## **Rearrangements of Carbocation Sulfinate Ion Pairs**<sup>☆</sup>

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The chirality of alkyl *p*-toluenesulfinates and of <sup>18</sup>O-labeled *p*-toluenesulfinate ions was utilized to study the stereoselectivity of ion-pair recombinations. The diastereomers of 2-norpinyl (13), 2-norbornyl (16), 2-methyl-2-norbornyl (25), and exo-4-protoadamantyl (34) *p*-toluenesulfinates were rearranged in formamide or trifluoroacetic acid (TFA). Solvolysis competed to a minor extent. Predominant return of the carbocations to the oxygen atoms of  $ArSO_2^-$  was observed if the isomeric *p*-toluenesulfinates persisted (kinetic control). On repeated ionization (thermodynamic control), sulfones were eventually formed. With the exception of 25, 1,2 shifts of the *p*-toluenesulfinate anion proceed faster than oxygen exchange. The migration origin of the carbocation returns preferentially to the oxygen atom of  $ArSO_2^-$  from which the migration terminus departed. Conversely, the sulfinate anion

The concept of ion pairs in nucleophilic substitution, introduced by Winstein<sup>[1]</sup>, is now generally accepted<sup>[2]</sup> (Eq. 1). Contact (intimate) as well as solvent-separated ions pairs have been invoked to explain the products, stereochemistry, and kinetics of solvolysis reactions. Evidence for the recombination of ion pairs (internal return) was obtained from rearrangement or racemization of the cationic component  $(RX \rightarrow R'X)$  and from exchange processes (isotopic scrambling) of the anionic component  $(RX \rightarrow RX')$ . Most often, either technique was applied. More insight can be gained from the combination of both methods, as illustrated by the seminal work of Goering and Thies<sup>[3]</sup> on <sup>18</sup>O labeled, enantiomerically enriched bicyclo[3.2.1]oct-endo-2-yl tosylate (4). The intervening carbocation was found to return preferentially to the oxygen atom from which it departed (4a'/4b' ca. 2:1).

The substrates used in previous studies were largely carboxylates  $(1)^{[4]}$  and sulfonates  $(2)^{[3,5]}$ . Our efforts were directed to sulfinates (3) since we anticipated opportunities with 3 that are not provided by 1 and  $2^{[6]}$ . The ambident character of the sulfinate ion suggests that sulfones as well as sulfinates should arise from ion-pair recombination. Owing to the chirality of 3, migration of R from oxygen to oxygen results in racemization (if R is achiral) or diastereomerization (if R is chiral). The rearrangement of alkyl sulfinates to sulfones is known<sup>[7,8]</sup>, but we are aware of only one report on the recombination of a carbocation with the oxygen atoms of a sulfinate ion: Fava et al. observed that the racemization of optically benzhydryl *p*-toluenesulfinate discriminates between positions 1 and 2 of the symmetrical, bridged 2-norbornyl cation in favor of the carbon atom from which it departed. The selectivity of ion-pair recombination decreases in the order 2-norpinyl  $\approx$  4-protoadamantyl > 2-norbornyl > 2-methyl-2-norbornyl, i.e., with increasing stability of the carbocation. The rearrangements of **13** and **34** proved to be more selective in TFA at 0°C than in formamide at 120–130°C. The *p*-toluenesulfinates **13** and **34** were compared with the analogous tosylates and 3,5-dinitrobenzoates. More oxygen scrambling was observed with less nucleophilic anions (tosylate  $\geq p$ -toluenesulfinate > 3,5-dinitrobenzoate). Oxygen scrambling is also enhanced if the anion migrates over a longer distance (2-norpinyl  $\rightarrow$  exo-2-norbornyl vs. 2-norpinyl  $\rightarrow$  endo-2-norbornyl).



(3, R = Ph<sub>2</sub>CH) competes with the rearrangement to sulfone<sup>[9]</sup>. We have utilized the chirality of the <sup>18</sup>O-labeled p-toluenesulfinate ion to study such reactions in more detail.

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2-Norpinyl (bicyclo[3.1.1]hept-2-yl) substrates (5, X = ODBN, OMs, N<sub>2</sub><sup>+</sup>) were reported to solvolyze with formation of *endo*- and *exo*-2-norbornyl products (7, 10)<sup>[10-12]</sup>. The fraction of *endo* products 7 increases with the nucleophilicity of the reactant Y<sup>-</sup>, i.e., trapping of an *endo*-selective intermediate 6 competes with rearrangement to the *exo*-selective, achiral 2-norbornyl cation 11. Ion-pair recombination also enhances the 7/10 ratio, as was observed for

the formation of 7-ODNB and 10-ODNB from 5-ODNB<sup>[11]</sup>. Nucleophilic capture of 6 gives mainly 7, owing to unsymmetrical distribution of charge and product stability. As a rule, only traces of 8 are found in solvolyses of 5, except for conditions which favor inverting displacement ( $k_s$ , Scheme 1). High-level ab initio calculations support the bridged structure 6 of the 2-norpinyl cation which is separated from 11 by a barrier of only 1.2 kcal/mol<sup>[13]</sup>. The "classical" 2-norbornyl cation 9 represents the transition state on the reaction path from 6 to 11. Scheme 1



2-Norpinyl *p*-toluenesulfinate (13)<sup>[14]</sup> was prepared from norpinan-2-ol (5, X = OH or <sup>18</sup>OH<sup>[15]</sup>) and *p*-toluenesulfinyl chloride. The ester <sup>18</sup>O atom caused a shift of  $\Delta \delta$  = 0.04 to higher field for the <sup>13</sup>C-NMR signal of C-2. All <sup>18</sup>O distributions of the present work were estimated by means of <sup>13</sup>C-NMR spectroscopy (see ref.<sup>[5h]</sup> for previous applications of this method). The mixture of diastereomers (13a/ 13b = 1:1) was readily analyzed by GC but gave overlapping peaks on HPLC. Repeated chromatography afforded one of the diastereomers with >99% purity. Crystals suitable for X-ray analysis were not obtained; the assignment of configuration in Scheme 2 is arbitrary. (Lower case letters attached to formula numbers indicate stereoisomers whereas capital letters refer to isotopomers.)

Solvolyses of **13a** were performed in formamide at 130°C and in trifluoroacetic acid (TFA) at 0°C. The widey different reaction conditions reflect the polarity of the solvents ( $Y_{C1} = 0.60^{[16]}$  for HCONH<sub>2</sub>,  $Y_{C1} = 1.84^{[17]}$ ,  $4.6^{[18]}$  for CF<sub>3</sub>CO<sub>2</sub>H). Ion-pair recombination (Scheme 2) was found to compete efficiently with solvolysis (Table 1). Carbocations attack the oxygen atom of formamide with formation of iminium salts which are hydrolyzed on aqueous workup to give alcohols and alkyl formates, Eq. (2).

Scheme 2



$$R-X + HCONH_2 \rightarrow R-O-CH = \stackrel{+}{N}H_2X^{-} \xrightarrow{H_2O} R-OH + R-O-CH = O$$
(2)

In formamide, a 10/7 ratio of ca. 2 is observed, similar to earlier results in aqueous solvents<sup>[11]</sup>. Ion-pair recombination gives 2-norbornyl sulfinates (15, 16) in excess over 2norbornyl sulfones (12, 18). In each series, *endo* products predominate over *exo* products (15/16 = 7.9, 12/18 = 8.6). The *endo* sulfinate 15 is formed diastereoselectively (15a/ 15b = 5.8), in contrast to the *exo* sulfinate 16 (16a/16b  $\approx$ 1). Under the reaction conditions of Table 1, 15 is stable and 16 reacts very slowly. Hence the diastereomeric ratios

Table 1. Product distributions (%) obtained from 13a

Conditions	7	8	10	12	15a	15b	16a	16b	18
HCONH <sub>2</sub> , 130°C, 2 h	5.3 <sup>[a]</sup> 0.6 <sup>[b]</sup>	0.5 <sup>[a]</sup> trace <sup>[b]</sup>	10.9 <sup>[a]</sup> 1.4 <sup>[b]</sup>	8.6	54.3	9.3	4.1	4.0	1.0
CF <sub>3</sub> CO <sub>2</sub> H, 0°C, 25 min	1.8 <sup>[c]</sup>	-	61.2 <sup>[c]</sup>	-	31.7	0.8	2.2	2.3	-

<sup>[a]</sup>  $X = OH. - {}^{[b]} X = OCHO. - {}^{[c]} X = OCOCF_3$ 

are not significantly affected by equilibration of the products. The fraction of ion-pair recombination decreases in TFA, relative to formamide, whereas the **10/7** and **15a/15b** ratios are enhanced. These changes are explicable in terms of the low nucleophilicity and strong ionizing power of TFA.

Besides the product distributions, the following findings are important: (1) Interconversion of the 2-norpinyl p-toluenesulfinates 13a and 13b did not occur. Hence thermally induced inversion of the sulfur atom of alkyl sulfinates is excluded under the reaction conditions of Table 1. (2) Starting from 13a, the following distributions of <sup>18</sup>O were observed: In the more abundant diastereomer 15a of endo-2norbornyl p-toluenesulfinate only the singly bonded ("ester") oxygen atom was labeled. The less abundant diastereomer 15b bore the label only at the doubly bonded ("sulfone") oxygen atom. Obviously, the configuration of the  $[^{18}O]$ -*p*-toluenesulfinate ion must be retained during the lifetime of the ion pair 14, otherwise the label would be scrambled in both 15a and 15b. (3) The distributions of  $^{18}O$ in the exo-2-norbornyl p-toluenesulfinates 16a and 16b were the same, within experimental error. However, the isotopomers A were formed in slight excess over B (A/B =  $1.6 \pm$ 0.2:1).

