63. Reduction of 5,6-Dimethylidene-*exo*-2,3-epoxynorbornane with Metal Hydrides. Efficient Syntheses of 6-Methyl-5-methylidene-*anti*-3-nortricyclanol and of 2,3-Dimethylidene-*anti*-7-norbornanol

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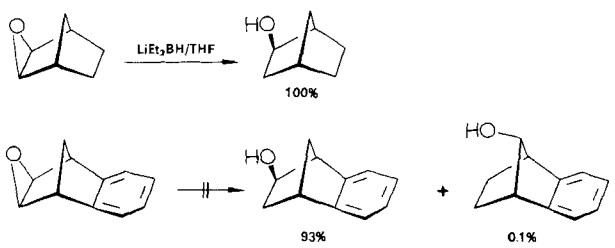
Summary

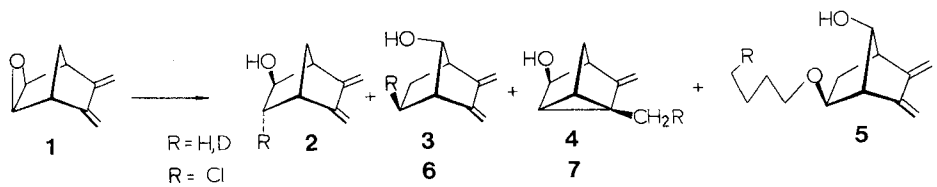
5,6-Dimethylidene-*exo*-2,3-epoxynorbornane (**1**) is reduced slowly by $LiAlH_4$ in boiling tetrahydrofuran (THF) and furnishes a mixture of 5,6-dimethylidene-*exo*-2-norbornanol (**2**), 2,3-dimethylidene-*anti*-7-norbornanol (**3**) and principally 6-methyl-5-methylidene-*anti*-3-nortricyclanol (**4**). The yield of **4** is the highest for low initial concentrations of $LiAlH_4$; it decreases in favour of alcohols **2** and **3** at high concentration of $LiAlH_4$. The reduction of **1** with AlH_3 in THF yields **3** as the major product, thus revealing an efficient synthesis of 7-substituted-2,3-dimethylidenenorbornane derivatives. No alcohol **2** could be isolated by $LiEt_3BH$ reduction of **1**. $LiAlD_4$ reduces **1** into the monodeuterated alcohols **2**-d, **3**-d and **4**-d. The deuterium label is found in the *endo*-position at C(3) in **2**-d, in the *exo*-position at C(5) in **3**-d and in the methyl group of the tricyclic alcohol **4**-d. Mechanistic limits for the formation of **2**, **3** and **4** are discussed briefly.

Introduction. – 5,6-Dimethylidene-*exo*-2,3-epoxynorbornane (**1**) is easily obtained from cyclopentadiene and *trans*-1,4-dichloro-2-butene in a three step synthesis [1]. This fact together with the presence of the epoxide was thought to render the diene **1** convenient starting material for the preparation of 2,3-dimethylidenenorbornane derivatives substituted in the bicyclic skeleton. In particular, we planned to prepare the 5,6-dimethylidene-*exo*-2-norbornanol (**2**) by reduction of **1** with the lithium triethylborohydride ('super hydride'), a strong nucleophile convenient for the facile reduction of both hindered and bicyclic epoxides without inducing rearrangements arising from carbocationic intermediates [2].



When the epoxy-diene **1** was treated in conditions similar to those used by *Brown et al.* [2b] for the reduction of *exo*-2,3-epoxynorbornane (or benzonorbornadiene epoxide) with $LiEt_3BH$, we were unable to isolate a trace of the expected 5,6-dimethylidene-*exo*-2-norbornanol (**2**). Only 6-methyl-5-methylidene-*anti*-3-nortricyclanol (**4**, R = H) could be isolated in a low yield. We then investigated the reactivity of **1** toward other metal hydrides, *e.g.*: $LiAlH_4$ ($LiAlD_4$) and AlH_3 and found that the outcome of these reductions depends strongly upon the reaction conditions.

