13. Hindered Nucleophilic Displacement (S_N2) Reactions of 2*exo*- and 2*endo*-Norbornyl Derivatives. Norbornane[1]) Series 4

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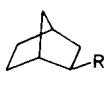
(28.X.80)

Summary

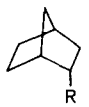
The reactions of 2*exo*- and 2*endo*-norbornyl bromide (**1e** and **2e**, respectively) in 90% ethanol with a large excess of potassium hydroxide, and of 2*exo*-norbornyl *p*-toluenesulfonate (**1g**) with excess sodium thiophenolate in methyl cellosolve, have been studied. They obey the first order rate law and are zero order with respect to the base-nucleophile. However, the ratio of 1,2- and 1,3-elimination to *exo*-substitution products depends strongly on the base-nucleophile concentration. Ion pair intermediates are indicated. The extreme inertness of 2-norbornyl derivatives in displacement reactions is due to severe steric hindrance of rearside nucleophilic attack, a feature they have in common with other bi- and tricyclic molecules bearing nucleofugal groups adjacent to one or two bridgehead atoms.

The literature contains surprisingly little evidence for bimolecular nucleophilic displacement reactions at C(2) of 2*exo*- and 2*endo*-norbornane derivatives[1]) **1** and **2**, respectively, when R represents a nucleofugal group.



1

R =



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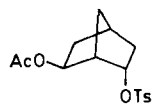

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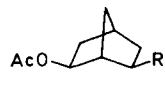

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a *p*-$BrC_6H_4SO_3$ **e** Br

b *p*-$CH_3C_6H_4S$ **f** C_6H_5S

c D **g** *p*-$CH_3C_6H_4SO_3$

d HO **h** C_2H_5O

i $CH_3OCH_2CH_2O$

a R = CH_3S

b R = Br

Claims that such reactions occur are based mainly on the formation of inverted products by reaction with strong nucleophiles under non-solvolytic conditions. Thus, 2*exo*- and 2*endo*-norbornyl *p*-bromobenzenesulfonate (**1a** and **2a**, respec-

[1]) According to the IUPAC nomenclature 'norbornane' is now called '8,9,10-trinorbornane'.

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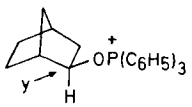
tively) are converted to the *endo*- and *exo*-sulfides **2b** and **1b**, respectively, by reaction with lithium thio-*p*-cresoxide (*p*-$CH_3C_6H_4SLi$) in acetone [1]; and the 2*endo*-*p*-bromobenzenesulfonate **2a** yields 2*exo*-deuterionorbornane (**1c**) with lithium aluminum deuteride in ether [2].

Recent examples of substitution with inversion are the conversion in high yields of 3-acetoxy-2*endo*-norbornyl *p*-toluenesulfonate (**3**) into the 2*exo*-sulfide **4a** with sodium methanethiolate (CH_3SNa) in *t*-butyl alcohol and to the 2*exo*-bromide **4b** with lithium bromide in dimethoxyethane [3]. Although the reaction conditions are conductive to concerted displacement reactions in all the above cases, two-step processes *via* intermediate ion pairs should also be considered.



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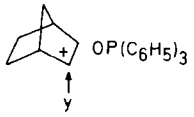

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A strong argument in favor of a concerted displacement reaction was supplied by *Schaefer & Weinberg* [4] who observed that optically active 2*exo*-norborneol (**1d**) yielded 12% of optically active inverted 2*endo*-bromide **2e** beside 79% of racemic 2*exo*-bromide **1e** when treated with triphenylphosphine and bromine in triglyme. The fact that attack on 2-norbornyl cations normally occurs predominantly, if not exclusively, on the *exo*-side [5][2]) strengthens their argument that the *endo*-bromide **2e** was formed by concerted displacement of triphenylphosphine oxide in the intermediate 2*exo*-norbornyloxy-triphenylphosphonium bromide (**5**, Y = Br^-). Subsequently *Tanigawa et al.* [7] reported a 72% yield of inverted *endo*-sulfide **2f** upon reaction of the phosphonium cation **5**, Y = C_6H_5SH, with thiophenol. However, even in these cases an intermediate norbornyl cation **6**, shielded on the *exo* side by the bulky triphenylphosphine oxide molecule, cannot be excluded.

On the other hand it is now well established that the solvolyses of 2*exo*- and 2*endo*-norbornyl sulfonates, such as **1a** and **2a**, in nucleophilic solvents (*e.g.* aqueous ethanol) take place without appreciable nucleophilic solvent participation [8] and must therefore be regarded as S_N1 processes.

