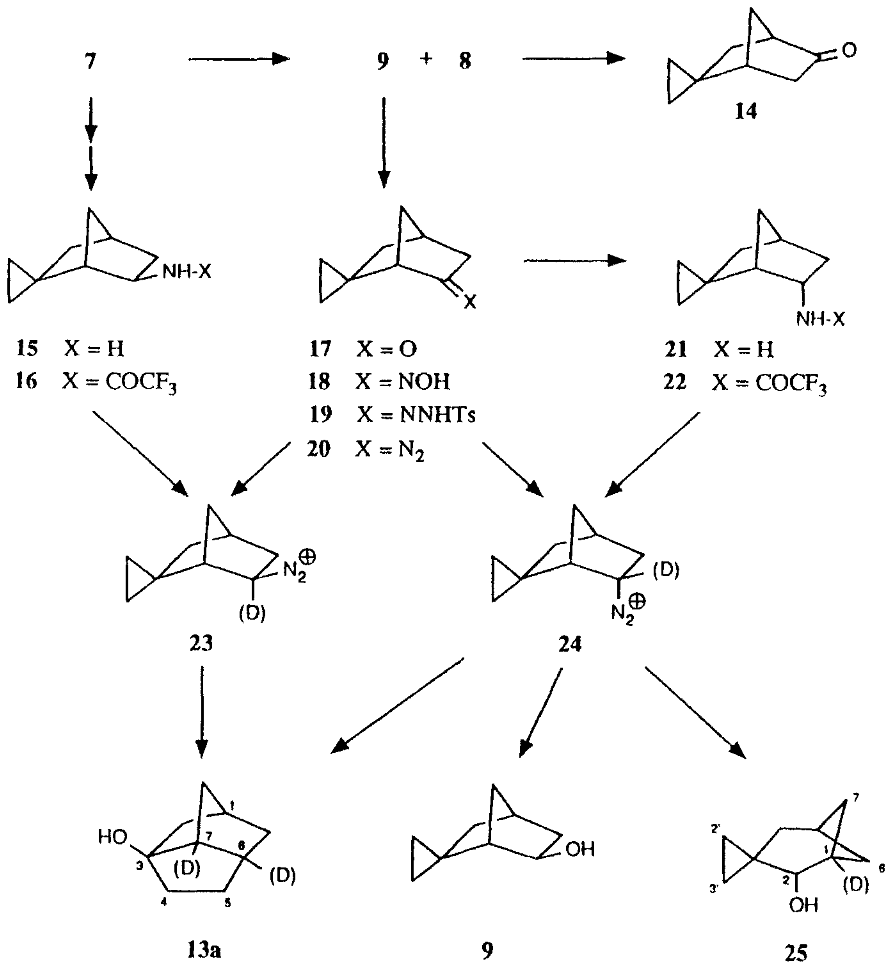
solvolysis of *exo*-2-norbornyl trifluoroacetate was studied by the same technique. Extrapolation of the data reveals that the solvolysis of **12b** in TFE is accelerated by a factor of 64 relative to that of *exo*-2-norbornyl trifluoroacetate.

Dediazoniation of spiro(bicyclo[2.2.1]heptane-2,1′-cyclopropane)-6-diazonium ions (23, 24). Degeneracy of the intermediate(s)

For further insight into the ring expansion reaction leading from spiro(norbornane-2,1′-cyclopropane) substrates to brendane products, we generated the intermediate carbocation(s) from diazonium ion precursors. Our first approach was by way of the tosylhydrazone **19**, derived from the ketone **17**. The mixture of alcohols, **8** and **9**, obtained by hydroborations of **7** was oxidized to give a mixture of the ketones **14** and **17**. Separation of the ketones by HPLC was easier than separation of the alcohols. Pure **17** was then converted into the tosylhydrazone **19** (Scheme 2). The photolysis of tosylhydrazone anions is known to generate diazo compounds,[14] which are protonated by hydroxylic solvents to give diazonium ions and products derived therefrom.[15] Irradiation of **19** in 0·2 M NaOH afforded **13a** as the major product, along with minor amounts of **7** and **25** (Table 2). While **7** and **13a** have been prepared by unequivocal routes,[10] the structural assignment of **25** rests mainly on spectral data. In particular, the ^{1}H NMR spectrum points to the cyclopropane ring (four distinct protons absorbing at δ 0·29, 0·47, 0·58 and 0·72) and to the bicyclo[3.1.1]heptane skeleton (W coupling of *endo*-6-H and *endo*-7-H, $J = 7·5$ Hz). The α-proton (2-H; $\delta = 3·57$) is shielded by the cyclopropane ring and couples only to one vicinal proton ($J = 5$ Hz).

Precedent with norbornanone tosylhydrazone[16] suggests that the photolysis of **19** should generate mixtures of the epimeric diazonium ions **23** and **24**. In order to elucidate the individual reaction patterns of **23** and **27**, we studied the nitrous acid deamination of the amines **15** and **21**, respectively. Aminoboration of **7** provided a mixture of **15** and of the 5-amino isomer (53 : 47), which was separated by HPLC of the trifluoroacetamides. A mixture of **21** and **15** (86 : 14) was obtained by reduction (Na–EtOH) of the oxime **18**. HPLC of the trifluoroacetamides afforded pure **22**, which was hydrolysed to give **21**. From the results of the nitrous acid deaminations (Table 2), it can be seen that **9** and **25** arise from the *endo*-diazonium ion **24**, whereas the *exo*-diazonium ion **23** gives ⩾99·8% of **13a**. The product distributions indicate that the tosylhydrazone **19** reacts predominantly by way of the *endo*-diazonium ion **24**.

The deuteriated diazonium ions [6-^{2}H]-**23** and [6-^{2}H]-**24** were generated by photolysis of the tosylhydrazone **19** in 0·2 M NaOD–D_2O, and the products [^{2}H]-**13** and [^{2}H]-**25** were isolated from the reaction mixture. The broad ^{2}H NMR signal of [^{2}H]-**13a** was resolved into two peaks of equal intensity by addition of Eu(fod)$_3$. The deuterium was located by means of ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of **13a** displays three peaks due to tertiary carbons at δ 52·42, 36·48 and 35·98. The low-field signal may be safely



Scheme 2

Table 2. Dediazoniation reactions of **23** and **24**

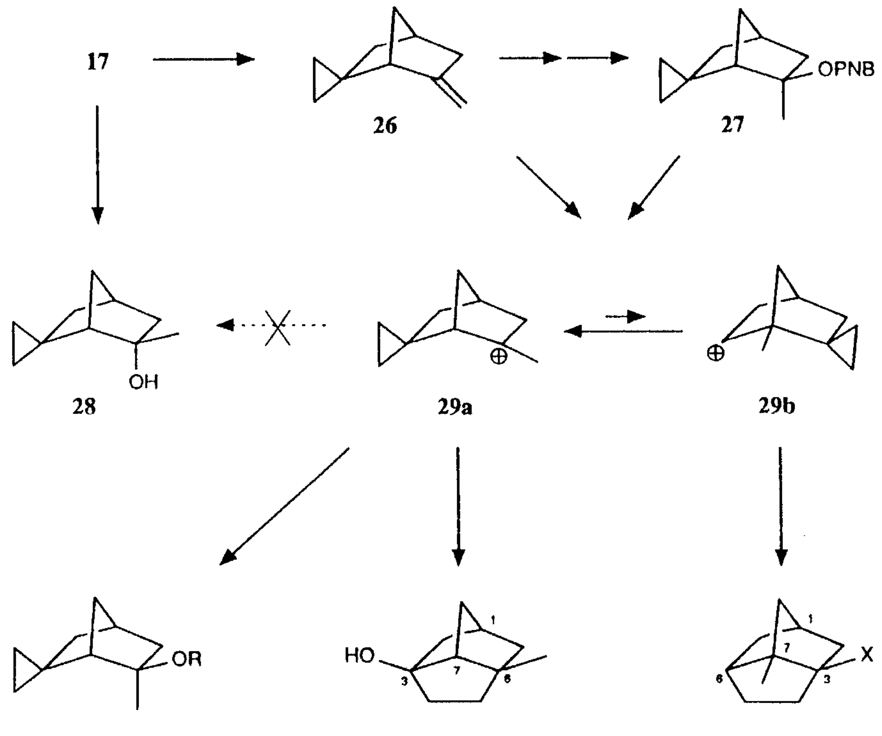
Precursor, conditions	Product distribution (%) 13a	9	25
19, 0·2 M naOH, $h\nu$	88·4	2·4	9·2
15, $NaNO_2$, aq. $HClO_4$ (pH 3·7), Et_2O	99·8	0·2	—
21, $NaNO_2$, aq. $HClO_4$ (pH 3·7), Et_2O	86·8	3·3	10·7