On recombination of the ion pairs 14 and 17, the oxygen atom of the *p*-toluenesulfinate ion is clearly favored over the sulfur atom as binding site (15/12 = 7.4, 16/18 = 8.1). The carbocation returns preferentially to the oxygen atom of the *p*-toluenesulfinate ion from which if dissociated. This tendency is much stronger for the  $13 \rightarrow 15$  rearrangement (the anion remains on the *endo* side) than for the  $13 \rightarrow 16$ rearrangement (the anion migrates to the *exo* side).

In the 2-methyl-2-norpinyl cation (20) the positive charge is more evenly distributed than in the parent species 6 (norpinyl strain is balanced by the stabilizing effect of the methyl substituent). As a consequence, 2-methyl-2-norpinyl substrates (19, X = OPNB, N<sub>2</sub><sup>+</sup>) were found to give comparable amounts of 2-methyl-2-norpinyl (19, X = OR) and 1-methyl-endo-2-norbornyl products (22, X = OR)<sup>[19]</sup>. The rearrangement of 20 leads to the weakly delocalized 2methyl-2-norbornyl cation (21)<sup>[20]</sup> from which a minor fraction of the products is derived.

Scheme 3



2-Methyl-2-norpinyl p-toluenesulfinate (19a) was readily obtained from the analogous alcohol 19c<sup>[21]</sup>. The diastereomers of **19a** were distinguished by <sup>13</sup>C NMR but all attempts to separate them by HPLC failed. A solution of the diastereomeric mixture (73.1:26.9) in formamide was heated at 50°C. After 50% conversion, the recovered 19a showed no significant change in the ratio of diastereomers (72.2:27.8). When the reaction of 19a was carried to completion, the major product was 1-methyl-endo-2-norbornyl p-toluene-sulfinate (22a, 69.4%, ratio of diastereomers 65.5:34.5). The analogous solvolysis products 22c (2.4%) and 22d (18.9%) were formed in substantial amounts while only traces of 19c, d and 23c, d were detected. A sulfone (8.3%) was also obtained whose  $\alpha$  carbon was quaternary (<sup>13</sup>C NMR). Since the spectra were different from those of 23b (see below), the sulfone is assigned as 19b.

Although ion pair recombination is obvious, our failure to separate the diastereomers of **19a** precludes a detailed analysis. It appears that the sulfur atom of the *p*-toluenesulfinate ion returns to the tertiary position of **20** ( $\rightarrow$  **19b**) whereas the oxygen atoms bond to the secondary position ( $\rightarrow$  **22a**). However, internal return to give **19a** would not affect the ratio of distereomers if our sample of **19a** was an equilibrium mixture.

### Norbornyl -> Norbornyl Rearrangements

The reversible dissociation-recombination of *exo*-2-norbornyl *p*-toluenesulfinate (16) was studied by means of <sup>18</sup>O (Scheme 4a) and deuterium labels (Scheme 4b). The reaction proceeded at a convenient rate in formamide at 150°C and in trifluoroacetic acid at room temperature (Table 2). With increasing reaction time, the diastereomers and isotopomers of 16 approach equilibrium (compare runs 1 and 2, or 4 and 5, in Table 2); moreover, solvolysis products and sulfone 18 increase at the expense of 16. In principle, the preferences of ion-pair recombination would be seen most clearly at low conversion. However, the experimental error is then large. We chose 15-30% conversion as a compromise between the divergent requirements.





Scheme 4b



According to Scheme 4a, the ion pair 17 may recombine in four ways: (a)  ${}^{18}\text{O} \rightarrow \text{C-2}$ , (b)  ${}^{18}\text{O} \rightarrow \text{C-1}$ , (c)  ${}^{16}\text{O} \rightarrow \text{C-2}$ , and (d)  ${}^{16}\text{O} \rightarrow \text{C-1}$ . With 16aA as starting material, path (a) is not measurable (regeneration of starting material) and (b) is favored over (c) by a factor 3–4. The 2-norbornyl cation returns mainly to the oxygen atom of the *p*-toluenesulfinate ion from which it dissociated. This preference was confirmed by labeling the norbornyl residue (Scheme 4b): deuterium from the 2-position of 16a appears predominantly in the 1-position of 16b. The distributions of  ${}^{18}\text{O}$  and D agree well (runs 1 and 3, and 4 and 6 of Table 2).

 Table 2. Product distributions (%) for the dissociation-recombination of 16

No.	Substrate, conditions	16aA	16bA	16bB	16aB
1	<sup>18</sup> O]-16a, formamide, 150°C, 2 h	75.9	17.3	5.4	1.4
2	<sup>18</sup> O]- <b>16a</b> , formamide, 150°C, 5 h	49.9	30.3	11.5	8.3
3	<sup>2</sup> H]-16a, formamide, 150°C, 2 h	79.2	14.3	4.4	2.1
4	[ <sup>18</sup> O]- <b>16a</b> , CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 30 min	82.7	12.6	3.1	1.6
5	[ <sup>18</sup> O]- <b>16a</b> , CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 45 min	52.5	29.7	11.3	6.5
6	<sup>2</sup> H] <b>-16a</b> , CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 30 min	73.4	19.8	5.1	1.7
7	[ <sup>18</sup> O]- <b>16b</b> , formamide, 150°C, 2 h	16.4	76.8	2.1	4.7
8	[ <sup>18</sup> O]- <b>16b</b> , CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 30 min	12.3	83.4	1.7	2.9

The data in Table 2 also reveal that C-1 and C-2 of the 2-norbornyl cation are not equivalent in ion pair recombination. For **16aA** the recombination path (c) is favored over (d) by a factor of 2–3. When **16bA** was treated analogously, the recombination paths (a), (d), and (c) were observed in a ratio of about 8:2:1 (runs 7 and 8 of Table 2). The complementary results for **16aA** and **16bA** preclude the predominant formation of one diastereomer in the recombination of **17**. It appears that the *p*-toluenesulfinate ion returns preferentially to the carbon atom of the 2-norbornyl cation from which it departed (C-2). The data in Table 2 demonstrate regioselective recombination *after* oxygen exchange, i.e., in rebonding to the <sup>16</sup>O atom. An even stronger preference should be valid *before* oxygen exchange, i.e., in recombination reactions involving the <sup>18</sup>O atom.

As a rule, nucleophiles do not discriminate between C-1 and C-2 of the symmetric, bridged 2-norbornyl cation<sup>[22]</sup>. Exceptions are known, however, where the 2-norbornyl cation is trapped in an unsymmetrical state: for example, the addition of HX to norbornene or the decomposition of 2norbornanediazonium ions<sup>[23]</sup>. The influence of the solvent on these processes<sup>[24]</sup> points to the intervention of unsymmetrical ion pairs in which the counterion is closer to C-2 than to C-1. However, earlier studies failed to detect selective recombination if the ion pairs were generated by heterolysis of 2-norbornyl esters<sup>[25]</sup>. This apparent discrepancy has now been resolved.

Scheme 5



**25a**, formamide, 70 °C, 1 h → **25b** : **27a** : **27b** = 5.3 : 1 : 1 **25b**, formamide, 70 °C, 1 h → **25a** : **27a** : **27b** = 6.6 : 1 : 1



Owing to the charge distribution of the 2-methyl-2-norbornyl cation  $(21)^{[20]}$ , kinetically controlled reactions lead to almost exclusive formation of *endo*-2-methyl-*exo*-2-norbornyl products (23). On the other hand, reversible dissociation-recombination affords the thermodynamically more stable 1-methyl-*exo*-2-norbornyl products in addition to  $23^{[26]}$ . Accordingly, *endo*-2-methyl-*exo*-2-norbornyl *p*toluenesulfinate (25) was found to give 1-methyl-*exo*-2-norbornyl *p*-toluenesulfinate (27) on heating (formamide, 70°C). Interconversion of the diastereomers 25a and 25b proceeds ca. 3 times faster than the isomerization leading to 27, i.e., the *p*-toluenesulfinate ion returns preferentially to the tertiary carbon (Scheme 5). Within experimental error, the diastereomers 27a and 27b are formed in equal amounts. Owing to the enhanced stability of the carbocation, the ion pair 26 should be less tight and longer lived than the parent species 17. Therefore, indiscriminate recombination at C-1 is observed.

On prolonged reaction, the sulfones **24** (15%) and **28** (0.2%) are formed, along with products of elimination (79%) and solvolysis (4%), at the expense of **25** and **27**. The ratio of **24** to **28**, ca. 75:1, approximates the selectivity of 2-methyl-2-norbornyl cations towards external nucleophiles. In order to identify **28**, an authentic sample was prepared from 1-methyl-*endo*-2-norbornyl brosylate (**29**)<sup>[19b]</sup> by inverting displacement with ArSLi, followed by oxidation of the sulfide **30**.

## **Protoadamantyl** $\rightarrow$ **Adamantyl Rearrangements**

Much effort has been directed to the 4-protoadamantyl  $\rightarrow$  2-adamantyl rearrangement, an important step in the synthesis of adamantoid hydrocarbons<sup>[27-30]</sup>. The prominent role of the bridged cation **32** has recently been confirmed: The acid-catalyzed rearrangement of optically active [4-<sup>2</sup>H]-*exo*-4-protoadamantanol (**31**) was found to give [1-<sup>2</sup>H]-2-adamantanol (**33**) with 97% *ee* (Scheme 6)<sup>[31]</sup>.

