Rearrangements of Spirocyclobutane-Substituted 2-Norbornyl Cations

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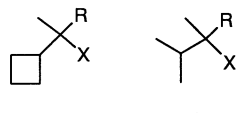
Received October 27, 1997

Keywords: Carbocations / Ion pairs / Rearrangements / Solvolysis / Spiro compounds

2-Norbornyl cations with spiroannellated cyclobutane rings were generated for comparison with the previously studied cyclopropane analogues. Starting with the Diels-Alder reaction of cyclopentadiene with methylenecyclobutane, spiro-[bicyclo[2.2.1]heptane-2,1′-cyclobutan]-6-one (**11**) was prepared. The tosylhydrazone **12** of **11** was photolyzed in $NaOD/D_2O$ to give the analogous alcohol **13** with a ca. 1:1 distribution of deuterium. Ring expansion was not observed, in contrast to the cyclopropane analogue. − The tosylhydrazone **22** of spiro[bicyclo[2.2.1]heptane-2,1′-cyclobutan]-3-one (**21**) and the related tosylates (**28**, **32**) rearranged, in part, to afford derivatives of spiro[bicyclo[2.2.1]heptane-7,1′-cyclobutane] (**29**, **33**, **34**). In both series, ring expansion of the spiroannellated cyclobutane, by *exo*-3,2-C shift, was the major reaction, giving rise to a uniquely *endo*-selective tertiary cation (**36**). Analogously positioned cyclopropane rings remain intact, due to stabilizing interactions with the neighboring positive charge which are lacking in the cyclobutane systems. − In $CDCl_3$ solution, the tosylate **32** produced mixtures of isomeric tosylates by way of ion pair recombination. We observed that *exo* → *exo* shifts of the counterion proceed with little scrambling of ^{18}O whereas complete equilibration of the tosylate oxygens is attained in *exo* → *endo* shifts.

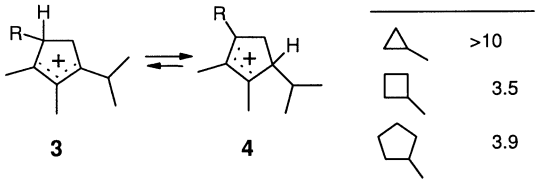
Cyclopropane is unique among carbocycles in its conjugative properties[1]. The largest effects are seen if the cyclopropane ring is attached to electron-deficient centers. Thus, the ability of cyclopropyl groups to stabilize an adjacent carbocation is close to that of phenyl groups[2]. Although the ring strain and the ionization potentials of cyclobutane and cyclopropane are similar, σ-p(π) interactions are much smaller in cyclobutyl than in cyclopropyl derivatives. Thus, the solvolysis rates of **1** are but slightly enhanced over those of **2**[3][4][5]. The effect of R = cyclobutyl on the equilibrium **3** ⇄ **4** does not differ significantly from that of R = cyclopentyl[6]. On the other hand, the technique of increasing the electron demand (by variation of Ar) was able to detect a small amount of conjugative stabilization in the cyclobutylcarbinyl system **6**[4][7].

The degenerate rearrangements of the 2-norbornyl cation[8] have often been used to probe the influence of substituents[8][9][10]. Dramatic changes (see below) were induced by cyclopropane rings which were spiroanellated to the 3-[11][12], 6-[13][14], and 7-positions[11][12] of the 2-norbornyl system. We now report on analogous spiroanellations of cyclobutane, in order to compare the effects of three- and four-membered rings.

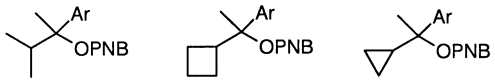


1 **2**

R	X	k_1/k_2	
H	OTs	86	AcOH, 25 °C[3]
Me	OPNB	3.4	60% acetone, 100 °C[4]
Ph	OPNB	5.7	80% acetone, 25 °C[5]



3 **4**



5 **6** **7**

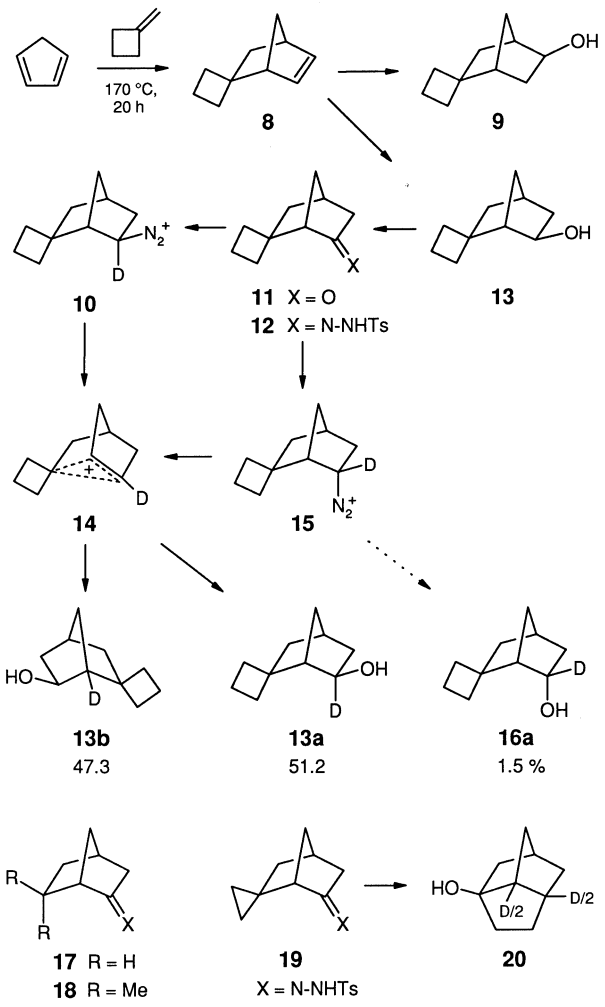
ρ^+ -4.65[7] -3.94[5] -2.78[7]

Spiro[bicyclo(2.2.1)heptane-2,1′-cyclobut]-6-yl Cation (14)

Forcing conditions were required for the Diels-Alder reaction of methylenecyclobutane with cyclopentadiene. The resulting mixture of the desired spiroalkene **8** and cyclopentadiene dimers had to be separated by PGC; hence the isolated yield of **8** was only 17%. The cycloaddition proceeded more smoothly with hexachlorocyclopentadiene (73%). However, a complex product mixture was obtained on dechlorination of the adduct. Hydroboration of **8** afforded the alcohols **9** and **13** (46:54) which were separated by HPLC. Oxidation of **13** with pyridinium chlorochromate (PCC) provided the ketone **11** from which the tosylhydrazone **12** was prepared.