assigned to C-7, the only tertiary carbon β to the hydroxy group.[17] In the ^{13}C NMR spectrum of [^2H]-**13a**, triplets (1 : 1 : 1) originating from deuteriated carbons were recorded at δ 51·69 and 36·01. The corresponding singlets were reduced in intensity and shifted upfield to δ 52·03 and 36·31, respectively, owing to the isotope effect of β-^2H.[18] We conclude, therefore, that the deuterium is equally distributed between C-6 and C-7 of [^2H]-**13a**. In the ^1H NMR spectrum of [^2H]-**25**, the signal of 1-H at δ 2·53 was missing, as was the coupling of 2-H with 1-H. Thus the deuterium resides exclusively at C-1 of [^2H]-**25**. The distribution of deuterium indicates that different intermediates are involved in the formation of **13a** and of **25** (see below).

6(1)-Methylspiro(bicyclo[2.2.1]heptane-2,1′-cycloprop-6-yl) cations (29)

Methyl substitution at C-2 has a profound influence on the structure and reactivity of the 2-norbornyl cation.[1] Hyperconjugative stabilization by methyl predominates in the tertiary ion whereas σ delocalization plays a minor role. We were intrigued to see how analogous methyl substitution affects the spiro tricyclic cation **3**. Wittig methylenation of the ketone **17**, followed by oxymercuration of the alkene **26**, afforded the tertiary *exo*-alcohol **30**. Solvolysis of the *p*-nitrobenzoate **27** in methanol was found to proceed without rearrangement. Predominant formation of the methyl ether **31** attests to S_N1 reactivity of **27** even in strongly nucleophilic media. We infer, therefore, that the major product obtained from **27** in aqueous organic solvents, the tertiary *exo*-alcohol **30**, arises from the carbocation **29a**. The tertiary *endo*-alcohol **28** (prepared by addition of methyl lithium to **17**) was not detected in the reaction mixtures, but the isomeric brendanols **32** and **33** were present in minor amounts (Scheme 3 and Table 3).

Acid-catalysed hydration of **26** provided a more convenient access to **32** and **33**. The hydration conditions slowly convert **30** into **32** and **33**, but do not equilibrate the brendanols. Downfield shifts, due to β-OH, of a tertiary carbon in the ^{13}C NMR spectrum of **32**, and of a quaternary carbon in the ^{13}C NMR spectrum of **33**,



30 R = H
31 R = CH_3

33 X = OH
34 X = I
35 X = H

Scheme 3

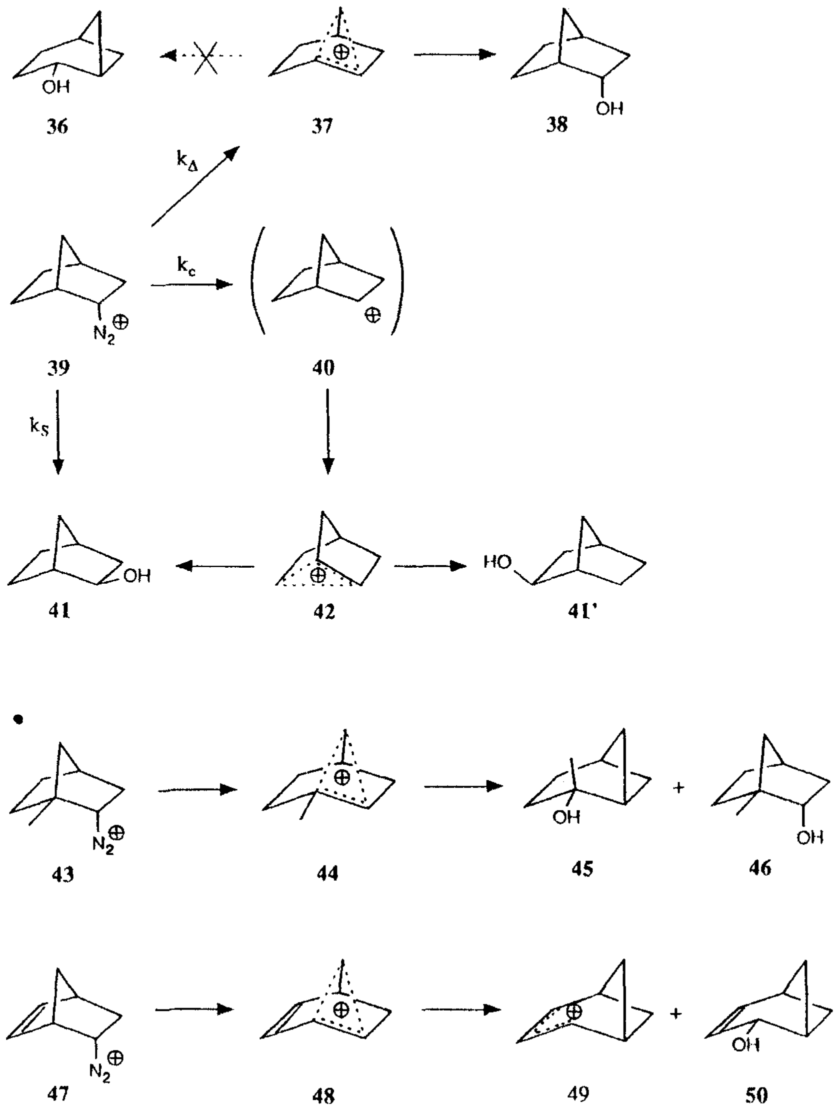
Table 3. Products derived from **29**

Precursor, conditions	Product distribution (%) **30**	**31**	**32**	**33**
27, MeOH, 5 d reflux	16·0	84·0	—	—
27, acetone–H_2O (1 : 1), 12 h reflux	85·5	—	4·3	10·2
27, dioxane–H_2O (7 : 3), 12 h reflux	82·1	—	4·6	13·3
26, dioxane–0·5 M H_2SO_4 (7 : 3), 40 °C:				
30 min, 17% conversion	30·8	—	13·8	55·4
90 min, 63% conversion	29·5	—	11·3	59·2
14 h, 100% conversion	—	—	16·7	83·3

served to assign the structures of the isomers. The assignment was confirmed by replacing the OH group of **33** with hydrogen, by way of the iodide **34**. The C_v symmetry of the hydrocarbon **35** is evident from its ^{13}C NMR spectrum. We note that the tertiary carbon of the cation **29** is the exclusive site of solvent capture whereas the intramolecular alkyl shift terminates preferentially at the secondary carbon.