Scheme 6



The diastereomers of *exo*-4-protoadamantanyl *p*-toluenesulfinate (**34**) were readily separated by HPLC, and the enantiomers of **34aA** (arbitrary assignment) were resolved on a chiral column. On heating a solution of **34aA** in formamide at 120°C, 2-adamantyl *p*-toluenesulfinate (**37**, 67%), 2-adamantyl *p*-tolyl sulfone (**38**, 6%), 2-adamantanol (21%), and 2-adamantyl formate (**39**, 6%) were obtained. The diastereomer **34aA** was not detected in the course of this reaction, and **37** did not undergo solvolysis under analogous conditions. Relative to formamide, more internal return ( $\rightarrow$ **37**, 90%) and less solvolysis ( $\rightarrow$ **40**, 8%) was observed with **34aA** in trifluoroacetic acid at 0°C.

The dissociation-recombination process,  $34 \rightarrow 37$ , was probed with [<sup>18</sup>O]-34aA (made from [<sup>18</sup>O]-exo-4-protoadamantanol), nonracemic 34aA, and deuterium-labeled 34aB (Table 3). The oxygen exchange measured with [<sup>18</sup>O]-34aA and the enantiomerization observed with nonracemic 34aA are in reasonable agreement. The ee of 37 was not affected by prolonged heating, i.e., oxygen exchange is the only process that inverts the configuration of sulfinic esters at moderate temperatures. The stereochemistry of the carbocation is not revealed by reactions of 34aA since the 2-adamantyl group (R = H) is achiral. In contrast, the  $[1-^{2}H]$ -2-adamantyl group (R = D) is chiral; 37aB and 37bB are diastereomers rather than enantiomers. The diastereomer 37bB could arise from configurational leakage of the carbocation,  $35 \rightarrow 36$ , as well as by exchange of the sulfinate oxygens. The close agreement of 37aB/37bB ratios with 37aA/37bA ratios (Table 3) indicates that such leakage does not occur. Among the carbocation-sulfinate ion pairs studied to date, **35** appears to be most tightly associated.

Table 3. Product ratios for the dissociation-recombination of 34

Substrate, conditions	37a	37b
<sup>18</sup> O]- <b>34aA</b> , formamide, 120°C, 8.5 h	87.6	12.4
34aA, nonracemic, formamide, 120°C, 3 h	89.8	10.2
34aB, formamide, 120°C, 8.5 h	90.7	9.3
[ <sup>18</sup> O]- <b>34aA</b> , CF <sub>3</sub> CO <sub>2</sub> H, 0°C, 40 min	97.7	2.3
34aA, nonracemic, CF <sub>2</sub> CO <sub>2</sub> H, 0°C, 5 min	97.6	2.4
<b>34aB</b> , CF <sub>3</sub> CO <sub>2</sub> H, 0°C, 40 min	97.4	2.6

#### **Comparison of Leaving Groups**

In the preceding sections, *p*-toluenesulfinates served to uncover novel aspects of ion pair recombination. Therefore, a comparison of sulfinates with more popular leaving groups, such as sulfonates and carboxylates, would be in order. The scrambling of <sup>18</sup>O labels was employed as a generally applicable tool. Tosylation of 2-norpinanol was reported to yield endo-2-norbornyl tosylate (43)<sup>[11,32]</sup> rather than the labile 2-norpinyl tosylate (42)<sup>[14]</sup>. On tosylation of  $[^{18}O]$ -2-norpinanol (41) we obtained 43 with substantial scrambling of the <sup>18</sup>O label (Table 4).Similarly, tosylation of exo-4-protoadamantanol gave only the rearranged 2-adamantyl tosylate (46); exo-4-protoadamantyl tosylate (45) could not be prepared<sup>[28a]</sup>. We found that the rearrangement is associated with partial redistribution of an <sup>18</sup>O label, albeit to a lesser extent than was observed for the 41  $\rightarrow$  43 transformation. The intermediate sulfonates 42 and 45 are thought to be formed from 41 and 44, respectively, without loss of <sup>18</sup>O. The sulfonate groups of 42 and 45 should be labeled only in the "ester" position. Column 5 of Table 4 records the <sup>18</sup>O that is recovered in the "ester" position of the products, relative to starting material. If the label

is distributed equally between the three oxygen atoms of the *p*-toluenesulfonate ion, 33% <sup>18</sup>O would be recovered in the "ester" position. This is taken into account in column 6 (% equilibration) of Table 4, in order to compare adequately anions with three and two oxygen atoms.



Table 4. Distribution of <sup>18</sup>O in dissociation-recombination processes

Substrate	Conditions <sup>[a]</sup>	Product	Anion <sup>[b]</sup>	"Ester"- <sup>18</sup> O (%) <sup>[c]</sup>	Equilibration (%)			
2-Norpinyl $\rightarrow$ endo-2-Norbornyl								
42	Py, 0 °C	43	TsO	65	52			
13	TFA, 0 °C	15	Ts	98	4			
47	TFA, 22 °C	48	ODNB	100	0			
2-Norpinyl $\rightarrow exo$ -2-Norbornyl								
13	TFA, 0 °C	16	Ts	62	76			
47	TFA, 22 °C	49	ODNB	92	16			
$exo$ -4-Protoadamantyl $\rightarrow$ 2-Adamantyl								
45	Py, 0 °C	46	TsO	81	28			
34	TFA, 0 °C	37	Ts	98	4			
50	TFA, 22 °C	51	ODNB	100	0			

<sup>[a]</sup> Py = pyridine, TFA = trifluoroacetic acid. - <sup>[b]</sup> TsO = *p*-toluenesulfonate; Ts = *p*-toluenesulfinate; ODNB = 3,5-dinitrobenzoate. - <sup>[c]</sup> Relative to substrate.

The 3,5-dinitrobenzoates  $47^{[11,12]}$  and  $50^{[28a]}$  were readily prepared, in contrast to the analogous tosylates. The rearrangement of 47 in trifluoroacetic acid (22°C, 6–7 h) afforded *endo*- (48) and *exo*-2-norbornyl 3,5-dinitrobenzoate (49) in a ratio of 92:8. Within experimental error (±2%), the <sup>18</sup>O label of 47 was completely recovered in the "ester" position of 48. Even the migration of ODNB from *endo* to *exo* ( $\rightarrow$  49) proceeds with a remarkably small amount of scrambling. Similarly, the 2-adamantyl group of 51 returns exclusively to the oxygen from which the 4-protoadamantyl group of 50 departed.

Owing to widely different reactivities, the various leaving groups could not be studied under the same reaction conditions. However, the range of <sup>18</sup>O distributions would be widened, rather than narrowed, by using more polar solvents for the tosylates and lower temperatures for the dinitrobenzoates of Table 4. The data indicate that the tightness of the intervening ion pairs increases in the order *p*-toluenesulfonate < p-toluenesulfinate < 3,5-dinitrobenzo-ate. An inverse relationship of <sup>18</sup>O scrambling with rates of



ionization (solvolysis) is anticipated. Rate ratios  $k_{OTs}/k_{OPNB}$ = 3.3  $\cdot$  10<sup>9</sup> (80% ethanol, 25°C)<sup>[33]</sup> and  $k_{ODNB}/k_{OPNB}$  = 16–17<sup>[34]</sup> (OPNB = *p*-nitrobenzoate) have been reported which lead to  $k_{OTs}/k_{ODNB}$  = 2  $\cdot$  10<sup>8</sup>. Rates of ionization (= rearrangement + solvolysis) were determined for 2-norpinyl *p*-toluenesulfinate (13) and 2-norpinyl tosylate (42)<sup>[35]</sup> (Table 5):  $k_{42}/k_{13}$  = 1.4  $\cdot$  10<sup>7</sup> (80% EtOH, 25°C). The rate ratios parallel the pK<sub>a</sub> values of the corresponding acids: *p*-toluenesulfinic -6.6<sup>[36]</sup>, *p*-toluenesulfinic 1.24<sup>[37]</sup>, and 3,5-dinitrobenzoic 2.82<sup>[38]</sup>. As a leaving group, *p*-toluenesulfinate ranges closer to 3,5-dinitrobenzoate than to tosylate. The same tendency is obvious for ion-pair recombination (Table 4). With respect to *endo*  $\rightarrow exo$  migration, however, *p*-toluenesulfinate and 3,5-dinitrobenzoate differ significantly (13  $\rightarrow$  16 vs. 47  $\rightarrow$  49).

 Table 5. Reaction rates of 2-norpinyl p-toluenesulfinate (13) in 80% ethanol

Substrate	Temp. (°C)	$k(s^{-1})$
13	138.2	8.87±0.07·10 <sup>-4</sup>
	130.3	$4.94 \pm 0.04 \cdot 10^{-4}$
	119.8	$2.00\pm0.03\cdot10^{-4}$
	109.5	$0.755 \pm 0.005 \cdot 10^{-4}$
	25.0 <sup>[a]</sup>	$3.41 \cdot 10^{-9}$
<b>42</b> <sup>[35]</sup>	25.0 <sup>[b]</sup>	$4.88 \cdot 10^{-2}$

<sup>[a]</sup> Extrapolated from higher temperatures. – <sup>[b]</sup> Extrapolated from lower temperatures.