  1434−193X/98/0202−0213 $ 17.50+.50/0

Scheme 1

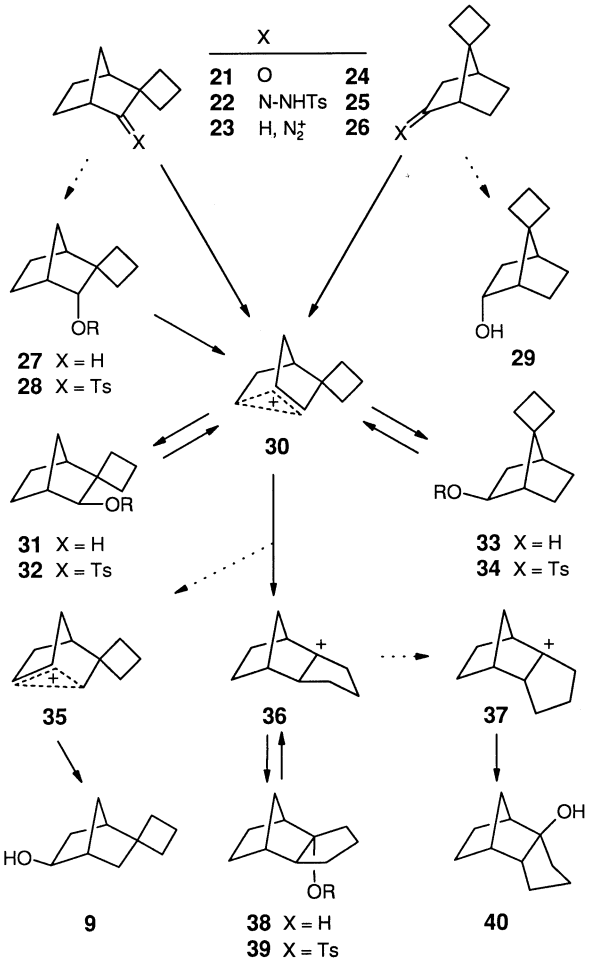


The photolysis of **12** in 0.5 N NaOH, proceeding by way of the diazonium ions **10** and **15**, gave rise to the alcohols **13** and **16** (98.5:1.5). The *endo* product **16** was identified by comparison with a sample obtained by $LiAlH_4$ reduction of **11**. When the photolysis of **12** was performed in 0.5 N $NaOD/D_2O$, the isotopomers **13a** and **13b** were formed in the ratio of 52:48 (^2H NMR). The data point to the bridged ion **14** as the predominant intermediate. The small amount of **16** and the slight excess of **13a** over **13b** are attributed to competing displacement reactions of the *endo* diazonium ion **15**[15]. Very similar results were previously obtained with the tosylhydrazones **17**[15] and **18**[16], derived from 2-norbornanone and 6,6-dimethyl-2-norbornanone, respectively. In contrast, the intermediate generated from the tosylhydrazone **19** of spiro[bicyclo[2.2.1]heptane-2,1′-cyclopropan]-6-one underwent ring expansion to give **20** almost exclusively, C-6 and C-1 being equivalent migration termini[14]. The lack of an analogous ring expansion in the case of **14** indicates that the cationic site interacts much less with a cyclobutane than with a cyclopropane ring.

Spiro[bicyclo[2.2.1]heptane-2,1′-cyclobut]-3-yl and Spiro-[bicyclo[2.2.1]heptane-7,1′-cyclobut]-2-yl Cation(s) (30)

Alkylation of norbornan-2-one with 1,3-dibromopropane afforded the ketone **21**[17] from which the tosylhydrazone **22** was prepared. Reduction of **21** with $LiAlH_4$ gave the alcohols **27**[17a] and **31** (95:5). This mixture was equilibrated with aluminum 2-propoxide to obtain sufficient amounts of **31**. After separation by HPLC, the alcohols **27** and **31** were converted into the tosylates **28** and **32**, respectively. The photolysis of **22** in 0.5 N NaOH gave rise, in part, to **33** which was isolated from the product mixture and tosylated to give **34**. Oxidation of **33** provided the ketone **24** from which the tosylhydrazone **25** and the *endo* alcohol **29** were made.

Scheme 2



With these substrates at hand, the potentially degenerate cation **30** was approached from both sides and with diverse leaving groups (N_2^+, OTs). No systematic changes in product distribution were found although some scatter is obvious (Table 1). The following observations deserve comment: (a) As to the yield of *endo* products, **25** conforms with the H and Me analogues **17**[15], **43**[18], and **44**[18] rather than with the cyclopropyl analogue **46**[12] (Scheme 3). The tosylhydrazone **45** of 7,7-dimethylnorbornan-2-one is not suitable for comparison as the *endo*-selective intermediate **41**

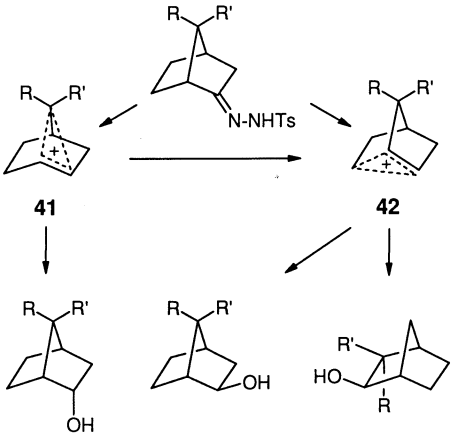
Table 1. Product distributions (%)[a] obtained from spiro[bicyclo-[2.2.1]heptane-2,1′-cyclobutane] and spiro[bicyclo[2.2.1]heptane-7,1′-cyclobutane] substrates