DISCUSSION

Solvolyses of **10** and **12b**, as well as extrusion of nitrogen from the *exo*-diazonium ion **23**, proceed with virtually complete rearrangement to give 3-brendanol (**13a**). The dediazoniation of the *endo*-diazonium ion **24** is different, leading to **9** and **25** in addition to **13a**. Detailed studies of norbornane-*endo*-2-diazonium ions (**39**) have provided evidence for inverting solvolytic displacement (k_S) as a minor reaction path.[16] The formation of **9** from **24**, clearly bypassing the stage of a carbocation, is thought to proceed analogously. Another minor reaction path (k_Δ) of **39** is participation of C-7, generating the unsymmetrically bridged ion **37**. Charge distribution and ring strain in **37** favour nucleophilic attack at C-2, leading to *endo*-2-norbornanol (**38**) rather than to bicyclo[3.1.1]heptan-



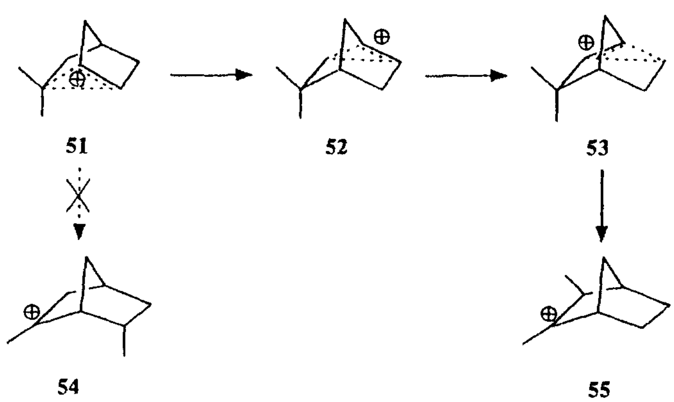
Scheme 4

2-ol (**36**). The balance is improved by a methyl group at C-1: the 7-bridged ion **44**, generated from **43**, gives rise to 2-methylbicyclo[3.1.1]heptan-2-ol (**45**) and 1-methyl-*endo*-2-norbornanol (**46**) in a 1·1 : 1 ratio.[19] With the 5-norbornene-*endo*-2-diazonium ion (**47**) as the precursor, the 7-bridged species **48** proceeds to give bicyclo[3.1.1]hept-3-en-2-ol (**50**) exclusively, owing to the allylic stabilization of **49**[20] (Scheme 4). Not surprisingly, **24** follows a similar course, leading to **25** by way of a cyclopropyl carbinyl cation.

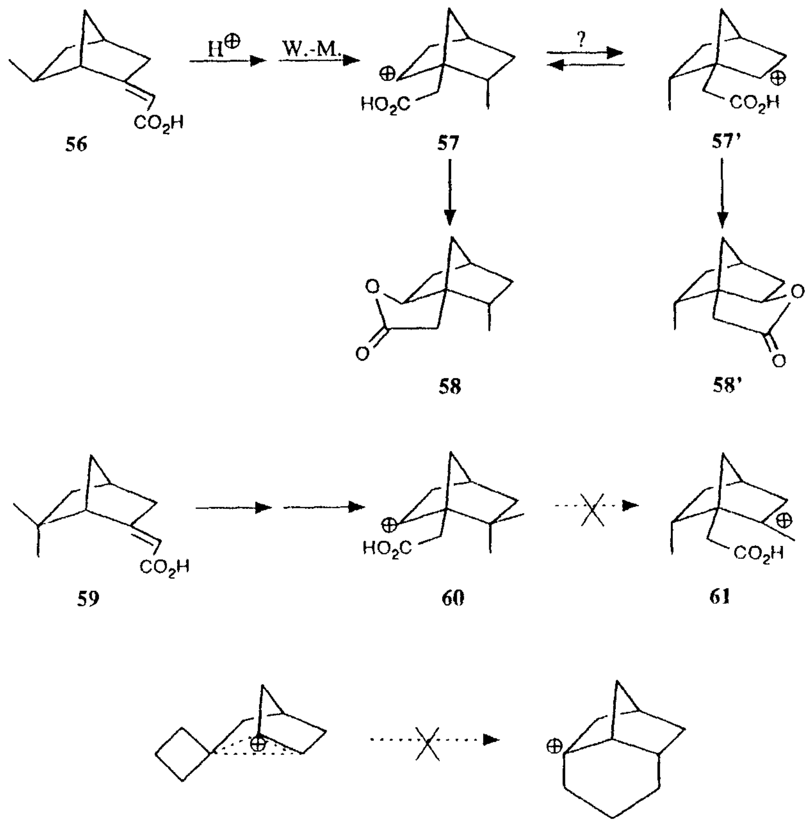
In the following discussion, we focus on the 6,2-carbon shift which transforms spiro(norbornane-2,1′-cyclopropyl) cations (**3**) into 3-brendyl derivatives (**13**). Whereas 6,2-hydride shifts have been observed with a wide variety of 2-norbornyl cations, analogous alkyl migrations appear to be limited to spirocyclopropane substituents. For instance, the generation of 6,6-dimethyl-2-norbornyl cations (**51**) by solvolysis[9,10] or deamination[21] fails to induce 6,2-methyl shifts. A deep-seated reorganization of **51** does occur under stable ion conditions (SbF_5–SO_2ClF, $-110\,^{\circ}C$). However, the tertiary cation thus formed was identified by NMR as **55**, rather than **54**.[22] We are forced to conclude that the sequence of 3,2-H, 6,2-H and 3,2-Me shifts, proceeding via **52** and **53**, is energetically more favoured than the 6,2-Me shift, **51** → **54** (Scheme 5). A degenerate 6,2-methyl shift, **57** ⇌ **57′**, has been invoked to account for racemization in the acid-catalysed formation of lactone **58** from optically active **56**[23] (Scheme 6). However, the lack of an analogous yet exoergic shift, **60** → **61**, in the lactonization of **59**[24] argues strongly against the purported mechanism. Attempts to promote 6,2-alkyl shifts by relief of ring strain were also unsuccessful. Exploratory studies of **62**, the cyclobutane analogue of **3**, gave no evidence of ring expansion, leading to **63**. It has been noted previously that cyclobutane is virtually inert toward electrophiles whereas cyclopropane has substantial reactivity.[25] The parent β-cyclopropylethyl system shows both kinetic and stereochemical evidence for partial cyclopropyl participation to form a symmetrical intermediate which opens to a cyclopentyl derivative,[26] analogous to the current case.

The ring expansion of spiro(norbornane-2,1′-cyclopropanes) was first described by Adam and co-workers.[27] They reported that addition of *p*-toluenesulphenyl chloride to **7** afforded the brendane derivatives **64** and **65**. Similar results were obtained on treatment of the oxirane **67a** and of the aziridine **67b** with acids (Scheme 7).[27b] In the formation of **65** and **69**, the 6,2-alkyl shift is preceded by Wagner–Meerwein rearrangement. However, the influence of the heteroatoms on product ratios is difficult to assess. In the present study, the parent spiro(norbornane-2,1′-cycloprop-6-yl) cation (**3**), minimally disturbed by deuterium, is shown to achieve equivalence of C-1 and C-6 prior to ring expansion. The enhanced rates of solvolysis of **10** and of **12b**, relative to analogous 2-norbornyl esters, must then be taken as evidence that **3** is lower in energy than the 2-norbornyl cation. In principle, label distributions cannot distinguish symmetrical bridged ions from rapidly equilibrating unsymmetrical species. The case of **3**, however, is particularly favourable for kinetic analysis. Since virtually no spirotricyclic products (e.g. **9**) are found, the rate of solvent capture (close to diffusion-controlled, $k_S = 10^9$–$10^{10}\ l\,mol^{-1}\,s^{-1}$) must be slower by a factor of at least 10^2 than the rate of ring expansion, which is thus estimated as $k_e = 10^{11}$–$10^{12}\ s^{-1}$. On the other hand, the formal Wagner–Meerwein rearrangement must proceed *ca* 100 times faster than ring expansion, in order to achieve an even distribution of the label. For the rate of the formal Wagner–Meerwein rearrangement, we arrive at an estimated $k_r = 10^{13}$–$10^{14}\ s^{-1}$, within the range of molecular vibrations. These arguments support the symmetrical bridged structure of **3**.