### Summary and Conclusion

Dissociation-recombination processes dominate the chemistry of the bicycloalkyl and tricycloalkyl p-toluenesulfinates we have studied. Kinetic control favors return of the carbocations to the oxygen atoms of the p-toluenesulfinate ion; thermodynamic control leads eventually to sulfones. With exception of the 2-methyl-2-norbornyl system, 1,2-shifts of the p-toluenesulfinate ion proceed faster than oxygen exchange. The migration origin of the carbocations returns preferentially to the oxygen atom of the sulfinate group from which the migration terminus departed. Conversely, the returning p-toluenesulfinate ion discriminates between positions 1 and 2 of the symmetrical 2-norbornyl cation (11) in favor of the carbon atom from which it dissociated. The selectivity of recombination decreases with increasing stability of the carbocations. In the series 2-norpinyl (6), 2-norbornyl (11), 2-methyl-2-norbornyl (21), 6 is less stable than 11 by 12.2 kcal/mol<sup>[13]</sup>, and 21 is more stable than 11 by 7.4 kcal/mol (solution)<sup>[39]</sup> to 8.7 kcal/mol (gas phase)<sup>[40]</sup>. The selectivities of ion-pair recombination, ca. 50:1 for 14, ca. 10:1 for 17, and ca. 1:1 for 26, follow an analogous order. The relative stability of the 4-protoadamantyl cation (32) is more difficult to assess. However, the solvolysis rates of 42 (Table 5)<sup>[35]</sup> and 45<sup>[28a]</sup>, as well as those of 43 and 46<sup>[41]</sup>, are similar, and so are the recombination selectivities of the corresponding ion pairs 14 and 35.

Alkyl p-toluenesulfinates rearrange more rapidly in trifluoroacetic acid (TFA; Y = 1.8) than in formamide (Y = 0.6). On the other hand, return of the counterion proceeds more selectively in TFA at  $0-25^{\circ}$ C than in formamide at  $120-150^{\circ}$ C. It appears that the temperature is more influential than the polarity of the solvent in promoting ionpair reorganization. The relative stability of the anions, ptoluenesulfonate > p-toluenesulfinate > 3,5-dinitrobenzoate, also exerts a strong effect, as discussed in the preceding Section.

### **Experimenal Section**

<sup>1</sup>H NMR: Bruker WP 80 and Bruker AM 400;  $\delta = 0$  for tetramethylsilane as internal standard,  $\delta = 7.26$  for chloroform. – <sup>13</sup>C NMR (100.6 MHz) and <sup>2</sup>H NMR (61.4 MHz): Bruker AM 400. Analyses of <sup>18</sup>O by means of <sup>13</sup>C isotopic shifts<sup>[5h]</sup> are most accurate if <sup>13</sup>C-<sup>18</sup>O and <sup>13</sup>C-<sup>16</sup>O signals are of similar intensity. Therefore, <sup>18</sup>OH<sub>2</sub> with 50–55% <sup>18</sup>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 dectection. – Melting points: Kofler hot plate (Reichert), not corrected.

Bicyclo[3.1.1]hept-2-yl p-Toluenesulfinate (13): To a solution of bicyclo[3.1.1]heptan-2-ol<sup>[12,42]</sup> or [<sup>18</sup>O]bicyclo[3.1.1]heptan-2-ol  $(41)^{[15]}$  (0.55 g, 4.9 mmol) in anhydrous pyridine (5.5 ml) was added at 0°C p-toluenesulfinyl chloride<sup>[43]</sup> (0.89 g, 5.1 mmol). After the mixture had been stirred at room temp. for 16 h, it was diluted with diethyl ether (60 ml). The ether solution was washed with 2 N HCl, aqueous NaHCO<sub>3</sub>, and water, dried (MgSO<sub>4</sub>), and concentrated in vacuo to give 1.2 g (98%) of 13<sup>[14]</sup>. HPLC (Polygosil 60-10-C<sub>18</sub>, methanol/water, 7:3) of the **13a**, **b** mixture (50.1:49.9, GC) afforded the first eluting diastereomer, arbitrarily assigned as 13a, with de > 99% (GC: 32 m Carbowax + KOH, 165°C). – <sup>1</sup>H NMR  $(CDCl_3)$ :  $\delta = 1.07$  (dd, J = 9.5/8.0 Hz, 1H), 1.62 (m, 1H), 1.66 (dd, J = 9.5/8.1 Hz, 1H), 1.84-2.02 (m, 3H), 2.11 (m, 1H),2.22-2.38 (m, 3H), 2.40 (s, 3H), 4.69 (td, J = 7.0/2.7 Hz, 1H), 7.29 and 7.57 (AA'BB', 4H).  $- {}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta = 21.46$  (CH<sub>3</sub>), 25.16 (CH<sub>2</sub>), 26.15 (CH<sub>2</sub>), 26.45 (CH<sub>2</sub>), 33.11 (CH), 33.6 (CH<sub>2</sub>), 40.16 (CH), 79.761 (18O-CH), 79.805 (16O-CH), 125.03 (CH), 129.53 (CH), 142.33 (C), 142.78 (C). - A solution of 13a (50 mg, 0.2 mmol) in formamide (3 ml) was heated at 130°C. The progress of the reaction (30 min: 80%; 75 min: 97%; 120 min: 100%) was monitored by extracting aliquots with pentane, and analyzing the extracts by GC (Table 1). A solution of 13a (25 mg, 0.1 mmol) in trifluoroacetic acid (TFA, 1.5 ml) was stirred at 0°C for 25 min.

# **FULL PAPER**

Diethyl ether was added (10 ml), the mixture was washed with aqueous NaHCO<sub>3</sub>, dried (MgSO<sub>4</sub>), concentrated by distillation (Vigreux column), and analyzed by GC (Table 1). In each case, mixtures of **15a**, **b** and **16a**, **b** were isolated by HPLC (Si 100-5, hexane/ ether, 9:1) and analyzed by <sup>13</sup>C NMR (the C-2 signals of all components were cleanly separated, see below). The reaction of **13a** (32.0  $\pm$  0.5% <sup>18</sup>O) in formamide afforded products with the following % "ester"-<sup>18</sup>O: **15a**, 32.0  $\pm$  0.5; **15b**, 0  $\pm$  1; **16a**, 20.5  $\pm$  2; **16b** 17.1  $\pm$ 2. The analogous data for the reaction of **13a** (52.5  $\pm$  0.5% <sup>18</sup>O) in TFA were: **15a**, 52.6  $\pm$  0.5; **15b**, 0  $\pm$  1; **16a**, 31.4  $\pm$  2; **16b** 33.6  $\pm$  2.

*Bicyclo*[2.2.1]*hept-endo-2-yl p-Tolyl Sulfone* (12): To a solution of bicycylo[2.2.1]*hepta-2*,5-dien-2-yl *p*-tolyl sulfone<sup>[44]</sup> (0.40 g, 1.61 mmol) in ethyl acetate (50 ml) was added 10% Pd/C (20 mg). The mixture was hydrogenated at normal pressure and room temp. for 12 h. The solution was filtered, the solvent evaporated, and the residue purified by HPLC (Polygosil 60-10-C<sub>18</sub>, methanol/water, 7:3) to give 0.38 g (94%) of 12, m.p. 62°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.28 (dquint, *J* = 10/2 Hz,1H), 1.33–1.50 (m, 3H), 1.57 (m, 1H), 1.68–1.77 (m, 2H), 2.29–2.38 (m, 2H), 2.42 (s, 3H), 2.50 (m, 1H), 3.30 (dddd, *J* = 10.5/6.5/3.9/2.0 Hz, 1H), 7.31 and 7.73 (AA'BB', 4H). – C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>S (250.4): calcd. C 67.16, H 7.25; found C 67.10, H 7.18.

*Bicyclo*[2.2.1]*hept-endo-2-yl p-Toluenesulfinate* (**15**): Following the procedure for **13**, bicyclo[2.2.1]*heptan-endo-2-ol* (0.60 g, 5.35 mmol) was treated with *p*-toluenesulfinyl chloride (0.99 g, 5.67 mmol) to give 1.32 g (98%) of **15**. The mixture of diastereomers was purified by HPLC (Polygosil 60-10-CN, hexane/ether, 9:1) but could not be separated. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.8-2.2$  (m, 9H), 2.40 (s, 3H), 2.47 (br. s, 1H), 4.63 (dt, J = 10.4/3.9 Hz, 1H), 7.28 and 7.58 (AA'BB', 4H). – <sup>13</sup>C NMR (CDCl<sub>3</sub>): **15a**  $\delta = 21.07$ (CH<sub>2</sub>), 21.78 (CH<sub>3</sub>), 29.61 (CH<sub>2</sub>), 36.74 (CH), 37.61 (CH<sub>2</sub>), 38.23 (CH<sub>2</sub>), 42.12 (CH), 78.83 (CH), 125.41 (CH), 129.85 (CH), 142.71 (C), 142.92 (C). **15b**  $\delta = 21.04$  (CH<sub>2</sub>), 21.78 (CH<sub>3</sub>), 29.66 (CH<sub>2</sub>), 36.71 (CH), 37.48 (CH<sub>2</sub>), 38.23 (CH<sub>2</sub>), 42.19 (CH), 78.70 (CH), 125.35 (CH), 129.88 (CH), 142.77 (C). – C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>S (250.4): calcd. C 67.16, H 7.25; found C 67.12, H 7.19.