Sub-strate	Conditions	**27**	**29**	**31**	**33**	**9**	**38**	**40**
22	0.5 N NaOH, hν	0.2	–	4.9	13.5	1.2	74.6	0.3
25	0.5 N NaOH, hν	–	5.2	3.7	15.0	1.4	68.1	trace
28	Dioxane/H_2O, 1:1, 80°C	0.1	–	2.7	6.5	2.0	85.3	0.4
32	Dioxane/H_2O, 1:1, 80°C	trace	–	2.6	10.3	2.4	82.6	0.2
34	Dioxane/H_2O, 1:1, 80°C	–	–	4.7	16.6	3.6	73.0	trace
39	Dioxane/H_2O, 1:1, 80°C	–	–	–	–	–	99.3	0.2

[a] Alkenes account for the difference to 100%.

(R = R′ = Me) undergoes fragmentation faster than solvent capture[19]. The role of **41** is strongly enhanced by spiroannellation of a cyclopropane ring at C-7 but not by analogous annellation of a cyclobutane ring. (b) The ratios of 7- to 3-substituted norbornan-*exo*-2-ols reflect the relative rates of solvent attack at positions 3 and 4, respectively, of the *exo*-selective intermediate **42**. Again, **25** behaves very much like **43**-**45**, in accordance with predominantly steric effects of the substituents. The extreme product ratio observed with **46**[12] is clearly different in origin. Charge stabilization by the neighboring cyclopropyl group is thought to override the σ delocalization of **42**. Spiroannellated cyclobutane does not cause an analogous perturbation.

Scheme 3



	R	R'	
17	H	H	5.8%
25	-$(CH_2)_3$-		5.2
43	Me	H	4.1
44	H	Me	4.7
45	Me	Me	- [a]
46	-$(CH_2)_2$-		29.5

77	23
40	60
92	8
83	17
<1	100

[a] 8% of fragmentation, see text

Isomerization of **30** is competitive with nucleophilic capture. A minor fraction of **30** undergoes 6,2-H shift (→ **35** → **9**). The product **9** was identified by comparison with the sample obtained from **8**. The major reaction of **30** is ring expansion by way of an *exo*-3,2-C shift, with formation of **36** and, eventually, **38**. In principle, **36** could also arise by concerted ionization and rearrangement of *endo* precursors, such as **28**. However, the product distributions recorded in Table 1 argue against a significant contribution of this mechanism. Generation of **36** from the tosylate **39** does not lead to isomerization, i.e., the conversion of **30** into **36** is irreversible. The ring expansion is unparalleled by the cyclopropyl analogue of **30**[11][12].

The tertiary norbornyl cation **36** shows exceptional *endo* selectivity in its reaction with water, leading to **38**. The reason is trivial: *exo* attack of the solvent at **36** would result in *trans* annellation of the cyclopentane ring, thus creating excessive strain (80–85 kJ/mol, according to force field calculations[20]). Although the isomeric tertiary ion **37** appears to predominate in nonbasic media[21], the present results (Table 1) exclude significant rearrangement of **36** (→ **37** → **40**) in nucleophilic solvents. Even in the acid-catalyzed isomerization of **31**, which involves repeated ionization of the intervening alcohols, **40** was found to accumulate but slowly (Table 2).

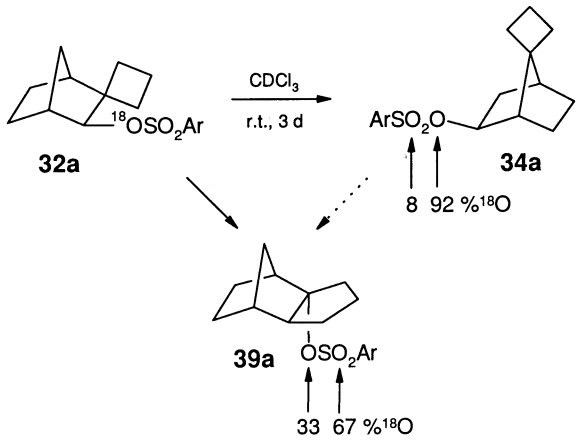
Table 2. Acid-catalyzed isomerization of spiro[bicyclo[2.2.1]-heptane-2,1′-cyclobutan]-*exo*-3-ol (**31**) (Dioxane/H_2O, 3:2, 1.75 M $HClO_4$, 60°C)

t [h]	**31**	**33**	**38**	**40**
1.5	53.6	1.1	44.5	0.8
3.5	19.2	1.3	78.6	0.9
5	5.2	1.3	91.6	1.9
23	0.7	trace	95.5	3.8

On standing in $CDCl_3$ solution, the tosylate **32** was found to rearrange with formation of both **34** and **39**. This behavior provides the unique opportunity to compare *exo* → *exo* and *exo* → *endo* shifts of the leaving group in a norbornyl-tosylate ion pair (only *exo* → *exo* shifts are regularly observed[8]). Exchange of **21** with $^{18}OH_2$ provided ^{18}O-**21** which was converted into **32a**. After a solution of **32a** in $CDCl_3$ was kept for 3 days at room temperature, the tosylate distribution was ca. 71% of **32a**, 12% of **34a**, and 17% of **39a** (NMR). Relative to starting material, the fraction of carbon-bound ^{18}O was 100% in **32a**, 92% in **34a**, and 33% in **39a**. In the course of the *exo* → *exo* shift, **32a** → **34a**, the carbocation returns preferentially to the oxygen atom of the tosylate ion from which it departed. This type of selectivity is generally observed if dissociation and recombination occur on the same side of the molecular plane[22]. The unprecedented *exo* → *endo* shift, **32a** → **39a**, proceeds with complete scrambling of the ^{18}O label between all oxygen atoms of the sulfonate ion. The present data confirm the notion that the scrambling of ^{18}O increases with the distance by which the counterion migrates[22].