Obviously, the question whether nucleophilic displacement reactions are feasible at C(2) of norbornane derivatives cannot be answered without resorting to product *and* kinetic measurements; *i.e.* a second order reaction, first order in the nucleophile, and inversion of configuration at C(2) in the product should be demonstrated in order to substantiate the afore-mentioned claims.

Consequently, three series of rate and product studies were carried out involving the reactions of 2*exo*- and 2*endo*-norbornyl bromide (**1e** and **2e**, respectively) with KOH in ethanol/water, 9:1 *(v/v)*, and of 2*exo*-norbornyl *p*-toluenesulfonate (**1g**) with sodium thiophenolate (C_6H_5SNa) in methyl cellosolve ($CH_3OCH_2CH_2OH$).

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[2]) Notable exceptions are recently published cases in which a nucleophilic 6*endo* substituent led to *endo*-cyclization [6].

Table 1. *First order rate constants*[a]) *for the reaction of 0.1* M 2exo- *and* 2endo-*norbornyl bromide with KOH in ethanol/water 9:1* (v/v)[b])

2*exo*-Bromide **1e** (T = 85.00°)		2*endo*-Bromide **2e** (T = 110.00°)	
KOH [mol/l]	$k \cdot 10^4$ [s^{-1}]	KOH [mol/l]	$k \cdot 10^4$ [s^{-1}]
–	2.11	–	1.10
0.102	2.27	0.102	0.68
0.204	2.24	0.204	0.67
0.510	2.07	0.510	0.72
1.02	1.65	1.02	0.79

[a]) Average of 2–4 runs; mean deviation ±4%.
[b]) Measured by titration of bromide ion with $AgNO_3$.

Results. In the first two reactions 90% ethyl alcohol was chosen as the solvent because it dissolves the bromides **1e** and **2e** and KOH in sufficiently high concentrations to favor a second order reaction. Nevertheless, in the range of concentrations employed, *i.e.* 0.1 M in **1e** and **2e** and zero to 1.0 M in KOH, the reactions accurately obeyed the first order rate law and were zero order in KOH. As *Table 1* shows the addition of increasing amounts of KOH to **1e** produces first a 7.5% increase and then a 22% decrease of the first order rate constant. These fluctuations are probably caused by the turn of a positive ionic strength effect into a negative one as more water is bound by solvation to KOH. In the *endo* series the rate constants first drop markedly upon addition of KOH only to increase again by 16%.

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Table 2. *Yields of products (in %) from the reaction of 0.1* M 2exo- *and* 2endo-*norbornyl bromide with KOH in ethanol/water 9:1* (v/v)

	KOH [mol/l]	Norbornene (**7**)	Nortricyclene (**8**)	2*exo*-Ethoxynorbornane (**1h**)	2*exo*-Norborneol (**1d**)
2*exo*-Bromide[a])	–	2	6	88	4
1e	0.102	2.5	8	82	7.5
	0.204	4	21	71	4
	0.510	7	34	55	4
	1.02	18.5	43	37	1.5
2*endo*-Bromide[b])	–	<0.1	0.1	75	24
2e	0.102	0.1	17	60	23
	0.204	2	15	61	22
	0.510	6	18	58	18
	1.02	13	20	54	13

[a]) T = 85°. [b]) T = 110°.

Table 3. *First order rate constants*[a]) *for the reaction of* 2exo-*norbornyl* p-*toluenesulfonate* (**1g**) *with* C_6H_5SNa *in methyl cellosolve at 50.0°*

1g [mol/l]	C_6H_5SNa [mol/l]	$k \cdot 10^4$ [s^{-1}]
0.50	–	0.97 ± 0.04
0.50	0.50	1.51 ± 0.02
0.52	0.52	1.56 ± 0.03
0.48	0.98	2.17 ± 0.06

[a]) Average of two runs.

Table 4. *Yields of products (%) from the reaction of 0.50*M 2exo-*norbornyl* p-*toluenesulfonate with* C_6H_5SNa *in methyl cellosolve at 50°*

C_6H_5SNa [mol/l]	Norbornene (7)	Nortricyclene (**8**)	2*exo*-Norbornyl phenyl sulfide (**1f**)	2*exo*-(2'-Methoxy-ethoxy)norbornane (**1i**)
–	4	15	–	81
0.54	1.5	27	12	60
0.98	3	31	25	41

The reaction of the bromides **1e** and **2e** with KOH in 90% ethyl alcohol led to four products, namely 2-norbornene (**7**), nortricyclene (= tricylco[2.2.1.$0^{2,6}$]heptane; **8**), 2*exo*-ethoxynorbornane (**1h**) and 2*exo*-norborneol (**1d**), the relative yields of which varied considerably with base concentration *(Table 2)*[3]).