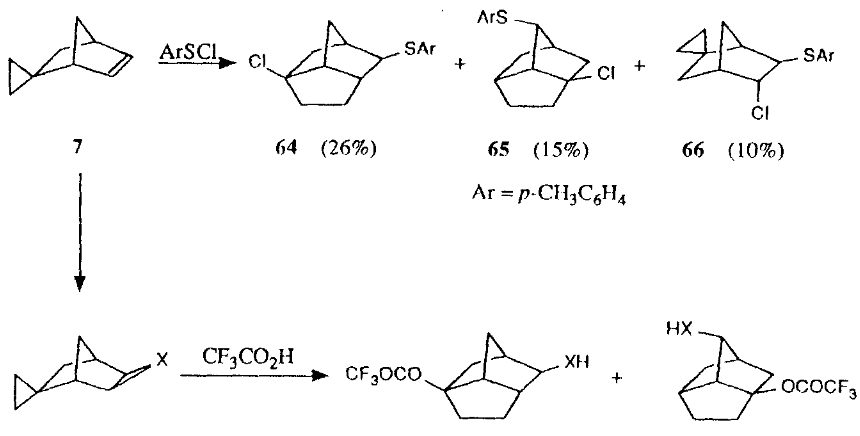
In contrast, the product pattern obtained from the 6-methyl derivative **29** is most reasonably interpreted in terms of two distinct cations, **29a** and **29b**. As a result



Scheme 5



Scheme 6



	X	68		69
a	O	12	:	88
b	NPh	20	:	80

Scheme 7

of hyperconjugative stabilization, the tertiary cation **29a** undergoes nucleophilic substitution, **29a** → **30**, faster than ring expansion (**29a** → **32**) (Scheme 3). The secondary cation **29b**, on the other hand, is expected to behave very much like **3**, i.e., ring expansion (**29b** → **33**) is much faster than solvent capture (not observed). The small concentration of **29b** in equilibrium with **29a** would thus be compensated by the enhanced rate of rearrangement, resulting in an excess of **33** over **32**. Although partial bridging in both **29a** and **29b** is likely, our data are difficult to reconcile with a *single* intermediate, i.e. a hybrid of **29a** and **29b**.

CONCLUSION

Spiro(norbornane-2,1′-cycloprop-6-yl) esters (**10** and **12b**) solvolyse faster than the analogous 2-norbornyl derivatives. The kinetic data confirm the stabilizing effect of spirocyclopropyl substitution at C-6 of the 2-norbornyl cation which was predicted from theory.[8b] The intervening carbocation **3** achieves equivalence of C-1 and C-6 prior to the ring expansion (6,2-alkyl shift) leading to 3-brendyl products. The estimated rate of the formal Wagner–Meerwein rearrangement is of the order of molecular vibrations, thus supporting the symmetrical bridged structure of **3**. Methyl substitution at C-6 disturbs the parent system substantially. Nucleophilic attack now occurs exclusively at the tertiary carbon (C-6) whereas the secondary carbon (C-1) is the preferred terminus of ring expansion. These observations point to the intervention of two distinct cations (**29a** and **b**), rather than to a single bridged intermediate.

EXPERIMENTAL

General. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were obtained at 80 MHz (Bruker WP 80) and 400 MHz (Bruker AM-400). ^{2}H (61·42 MHz) and ^{13}C (100·61 MHz) NMR spectra were recorded on a Bruker AM-400 spectrometer. Chemical shifts in $CDCl_3$ are reported in δ (ppm) relative to tetramethylsilane as an internal standard, unless indicated otherwise. GC was performed by the use of a Siemens Sichromat equipped with glass capillary columns. Varian Aerograph 920 instruments equipped with packed glass columns were used for preparative GC (PGC). HPLC was carried out with LDC (Milton Roy) chromatographs with refractometric or UV detection.

Spiro(bicyclo[2.2.1]heptane-2,1′-cycloprop-exo-6-yl) p-toluenesulphonate (10). Diborane, generated from sodium tetrahydroborate (20·3 g, 0·54 mol) and boron trifluoride etherate (70·2 g, 63 ml, 0·50 mol) in diglyme (400 ml) was introduced with a slow stream of nitrogen into a cooled (0 °C) solution of spiro(bicyclo[2.2.1]hept-5-ene-2,1′-cyclopropane) (**7**)[13] (20·0 g, 0·17 mol) in diethyl ether (70 ml). The mixture was stirred for 1 h at 0 °C and for 1 h at room temperature. Ice (50 g) was added slowly, followed by 3 M NaOH (150 ml) and 30% H_2O_2 (120 ml). The reaction was stirred at room temperature for 1 h and then extracted with diethyl ether (3 × 200 ml). The combined organic extracts were washed with aqueous $FeSO_4$ and brine, dried ($MgSO_4$) and concentrated *in vacuo*. Distillation of the residue afforded a mixture of spiro(bicyclo[2.2.1]heptane-2,1′-cyclopropane)-*exo*-5-ol (**8**) and -*exo*-6-ol (**9**) (55:45, GC), b.p. 98–101 °C/10 Torr, (1 Torr = 133·3 Pa), yield 17·4 g (76%), which was separated by HPLC (Polygosil 60-10-C_{18}, water–acetonitrile, 3:8). **8**: ^{1}H NMR, δ 0·22 (m, 1H), 0·30–0·38 (m, 2H), 0.50 (m, 1H), 1·01 (dd, J = 12·5, 2 Hz, *endo*-3-H), 1·25 (ddd, J = 13, 4, 2 Hz, *exo*-6-H), 1·39 (d, J = 4 Hz, 1-H), 1·50 (dd, J = 12·5, 5 Hz, *exo*-3-H), 1·55 (d, br, J = 9·5 Hz, *syn*-7-H), 1·64 (dd, J = 9·5, 2 Hz, *anti*-7-H), 1·70 (s, br, OH), 1·98 (ddd, J = 13, 6·8, 2 Hz, *endo*-6-H), 2·21 (d, J = 5 Hz, 4-H), 3·88 (d, J = 6·8 Hz, 5-H). Analysis: calculated for $C_9H_{14}O$, C 78·21, H 10·21; found, C 78·55; H 10.11%. **9**: ^{1}H NMR, δ 0·17 (m, 1H), 0·32 (m, 1H), 0·38–0·48 (m, 2H), 0·92 (dd, J = 12, 2 Hz, *endo*-3-H), 1·26 (m, *exo*-5-H), 1·31 (s, 1-H), 1·43–1·54 (m, *exo*-3-H and *syn*-7-H), 1·57 (dd, J = 9·5, 2 Hz, *anti*-7-H), 1·70 (ddd, J = 13, 6·8, 2 Hz, *endo*-5-H), 2·28 (t, J = 4 Hz, 4-H), 2·65 (s, br, OH), 3·95 (d, J = 6·8 Hz, 6-H). ^{13}C NMR, δ 9·0 (t), 14·4 (t), 21·8 (s), 35.7 (t), 37·9 (d), 40·3 (t), 42·1 (t), 53·2 (d), 73·6 (d). Analysis: calculated for $C_9H_{14}O$, C 78·21, H, 10·21; found, C 78·22, H 10·22%.

To a solution of **9** (0·80 g, 5·8 mmol) in anhydrous pyridine (10 ml) was added at 0 °C with stirring *p*-toluenesulphonyl chloride (1·2 g, 6·4 mmol). After 30 min at 0 °C, the reaction mixture was maintained at −20 °C for 3 d. Ice (20 g) and concentrated HCl (10 ml) were then added with stirring. After 10 min, the mixture was extracted with diethyl ether (3 × 30 ml). The combined extracts were washed with saturated aqueous $NaHCO_3$ solution and water, dried ($MgSO_4$) and evaporated *in vacuo*. HPLC (Polygosil 60-5-CN, hexane–diethyl ether, 8:2) of the residue gave unreacted *p*-toluenesulphonyl chloride (37%), **11** (2·5%, see below) and **10** (60·5%); m.p. 57·5–58·5 °C; ^{1}H NMR, δ 0·22–0·50 (m, 4H), 0·95 (d, br, 1H), 1·25–1·95 (m, 6H), 2·20 (m, 1H), 2·42 (s, 3H), 4·68 (dd, J = 6, 3·5 Hz, 1H), 7·28 (AA′, 2H), 7·75 (BB′, 2H). On standing, and on attempted recrystallization, **10** was found to rearrange with formation of **11**. The ^{1}H NMR spectrum reported by Schaffner[10b] is similar to ours, whereas her m.p. 93–94·6 °C[10b] (presumably taken after recrystallization) is in agreement with that of **11**.