Results. – *Table 1* summarizes the results obtained for the hydride reduction of 5,6-dimethylidene-*exo*-2,3-epoxy-norbornane (**1**) with $LiEt_3BH$, $LiAlH_4$ and AlH_3 in tetrahydrofuran (THF). In the presence of a 2 to 10 fold molar excess of $LiAlH_4$ at 0.02 to 0.1 M initial concentration, **1** is reduced relatively slowly into the tricyclic alcohol **4**. By increasing the initial concentration of $LiAlH_4$, the yield in **4** decreases



and some norbornanol **2** is formed together with some 2,3-dimethylidene-*anti*-7-norbornanol (**3**). These three alcohols can be separated easily by preparative gas chromatography (GC.) or by elution chromatography on SiO_2. The best yield of **3** was obtained when AlH_3 (prepared according to $2\ LiAlH_4 + H_2SO_4 \longrightarrow 2\ AlH_3 + 2\ H_2 + Li_2SO_4$ [3]) was used for the reduction of **1**. The ratio **3**/(**2** + **4**) was found to increase with the dilution of AlH_3. The corresponding alcoholates of **2**, **3** and **4** were found to be stable under the conditions used for the $LiAlH_4$ and AlH_3 reductions. A small amount of compound **5** bearing an alcohol and ether function was found in the reaction mixture when AlH_3 was used as reducing agent.

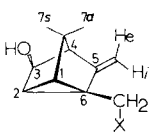
The structure of alcohols **2**–**5** were determined by their spectroscopic data (UV., IR., ^{1}H- and ^{13}C-NMR., MS.) and by their elementary analysis. Only the dienes **2**, **3** and **5** furnished the expected *Diels-Alder* adducts with tetracyanoethylene (TCE) or dimethyl acetylenedicarboxylate (DAD). Alcohol **2** was identical with 5,6-dimethylidene-*exo*-2-norbornanol (mixed melting point of the corresponding adducts with TCE) obtained by another route [4]. The diene **3** had physical and spectroscopic characteristics identical with those reported by *Tanida et al.* [5] for 2,3-dimethylidene-*anti*-7-norbornanol prepared by a much more complicated route. The AlH_3 reduction of **1** is thus an efficient, new method for the preparation of 7-substituted 2,3-dimethylidene-norbornanes. The structure of the tricyclic alcohol **4** is supported by comparison of its ^{13}C-NMR. characteristics (δ (C) and C,H-coupling constants ^1J) with those reported for nortricyclanol and other nortricyclane derivatives [6]. The addition of HCl to **1** (ether or pentane, 0°) yielded a 3:1 mixture of the chloro-alcohols **6** and **7** whose spectroscopic data were analogous to those of **3** and **4**, respectively (see experimental section).

Table 1. *Reduction of 5,6-dimethylene-exo-2,3-epoxynorbornane* (**1**) *with metal hydrides in THF (60–65°)*

Metal hydride	Initial conc. of the metal hydride [M]	Initial conc. of **1** [M]	Molar excess of the metal hydride	Time of reaction [h]	Isolated material [%]	Product distribution [%]					
						1	**2**	**3**	**4**	**5**	unknown
$LiEt_3BH$	0.5	0.092	5.4	6	< 10	–	–	–	100	–	
,,	0.5	0.19	2.6	6	< 10	–	–	–	100	–	
$LiAlH_4$	0.105	0.034	3.1	110	54	–	< 0.5	< 0.5	> 99	–	
,,	0.21–0.27	0.027–0.105	10–2	24	60–62	10±2	8±1	0–0.5	82±3	–	–
,,[a])	0.70	0.096	7.3	72	71	9±1	37±2	12±1	38±2	–	4±1
AlH_3[a])	0.131	0.126	1.04	22	63	–	1–2	70±2	24±1	4±1	< 1
,,	0.013	0.013	1.	30	72	15±1	1–2	59±2	13±1	4±1	7±1

[a]) Similar conditions were used for the reduction of **1** with metal deuterides in THF.