Conclusion

The chemistry of 2-norbornyl cations with spiroannellated cyclobutane rings deviates strongly from that of the cyclopropane analogues. The differences with regard to ring expansion are most obvious. A cyclobutane ring spiroannellated to the 6-position does not undergo ring expansion



(6,2-C shift) whereas a cyclopropane ring does. On the other hand, a cyclobutane ring spiroannellated to the 3-position expands readily (*exo*-3,2-C shift), giving rise to a uniquely *endo*-selective tertiary cation (**36**). An analogously positioned cyclopropane ring remains intact. The Wagner-Meerwein pairs (delocalized ions, **42**) generated from 3- and 7-spiroannellated substrates accept nucleophiles preferentially β to the cyclobutane ring and α to the cyclopropane ring. The divergent effects confirm that cyclobutane does not interact strongly with a neighboring positive charge, in contrast to cyclopropane. Spiroannellated cyclobutane rings behave like geminal alkyl groups, except that the *exo*-3,2-C shift is promoted by ring strain. − The rearrangements mentioned above were used to scrutinize the recombination of carbocation-sulfonate ion pairs. Little scrambling of oxygen occurs in *exo* → *exo* shifts whereas *exo* → *endo* shifts are associated with complete equilibration of the sulfonate counterion. These data are thought to reflect the "tightness" of the intervening ion pairs.

We thank *Jutta Hartmann* for preliminary experiments and *Barbara Schröder* for technical assistance. Financial support by the *Fonds der Chemischen Industrie* is gratefully acknowledged.

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. Analyses of ^{18}O by means of ^{13}C-isotopic shifts are most accurate if ^{13}C-^{18}O and ^{13}C-^{16}O signals are of similar intensity. Therefore, $^{18}OH_2$ with 50−55% ^{18}O was used for the preparation of labeled compounds. − 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, refractometric detection. − Melting points: Kofler hot plate (Reichert), not corrected.

Spiro[bicyclo[2.2.1]hept-5-ene-2,1′-cyclobutane] (**8**): A mixture of methylenecyclobutane (10.0 g, 0.15 mol), freshly distilled cyclopentadiene (18.4 g, 0.28 mol), and hydroquinone (0.20 g, 1.8 mmol) was heated at 170°C (stainless steel autoclave) for 20 h. Short-path distillation afforded a product mixture (34% of **8**, 56% of *endo*-dicyclopentadiene, 10% of *exo*-dicyclopentadiene) from which **8** (3.4 g, 17%) was isolated by PGC (3 m Carbowax + KOH, 150°C). − IR (film): $\tilde{\nu}$ = 1580 (C=C) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.19 (dd, *J* = 11.5/2.8 Hz, 1 H), 1.27 (dt, *J* = 8.2/1.0 Hz, 1 H), 1.38 (ddt, *J* = 8.2/2.8/1.5 Hz, 1 H), 1.72 (dd, *J* = 11.5/3.5 Hz, 1 H), 1.74-1.85 (m, 3 H), 1.86-1.98 (m, 2 H), 2.11 (m, 1 H), 2.72 (m, 1 H), 2.75 (m, 1 H), 6.07 (dd, *J* = 5.5/2.8 Hz, 1 H), 6.12 (dd, *J* = 5.5/3.0 Hz, 1 H). − $C_{10}H_{14}$ (134.2): calc. C 89.49, H 10.51; found C 89.48, H 10.62.

Spiro[bicyclo[2.2.1]heptane-2,1′-cyclobutan]-exo-5- and -exo-6-ol (**9**, **13**): A solution of $BF_3 \cdot OEt_2$ (4.8 ml, 39 mmol) in diglyme (8 ml) was added dropwise to a solution of $NaBH_4$ (1.5 g, 39 mmol) in diglyme (60 ml). The diborane thus generated was carried by a stream of nitrogen into a cooled (0°C) and stirred solution of **8** (2.0 g, 15 mmol) in diethyl ether (50 ml). After the transfer was complete, stirring was continued for 1 h at 0°C and for 12 h at room temp. At 0°C, ice (20 g) and 2 N NaOH (20 ml) were added carefully, followed by 30% H_2O_2 (10 ml). The mixture was allowed to warm to room temp., and stirring was continued for 1 h. The aqueous phase was saturated with NaCl and extracted with diethyl ether. The combined extracts were washed with aqueous $FeSO_4$ and aqueous NaCl, dried ($MgSO_4$), and concentrated in vacuo. GC (39 m Carbowax, 130°C) indicated the presence of **9** and **13** (46:54). HPLC (Polygosil 60-5, pentane/ether, 2:1) afforded 0.75 g (33%) of **9** and 0.94 g (41%) of **13**. − ^{1}H NMR ($CDCl_3$) of **9**-OD: δ = 0.99 (dd, *J* = 13.0/2.5 Hz, 1 H), 1.11 (ddd, *J* = 13.5/4.0/1.0 Hz, 1 H), 1.24 (dm, *J* = 10 Hz, 1 H), 1.49 (ddt, *J* = 10.0/2.5/1.0 Hz, 1 H), 1.59 (dd, *J* = 13.0/5.5 Hz, 1 H), 1.65−1.75 (m, 4 H), 1.79 (ddd, *J* = 13.5/6.8/ 2.5 Hz, 1 H), 1.84−1.90 (m, 2 H), 2.00−2.07 (m, 2 H), 3.65 (dt, *J* = 6.8/1.0 Hz, 1 H). − ^{1}H NMR ($CDCl_3$) of **13**: δ = 1.12 (dd, *J* = 12.5/2.5 Hz, 1 H), 1.17−1.28 (m, 2 H), 1.42 (ddt, *J* = 10.0/2.5/1.0 Hz, 1 H), 1.48 (br. s, OH), 1.59 (ddd, *J* = 12.5/4.5/3.0 Hz, 1 H), 1.62 (ddd, *J* = 13.0/7.0/2.5 Hz, 1 H), 1.66−1.84 (m, 4 H), 1.91 (m, 1 H), 2.02 (s, 1 H), 2.07 (m, 1 H), 2.18 (td, *J* = 4.0/1.0 Hz, 1 H), 3.90 (dt, *J* = 7.0/1.0 Hz, 1 H). − $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 79.00, H 10.60.