Kinetic procedure. Solutions of **10** in 80% ethanol (*ca* 10^{-3} M) were prepared at 0 °C and thermostated at the appropriate temperature (Table 1). Benzene was added as an internal standard. Sampling with a syringe through a septum was followed immediately (without work-up) by HPLC (Polygosil 60-5-CN, hexane–diethyl ether, 8 : 2, UV detector). The decrease in **10** relative to the internal standard was first order to >90% conversion. Concomitantly, **11** approached a level which accounted for 10–15% of the initial concentration of **10**. Solvolysis products were not monitored by the HPLC detector, but GC indicated **13a** and **13b** (not isolated) in a 14 : 86 ratio.

Tricyclo[4.2.1.0^3,7]non-3-yl p-toluenesulphonate (11). The acid-catalysed hydration of **7** is a convenient route to **13a** (for an unequivocal synthesis, see Ref. 10b). A solution of **7** (2·0 g, 17 mmol) in dioxane (20 ml) and 2·5 M H_2SO_4 (20 ml) was heated at reflux for 5 h. After cooling to 20 °C, the mixture was saturated with NaCl and extracted with diethyl ether (3 × 30 ml). The combined organic extracts were washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$) and concentrated to give a mixture of **8** (20%) and **13a** (77%). For better separation, the mixture was oxidized with CrO_3 (2·0 g, 20 mmol) in pyridine (25 ml) (20 °C, 24 h). Conventional work-up yielded a mixture of **13a** (80%) and **14** (15%), from which **13a** (0·82 g, 36%) was isolated by HPLC (Polygosil 60-10, diethyl ether–hexane, 1 : 1) m.p. 88–90·5 °C (87.9–89·6 °C[10b]). ^{1}H NMR, δ 0·75 (dt, *J* = 12, 2·5 Hz, *endo*-9-H), 1·24–1·33 (m, 2H), 1·38 (dd, *J* = 12·5, 2 Hz, *endo*-2-H), 1·60 (d, br, *J* = 10 Hz, *syn*-8-H), 1·60–1·74 (m, 2H), 1·78 (ddd, *J* = 13·5, 7, 1·5 Hz, 1H), 1·85–1·96 (m, 3H), 2·02 (d, *J* = 4·5 Hz, 7-H), 2·05–2·15) (m, 1-H and 6-H). ^{13}C NMR, δ 28·49 (t, C-5), 35·98 (d, C-1), 36·48 (d, C-6), 37·54 (t, C-8), 38·30 (t, C-4), 40·45 (t, C-9), 49·25 (t, C-2), 52·42 (d, C-7), 84·32 (s, C-3). These assignments are supported by ^{1}H–^{13}C correlation and by partial deuteriation (see below).

To a solution of **13a** (0·40 g, 2·9 mmol) in pyridine (10 ml) were added 4-dimethylaminopyridine (0·35 g, 2·9 mmol) and *p*-toluenesulphonyl chloride (0·83 g, 4·4 mmol). The mixture was stirred at 20 °C for 2 d. Conventional work-up (cf. **10**) was followed by HPLC (Polygosil 60-10, pentane–diethyl ether, 2 : 1) to give 0·64 g (75%) of **11**, m.p. 94–95·5 °C. ^{1}H NMR, δ 0·79 (d, *J* = 12 Hz, 1H), 1·2–2·25 (m, 11H), 2·42 (s, 3H), 2·55 (m, 1H), 7·24 (AA', 2H), 7·75 (BB', 2H). Analysis: calculated for $C_{16}H_{20}O_3S$, C 65·73, H 6·89; found, C 65·78, H 6·94%.

The kinetic procedure described for **10** was applied, with the exception of the internal standard (benzophenone). The rate constants for the solvolysis of **11** in 80% EtOH (Table 1) are slightly greater than those reported for **10** by Altmann-Schaffner and Grob,[10a] who used a conductimetric technique.

Spiro(bicyclo[2.2.1]]heptane-2,1'-cycloprop-exo-6-yl) p-nitrobenzoate (12a) and trifluoroacetate (12b). To a solution of **9** (1·0 g, 7·2 mmol in pyridine (10 ml) was added with cooling *p*-nitrobenzoyl chloride (2·1 g, 11·3 mmol). The mixture was maintained at 40 °C for 30 min and at 25 °C for 4 d. The mixture was then diluted with water (40 ml) and extracted with diethyl ether (3 × 30 ml). The combined extracts were washed with 2 M HCl, saturated $NaHCO_3$ solution and water, dried ($MgSO_4$) and evaporated. The crude product (1·2 g, 58%) was purified by HPLC (Polygosil 60-10, hexane–diethyl ether, 99 : 1) to give **12a**, m.p. 89–91 °C. ^{1}H NMR, δ 0·31 (m, 1H), 0·48 (m, 1H), 0·63 (m, 2H), 1·13 (dd, *J* = 12, 2 Hz, 1H), 1·58–1·70 (m, 5H), 2·0 (ddd, *J* = 11·8, 7, 2 Hz, 1H), 2·48 (t, br, *J* = 4 Hz, 1H), 5·15 (dd, *J* = 7, 2 Hz 1H), 8·13 (AA', 2H), 8·25 (BB', 2H). Analysis: calculated for $C_{16}H_{17}NO_4$, C 66·88, H 5·96, N 4·88; found, C 66·90, H 5·96, N 4·84%.

Solvolyses of **12a** (30 mg, 0·10 mmol) were attempted in dioxane–water (7 : 3, 7 ml, 2 d reflux) and in 97% trifluoroethanol (8 ml, 3 d at 110 °C, sealed ampoule), in the presence of 2,6-lutidine (110 mg, 1·0 mmol). In both runs, **9** was the only product detected by GC whereas up to 70% of **12a** was recovered by HPLC.

To a solution of **9** (0·20 g, 1·45 mmol) in anhydrous pyridine (3 ml) was added at 0 °C trifluoroacetic anhydride (0·44 g, 2·1 mmol). The mixture was stirred at 0 °C for 1 h and at 20 °C for 3 d. Conventional work-up (cf. **12a**) afforded 0·33 g (98%) of **12b**. ^{1}H NMR, δ 0·32 (m, 1H), 0·45 (m, 1H), 0·61 (m, 2H), 1·08 (dd, *J* = 11, 2·5 Hz, 1H), 1·25 (s, 1H), 1·58–1·72 (m, 4H), 1·95 (ddd, *J* = 11, 7·5, 2·5 Hz, 1H), 2·45 (m, 1H), 5·08 (dm, *J* = 7·5 Hz, 1H). ^{19}F NMR, δ −76·8 (s).