Table 2. *^1H- and ^{13}C-NMR. characteristics of alcohols* **4** (X = H) *and* **7** (X = Cl). *Effects of added LIS reagents on chemical shifts* (LIS extrapolated to [LIS reagent]/[alcohol] = 1)



		^{1}H-NMR.	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H(7s)	H(7a)	H(e)	H(i)	$-CH_2-X$
	4	δ(H):	1.51 (*m*, 1 H)	1.42 (*m*, 1 H)	3.88 (*m*, 1 H)	2.18 (br.*s*, 1 H)	1.87 (*m* with *a d*, 10.: 1 H)	1.58	4.46 (br.*s*, 1 H)	4.68 (br.*s*, 1 H)	1.19 ppm[b]) (*s*, 3 H)
		LIS[a]):	4.16	7.06	13.37	6.47	9.23	4.06	1.20	1.09	1.80 ppm[b])
	7	δ(H):	[c])	[c])	3.88 (*m*, 1 H)	2.20 (br.*s*, 1 H)	[c])	[c])	4.63 (br.*s*, 1 H)	4.74 (br.*s*, 1 H)	3.73 ppm[b]) (*s*, 2 H)
		^{13}C-NMR.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	CH_2=C(5)	$-CH_2-X$
	4	δ(C):	22.9	28.6	74.8	44.2	155.35	26.9	30.4	97.5	11.1 ppm[d])
		^1J(C,H):	(*d*, 178)	(*d*, 178)	(*d*, 154)	(*d*, 150)	(*s*)	(*s*)	(*t*, 137)	(*t*, 159)	(*qa*, 126)
		LIS[e]):	41.4	62.3	136.9	58.2	26.8	29.6	46.2	14.4	14.1 ppm[d])
	7	δ(C):	24.2	29.4	75.2	44.5	150.5	33.3	30.5	99.9	42.25 ppm[d])
		^1J(C,H):	(*d*, 178)	(*d*, 178)	(*d*, 154)	(*d*, 150)	(*s*)	(*s*)	(*t*, 136)	(*t*, 158)	(*t*, 151)

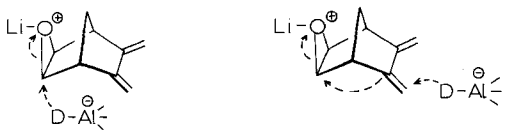
[a]) Eu(dpm)$_3$ in $CDCl_3$/40°; [b]) in $CDCl_3$/40°; [c]) δ(H) = 1.4–2.1 (*m*, 4 H); [d]) in $CDCl_3/CCl_4$ 1:1/30°; [e]) Yb(dpm)$_3$ in $CDCl_3/CCl_4$ 1:1/30°

Reduction of **1** with an excess of $LiAlD_4$ in THF (0.7 M; 7 fold excess) followed by hydrolysis with KOH/H_2O or KOD/D_2O yielded a mixture of monodeuterated (mass spectrometric evidence) alcohols **2**-d, **3**-d and **4**-d. There was no deuterium incorporation in **2**, **3** and **4** when KOD/D_2O was used for the work-up of the $LiAlH_4$ reduction products. The position of the deuterium label in **2**-d, **3**-d and **4**-d was determined by ^{1}H-NMR. analysis and with the help of lanthanide chelates (LIS reagents [7]; see experimental section). At least 95% of the deuterium in alcohol **2**-d is found in the *endo*-position at C(3); at least 95% of the deuterium label in **3**-d is located in the *exo*-position at C(5). Line shape analysis of the methyl multiplet of **4**-d as well as peak integration showed that at least 95% of the deuterium incorporated was located in the methyl group in the tricyclic alcohol.

AlD_3 reduction of **1** yielded a mixture of the monodeuterated alcohols **3**-d and **4**-d and compound **5**-d. In the latter the deuterium was located in the methyl group of the butyloxy chain.