Bicyclo [2.2.1] hept-exo-2-vl p-Toluenesulfinate (16): Bicyclo [2.2.1]heptan-exo-2-ol, [endo-2-2H]bicyclo[2.2.1]heptan-exo-2-ol[45], and <sup>[18</sup>O]bicyclo[2.2.1]heptan-exo-2-ol (prepared by oxymercuration<sup>[46]</sup> of bicyclo[2.2.1]hept-2-ene with <sup>18</sup>OH<sub>2</sub>) were treated with *p*-toluenesulfinyl chloride according to the procedure reported for 13. The mixture of diastereomers (1:1), obtained in 98% yield, was separated by HPLC (Polygosi 60-10-C<sub>18</sub>, methanol/water, 7:3) to give 16a and 16b with  $de \ge 099\%$ .  $- {}^{1}H$  NMR (CDCl<sub>3</sub>): 16a  $\delta =$ 0.93-1.05 (m, 2H), 1.11 (ddq, J = 10.0/2.5/1.2 Hz, 1H), 1.33-1.48 (m, 2H), 1.55 (dquint, J = 10.0/2.0 Hz, 1H), 1.62 (dm, J = 13.8Hz, 1H), 1.75 (ddd, J = 13.8/6.9/2.5 Hz, 1H), 2.25 (m, 2H), 2.38 (s, 3H), 4.28 (br. d, J = 6.9 Hz, 1H), 7.28 und 7.57 (AA'BB', 4H). **16b**  $\delta = 0.94 - 1.07$  (m, 2H), 1.15 (br. d, J = 10.0 Hz, 1H), 1.33-1.42 (m, 2H), 1.46-1.55 (m, 2H), 1.55 (dquint, J = 10.0/2.0Hz, 1H), 2.22 (br. s, 1H), 2.38 (s, 3H), 2.47 (br. d, J = 5 Hz, 1H), 4.26 (t, J = 4.6 Hz, 1H), 7.28 und 7.56 (AA'BB', 4H).  $- {}^{2}$ H NMR (CHCl<sub>3</sub>): 16a  $\delta = 4.28$ .  $-^{13}$ C NMR (CDCl<sub>3</sub>): 16a:  $\delta = 21.49$ (CH<sub>3</sub>), 24.24 (CH<sub>2</sub>), 28.08 (CH<sub>2</sub>), 34.99 (CH<sub>2</sub>), 35.40 (CH), 40.87 (CH<sub>2</sub>), 42.91 (CH), 81.656 (<sup>18</sup>O-CH), 81.690 (<sup>16</sup>O-CH), 124.99 (CH), 129.55 (CH), 142.36 (C), 142.95 (C); 16b:  $\delta = 21.48$  (CH<sub>3</sub>), 24.13 (CH<sub>2</sub>), 28.03 (CH<sub>2</sub>), 34.90 (CH<sub>2</sub>), 35.34 (CH), 40.36 (CH<sub>2</sub>), 42.88 (CH), 80.443 (18O-CH), 80.488 (16O-CH), 125.10 (CH), 129.58 (CH), 142.32 (C), 142.67 (C).  $-C_{14}H_{18}O_2S$  (250.4): calcd. C 67.16, H 7.25; found for 16a, b C 67.32, H 7.25. - The procedures reported for 13a were applied to reactions of 16a and 16b in TFA (25°C) and formamide (150°C). The products observed by

GC (20 m Carbowax + KOH, 150°C) were bicyclo[2.2.1]hept-*exo*-2-yl *p*-tolyl sulfone (**18**)<sup>[47]</sup>, *exo*-2-norbornanol, *exo*-2-norbornyl trifluoroacetate (in TFA), and *exo*-2-norbornyl formate (in formamide). The sulfinates **16a** and **16b** were recovered by HPLC (Polygosil 60-10-C<sub>18</sub>, methanol/water, 7:3) for analysis of the isotopic distribution by NMR. Table 6 records the data from which the product distributions in Table 2 were calculated. Since the fraction of **16aB** (Table 2) is obtained from the difference of columns 2 and 5 of Table 6, the estimated error of  $\pm 0.3$  in % <sup>18</sup>O can lead to errors up to  $\pm 0.9$  in **16aB**. However, the data for **16bB** are more accurate ( $\pm 0.3$ ), and **16bB** > **16aB** is consistenly found in all rearrangements of **16aA**.

Table 6. Distribution of diastereomers and labels from the dissociation-recombination of 16

Substrate	<sup>18</sup> O (%)	Conditions	16a : 16b	"Ester"-	<sup>18</sup> O (%)
				16a	16b
[ <sup>18</sup> 0]-16a	50.4	formamide, 150°C, 2 h	77.3 : 22.7	49.5	38.5
<sup>18</sup> 0]-16a	53.6	formamide, 150°C, 5 h	58.2 : 41.8	46.0	38.9
<sup>18</sup> 0]-16a	53.6	CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 30 min	84.3:15.7	52.6	42.9
<sup>18</sup> 0]-16a	53.4	CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 45 min	59.0 : 41.0	47.5	38.7
<sup>18</sup> 0]-16b	53.6	formamide, 150°C, 2 h	21.1 : 78.9	41.6	52.2
[ <sup>18</sup> 0]- <b>16b</b>	53.6	CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 30 min	15.2 : 84.8	43.3	52.7
<sup>2</sup> H (%)				<sup>2</sup> H (%)	
	. ,			16a	16b
<sup>2</sup> H]-16a	>99.8	formamide, 150°C, 2 h	81.3 : 18.7	97.4	23.5
[ <sup>2</sup> H]-16a	>99.8	CF <sub>3</sub> CO <sub>2</sub> H, 25°C, 30 min	75.1 : 24.9	97.7	20.3

2-Methylbicyclo[3.1.1]hept-2-yl p-Toluenesulfinate (19a): To a solution of 1.60 g (12.7 mmol) of 2-methylbicyclo[3.1.1]heptan-2ol (19c)<sup>[21]</sup> in pyridine (15 ml) was added at 0°C p-toluenesulfinyl chloride (2.32 g, 13.3 mmol), and the mixture was stirred for 3 h at room temp. Conventional workup (see 13) afforded 3.1 g (92%) of 19a whose diastereomers could not be separated by HPLC. A sample containing 73% (NMR) of diastereomer 1 was obtained by cutting of the overlapping peaks (Polygosil 60-10-CN, hexane/ether, 9:1).  $- {}^{1}$ H NMR (CDCl<sub>3</sub>):  $\delta = 1.07 - 2.65$  (m, 10H), 1.57 (s, 3H), 2.34 (s, 3H), 7.23 and 7.52 (AA'BB', 4H). - <sup>13</sup>C NMR (CDCl<sub>3</sub>): diastereomer 1 (major):  $\delta = 21.72$  (CH<sub>3</sub>), 26.34 (CH<sub>2</sub>), 27.65 (CH<sub>3</sub>), 30.59 (CH<sub>2</sub>), 30.66 (CH<sub>2</sub>), 31.93 (CH<sub>2</sub>), 33.38 (CH), 45.38 (CH), 88.84 (C), 125.00 (CH), 129.79 (CH), 142.20 (C), 144.15 (C); diastereomer 2 (minor):  $\delta = 21.72$  (CH<sub>3</sub>), 26.45 (CH<sub>2</sub>), 27.59 (CH<sub>3</sub>), 30.56 (CH<sub>2</sub>), 30.92 (CH<sub>2</sub>), 31.65 (CH<sub>2</sub>), 33.35 (CH), 45.95 (CH), 88.80 (C), 125.12 (CH), 129.79 (CH), 142.14 (C), 144.15 (C). - C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S (264.4): calcd. C 68.15, H 7.63; found C 68.13, H 7.55. - A solution of 19a (0.10 g, 0.38 mmol, ratio of diastereomers 73.1:26.9) in formamide (6 ml) was heated at 50°C for 20 min. The mixture was extracted with pentane. The extracts were washed with water, dried (MgSO<sub>4</sub>), and concentrated in vacuo. The sulfinates 19a (49.9%) and 22a (50.1%, see below) were separated by HPLC. <sup>13</sup>C NMR revealed diastereomeric ratios of 72.2:27.8 for 19a and 65.5:34.5 for 22a. Heating at 50°C for 2 h led to complete conversion of 19a. HPLC of the product mixture indicated the presence of 19b (8.3%, see below), 22a (69.4%), 22c (2.4%), and 22d (18.9%). Traces of 19c, 23c, and 23d were also detected; the mixture was not analyzed for alkenes.

2-Methylbicyclo[3.1.1]hept-2-yl p-Tolyl Sulfone (19b): The rearrangement of 19a (2.0 g, 7.6 mmol) in 120 ml of formamide (50°C, 2 h), followed by HPLC (Polygosil 60-10-CN, hexane/ether, 9:1) of the product mixture, afforded 52 mg (2.6%) of 19b, m.p. 82°C.  $^{-1}$ H NMR (CDCl<sub>3</sub>):  $\delta = 1.32$  (s, 3H), 1.38 (dd, J = 10.0/ 8.5 Hz, 1H), 1.57 (ddd, J = 14.5/7.5/3.0 Hz, 1H), 1.73–2.09 (m,

5H), 2.26 (m, 1H), 2.44 (s, 3H), 2.50 (q, J = 5.5 Hz, 1H), 2.60 (dt, J = 14.5/8.5 Hz, 1H), 7.31 and 7.73 (AA'BB', 4H).  $- {}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta = 21.08$  (CH<sub>3</sub>), 21.84 (CH<sub>3</sub>), 24.26 (CH<sub>2</sub>), 26.20 (CH<sub>2</sub>), 29.52 (CH<sub>2</sub>), 33.25 (CH), 33.36 (CH<sub>2</sub>), 40.59 (CH), 65.87 (C), 129.56 (CH), 130.50 (CH), 133.59 (C), 144.50 (C).  $- C_{15}H_{20}O_{2}S$  (264.4): calcd. C 68.15, H 7.63; found C 68.19, H 7.74.