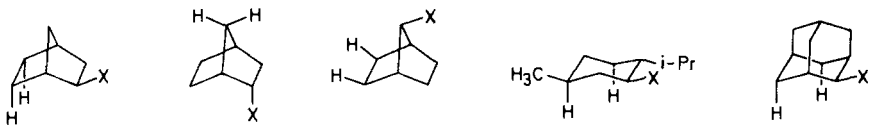
The reactions of 2*exo*-norbornyl *p*-toluenesulfonate (**1g**) with varying amounts of sodium thiophenolate in methyl cellosolve again obeyed the first order rate law and were zero order with respect to the strong nucleophile C_6H_5SNa *(Table 3).* However, a considerable positive salt effect was observed, since doubling the salt concentration led to a 40% increase of the rate constant. The product consisted of a mixture of norbornene (**7**), nortricyclene (**8**), 2*exo*-norbornyl phenyl sulfide (**1f**) and 2*exo*-(2'-methoxyethoxy)norbornane (**1i**) in yields which were dependent on the concentration of the sodium salt *(Table 4).* These results suggest that previous claims that displacement reactions occur at C(2) of norbornane should be checked by kinetic methods.

Discussion. – As *Table 1* shows the rates of 0.1 M solutions of 2*exo*- and 2*endo*-norbornyl bromide (**1e** and **2e**, respectively) obey the first order rate law and are independent of KOH concentration in the range studied (0.1–1.0 M). Small fluctuations of the rate constants can be ascribed to ionic strength effects and do not affect the conclusion that KOH does not participate in the rate-determining ionization step.

On the other hand product composition depends markedly on base-nucleophile concentration *(Table 2)*, which proves that KOH participates in the fast step leading to products. These conclusions also apply to the reaction of the strong nucleophile thiophenolate ion with 2*exo*-norbornyl *p*-toluenesulfonate (**1g**) (*Tables 3* and *4*).

[3]) The product distribution was determined by gas chromatography.

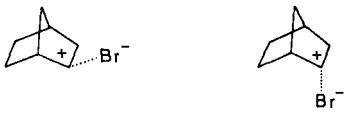
Taken in conjunction with the aforementioned solvolyses studies [8], these results indicate that 2*exo*- and 2*endo*-norbornyl derivatives are unusually inert towards nucleophilic (S_N2) displacement at C(2).



9 **10** **11** **12** **13**

This inertness must be attributed to severe steric hindrance to rearside attack at C(2) of *exo*- and *endo*-norbornane derivatives, due to the H-atoms at C(5), C(6) and C(7) [9], as illustrated in **9** and **10**. Obstruction of the reaction site by CH-groups is also pronounced in 7-norbornyl derivatives **11** [9] [10] and in rigid chair-form cyclohexanes, such as menthyl **12** [8b] and 2-adamantyl derivatives **13** [11] [8b]. According to molecular models *hindrance to rearside attack by nucleophiles is expected in bi- and tricyclic molecules in which the nucleofugal group is adjacent to one or two bridgehead atoms*[4])[5]). Since the positive charge generated in the ionization step cannot be transferred to an external nucleophile it will tend to be stabilized internally by induction, C,H- and C,C-hyperconjugation, rearrangement or fragmentation [12]. If these internal modes of stabilization are also lacking, very low reactivity will result.

In the case of 2*exo*- and 2*endo*-norbornyl bromides and *p*-toluenesulfonates the conclusion is that they ionize without nucleophilic assistance, *i.e.* they react by the S_N1 mechanism, even in the presence of high concentrations of base-nucleophile. However, the markedly different yields of norbornene (**7**), nortricyclene (**8**), 2*exo*-ether **1h** and 2*exo*-norborneol (**1d**), which result from the reaction of the bromides **1e** and **2e** with KOH in 90% ethanol *(Table 2)*, militate against a free carbenium ion as the common intermediate; more likely these products arise by attack of the base-nucleophile on the stereoisomeric ion pairs **14** and **15**[6]).



14 **15**

The variation of product composition as the concentration of the KOH-solution is increased is noteworthy. In the absence of base substitution leading to *exo*-ether **1h** and *exo*-alcohol **1d** far outweighed 1,2- and 1,3-elimination, as also observed in dioxane/water 7:3 [6]. However, as the concentration of the KOH-solution was

[4]) A similar steric situation is found in the acyclic 1,2,2-trimethylpropyl (pinacolyl) derivatives $(CH_3)_3C-CH(CH_3)X$ [9].