Discussion. – The rigorous conditions required for the $LiAlH_4$ reduction of **1** illustrate the high resistance of the epoxide function in this bicyclic compound toward nucleophilic reagents. We have been unable to open **1** by prolonged heating in KOH/DMSO/18-crown-6 ether. In contrast, the 4,5-dimethylidene-1,2-epoxycyclohexane has been found to open in aqueous NaOH [8]. The extraordinary stability of the *exo*-2,3-epoxynorbornane derivatives toward strong nucleophilic reagents has been reported several times [2b] [9]. As expected from comparison with the reaction of *exo*-2,3-epoxynorbornane and benzonorbornadiene epoxide with metal hydrides [2b], **1** reacts faster with $LiEt_3BH$ than with $LiAlH_4$ in THF. The formation of the tricyclic alcohol **4** as sole product[1]) suggests that steric effects arising in the norbornane skeleton and the bulkiness of the "super hydride" prohibit the attack of the nucleophile on the *endo* site of **1**. Thus, the nucleophile prefers to attack the methylene carbon atom C(5′) or C(6′) to engender the nortricyclanol derivative **4** probably by an homoallyl S_N2'-type ring opening of the epoxide *(Scheme 1)*. Similar arguments explain the reduction of **1** with $LiAlH_4$. The bulkiness of the lithium aluminium hydride reagent due to aggregation (*cf.* [10]) can also play a role. However, it is possible that the Li^+ cation (*cf.* [11]) intervenes and accelerates the reactions by electrophilic assistance of the opening of the epoxide ring. Since we found more than 95% of the deuterium label in the *endo*-position at C(3) in **2**-d obtained in the $LiAlD_4$ reduction of **1**, it seems that the electrophilic opening of the epoxide does not precede the hydride attack that leads to **2** *(Scheme 1)*.

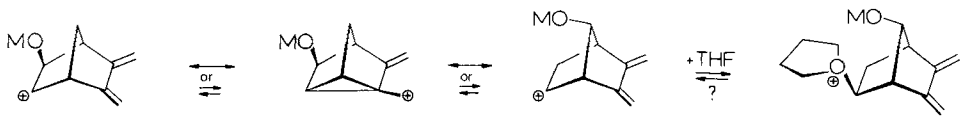
Scheme 1



[1]) The alcohols **2** and **3** are destroyed slowly when treated by a large excess of $LiEt_3BH$ in boiling THF. We have established that, nevertheless, if **2** and **3** were formed under the conditions used for the reduction of **1** with this reagent, they could not have been decomposed completely and that at least a fraction of these products should have been detected if formed.

The electrophilic ring opening of *exo*-2,3-epoxynorbornanes is considered to engender transient 3-oxy-2-norbornyl cationic species which normally rearrange into the more stable 7-oxy-2-norbornyl cation intermediates [12]. In our case, these species would be further stabilized as cyclopropylmethyl cationic intermediates [13] and are expected to generate *exo*-3-deuterio-5,6-dimethylidene-*exo*-2-norbornanol (instead of **2**-d) besides **3**-d and **4**-d. Therefore, if this mechanism *(Scheme 2)* is operative, it does not lead to **2** in the reduction of **1** by $LiAlH_4$.

Scheme 2



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The position of the deuterium label suggests that the 2-norbornanol **2** and the nortricyclanol **4** can be envisioned as arising from a direct nucleophilic attack of $LiAlH_4$ (or an aggregate in THF) at C(3) on the *endo* side and on the methylidene group in **1**, respectively *(Scheme 1)*. The formation of the 7-norbornanol derivative **3** would arise from the electrophilic opening of the epoxide ring *(Scheme 2)*[2]). It is expected that the distribution of the positive charge can also lead to the tricyclic alcohol **4**.