*1-Methylbicyclo*[2.2.1]*hept-endo-2-yl p-Toluenesulfinate* (22a): The sulfinylation of 1-methylbicyclo[2.2.1]*heptan-endo-2-ol* (22c)<sup>[19b]</sup> was performed as described for 13a to give 94% of 22a. Solutions of 22a in formamide did not react at 50°C whereas solvolysis was complete after 20 h at 150°C (→ 22c, 34%, +22d, 65%). The diastereomers of 22a were distinguished by <sup>13</sup>C NMR but could not be separated by HPLC. – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 18.35, 18.63 (1-CH<sub>3</sub>), 21.76 (Ar-CH<sub>3</sub>), 28.09 (CH<sub>2</sub>), 31.03 (CH<sub>2</sub>), 36.90, 36.99 (CH), 39.04, 39.77 (CH<sub>2</sub>), 44.22, 44.33 (CH<sub>2</sub>), 47.99, 48.15 (C), 82.84, 83.81 (CH), 125.30, 125.51 (CH), 129.76, 129.81 (CH), 142.64 (C), 142.89, 143.00 (C). – C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S (264.4): calcd. C 68.15, H 7.63; found C 68.23, H 7.80.

*1-Methylbicyclo*[2.2.1]hept-endo-2-yl Formate (22d): To acetic anhydride (0.27 g, 2.65 mmol) was added formic acid (122 mg, 2.65 mmol). The mixture was kept at 45°C for 1 h. One drop of pyridine and 0.30 g (2.4 mmol) of **22c** were then added, and stirring was continued for 16 h at room temp. The mixture was diluted with diethyl ether and washed with aqueous NaHCO<sub>3</sub>. The organic phase was dried (MgSO<sub>4</sub>) and concentrated in vacuo. Chromatography (Polygosil 60-10-CN, hexane/ether, 9:1) afforded 0.34 g (93%) of **22d** which was further purified by PGC (1.6 m OV 101, 130 cm<sup>-1</sup>). -<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.05$  (dt, J = 13.0/3.2 Hz, 1H), 1.09 (s, 3H), 1.18 (tdd, J = 12.5/4.6/2.0 Hz, 1H), 1.23–1.32 (m, 2H), 1.37 (dddd, J = 12.5/9.1/4.6/2.1 Hz, 1H), 1.68 (ttd, J = 12.5/4.8/3.2 Hz, 1H), 1.87 (dddd, J = 12.5/9.1/4.8/2.1 Hz, 1H), 2.12–2.20 (m, 2H), 4.79 (br. d, J = 10.0 Hz, 1H), 8.07 (s, 1H). – C<sub>9</sub>H<sub>14</sub>O<sub>2</sub> (154.2): calcd. C 70.10, H 9.15; found C 70.16, H 9.12.

endo-2-Methylbicyclo[2.2.1]hept-exo-2-yl p-Toluenesulfinate (25): To solution of *endo*-2-methylbicycylo[2.2.1]heptan-*exo*-2-ol<sup>[48]</sup> (0.80 g, 6.3 mmol) in pyridine (8 ml) was added at 0°C p-toluenesulfinyl chloride (1.16 g, 6.6 mmol), and the mixture was stirred for 50 h at room temp. Conventional workup (see 13) afforded 1.40 g (83.5%) of 25 whose diastereomers were separated by HPLC (Polygosil 60-10-CN, hexane/ether, 9:1) to give 25a (assignment arbitrary, de > 99.8%) and **25b** (de = 95.8%). - <sup>1</sup>H NMR (CDCl<sub>3</sub>) of **25a**:  $\delta = 1.63$  (s, 3H), 1.0–2.15 (m, 8H), 2.26 (br. s, 1H), 2.38 (s, 3H), 2.63 (br. s, 1H), 7.27 and 7.54 (AA'BB', 4H). - <sup>13</sup>C NMR  $(CDCl_3)$  of 25a:  $\delta = 21.69$  (Ar-CH<sub>3</sub>), 23.94 (CH<sub>2</sub>), 24.57 (2-CH<sub>3</sub>), 28.35 (CH<sub>2</sub>), 37.49 (CH), 37.53 (CH<sub>3</sub>), 47.90 (CH<sub>2</sub>), 47.96 (CH), 92.23 (C), 124.95 (CH), 129.82 (CH), 142.20 (C), 144.00 (C). -C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S (264.4): calcd. C 68.15, H 7.63; found C 68.11, H 7.60. - <sup>1</sup>H NMR (CDCl<sub>3</sub>) of **25b**:  $\delta = 1.66$  (s, 3H), 1.05–2.12 (m, 8H), 2.22 (br. s, 1H), 2.37 (s, 3H), 2.52 (br. s, 1H), 7.27 and 7.55 (AA'BB', 4H). – <sup>13</sup>C NMR (CDCl<sub>3</sub>) of **25b**:  $\delta = 21.69$  (Ar-CH<sub>3</sub>), 23.98 (CH<sub>2</sub>), 24.72 (2-CH<sub>3</sub>), 28.51 (CH<sub>2</sub>), 37.61 (CH), 37.66 (CH<sub>2</sub>), 47.96 (CH<sub>2</sub>), 48.41 (CH), 92.33 (C), 125.06 (CH), 129.82 (CH), 142.23 (C), 144.03 (C). - A solution of 25a (0.10 g, 0.38 mmol) in formamide (6 ml) was heated for 1 h at 70°C and was then extracted with pentane. Analysis of the extracts by HPLC indicated 79.1% of 25a, 15.2% of 25b, 2.8% of 27a, and 2.8% of 27b. An analogous experiment with 25b (containing 2.1% of 25a) gave 19.2% of **25a**, 75.6% of **25b**, 2.6% of **27a**, and 2.6% of **27b**. – The conversion of 25a was complete after 4 h at 70°C, and the resulting product mixture consisted of 2-methylbicyclo[2.2.1]hept-2-ene<sup>[49]</sup> (27.0%), 2-methylenebicyclo[2.2.1]heptane<sup>[50]</sup> (52.3%), endo-2methylbicyclo[2.2.1]heptan-exo-2-ol<sup>[48]</sup> (0.3%), endo-2-methylbicyclo[2.2.1]heptan-*exo*-2-yl formate<sup>[51]</sup> (2.5%), 1-methylbicyclo-[2.2.1]heptan-*exo*-2-yl formate<sup>[51]</sup> (1.3%), **27a** (0.88%), **27b** (0.85%), **24** (14.7%), and **28** (0.2%).

*1-Methylbicyclo*[2.2.1]*hept-exo-2-yl p-Toluenesulfinate* (**27**): The standard sulfinylation procedure (see **13**) was applied to 1-methylbicyclo[2.2.1]*heptan-exo-2-ol*<sup>[26a,52]</sup> (0.51 g, 4.0 mmol) to give 1.0 g (95%) of **27** as a mixture of diastereomers (1:1, GC). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 16.72, 16.90 (1-CH<sub>3</sub>), 21.43 (Ar-CH<sub>3</sub>), 29.76, 29.85 (CH<sub>2</sub>), 32.93, 33.01 (CH<sub>2</sub>), 36.14, 36.28 (CH), 41.22 (CH<sub>2</sub>), 42.06, 42.49 (CH<sub>2</sub>), 82.90, 83.71 (CH), 124.94, 125.15 (CH), 129.43, 129.46 (CH), 142.28 (C), 142.73 (C). – C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S (264.4): calcd. C 68.15, H 7.63; found C 68.23, H 7.62.

endo-2-Methylbicyclo[2.2.1]hept-exo-2-yl p-Tolyl Sulfone (24): The rearrangement of 25a, b (0.50 g, 1.9 mmol) in formamide (70°C, 4 h), followed by HPLC (Polygosil 60-10-CN, hexane/ether, 9:1) of the product mixture, afforded 40 mg (8%) of 24, m.p. 93°C.  $^{-1}$ H NMR (CDCl<sub>3</sub>):  $\delta = 1.06-1.23$  (m, 3H), 1.28 (s, 3H), 1.37 (m, 1H), 1.48-1.62 (m, 2H), 2.28-2.37 (m, 2H), 2.42 (s, 3H), 2.47-2.55 (m, 2H), 7.32 and 7.55 (AA'BB', 4H).  $^{-13}$ C NMR (CDCl<sub>3</sub>):  $\delta = 21.82$  (CH<sub>3</sub>), 22.13 (CH<sub>3</sub>), 26.13 (CH<sub>2</sub>), 27.69 (CH<sub>2</sub>), 37.54 (CH), 39.02 (CH<sub>2</sub>), 40.62 (CH<sub>2</sub>), 43.66 (CH), 68.97 (C), 129.64 (CH), 130.40 (CH), 134.32 (C), 144.43 (C).  $- C_{15}H_{20}O_2S$ (264.4): calcd. C 68.15, H 7.63; found C 68.07, H 7.55.