[5]) Nucleofugal groups at the bridgehead itself are necessarily inaccessible to rearside attack.

[6]) It is of course recognized that the cations can undergo rapid degenerate rearrangement before products are formed.

raised elimination increased at the expense of substitution. Reaction of a tenfold excess of KOH with the *exo*-bromide **1e** led to a substitution/elimination ratio of 0.6:1; with the *endo*-bromide **2e** this ratio was reversed to 2:1. This reversal reflects the easier access of reagents to the *exo* side of the *endo* ion pair **15**. It is also noteworthy that 1,3-elimination to nortricyclene (**8**) outweighed 1,2-elimination to norbornene **7** in both series and at all concentration of the KOH-solutions[7]).

In the reaction of 2*exo*-norbornyl *p*-toluenesulfonate (**1g**) with sodium thiophenolate in methyl cellosolve 1,2- and 1,3-elimination again accompanied substitution to the *exo*-thioether **1f** and the *exo*-methoxyethyl ether **1i**. Formation of the latter products with complete retention of configuration confirms the formation of a cationic intermediate which undergoes *exo*-attack by solvent and by the thiophenolate ion, and which yields increasing amounts of nortricyclene as the concentration of the base-nucleophile $C_6H_5S^-$ is raised.

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Experimental Part

General remarks. Melting points (m.p.) were determined on a *Kofler* block and are corrected (±1°). Analyses by gas chromatography (GLC.) were carried out on the *Perkin-Elmer* models F11 and Sigma 3.

Syntheses. - The *2exo-norbornyl bromide* (**1e**) [14] and its *2endo-isomer* **2e** [15] were prepared according to known procedures. Spectral and physical (b.p.) data were in agreement with the literature and samples were shown to be pure by GLC. (5% *FFAP* on *Chromosorb W*, 90°). The *2exo-Norbornyl* p-*toluenesulfonate* (**1g**) was prepared according to [16]; after crystallization from ether/pentane, m.p. 55–56° ([16]: m.p. 53–56°). Tricyclo[2.2.1.$0^{2,6}$]heptane (nortricyclene; **8**) was prepared according to [17]. Norbornene (**7**) and 2*exo*-norborneol (**1d**) were commercially available *(Aldrich)*.

Preparation of 2exo-*ethoxynorbornane* (**1h**)[8]). A mixture of 0.5 g (4.46 mmol) of **1d** in 8.0 g of ethyl iodide (51 mmol) was heated under reflux over 1.0 g (4.3 mmol) of silver(I)oxide for 4 h. Then further 0.6 g of Ag_2O were added and heating was continued for 4 h. Having repeated the procedure again the mixture was diluted with pentane and filtered through aluminum oxide (neutral, act. I) to remove the precipitate and the unreacted alcohol. The solvent was distilled off through a *Vigreux* column and the remaining ether **1h** purified by prep. GLC. (10% *SE 52* on *Chromosorb W*): volatile oil, b.p. 95–97°/740 Torr. - IR. (film): 2960 and 2870 (CH, alkyl), 1105 (C–O, ether). - ^{1}H-NMR. ($CDCl_3$): 0.85–1.65 (*m*, 8 H, 4 ring CH_2); 1.15 (*t*, 3 H, CH_3CH_2O); 2.25 (*m*, 2 H, H–C(1), H–C(4)); 3.30 (*m*, 1 H, H_{endo}–C(2)); 3.40 (*qa*, 2 H, CH_3CH_2O). - MS.: 140 (5.8, M^+), 111 (8.5), 94 (100), 66 (91).

$C_9H_{16}O$ (140.226) Calc. C 77.09 H 11.50% Found C 77.18 H 11.67%

The ether **1h** was also obtained by warming 5.6 g (21 mmol) of **1g** in 90 ml of abs. ethanol, containing 3 ml (21 mmol) of triethylamine, to 50° for 12 h. After adding pentane and washing with 1N HCl and water, the pentane solution was filtered through 30 g of Al_2O_3. Distillation yielded 2.42 g (82%) of **1h**, b.p. 95–97°/atmospheric pressure.

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[7]) This result is at variance with the behaviour of 2*exo*- and 2*endo* norbornyl *p*-toluenesulfonate with *t*-butoxide in *t*-butyl alcohol where norbornene formation predominated at higher base concentration [13].