If the metal hydride is a stronger *Lewis* acid than $LiAlH_4$ (and its aggregate in THF), the probability of electrophilic ring opening of the epoxide will increase. In that case, the yield in 2-norbornanol derivative should decrease in favour of the 7-norbornanol and nortricyclanol derivatives **3** + **4**. This is indeed what is observed in the reduction at **1** by AlH_3 in THF. Furthermore, it is interesting to note that the ratio **3**/**4** increases as the initial concentration of AlH_3 is reduced. This can be understood by assuming that the addition of the hydride to the cationic intermediate arising from the electrophilic opening of the epoxide is intramolecular for **3** whereas it has to be intermolecular in the reaction yielding **4**. The electrophilic character of AlH_3 and the intermediacy of carbocationic species are demonstrated by the isolation of compound **5** bearing an ether and alcohol function (see *Scheme 2*). No deuterium could be detected in the *endo*-position at C(5) of **3**-d obtained in the AlD_3 reduction of **1**, *i.e.* **8** cannot be an intermediate for the formation of **3**.

The participation of the methylidene double bond homoconjugated to the epoxide is not without analogy. Norbornadiene epoxide is reduced by $LiAlH_4$ to yield *endo*-6-hydroxymethyl-bicyclo[3.1.0]hex-2-ene [14]. Intermediates of the cyclopropylmethyl cation type [13] are probably involved in these electrophilic ring openings of the epoxides by reducing agents (*cf.* [9a] [15]).

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[2]) Similarly, reduction of *exo*-2,3-epoxynorbornane with $LiAlD_4$ was found to generate a 92:2 mixture of *endo*-3-deuterio-*exo*-2-norbornanol and *exo*-2-deuterio-*syn*-7-norbornanol [9b].

Conclusion. – 6-Methyl-5-methylidene-*anti*-3-nortricyclanol (**4**) could be prepared by reduction of 5,6-dimethylidene-*exo*-2,3-epoxynorbornane (**1**) with $LiAlH_4$. The reduction of **1** with AlH_3 furnished 2,3-dimethylidene-*anti*-7-norbornanol (**3**) as major product thus uncovering a new, efficient method for the preparation of 7-substituted-2,3-dimethylidene-norbornanes. Electrophilic ring opening of the epoxide generating transient cationic species was found to compete with direct attack of the hydride on the methylidene double bond (homoallyl S_N2') in the metal hydride reduction of **1**.

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Experimental Part

The m.p. are not corrected on a Tottoli apparatus. – IR. spectra ($\tilde{\nu}$ [cm^{-1}]) on a *Beckman* IR-20A spectrometer. – UV. spectra on a *Carl Zeiss* RPQ 20 A/C instrument (λ_{max} [nm]; (ε), sh = shoulder). – Mass spectra (MS.(EI.)) at 70 eV with a *CEC* 21-490 Bell-Howell spectrometer (m^+/e[amu](% base peak)); MS. in chemical ionization mode (MS.(CI./ionizing gas).) on a GC./MS. system HP 5980A *(Hewlett-Packard)*. ^{1}H-NMR. spectra (δ [ppm], J [Hz]) on a *Varian* A 60A spectrometer. ^{13}C-NMR. spectra with a *Bruker* WP60 instrument (15.08 MHz) in FT. mode, using $CDCl_3$ ($30\pm2°$) as solvent and deuterium lock; chemical shift (δ(C)) to internal TMS, precision 0.1 ppm (spectrum width: 3750 Hz, 4096 points). Accuracy of ^1J(C,H) coupling constants (Hz) 1 Hz (s = singlet, br. = broad; d = doublet; t = triplet; m = multiplet; qa = quartet); $\delta_{TMS} = 0.0$ ppm. Elementary analysis were performed by the 'Microlabor' of the University of Geneva (Dr. *K. Eder*). $LiAlH_4$, $LiAlD_4$ (> 99% atom D) and D_2O (> 99.8%) were from *Fluka AG*, Buchs, Switzerland. The lanthanide chelates (LIS reagents) were from *Willow Brook Labs*, Waukesha, Wis., USA. Linear induced shifts of the δ(C) and δ(H) were observed for concentration ratios: $0.05 < [\text{LIS reagent}]/[\text{alcohol}] < 0.4$; a correlation coefficient ≥ 0.999 was obtained for up to 5–7 successive additions of the LIS reagent to $CDCl_3$ solutions of the alcohols. Analytical gas chromatography (GC.) with a HP 5712A chromatograph *(Hewlett-Packard)* and preparative GC. with a model *Aerograph, Wilkens Instruments and Research*, No. 31.012. Abbreviations: i.V. = *in vacuo*, RT. = room temperature, anh. = anhydrous.