Solvolyses of **12b** (20 mg, 85 μmol) in various solvents (5 ml) were monitored by GC, with the following results: dioxane–water (7 : 3)–2,6-lutidine, 97% **9**, 3% **13a**; dioxane–water (1 : 1)–2,6-lutidine, 81% **9**, 19% **13a**; dioxane–water (1 : 1), 68% **9**, 32% **13a**; 97% trifluoroethanol, 89% **13c**, 11% **13d**. **13c**: ^{1}H NMR, δ 0·82 (dm, *J* = 12 Hz, 1H), 1·2–2·4 (m, 12H), 3·82 (q, *J* = 16 Hz, 1H), 3·93 (q, *J* = 16·8 Hz, 1H); ^{19}F NMR, δ −75·0 (t, *J* = 16·8 Hz). **13d**: ^{1}H NMR, δ 0·55 (dm, *J* = 12 Hz, 1H), 0·88 (m, 2H), 1·3–2·35 (m, 9H), 2·54 (m, 1H); ^{19}F NMR, δ −76·37 (s). Rate constants (Table 1) were estimated by monitoring the decrease in **12b** (10^{-3} M in TFE) relative to an internal standard (anisole) by GC. Analogous measurements with *exo*-2-norbornyl trifluoroacetate[28] were made in sealed ampoules at 100–115 °C (Table 1).

Spiro(bicyclo[2.2.1]heptane-2,1'-cyclopropan)-6-one p-toluenesulphonylhydrazone (19). To Sarett reagent[29] prepared from CrO_3 (6·2 g, 62 mmol) and pyridine (70 ml) was added with cooling (0 °C) a mixture of **8** and **9**, as obtained from the hydroboration of **7** (see above). The reaction mixture was maintained at 0 °C for 30 min and at 20 °C for 24 h, then diethyl ether (100 ml) was added. The solution was filtered, washed with 2 M HCl, saturated $NaHCO_3$ solution and water, dried ($MgSO_4$) and evaporated. Distillation of the residue afforded a mixture of **14** and **17** (54 : 46, 1·5 g = 76%, b.p. 102 °C/28 Torr), which was separated by HPLC (Polygosil 60-10-C_{18}, water–acetonitrile, 2 : 1). Spiro(bicyclo[2.2.1]heptane-2,1′-cyclopropan)-5-one (**14**): ^{1}H NMR, δ 0·41 (m, 1H), 0·48–0·56 (m, 2H), 0·68 (m, 1H), 1·52 (dd, J = 12·5, 2 Hz, 1H), 1·81 (dd, J = 9·5, 3 Hz, 1H), 1·82–1·88 (m, 2H), 1·97–2·05 (m, 2H), 2·14 (dd, J = 17·5, 4 Hz, 1H), 2·65 (d, J = 4·5 Hz, 1H); IR (CCl_4), ν (C=O) 1740 cm^{-1}. Analysis: calculated for $C_9H_{12}O$, C 79·30, H 8·88; found, C 79·43, H 8·91%. Spiro(bicyclo[2.2.1]heptane-2,1′-cyclopropan)-6-one (**17**): ^{1}H NMR, δ 0·42 (m, 1H), 0·47–0·58 (m, 2H), 0·69 (m, 1H), 1·36 (dd, J = 12, 2·2 Hz, 1H), 1·72 (s, 1H), 1·74 (dm, J = 10·5 Hz, 1H), 1·86–1·95 (m, 3H), 2·09 (dm, J = 18 Hz, 1H), 2·74 (m, 1H); IR (CCl_4), ν (C=O) 1750 cm^{-1}. Analysis calculated for $C_9H_{12}O$, C 79·30, H 8·88; found, C 79·36, H 8·86%.

p-Toluensulphonylhydrazine (527 mg, 2·8 mmol) was dissolved in hot, anhydrous methanol (4 ml). Six drops of saturated methanolic HCl were added, followed by **17** (0·35 g, 2·6 mmol). The mixture was heated at reflux for 2 h and was then allowed to cool slowly to 20 °C. The solid was filtered and recrystallized from ethanol to give 0·50 g (63%) of **19**, m.p. 129 °C. ^{1}H NMR, δ 0·1–0·75 (m, 4H), 1·13 (dd, J = 12, 2 Hz, 1H), 1·3–2·3 (m, 7H), 2·42 (s, 3H), 2·60 (m, 1H), 7·26 (AA′, 2H), 7·82 (BB′, 2H). Analysis: calculated for $C_{16}H_{20}N_2O_2S$, C 63·13, H 6·57, N 9·20; found, C 63·03, H 6·68, N 9·29%.

A solution of **19** (0·50 g, 1·6 mmol) in 0·2 M NaOH (50 ml) was irradiated for 3 h (medium-pressure mercury lamp, Pyrex vessel, 20 °C). The solution was extracted with diethyl ether (3 × 30 ml) and the combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated by distillation (15 cm Vigreux column). In addition to **13a**, **9** and **25** (Table 2), 1–2% of the ketone **17** was detected by GC. The alcohols **13a** and **25** were isolated by HPLC (Polygosil 60-10, diethyl ether–hexane, 1 : 1); **13a** was identified by comparison with the sample obtained from **7**. Spiro(bicyclo[3.1.1]heptane-3,1′-cyclopropan)-3-ol (**25**): ^{1}H NMR, δ 0·29, 0·47, 0·58, 0·72 (ddd, J = 9·5, 6, 4·5 Hz, 1H), 1·43 (ddd, J = 13, 4·5, 1·8 Hz, 1H), 1·55 (s, br, OH), 1·63 (dd, J = 9·5, 7·5 Hz, 1H), 1·68 (dd, J = 9·5, 7·5 Hz, 1H), 1·95 (m, 1H), 1·99 (d, J = 13 Hz, 1H), 2·05 (m, 1H), 2·41 (qd, J = 5, 2 Hz, 1H), 2·53 (q, J = 5 Hz, 1H), 3·57 (d, J = 5 Hz, 1H). Analysis: calculated for $C_9H_{14}O$, C 78·21, H 10·21; found, C 78·14, H 10·11%.

From an analogous photolysis of **19** in 0·2 M NaOD–D_2O, the major products were isolated as described above. [^{2}H]-**13a**: ^{2}H NMR (CCl_4), δ 2·0 (s, br); after addition of Eu(fod)$_3$, δ 2·11 and 2·17 (0·98 : 1·00); ^{13}C NMR (CCl_4), δ *28·47*, 28·60 (C-5), 35·91 (C-1), *35·80*, *36·01*, *36·22*, 36·31 (C-6), 37·43, *37·53* (C-8), 38·09 (C-4, *40·16*, 40·25 (C-9), 49·06 (C-2), 51·47, 51·69, 51·90, *52·03* (C-7), 84·01, *84·04* (C-3) (signals assigned to [6-^{2}H]-**13a** in italics). [^{2}H]-**25**: significant deviations from the ^{1}H NMR spectrum of **25** were found at δ 3·57 (s) and 2·53 (no absorption).

Spiro(bicyclo[2.1.1]heptane-2,1′-cyclopropan)-exo- and -endo-6-amine (15 and 21). A solution of **17** (0·80 g, 5·9 mmol), hydroxylamine hydrochloride (0·62 g, 8·9 mmol) and pyridine (1·0 g, 12·6 mmol) in ethanol (10 ml) was heated at reflux for 3 h. The solvent was evaporated *in vacuo* and the residue was extracted with diethyl ether (3 × 20 ml). The combined organic extracts were washed with water, dried ($MgSO_4$) and concentrated to give the oxime **18** (0·61 g, 68%). ^{1}H NMR, δ 0·15–0·85 (m, 4H), 1·20 (dm, J = 12 Hz, 1H), 1·35–2·0 (m, 5H), 2·05–2·4 (m, 2H), 2·55 (m, 1H).