1-Methylbicyclo[2.2.1]hept-exo-2-yl p-Tolyl Sulfone (28): To a solution of 1-methyl-bicyclo[2.2.1]hept-endo-2-yl p-bromobenzenesulfonate (29)<sup>[19b]</sup> (0.50 g, 1.45 mmol) in acetone (25 ml) was added lithium p-toluenethiolate (0.19 g, 1.46 mmol). The mixture was heated at 80°C for 12 h (sealed ampule) and was then diluted with diethyl ether (100 ml). The solution was washed with water, dried (MgSO<sub>4</sub>), and concentrated in vacuo. HPLC (Polygosil 60-10-CN, hexane/ether, 9:1) of the residue afforded 0.15 g (45%) of crude 1-methylbicyclo[2.2.1]hept-exo-2-yl p-tolyl sulfide (30). - <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 0.88 - 2.05$  (m, 8H), 1.18 (s, 3H), 2.18 (br. s, 1H), 2.30 (s, 3H), 3.18 (m, 1H), 7.05 and 7.27 (AA'BB', 4H). To a solution of 30 (0.15 g, 0.65 mmol) in acetic acid (1 ml) was added 30% H<sub>2</sub>O<sub>2</sub> (0.4 ml). The mixture was heated at 90°C for 30 min, and stirring was continued for 48 h at room temp. On dropwise addition of water, a precipitate was formed which was filtered off and purified by HPLC (as above) to give 0.10 g (59%) of 28, m.p. 114°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.12$  (ddt, J = 10.0/2.6/1.2Hz, 1H), 1.16 (m, 1H), 1.24-1.36 (m, 2H), 1.39 (dt, J = 12.5/5.2Hz, 1H), 1.48 (s, 3H), 1.65 (m, 1H), 1.87 (dddd, J = 13.3/6.3/4.4/2.7 Hz, 1H), 1.93 (dq, J = 10.0/2.0 Hz, 1H), 2.23 (br. t, J = 4.4Hz, 1H), 2.42 (s, 3H), 2.97 (dd, J = 8.5/6.3 Hz, 1H), 7.30 and 7.72 (AA'BB', 4H). - <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 18.65 (CH<sub>3</sub>), 21.54 (CH<sub>3</sub>), 29.72 (CH<sub>2</sub>), 35.67 (CH<sub>2</sub>), 36.01 (CH), 39.75 (CH<sub>2</sub>), 42.48 (CH<sub>2</sub>), 48.31 (C), 68.10 (CH), 128.30 (CH), 129.53 (CH), 137.03 (C), 143.89 (C).  $-C_{15}H_{20}O_2S$  (264.4): calcd. C 68.15, H 7.63; found C 68.20, H 7.69.

Tricyclo[4.3.1.0<sup>3,8</sup>]dec-exo-4-yl p-Toluenesulfinate (34): The standard sulfinylation procedure (see 13) was applied to tricyclo-[4.3.1.0<sup>3,8</sup>]decan-exo-4-ol<sup>[28a]</sup>, [4-<sup>2</sup>H]tricyclo[4.3.1.0<sup>3,8</sup>]decan-exo-4-ol (31)<sup>[28a]</sup>, and [<sup>18</sup>O]tricyclo[4.3.1.0<sup>3,8</sup>]decan-exo-4-ol<sup>[15]</sup> to give 93% of 34<sup>[28a]</sup>. The diastereomers (48:52) of 34 were separated by HPLC (Lichrospher Si 60-5, hexane/ether, 9:1), and the enantiomers of 34a (assignment arbitrary) were partially resolved (ee = 87-88%) on N-(3,5-dinitrobenzoyl)-(R)-phenylglycine coupled to aminopropylsilica (5 µm, hexane/propan-2-ol, 99:1). – 34a: M.p. 60–61°C (racemic mixture). –  $[\alpha]_D^{24} = 92.8 \pm 0.4$  (c = 1.99, acetone). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.28-1.39$  (m, 3H), 1.45 (dd, J = 11.0/2.5 Hz, 1H), 1.57-1.78 (m, 3H), 1.88-2.01 (m, 2H), 2.08-2.15 (m, 3H), 2.24 (q, J = 6.3 Hz, 1H), 2.40 (s, 3H), 2.43 (m,

# **FULL PAPER**

1H), 4.77 (q, J = 3.8 Hz, 1H), 7.30 and 7.58 (AA'BB', 4H).  $- {}^{13}C$ NMR (CDCl<sub>3</sub>):  $\delta = 21.76$  (CH<sub>3</sub>), 27.42 (CH), 32.42 (CH), 32.74 (CH<sub>2</sub>), 35.57 (CH<sub>2</sub>), 35.71 (CH), 37.17 (CH<sub>2</sub>), 39.46 (CH<sub>2</sub>), 40.90 (CH), 42.36 (CH<sub>2</sub>), 78.715 (<sup>18</sup>O-CH), 78.756 (<sup>16</sup>O-CH), 125.36 (CH), 129.81 (CH), 142.47 (C), 143.26 (C). - 34b: M.p. 89-90°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.26 - 1.39$  (m, 3H), 1.47 (dd, J = 11.0/2.5 Hz, 1H), 1.62-1.79 (m, 3H), 1.85-1.96 (m, 4H), 2.13 (m, 1H), 2.27 (br. q, J = 6.5 Hz, 1H), 2.39 (s, 3H), 2.71 (m, 1H), 4.78 (m, 1H), 7.28 and 7.57 (AA'BB', 4H).  $- {}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta = 21.75$ (CH<sub>3</sub>), 27.37 (CH), 32.52 (CH), 32.67 (CH<sub>2</sub>), 35.46 (CH<sub>2</sub>), 35.70 (CH), 36.80 (CH<sub>2</sub>), 39.39 (CH<sub>2</sub>), 40.54 (CH), 42.42 (CH<sub>2</sub>), 78.140 (18O-CH), 78.181 (16O-CH), 125.25 (CH), 129.84 (CH), 142.47 (C), 143.18 (C). - A solution of 34aA (0.20 g, 0.69 mmol) in formamide (12 ml) was heated at 120°C for 8.5 h (≥99% conversion). Analysis of the products by HPLC (Polygosil 60-10-CN, hexane/ether, 9:1) indicated the presence of 37 (67%), 38 (6%), 2-adamantanol (21%), and 39<sup>[52]</sup> (6%). Traces of exo-4-protoadamantanol and of exo-4protoadamantanyl formate were also detected. - An analogous reaction was performed with 34aB to give 134 mg (67%) of 37B whose diastereomers 37aB ( $\delta = 33.92, 90.7 \pm 0.5\%$ ) and 37bB ( $\delta$ = 33.75, 9.3  $\pm$  0.5%) were distinguished by <sup>13</sup>C NMR. – A solution of nonracemic 34aA (ee =  $88.2 \pm 0.5\%$ ) in formamide was kept at 120°C, and aliquots were taken after 1, 2, and 3 h. The ee of 37A was found to be 70.3, 70.7, and 69.7  $\pm$  0.5%, respectively, by HPLC on the chiral column described above. - The rearrangement of [<sup>18</sup>O]-**34bA** (56.9  $\pm$  0.3% <sup>18</sup>O) in formamide (120°C, 8.5 h) afforded 37A with 49.8  $\pm$  0.3% "ester"-<sup>18</sup>O, according to <sup>13</sup>C NMR. - A solution of 34aA (0.30 g, 1.03 mmol) in TFA (15 ml) was stirred for 40 min at 0°C (complete conversion). The products obtained after aqueous workup (see 13) were 37A (0.27 g, 90%) and 40<sup>[29a]</sup> (8%). – The same procedure was used to convert 34aB into 37B. In order to estimate the ratio of diastereomers, Eu(dpm)<sub>3</sub> (50 mg, 2.07 equiv.) was added to a solution of 37B (10 mg, 0.034 mmol) in CHCl<sub>3</sub> (0.7 ml).  $- {}^{2}$ H NMR (CHCl<sub>3</sub>):  $\delta = 5.76$  (2.6 ± 0.5%), 6.15 (97.4  $\pm$  0.5%). Alternatively, the signals of the deuterated carbon atoms were compared by <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 33.74 (2.9  $\pm$  0.5%), 33.91 (97.1  $\pm$  0.5%). – The reaction of nonracemic 34aA ( $ee = 86.9 \pm 0.5\%$ ) in TFA (0°C, 5 min) gave 37A with  $ee = 82.7 \pm 0.5\%$ . - The rearrangement of [<sup>18</sup>O]-34aA (55.6 \pm 0.3\%) <sup>18</sup>O) in TFA (0°C, 40 min) afforded 37A with 54.3  $\pm$  0.3% "ester"-<sup>18</sup>O, according to <sup>13</sup>C NMR.

*Tricyclo*[*3*.3.1.1<sup>3.7</sup>]*dec*-2-*y*l *p*-*Toluenesulfinate* (**37**A)<sup>[53]</sup>: Sulfinylation of 2-adamantanol by the standard procedure (see **13**) afforded 92% of **37A**, m.p. 96–97°C (reported<sup>[53]</sup> 95–96°C). – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.43-1.57$  (m, 2H), 1.6–1.9 (m, 9H), 1.98–2.06 (m, 2H), 2.13 (br. s, 1H), 2.48 (s, 3H), 4.48 (t, J = 3.5Hz, 1H), 7.28 and 7.58 (AA'BB', 4H). – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta =$ 21.49 (CH<sub>3</sub>), 26.73 (CH), 27.03 (CH), 31.17 (CH<sub>2</sub>), 31.22 (CH<sub>2</sub>), 33.44 (CH), 33.61 (CH), 36.37 (CH<sub>2</sub>), 36.48 (CH<sub>2</sub>), 37.19 (CH<sub>2</sub>), 81.889 (<sup>18</sup>O-CH), 81.929 (<sup>16</sup>O-CH), 124.91 (CH), 129.46 (CH), 142.18 (C), 142.91 (C).