Spiro[bicyclo[2.2.1]heptane-2,1′-cyclobutan]-6-one (**11**) *and p-Toluenesulfonylhydrazone* **12**: To a suspension of pyridinium chlorochromate (PCC, 1.35 g, 6.3 mmol) in CH_2Cl_2 (10 ml) was added dropwise a solution of **13** (0.64 g, 4.2 mmol) in CH_2Cl_2 (2 ml). After the mixture was stirred for 1.5 h at room temp., diethyl ether (10 ml) was added. The black residue was filtered off and washed with diethyl ether (3 × 5 ml). Flash chromatography (silica gel) of the ether solutions, followed by distillation of the solvent (10 cm Vigreux column), afforded 0.49 g (77%) of crude **11**. Part of the ketone was purified by PGC (0.5 m DC200, 95°C). − IR (film): $\tilde{\nu}$ = 1745 (CO) cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.47 (dd, *J* = 12.5/2.5 Hz, 1 H), 1.62 (dddd, *J* = 10.5/4.0/2.0/1.0 Hz, 1 H), 1.65 (ddt, *J* = 10.5/2.5/1.0, 1 H), 1.69 (dd, *J* = 17.5/4.0 Hz, 1 H), 1.75−2.03 (m, 8 H), 2.48 (s, 1 H), 2.56 (td, *J* = 4.5/2.5 Hz, 1 H). − $C_{10}H_{14}O$ (150.2): calcd. C 79.96, H 9.39; found C 79.92, H 9.40.

To a solution of **11** (0.20 g, 1.3 mmol) and *p*-toluenesulfonohydrazide (0.25 g, 1.3 mmol) in methanol (2 ml) was added 3 drops of saturated methanolic HCl. The mixture was heated at reflux for 3 h and was then cooled slowly to room temp. The solid was filtered off and recrystallized from ethanol to give 258 mg (61%) of **12**, m.p. 173°C. − IR (KBr): $\tilde{\nu}$ = 3215, 3060 cm^{-1} (NH), 1605 (C=N), 1320, 1180 (SO_2). − ^{1}H NMR ($CDCl_3$): δ = 1.22 (dm, *J* = 12.5 Hz, 1 H), 1.40−2.15 (m, 11 H), 2.35−2.55 (m, 4 H), 2.73 (m, 1 H), 7.34 and 7.88 (AA′BB′, 4 H). − $C_{17}H_{22}N_2O_2S$ (318.4): calcd. C 64.12, H 6.96, N 8.80; found C 63.99, H 6.86, N 8.70.

A solution of **12** (0.20 g, 0.63 mmol) in 0.5 N NaOH was degassed (ultrasound), purged with nitrogen, and irradiated (medium

pressure mercury arc, 150 W, pyrex vessel) at 20°C for 2 h. The mixture was saturated with NaCl and extracted with diethyl ether (4 × 30 ml). The combined extracts were dried ($MgSO_4$) and concentrated by distillation. GC (39 m Carbowax, 130°C, and 127 m Edenol, 150°C) indicated **11** (1.6%), **13** (97.0%), and **16** (see below, 1.4%). After oxidation of the product mixture with PCC, only **11** was found. − From an analogous photolysis of **12** in 0.5 N NaOD/D_2O, **13a**, **b** was isolated by HPLC (Polygosil 60-5, pentane/ether, 2:1). ^2H NMR ($CHCl_3$): δ = 1.98 (48%), 3.83 (52%).

Spiro[bicyclo[2.2.1]heptane-2,1′-cyclobutan]-endo-6-ol (**16**): To a suspension of $LiAlH_4$ (30 mg, 0.79 mmol) in diethyl ether (5 ml) was added a solution of **11** (0.10 g, 0.67 mmol) in diethyl ether (2 ml). The mixture was heated at reflux for 1 h and was then hydrolyzed by dropwise addition of water. The precipitate was filtered off and washed with diethyl ether. The combined ether solutions were washed with aqueous NaCl, dried ($MgSO_4$), and concentrated by distillation (10 cm Vigreux column). Sublimation of the residue afforded 72 mg (71%) of **16**, m.p. 65°C. − ^1H NMR ($CDCl_3$): δ = 0.85 (dt, *J* = 12.5/3.0 Hz, 1 H), 1.05−1.3 (m, 2 H), 1.35−1.6 (m, 2 H), 1.65−2-2 (m, 10 H, 4.25 (dt, *J* = 10/4 Hz, 1 H). − $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.91, H 10.62.

Spiro[bicyclo[2.2.1]heptane-2,1′-cyclobutan]-3-one (**21**) *and p-Toluenesulfonylhydrazone* **22**: To a stirred solution of bicyclo-[2.2.1]heptan-2-one (10.3 g, 93 mmol) and 1,3-dibromopropane (28.3 g, 140 mmol) in anhydrous diethyl ether (300 ml) was added with stirring under nitrogen sodium amide (9.4 g, 240 mmol). The mixture was heated at reflux for 24 h. After the mixture had cooled to room temp., water (150 ml) was added slowly. The phases were separated, and the aqueous phase was extracted with diethyl ether (3 × 50 ml). The combined ether solutions were washed with aqueous NaCl, dried ($MgSO_4$), and concentrated by distillation to give 6.3 g (45%) of crude ketone, b.p. 82−110°C/20 Torr. The product, containing ca. 12% of impurities (GC), was dissolved in pentane (100 ml) and was added to a solution of $KMnO_4$ (4.0 g, 25 mmol) in water (100 ml). After the mixture was stirred for 16 h at room temp., the phases were separated, and the aqueous phase was extracted with pentane (2 × 30 ml). The combined pentane solutions were dried ($MgSO_4$) and concentrated by distillation (30 cm Vigreux column). The residue was distilled in vacuo to give 4.3 g (31%) of pure (GC) **21**[17], b.p. 80−85°C/20 Torr.