[8]) This compound was prepared by Mr. *Bruno Schaub*.

Preparation of 2exo-*(2'-methoxyethoxy)norbornane* (**1i**). A solution of 4 g (15 mmol) of **1g** in 20 ml of 2-methoxyethanol (methyl cellosolve) and 1,21 ml (15 mmol) of pyridine was warmed to 60° for 15 h. The mixture was diluted with pentane and the solution washed with 2N HCl and water. Filtration through 50 g of Al_2O_3 and distillation through a *Vigreux* column yielded 1.98 g (78.5%) of pure **1i**, b.p. 218°. – IR. (film): 2960 and 2870 (CH), 1130 and 1100 (ether). – ^{1}H-NMR. ($CDCl_3$): 0.85–1.7 (*m*, 8 H, 4 ring CH_2); 2.15–2.5 (*m*, 2 H, H–C(1), H–C(4)); 3.2–3.7 (*m*, 1 H, H–C(2)); 3.35 (*s*, 3 H, CH_3O); 3.48 (*s*, 4 H, OCH_2CH_2O).

$C_{10}H_{18}O_2$ (170.25) Calc. C 70.54 H 10.66% Found C 70.38 H 10.67%

Preparation of 2exo-*norbornyl phenyl sulfide* (**1f**). To a solution of 0.1 g (4.35 mmol) of sodium in 9 ml (87.4 mmol) of thiophenol were added 1.4 g (5.27 mmol) of **1g**. The mixture was heated to 60° for 15 h, 20 ml of petroleum ether were added and the organic phase was extracted with 2N NaOH. The organic solution was concentrated to 5 ml when needles of dithiophenol separated upon cooling. The filtrate was diluted with petroleum ether and passed through 20 g of Al_2O_3. After evaporation to dryness 0.81 g (75%) of oily **1f** were obtained as a colorless oil. – IR. (film): 685, 735, 2870 and 2955 (CH), 1585 (arom.). – ^{1}H-NMR. ($CDCl_3$): 1.0–2.0 (*m*, 8 H, 4 CH_2); 2.2 (*m*, 2 H, H–C(1) and H–C(4)); 3.1 (*m*, 1 H, H–C(2)); 7.15 (*s*, 5 H, C_6H_5S).

$C_{13}H_{16}S$ (204.337) Calc. C 76.44 H 7.90 S 15.67% Found C 76.48 H 7.95 S 15.38%

Rate measurements. – The ethanol/water mixture 9:1 *(v/v)* was prepared by mixing 1000 g of 'superdry' ethanol (distilled over calcium) and 141.1 g of twice distilled water. Methyl cellosolve was purified by distillation over sodium, b.p. 123–124°.

Rates were followed by titration of the reaction solution contained in at least 18 ampoules. These were immersed in a thermostat (constancy ± 0.02°) for various lengths of time and then cooled in an ice bath.

In the case of the bromides **1e** and **2e** 5-ml aliquots were taken from the ampoules with an automatic pipette, added to 20 ml of 1N nitric acid/96% ethyl alcohol 1:1, and covered with a layer of 5 ml of petroleum ether. The bromide ions in the aqueous layer were titrated with 0.1N silver nitrate. The KOH-solutions in ethanol/water 9:1 *(v/v)* were prepared by dissolving clean potassium pieces in the solvent until it was approximately 2N in KOH, then diluting to the required molarity and checking by titration with 1.0N HCl.

Sodium thiophenolate solutions in methyl cellosolve were prepared by dissolving thiophenol in solutions of the sodium salt of methyl cellosolve ($CH_3OCH_2CH_2ONa$) in methyl cellosolve[9]). The latter were obtained by adding sodium to the solvent and titrating with 1.0N HCl. The reactions with **1g** were followed by titrating 5-ml aliquots of the alkaline solutions with 1.0N HCl and bromocresol green; acidic solutions were titrated with aqueous NaOH-solution and phenolphthalein.

Rate constants were calculated with the aid of a computer program. The experimental points coincided with the calculated first order curve with a mean deviation of ± 3.6%.

Preparative solvolyses were carried out under the same conditions as the kinetic runs. Reaction solutions were injected directly into the GLC. apparatus, *i.e.* model F11 (5% *FFAP* on *Chromosorb W*) for the bromides **1e** and **2e**, and model Sigma 3 (10% *FFAP* on *Chromosorb W*) for **1g**. Peak areas were calibrated with authentic samples.

[9]) Alkaline solutions of sodium thiophenolate were kept under argon to prevent oxidation to dithiophenol.

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