To a solution of the crude oxime (0·50 g, 3·3 mmol) in anhydrous ethanol (80 ml) was added sodium (4·6 g, 0·2 mol) in small chunks. The resulting solution was diluted with water (50 ml), saturated with NaCl and extracted with diethyl ether (5 × 40 ml). The combined organic phases were extracted with 2 M HCl (3 × 30 ml). The acidic aqueous phase was washed with diethyl ether, basified with sodium hydroxide and extracted with diethyl ether (3 × 40 ml). The combined organic extracts were dried (K_2CO_3) and concentrated by distillation (15 cm Vigreux column). The residue (0·30 = 66%, **15** : **21** = 14 : 86) was dissolved in anhydrous pyridine (5 ml). Trifluoroacetic anhydride (0·31 ml, 2·2 mmol) was added dropwise, and the reaction was maintained at 60 °C for 1 h. After cooling to 20 °C, the mixture was diluted with diethyl ether (80 ml), washed with 2 M HCl and water, dried ($MgSO_4$) and concentrated *in vacuo*. The trifluoroacetamides **16** (19·6%) and **22** (80·4%) were separated by PGC (2 m Carbowax column, 140 °C). **16**: m.p. 82 °C; ^{1}H NMR, δ 0·2–0·75 (m, 4H), 1·15 (dd, J = 12, 2 Hz, 1H), 1·25–1·8 (m, 5H), 2·03 (ddd, J = 13, 8, 2 Hz, 1H), 2·45 (m, 1H), 4·10 (td, J = 8, 4 Hz, 1H), 6·0 (s, br, NH). Analysis calculated for $C_{11}H_{14}F_3NO$, C 56·65, H 6·05, N 6·01; found, C 56·56, H 6·00, N 6·14%. **22**: m.p. 104 °C; ^{1}H NMR, δ 0·1–0·8 (m, 4H), 1·0 (dm, J = 12 Hz, 1H), 1·3 (d, J = 11 Hz, 1H), 1·35–1·9 (m, 4H), 2·15 (dm, J = 12 Hz, 1H), 2·40 (m, 1H), 4·32 (m, 1H), 6·8 (s, br, NH). Analysis: found, C 56·71, H 6·19, N, 6·10%.

Aminoboration[30] of **7** provided a mixture of **15** and the *exo*-5-isomer (53 : 47), which was converted into the trifluoroacetamides as described above. Compound **16** was isolated from the mixture by HPLC (Polygosil 60-10, hexane–diethyl ether, 40 : 1). Samples of pure **16** and **22** (233 mg, 1 mmol) were dissolved in methanol (2 ml) and water (8 ml), K_2CO_3 (230 mg, 1·6 mmol) was added and the mixtures were stirred at 20 °C under nitrogen for 20 h.[31] Methanol was evaporated *in vacuo* and the aqueous solution was extracted with diethyl ether (3 × 20 ml). Anhydrous HCl was introduced into the dried (K_2CO_3) organic extracts. Excess of HCl and diethyl ether were evaporated *in vacuo* and the residue was recrystallized from ethyl acetate–methanol. **15**·HCl: m.p. 254 °C (decomp.); ^1H NMR (D_2O), δ 0·25–0·8 (m, 4H), 1·15 (d, $J = 12$ Hz, 1H), 1·3–2·1 (m, 6H), 2·45 (m, 1H), 3·50 (m, 1H). **21**·HCl: m.p. 248 °C (decomp.); ^1H NMR (D_2O), δ 0·2 (m, 1H), 0·3–0·95 (m, 3H), 1·1–1·9 (m, 5H), 2·05–2·7 (m, 3H), 3·57 (dm, $J = 10$ Hz, 1H). Analyses: calculated for $C_9H_{16}ClN$, C 62·24, H 9·28, N 8·06; found, C 62·04, H 9·43, N, 8·28%.

Deamination procedure. Compound **15**·HCl or **21**·HCl (87 mg, 0·5 mmol) was dissolved in water (10 ml) and diethyl ether (10 ml) and 0·1 M $HClO_4$ and a solution of $NaNO_2$ (255 mg, 3·7 mmol) in water (2 ml) were added dropwise with stirring to the biphasic mixture. The rate of addition was adjusted to maintain pH 3·5–3·8 in the aqueous phase (glass electrode). After stirring at 20 °C for 16 h, the phases were separated and the aqueous phase was extracted with diethyl ether (3 × 15 ml). The combined organic extracts were washed with saturated $NaHCO_3$ solution and dried ($MgSO_4$). $LiAlH_4$ (50 mg) was then added, and the mixture was heated at reflux for 1 h (in order to convert alkyl nitrites to alcohols). After cooling to 20 °C, water was then added dropwise to obtain a flaky precipitate. The solution was filtered, dried ($MgSO_4$), concentrated by distillation (15 cm Vigreux column) to 1–2 ml and analysed by GC (39 m Carbowax column, 120 °C, and 127 m Edenol column, 140 °C) (Table 2).

6-Methylenespiro(bicyclo[2.2.1]heptane-2,1′-cyclopropane) (26). Methyltriphenylphosphonium bromide (5·4 g, 15 mmol), sodium amide (585 mg, 15 mmol) and diethyl ether (40 ml) was heated at reflux for 16 h. After cooling to 20 °C, a solution of **17** (1·0 g, 7·3 mmol) in diethyl ether (10 ml) was added dropwise. The mixture was heated at reflux for 4 h, cooled to 20 °C, and filtered. The solution was concentrated by distillation (15 cm Vigreux column) and the residue was purified by short-path distillation at 10^{-2} Torr to give 0·80 g (80%) of **26**. ^1H NMR, δ 0·29 (ddd, $J = 9·5, 6, 4$ Hz, 1H), 0·34–0·43 (m, 2H), 0·62 (ddd, $J = 9·5, 6, 4$ Hz, 1H), 1·21 (dd, $J = 12, 2·5$ Hz, 1H), 1·45 (dq, $J = 9, 2$ Hz, 1H), 1·56 (ddd, $J = 12, 4·5, 3$ Hz, 1H), 1·60 (ddt, $J = 9, 2·5, 1·5$ Hz, 1H), 1·65 (m, 1H), 1·97 ($J = 15·5, 2·5$ Hz, 1H), 2·21 (ddq, $J = 15·5, 4·5, 2·5$ Hz, 1H), 2·43 (tm, $J = 4·5$ Hz, 1H), 4·62 (m, 1H), 4·73 (m, 1H). Analysis calculated for $C_{10}H_{14}$, C 89·49, H 10·51; found, C 89·43, H 10·62%.

To a solution of **26** (0·20 g, 1·5 mmol) in dioxane (14 ml) and water (6 ml) was added concentrated H_2SO_4 (0·98 g, 10 mmol). The mixture was stirred at 40 °C while progress of the reaction was monitored by GC (41 m Carbowax column, 140 °C (Table 3). Complete conversion of **26** and of the intermediate **30** (see below) was achieved within 14–16 h. The solution was then saturated with NaCl and extracted with diethyl ether (3 × 40 ml). The combined organic extracts were washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$) and concentrated by distillation (15 cm Vigreux column). HPLC (Polygosil 60-10, diethyl ether–pentane, 1 : 2) afforded **32** and **33**. 6-Methyltricyclo[4.2.1.0^{3,7}]nonan-3-ol (**32**): m.p. 96–97 °C; ^1H NMR, δ 0·98 (dd, $J = 12, 2$ Hz, 1H), 1·00 (s, 3H), 1·31 (dtd, $J = 12, 3·5, 1$ Hz, 1H), 1·40–1·43 (m, 2H), 1·52 (ddd, $J = 13·5, 9·5, 6·6$ Hz, 1H), 1·55–1·70 (m, 5H), 1·84 (tdd, $J = 12·5, 6·5, 2·5$ Hz, 1H), 1·92 (ddd, $J = 12·5, 9·5, 5$ Hz, 1H), 2·14 (tm, $J = 3·5$ Hz, 1H); ^{13}C NMR, δ 27·8 (q), 36·1 (t), 36·5 (t), 37·1 (t), 38·1 (d), 43·4 (s), 47·6 (t), 49·5 (t), 58·6 (d), 84·8 (s). Analysis: calculated for $C_{10}H_{16}O$, C 78·90, H 10·59; found, C 78·83, H 10·56%. 7-Methyltricyclo[4.2.1.0^{3,7}]nonan-3-ol (**33**): m.p. 174–176 °C; ^1H NMR, δ 0·90 (dd, $J = 10·5, 2·5$ Hz, 1H), 1·01 (s, 3H), 1·22–1·31 (m, 2H), 1·46 (dt, $J = 10, 2$ Hz, 1H), 1·50 (s, br OH), 1·57 (dd, $J = 12·5, 2·5$ Hz, 1H), 1·69–1·78 (m, 2H), 1·91–2·07 (m, 4H), 2·00 (m, 1H); ^{13}C NMR, δ 13·4 (q), 26·6 (t), 34·6 (d), 36·8 (t), 42·2 (t), 42·9 (d), 43·6 (t), 50·2 (t), 54·1 (s), 84·2 (s). Analysis: found, C 78·65, H 10·47%.