To a solution of *p*-toluenesulfonohydrazide (1.3 g, 7.0 mmol) in methanol (4 ml) were added **21** (1.05 g, 7.0 mmol) and saturated methanolic HCl (10 drops). The mixture was heated at reflux for 5 h and was then cooled slowly to room temp. The solid was filtered off, washed with cold methanol, and dried at 0.1 Torr to give 2.05 g (92%) of **22**, m.p. 133−134°C. − IR (KBr): $\tilde{\nu}$ = 3180, 3050 cm^{-1} (NH), 1650 (C=N), 1340, 1185 (SO_2). − ^1H NMR (C_6D_6): δ = 0.85 (dm, *J* = 9 Hz, 1 H), 1.0−1.16 (m, 4 H), 1.29 (m, 1 H), 1.6−1.8 (m, 3 H), 1.88−2.12 (m + s, 7 H), 2.32 (m, 1 H), 2.81 (dm, *J* = 3 Hz, 1 H), 6.88 and 8.25 (AA′BB′, 4 H), 8.3 (br. s, NH). − $C_{17}H_{22}N_2O_2S$ (318.4): calcd. C 64.12, H 6.96, N 8.80; found C 64.14, H 6.96, N 8.87.

A degassed solution of **22** (32 mg, 0.1 mmol) in 0.5 N NaOH (5 ml) was irradiated (medium pressure mercury arc, 150 W, pyrex vessel, 20°C) for 1 h. The solution was saturated with NaCl and extracted with diethyl ether (5 ml). The ether extract was washed with water (1 ml), dried ($MgSO_4$), and analyzed by GC (57 m Edenol, 130°C); the results are recorded in Table 1. − For preparative runs, a solution of **22** (2.0 g, 6.3 mmol) in 1 N NaOH (60 ml) was photolyzed for 6 h while being circulated in a quartz apparatus. The solution was then extracted with diethyl ether (3 × 30 ml). The combined extracts were washed with water, dried ($MgSO_4$), and concentrated in vacuo. HPLC (LiChrospher 100-5, hexane/ether, 7:3) of the residue (0.98 g) afforded 20 mg (2.1%) of **31** (see below), 750 mg (78%) of *exo*-tricyclo[5.2.1.$0^{2,6}$]decan-*endo*-2-ol (**38**)[23], and 70 mg (7%) of spiro[bicyclo[2.2.1]heptane-7,1′-cyclobutan]-*exo*-2-ol (**33**), m.p. 53−55°C. − ^1H NMR ($CDCl_3$): δ = 0.92 (m, 2 H), 1.3−1.55 (m, 4 H), 1.7−2.05 (m, 8 H), 2.30 (m, 1 H), 3.76 (dd, *J* = 7.5/3.0 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 16.56 (CH_2), 23.15 (CH_2), 25.45 (CH_2), 27.01 (CH_2), 27.47 (CH_2), 40.81 (CH_2), 42.62 (CH), 50.57 (CH), 53.16 (C), 76.62 (CH). − $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.89, H 10.66.

Spiro[bicyclo[2.2.1]heptane-2,1′-cyclobutan]-3-ols (**27**, **31**) *and p-Toluenesulfonates* **28**, **32**: To a suspension of $LiAlH_4$ (0.25 g, 6.6 mmol) in diethyl ether (20 ml) was added slowly a solution of **21** (1.9 g, 12.6 mmol). The mixture was stirred for 2 h at room temp. and heated at reflux for 2 h. Aqueous workup (see **16**) afforded 1.59 g (81%) of crude product, **27**/**31** = 95:5[17]. A mixture of crude **27** (4.0 g, 26.3 mmol), $Al(OCHMe_2)_3$ (5.5 g, 27 mmol), acetone (0.8 ml), and 2-propanol (50 ml) was heated in a sealed tube at 130°C for 3 d. The contents of the tube were diluted with water (100 ml), and the mixture was extracted with diethyl ether (3 × 50 ml). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo to ca. 5 ml. HPLC (LiChrospher 100-5, ether/hexane, 1:1) of the concentrate afforded 1.0 g (25%) of **27** and 1.14 g (28%) of **31**.

Spiro[bicyclo[2.2.1]heptane-3,1′-cyclobutan]-endo-3-ol (**27**): ^1H NMR ($CDCl_3$): δ = 1.18 (dt, *J* = 10.0/1.5 Hz, 1 H), 1.23 (m, 1 H), 1.28−1.39 (m, 3 H), 1.50 (br. s, OH), 1.56 (m, 1 H), 1.68−1.83 (m, 5 H), 1.97 (m, 1 H), 2.08 (br. s, 1 H), 2.24 (br. t, *J* = 4.5 Hz, 1 H), 3.72 (d, *J* = 4.5 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 16.00 (CH_2), 19.59 (CH_2), 22.52 (CH_2), 22.69 (CH_2), 33.22 (CH_2), 36.93 (CH_2), 42.84 (CH), 46.68 (CH), 48.50 (C), 80.47 (CH). − $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.85, H 10.62. − *Spiro[bicyclo[2.2.1]heptane-3,1′-cyclobutan]-exo-3-ol* (**31**): M.p. 42−44°C. − ^1H NMR ($CDCl_3$): δ = 1.06 (m, 1 H), 1.11 (dq, *J* = 10.0/1.6 Hz, 1 H), 1.28−1.35 (m, 2 H), 1.4−1.57 (m, 5 H), 1.7−1.88 (m, 3 H), 1.93 (m, 1 H), 2.01 (dm, *J* = 4.5 Hz, 1 H), 2.08 (m, 1 H), 3.29 (d, *J* = 1.7 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 16.43 (CH_2), 22.66 (CH_2), 25.68 (CH_2), 27.13 (CH_2), 28.89 (CH_2), 33.55 (CH_2), 45.70 (CH), 46.09 (CH), 52.46 (C), 82.93 (CH). − $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.81, H 10.69. − The assignment of configuration is based on the chemical shifts and coupling constants ($J_{3,4}$) of 3-H.