*p*-*Tolyl Tricyclo*[*3.3.1.*]<sup>3,7</sup>]*dec-2-yl Sulfone* (**38**): The rearrangement of **34A** (0.40 g, 1.4 mmol) in formamide (120°C, 8.5 h), followed by HPLC (Polygosil 60-10-CN, hexane/ether, 9:1) of the product mixture, afforded 23 mg (6%) of **24**, m.p. 134–135°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 1.42–2.04 (m, 10H), 2.24–2.77 (m, 4H), 2.40 (s, 3H), 3.09 (br. s, 1H), 7.30 and 7.75 (AA'BB', 4H). – C<sub>17</sub>H<sub>22</sub>O<sub>2</sub>S (290.4): calcd. C 70.31, H 7.64; found C 70.21, H 7.51.

*Rearrangement of p-Toluenesulfonates:* To a solution of [<sup>18</sup>O]bicyclo[3.1.1]heptan-2-ol (**41**)<sup>[15]</sup> (80 mg, 0.71 mmol, 55.2  $\pm$  0.3% <sup>18</sup>O) in pyridine (1 ml) was added with stirring at 0°C *p*-toluenesulfonyl chloride (148 mg, 0.78 mmol). Stirring was continued for 16

h. The mixture was then diluted with diethyl ether (15 ml) and washed with 10% HCl and with aqueous NaHCO<sub>3</sub>. The organic phase was dried (MgSO<sub>4</sub>) and concentrated in vacuo. HPLC (Polygosil 100-5, hexane/ether, 9:1) of the residue afforded 0.15 g (79.5%) of bicyclo[2.2.1]hept-endo-2-yl p-toluenesulfonate (43)<sup>[54]</sup>, m.p. 29°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.07$  (dm, J = 13.5 Hz, 1H), 1.22-1.34 (m, 4H), 1.49 (m, 1H), 1.73-1.87 (m, 2H), 2.13 (br. s, 1H), 2.30 (br. s, 1H), 2.42 (s, 3H), 4.73 (dddd, J = 10.2/4.5/3.6/1.6Hz, 1H), 7.30 and 7.74 (AA'BB', 4H).  $- {}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta =$ 20.88 (CH<sub>2</sub>), 21.87 (CH<sub>3</sub>), 29.33 (CH<sub>2</sub>), 36.45 (CH), 36.82 (CH<sub>2</sub>), 37.24 (CH<sub>2</sub>), 41.30 (CH), 83.242 ( $^{18}$ O-CH, 36.0  $\pm$  0.3%), 83.288  $(^{16}\text{O-CH}, 64.0 \pm 0.3\%), 127.98$  (CH), 129.98 (CH), 134.45 (C), 144.71 (C). – A solution of  $[^{18}O]$ tricyclo $[4.3.1.0^{3.8}]$ decan-exo-4-ol  $(44)^{[15]}$  (0.10 g, 0.65 mmol, 54.5 ± 0.3% <sup>18</sup>O) in pyridine (2 ml) was treated analogously with p-toluenesulfonyl chloride (137 mg, 0.72 mmol) at 0°C (22 h) to give 118 mg (59%) of tricyclo[3.3.1.1<sup>3,7</sup>]dec-2-yl p-toluenesulfonate (46)<sup>[55]</sup>, m.p. 81-82°C. - <sup>13</sup>C NMR  $(CDCl_3): \delta = 21.87 (CH_3), 26.78 (CH), 27.03 (CH), 31.34 (CH_2),$ 32.89 (CH), 36.61 (CH<sub>2</sub>), 37.30 (CH<sub>2</sub>), 86.546 (<sup>18</sup>O-CH, 44.0 ± 0.3%), 86.595 (<sup>16</sup>O-CH, 56.0 ± 0.3%), 127.69 (CH), 129.95 (CH), 135.11 (C), 144.52 (C).

Rearrangement of Bicyclo[3.1.1]hept-2-yl 3,5-Dinitrobenzoate (47): According to the published procedure<sup>[11b]</sup>, a solution of [<sup>18</sup>O]bicyclo[3.1.1]heptan-2-ol (**41**)<sup>[15]</sup> (0.10 g, 0.88 mmol) in pyridine (2 ml) was treated with 3,5-dinitrobenzoyl chloride (0.22 g, 0.97 mmol) to give 0.25 g (92%) of 47, m.p. 74°C. - <sup>13</sup>C NMR  $(CDCl_3)$ :  $\delta = 23.21 (CH_2), 26.49 (CH_2), 26.79 (CH_2), 33.58 (CH_2),$ 33.69 (CH), 38.72 (CH), 78.301 (<sup>18</sup>O-CH, 55.2 ± 0.3%), 78.343 (<sup>16</sup>O-CH, 44.8 ± 0.3%), 122.37 (CH), 129.59 (CH), 134.84 (C), 148.80 (C), 161.97 (C). - A solution of 47 (0.19 g, 0.62 mmol) in TFA (10 ml) was stirred for 7 h at 22°C. The mixture was diluted with diethyl ether (80 ml) and washed with aqueous NaHCO<sub>3</sub>. The organic phase was dried (MgSO<sub>4</sub>) and concentrated in vacuo. HPLC (Polygosil 100-5, hexane/ether, 9:1) of the residue afforded 135 mg (71%) of 48 and 49 (92:8). - 48<sup>[56]</sup>: M.p. 121-122°C. -<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.18$  (dt, J = 13.8/3.5 Hz, 1H), 1.37 - 1.53(m, 4H), 1.65 (m, 1H), 1.83 (m, 1H), 2.13 (dddd, J = 13.8/10.3/4.3/3.0 Hz, 1H), 2.31 (br. t, J = 4.3 Hz, 1H), 2.65 (br. t, J = 3.5 Hz, 1H), 5.25 (dtd, J = 10.3/3.5/1.5 Hz, 1H), 9.08 (d, J = 2.1 Hz, 2H), 9.15 (t, J = 2.1 Hz, 1H).  $- {}^{13}$ C NMR (CDCl<sub>3</sub>):  $\delta = 21.45$  (CH<sub>2</sub>), 29.53 (CH<sub>2</sub>), 36.76 (CH), 37.14 (CH<sub>2</sub>), 37.62 (CH<sub>2</sub>), 40.69 (CH), 78.900 (<sup>18</sup>O-CH, 55.7  $\pm$  0.3%), 78.941 (<sup>16</sup>O-CH, 44.3  $\pm$  0.3%), 122.40 (CH), 129.48 (CH), 134.58 (C), 148.88 (C), 162.72 (C). -**49**<sup>[54a,56]</sup>: M.p. 104–105°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.11-1.25$ (m, 2H), 1.27 (ddg, J = 10.0/2.5/1.2 Hz, 1H), 1.48 (m, 1H), 1.56-1.67 (m, 3H), 1.86 (ddd, J = 13.5/7.0/2.5 Hz, 1H), 2.37 (br. s, 1H), 2.47 (br. d, J = 4.8 Hz, 1H), 4.92 (br. d, J = 7.0 Hz, 1H), 9.06 (d, J = 2.2 Hz, 2H), 9.13 (d, J = 2.2 Hz, 1H).  $- {}^{13}C$  NMR  $(CDCl_3): \delta = 24.42 (CH_2), 28.25 (CH_2), 35.70 (CH_2 + CH), 39.73$ (CH<sub>2</sub>), 41.83 (CH), 80.733 (<sup>18</sup>O-CH, 50.9 ± 0.3%), 80.776 (<sup>16</sup>O-CH, 49.1 ± 0.3%), 122.35 (CH), 129.47 (CH), 134.75 (C), 148.84 (C), 162.28 (C).

Rearrangement of Tricyclo [4.3.1.0<sup>3.8</sup>] dec-exo-4-yl 3,5-Dinitrobenzoate (**50**): According to the published procedure<sup>[28a]</sup>, a solution of [<sup>18</sup>O]tricyclo[4.3.1.0<sup>3.8</sup>] dec-exo-4-ol (44)<sup>[15]</sup> (0.12 g, 0.78 mmol) in pyridine (2 ml) was treated with 3,5-dinitrobenzoyl chloride (0.22 g, 0.97 mmol) to give 0.23 g (85%) of **50**, m.p. 157–158°C. – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 27.28 (CH), 32.41 (CH), 32.90 (CH<sub>2</sub>), 35.48 (CH<sub>2</sub>), 35.63 (CH), 35.77 (CH<sub>2</sub>), 38.74 (CH), 39.29 (CH<sub>2</sub>), 42.46 (CH<sub>2</sub>), 76.749 (<sup>18</sup>O-CH, 54.5 ± 0.3%), 76.793 (<sup>16</sup>O-CH, 45.5 ± 0.3%), 122.35 (CH), 129.49 (CH), 135.02 (C), 148.83 (C), 162.29 (C). – A solution of **50** (0.18 g, 0.52 mmol) in TFA (9 ml) was stirred for 7 h at 22°C. Aqueous workup (see **47**) afforded 145 mg (81%) of tricyclo[3.3.1.1<sup>3,7</sup>]dec-2-yl 3,5-dinitrobenzoate (**51**)<sup>[28a]</sup>, m.p. 157–158°C. – <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 26.77 (CH), 27.03 (CH), 31.85 (CH), 31.91 (CH<sub>2</sub>), 36.19 (CH<sub>2</sub>), 37.08 (CH<sub>2</sub>), 80.147 (<sup>18</sup>O-CH, 54.5 ± 0.3%), 80.191 (<sup>16</sup>O-CH, 45.5 ± 0.3%), 122.10 (CH), 129.24 (CH), 134.68 (C), 148.55 (C), 161.66 (C).

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<sup>\*</sup> Dedicated to Professor *Dieter Seebach* on the occasion of his 60th birthday.

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