A mixture of **33** (100 mg, 0·75 mmol), sodium iodide (225 mg, 1·5 mmol) and 95% phosphoric acid (3 ml) was maintained in a sealed flask at 80 °C for 4 h.[32] After cooling to 20 °C, the mixture was diluted with water (10 ml) and extracted with diethyl ether (3 × 10 ml). The combined organic extracts were washed with $Na_2S_2O_3$ solution and water, dried ($MgSO_4$) and concentrated. The iodide **34** was dissolved in methanol (10 ml), magnesium turnings (50 mg, 2 mmol) were added and the mixture was heated at reflux for 1 h. After cooling to 20 °C, the solution was diluted with diethyl ether (40 ml), washed with water, dried ($MgSO_4$) and concentrated by distillation (15 cm Vigreux column). The residue was purified by PGC (1·5 m Carbowax column, KOH, 95 °C) to give 20 mg (20%) of 7-methyltricyclo[4.2.1.0^{3,7}]nonane (**35**): m.p. 108–109 °C; ^1H NMR, δ 0·85 (dm, $J = 12$ Hz, 2H), 1·03 (s, 3H), 1·39 (m, 2H), 1·49 (m, 2H), 1·76 (m, 2H), 1·82–1·97 (m, 5H); ^{13}C NMR, δ 17·8 (q), 30·8 (t), 35·2 (d), 42·4 (t), 44·6 (d), 46·5 (t), 54·8 (s). Analysis: calculated for $C_{10}H_{16}$, C 88·16, H 11·84; found, C 88·05, H 11·87%.

endo-6-Methylspiro(bicyclo[2.2.1]heptane-2,1′-cyclopropan)-exo-5-ol p-nitrobenzoate (27). To a suspension of $Hg(OAc)_2$ (320 mg, 1 mmol) in THF (6 ml) and water (6 ml) was added **26** (134 mg, 1 mmol). The mixture was stirred at 20 °C for 30 min, then 3 M NaOH (4 ml) and 0·5 M $NaBH_4$ (4 ml) were added dropwise. The solution was filtered, saturated with NaCl and extracted with diethyl ether (4 × 20 ml). The combined organic extracts were washed with water, dried ($MgSO_4$) and concentrated to 2 ml. HPLC (Polygosil 60-10, diethyl ether–pentane, 1 : 2) of the residue gave 93 mg (61%) of *endo*-6-methylspiro(bicyclo[2.2.1]heptane-2,1′-cyclopropan)-*exo*-6-ol (**30**). ^{1}H NMR, δ 0·13 (ddd, J = 9·5, 6, ·4 Hz, 1H), 0·42 (ddd, J = 9·5, 6, 4 Hz, 1H), 0·52–0·69 (m, 2H), 1·10 (dd, J = 11·5, 2 Hz, 1H), 1·20 (s, 1H), 1·28 (s, br, OH), 1·37 (dd, J = 13, 3 Hz, 1H), 1·39 (s, 3H), 1·51 (ddd, J = 11·5, 4·5, 3 Hz, 1H), 1·62 (dm, J = 9·5 Hz, 1H), 1·65 (ddd, J = 13, 4·5, 2·5 Hz, 1H), 1·84 (dm, J = 9·5 Hz, 1H), 2·34 (tm, J = 4·5 Hz, 1H). Analysis: calculated for $C_{10}H_{16}O$, C 78·90, H 10·59; found, C 78·95, H 10·63%.

To a solution of **30** (304 mg, 2·0 mmol) in anhydrous THF (5 ml) was added under nitrogen *n*-butyllithium (1·6 M in hexane, 1·4 ml). After stirring at 20 °C for 30 min, a solution of *p*-nitrobenzoyl chloride (408 mg, 2·2 mmol) in THF (3 ml) was added and the mixture was heated at reflux for 2 h. After cooling to 20 °C, the mixture was diluted with diethyl ether (30 ml), washed with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$) and concentrated. Flash chromatography, followed by HPLC (Polygosil 60-10, diethyl ether–pentane, 1 : 2), afforded 180 mg (60%) of unreacted **30** and 100 mg (17%) of **27**; m.p. 101–103 °C (recrystallized from pentane). ^{1}H NMR, δ 0·2 (m, 1H), 0·35–0·95 (m, 3H), 1·19 (dm, J = 12 Hz, 1H), 1·42–1·85 (m, 4H), 1·77 (s, 3H), 1·95–2·5 (m, 3H), 8·13 (m, 4H). Analysis: calculated for $C_{17}H_{19}NO_4$, C 67·76, H 6·35, N 4·65; found, C 67·77, H 6·41, N 4·75%.

A solution of **27** (20 mg, 0·07 mmol) and 2,6-lutidine (75 mg, 0·7 mmol) in methanol (5 ml) was heated at reflux for 5 d. The mixture was partitioned between water and diethyl ether. The organic phase was washed with 1 M HCl and water, dried (Na_2SO_4), concentrated by distillation (15 cm Vigreux column) and analysed by GC (41 m Carbowax column, 140 °C). *exo*-6-Methoxy-*endo*-6-methylspiro(bicyclo[2.2.1]heptane-2,1′-cyclopropane (**31**) was identified by comparison with an authentic sample, obtained by methylation (CH_3I, NaH, THF, 8 h reflux) of **30**. ^{1}H NMR, δ 0·1–0·72 (m, 4H), 0·95–1·25 (m, 2H), 1·30 (s, 3H), 1·32–1·88 (m, 6H), 2·28 (m, 1H), 3·07 (s, 3H). Analysis: calculated for $C_{11}H_{18}O$, C 79·47, H 10·91; found, C 79·39, H 10·82%.

Analogous solvolyses of **27** (20 mg, 0·07 mmol) were carried out in acetone (2·5 ml)–water (2·5 ml)–K_2CO_3 (97 mg, 0·7 mmol) (12 h reflux) and in dioxane (3·5 ml)–water (1·5 ml)–2,6-lutidine (75 mg, 0·7 mmol) (12 h reflux), with the results recorded in Table 3. *exo*-6-Methylspiro(bicyclo[2.2.1]heptane-2,1′-cyclopropan)-*endo*-3-ol (**28**) was not detected (GC) in the solvolysis mixtures. A sample of **28** was prepared from the ketone **17** (136 mg, 1 mmol in 10 ml of diethyl ether) and methyllithium (1·6 M in diethyl ether, 1 ml). ^{1}H NMR, δ 0·16 (ddd, J = 9·5, 5·5, 4 Hz, 1H), 0·41 (ddd, J = 9·5, 5·5, 4 Hz, 1H), 0·69–0·72 (m, 2H), 1·23–1·26 (m, 4H), 1·30 (dd, J = 13, 3·5 Hz, 1H), 1·35 (dd, J = 12, 2 Hz, 1H), 1·53 (dm, J = 10 Hz, 1H), 1·61 (ddd, J = 12, 5, 3 Hz, 1H), 1·67 (ddt, J = 10, 3·5, 1·5 Hz, 1H), 1·71 (ddd, J = 13, 4·5, 2·5 Hz, 1H), 2·32 (tm, J = 5 Hz, 1H), 2·60 (s, br, OH). Analysis: calculated for $C_{10}H_{16}O$, C 78·90, H 10·59; found, C 78·72, H 10·50%.

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