To an ice-cooled solution of **27** (0.75 g, 4.9 mmol) in anhydrous pyridine (4 ml) was added in small portions *p*-toluenesulfonyl chloride (0.97 g, 5.1 mmol). The mixture was kept in a refrigerator at 6°C for 16 h and was then poured into ice (20 g) and 2 N HCl (20 ml). The aqueous solution was extracted with diethyl ether (3 × 30 ml). The combined extracts were washed with aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated in vacuo. The residue (913 mg, 61%) was purified by HPLC (Polygosil 60-5-NO_2, hexane/ether, 4:1) to give spiro[bicyclo[2.2.1]heptane-2,1′-cyclobutan]-*endo*-3-yl *p*-toluenesulfonate (**28**), m.p. 54−56°C. − ^1H NMR ($CDCl_3$): δ = 1.16 (m, 1 H), 1.18 (dt, *J* = 10.5/1.5 Hz, 1 H), 1.27 (dquin, *J* = 10.5/1.5 Hz, 1 H), 1.33−1.4 (m, 2 H), 1.55−1.7 (m, 6 H), 2.02 (m, 1 H), 2.08 (br. s, 1 H), 2.20 (br. t, *J* = 4 Hz, 1 H) 2.44 (s, 3 H), 4.39 (dd, *J* = 4.5/1.2 Hz, 1 H), 7.33 and 7.81 (AA′BB′, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 15.84 (CH_2), 20.76 (CH_2), 21.90 (CH_3), 22.41 (CH_2), 23.96 (CH_2), 33.75 (CH_2), 36.40 (CH_2), 41.91 (CH), 46.23 (CH), 48.05 (C), 90.31 (CH), 128.05 (CH), 129.95 (CH), 134.53 (C), 144.67 (C). − $C_{17}H_{22}O_3S$ (306.4): calcd. C 66.64, H 7.24; found C 66.60, H 7.28. − Analogous treatment of **31** for 4 h afforded 95% of spiro[bicyclo [2.2.1]heptane-2,1′-cyclobutan]-*exo*-

3-yl *p*-toluenesulfonate (**32**), m.p. 59−61°C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 0.96 (m, 1 H), 1.08 (dq, *J* = 10.3/1.5 Hz, 1 H), 1.24−1.38 (m, 2 H), 1.41 (m, 1 H), 1.5−1.75 (m, 5 H), 1.86 (m, 1 H), 2.10 (m, 2 H), 2.31 (m, 1 H), 2.43 (s, 3 H), 3.98 (d, *J* = 1.8 Hz, 1 H), 7.33 and 7.80 (AA′BB′, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 16.26 (CH_2), 21.90 (CH_3), 22.73 (CH_2), 25.36 (CH_2), 28.35 (CH_2), 29.07 (CH_2), 34.17 (CH_2), 43.79 (CH), 46.08 (CH), 51.96 (C), 92.69 (CH), 127.97 (CH), 129.99 (CH), 134.61 (C), 144.66 (C). − $C_{17}H_{22}O_3S$ (306.4): calcd. C 66.64, H 7.24; found C 65.72, H 7.14. − To a solution of **28** or **32** (31 mg, 0.1 mmol) in water/dioxane (1:1) (3 ml) was added 2,6-dimethylpyridine (107 mg, 1 mmol). The mixtures were stirred for 16 h at 80°C. After addition of powdered K_2CO_3 at room temp., the dioxane phase was separated, dried ($MgSO_4$), and analyzed by GC (57 m Edenol, 130°C). For results, see Table 1.

Spiro[bicyclo[2.2.1]heptane-7,1′-cyclobutan]-2-one (**24**) *and p-Toluenesulfonylhydrazone* **25**: To a solution of **33** (0.14 g, 0.92 mmol) in pentane (10 ml) was added PCC adsorbed on alumina[24] (2.0 g). The mixture was stirred for 1 d at room temp., solids were filtered off, and the filtrate was diluted with pentane (10 ml). The pentane solution was washed with water, dried ($MgSO_4$), and concentrated at reduced pressure (100 Torr) to give 0.12 g (87%) of crude **24**, ^{1}H NMR ($CDCl_3$): δ = 1.38 (m, 2 H), 1.70−1.92 (m, 8 H), 1.98 (m, 1 H), 2.13 (dm, *J* = 18 Hz, 1 H), 2.28 (br. t, *J* = 4.2 Hz, 1 H), 2.36 (br. d, *J* = 4.5 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 14.91 (CH_2), 21.96 (CH_2), 25.15 (CH_2), 25.53 (CH_2), 26.45 (CH_2), 42.74 (CH), 43.06 (CH_2), 52.98 (C), 57.10 (CH), 218.02 (CO).

To a solution of *p*-toluenesulfonohydrazide (50 mg, 0.27 mmol) in methanol (1 ml) were added **24** (40 mg, 0.26 mmol) and saturated methanolic HCl (2 drops). The mixture was stirred for 16 h at room temp. The precipitate was recrystallized from methanol to give 63 mg (76%) of **25**, m.p. 175−176°C (dec.). − ^{1}H NMR (C_6D_6): δ = 0.82 (ddd, *J* = 12.7/9.3/4.4 Hz, 1 H), 1.15 (ddd, *J* = 12.7/9.3/ 4.2 Hz, 1 H), 1.30 (m, 1 H), 1.42−1.58 (m, 8 H), 1.64 (br. t, *J* = 4.4 Hz, 1 H), 1.82 (m, 1 H), 1.86 (m, 1 H), 1.89 (s, 3 H), 2.47 (br. d, *J* = 4.4 Hz, 1 H), 6.82 and 8.19 (AA′BB′, 4 H). − $C_{17}H_{22}N_2O_2S$ (318.4): calcd. C 64.12, H 6.96, N 8.80; found C 64.26, H 7.01, N 8.80. − The photolysis of **25** was performed as described for **22**; see Table 1 for results.

Spiro[bicyclo[2.2.1]heptane-7,1′-cyclobutan]-2-ols (**29**, **33**) *and p-Toluenesulfonate* **34**: To a solution of **24** (0.13 g, 0.87 mmol) in diethyl ether (5 ml) was added a solution of $NaBH_4$ (0.20 g, 5.26 mmol) and $NaHCO_3$ (8.4 mg, 0.1 mmol) in water (2 ml). The mixture was stirred for 16 h at room temp. The phases were separated, and the aqueous phase was extracted with diethyl ether (2 × 10 ml). The combined ether solutions were dried ($MgSO_4$) and concentrated in vacuo (**29**/**33** = 53:47, GC). HPLC (LiChrospher 100-5, hexane/ether, 7:3) of the residue afforded 40 mg (30%) of **33**, identical with the compound described above, and 40 mg (30%) of spiro[bicyclo[2.2.1]heptane-7,1′-cyclobutan]-*endo*-2-ol, m.p. 58−59°C. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (dd, *J* = 13.1/3.3 Hz, 1 H), 1.23 (m, 1 H), 1.32−1.50 (m + br. s, 2 H), 1.61 (m, 1 H), 1.7−1.95 (m, 10 H), 2.06 (m, 1 H), 4.24 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 15.82 (CH_2), 17.87 (CH_2), 26.19 (CH_2), 27.12 (CH_2), 27.44 (CH_2), 38.07 (CH_2), 43.25 (CH), 49.00 (CH), 54.52 (C), 71.43 (CH).

The tosylation of **33** (30 mg, 0.20 mmol), according to the procedure given for **28**, provided 39 mg (64%) of **34**, m.p. 47−49°C. − ^{1}H NMR ($CDCl_3$): δ = 0.92 (m, 2 H), 1.48 (m, 1 H), 1.61 (dd, *J* = 14.0/7.4 Hz, 1 H), 1.68−1.9 (m, 7 H), 1.94 (br. t, *J* = 3.5 Hz, 1 H), 2.03 (br. d, *J* = 3.5 Hz, 1 H), 2.22 (m, 1 H), 2.43 (s, 3 H), 4.44 (dd, *J* = 7.3/3.2 Hz, 1 H), 7.31 and 7.74 (AA′BB′, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 16.21 (CH_2), 21.90 (CH_3), 22.99 (CH_2), 25.45 (CH_2), 26.56 (CH_2), 27.04 (CH_2), 38.07 (CH_2), 42.60 (CH), 48.20 (CH), 53.58 (C), 86.42 (CH), 127.68 (CH), 129.96 (CH), 134.88 (C), 144.53 (C). − $C_{17}H_{22}O_3S$ (306.4): calcd. C 66.64, H 7.24; found C 66.76, H 7.19. − The solvolysis products of **33** were obtained and analyzed as described for **28** (Table 1).

Tricyclo[5.2.1.0^{2,6}]dec-endo-2-yl p-Toluenesulfonate (**39**): The procedure reported for **28** was followed in the tosylation of **38**[23] (0.54 g, 3.55 mmol), giving 703 mg (69%) of **39**, m.p. 91−93°C. − ^{1}H NMR ($CDCl_3$): δ = 0.99 (m, 1 H), 1.20 (m, 2 H), 1.3−1.5 (m, 3 H), 1.5−1.62 (m, 3 H), 1.67−1.79 (m, 2 H), 1.81 (br. d, *J* = 4.5 Hz, 1 H), 2.0 (m, 1 H), 2.42 (s, 3 H), 2.58 (br. dd, *J* = 14/5 Hz, 1 H), 2.77 (br. d, *J* = 4 Hz, 1 H), 7.30 and 7.77 (AA′BB′, 4 H). − ^{13}C NMR ($CDCl_3$): δ = 21.81 (CH_3), 23.18 (CH_2), 25.32 (CH_2), 28.17 (CH_2), 32.37 (CH_2), 35.43 (CH_2), 37.55 (CH_2), 40.18 (CH), 46.11 (CH), 55.86 (CH), 109.52 (C), 127.16 (CH), 129.74 (CH), 137.39 (C), 143.94 (C). − $C_{17}H_{22}O_3S$ (306.4): calcd. C 66.64, H 7.24; found C 66.76, H 6.89. − The solvolysis of **39** in aqueous dioxane (see procedure for **28**) gave predominantly **38** (Table 1). Traces of **40** were identified by comparison with an authentic sample[25].

Studies on Ion Pair Recombination: To a solution of **21** (1.10 g, 7.73 mmol) in anhydrous THF (3 ml) were added $^{18}OH_2$ (ca. 55% ^{18}O, 2 ml) and conc. HCl (1 µl). After the mixture was heated at 80°C for 15 h, it was cooled to room temp. and extracted with pentane. The extracts were dried ($MgSO_4$) and concentrated by distillation to give 1.0 g (91%) of ^{18}O-**21**, IR (film): $\tilde{\nu}$ = 1738 (C=^{16}O) and 1708 (C=^{18}O) cm^{-1}. Following the procedures outlined for **32**, the labeled ketone was converted into **32a**, ^{13}C NMR ($CDCl_3$): δ = 92.591 (36±1%), 92.638 (64±1%). The NMR solution was kept at room temp. for 3 d when 12% of **34a**, ^{13}C NMR ($CDCl_3$): δ = 86.315 (33%), 86.363 (67%), and 17% of **39a**, ^{13}C NMR ($CDCl_3$): δ = 109.394 (88%), 109.451 (12%), had appeared. After 5d, **39a** was isolated by HPLC (Polygosil 60-5-NO_2, hexane/ether, 9:1). Within experimental error (±1%), the isotopic distribution was the same as that observed in situ.

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