trans-*5,6-Bis(chloromethyl)*-exo-*2,3-epoxynorbornane.* 115 g of a 40% solution of peracetic acid (0.767 mol) in 90 ml of ethyl acetate were added dropwise to a stirred solution of 53 g (0.277 mol) of *trans*-5,6-bis(chloromethyl)-norborn-2-ene [16] in 150 ml of ethyl acetate. After stirring for 5 h at 40° 200 ml of H_2O were added and the mixture was extracted 3 times with 100 ml of CH_2Cl_2. The organic extract was washed successively 3 times with an aq. sol. of $NaHCO_3$ and twice with H_2O; it was finally dried over anh. $MgSO_4$. The solvent was evacuated under reduced pressure and the epoxide was distilled: 48 g (84%), colourless oil; b.p. 100°/0.2 Torr. – IR. (film): 2980, 1460, 1390, 1330, 1310, 1300, 1010, 910, 860. – ^{1}H-NMR.(CCl_4): 3.8–3.4 (*m*, 4 H); 3.2 (*m*, 2 H); 2.7 (*m*, 1 H); 2.6 (*m*, 1 H); 2.3–1.7 (*m*, 2 H); 1.3 (*m* with a *d*, J = 10.0; 1 H); 0.95 (*m* with a *d*, J = 10.0; 1 H). – MS.(EI): 210 (0.1), 208 (0.6), 206 (1), 173 (1), 171 (3), 121 (11), 105 (11), 93 (14), 91 (41), 82 (100).

$C_9H_{12}Cl_2O$ (207.10) Calc. C 52.20 H 5.84% Found C 52.26 H 5.97%

5,6-Dimethylidene-exo-*2,3-epoxynorbornane* (**1**). 22.4 g (0.108 mol) of *trans*-5,6-bis(chloromethyl)-*exo*-2,3-epoxynorbornane mixed with 18 g (0.321 mol) of KOH were boiled in 100 ml of anh. ethanol for 3 days under N_2. 150 ml of H_2O were added and the mixture was extracted 5 times with 50 ml of pentane. The organic extract was washed with H_2O and dried over anh. $MgSO_4$. The solvent was

evacuated under reduced pressure by maintaining a reflux. The residue was distilled: 9.0 g (62%), colourless oil; b.p. 65°/15 Torr. This product contained less than 2% of volatile impurities (GC.). For a method yielding very pure epoxy-diene **1**, see [9c].

2,3-Dimethylidene-anti-*7-norbornanol* (**3**). 3.5 g (0.0261 mol) of **1** in 150 ml of anh. THF were added under N_2 to a solution of AlH_3 (0.024 mol) in 60 ml of anh. THF prepared according to [17]. The mixture was heated under reflux for 22 h. After cooling to 0°, 10 ml of a 90:10 mixture of THF:H_2O were added dropwise. After stirring for 1 h at RT., the precipitate was filtered off and the solution dried over anh. $MgSO_4$. The solvent was evacuated under reduced pressure. The residue was distilled (bulb to bulb) i.V.: 2.2 g (63%), mixture containing 1–2% of 5,6-dimethylidene-*exo*-2-norbornanol (**2**), 70± 1% of **3**, 24± 1% of the tricyclic alcohol **4** and 4–5% of the ether-alcohol **5** (GC., Carbowax 20M 5% on Chromosorb WAW 60/80 mesh). Column chromatography on SiO_2 (ethyl acetate/light petroleum 1:9) afforded 0.95 g (26.7%) of **3**. Its spectroscopic data were found identical to those reported by *Tanida et al.* [5].

6-Methyl-5-methylidene-anti-*3-nortricyclanol* (**4**). 1.1 g (0.0082 mol) of **1** in 40 ml of anh. THF were added in portions to a stirred mixture of 1.0 g (0.026 mol) of $LiAlH_4$ in 200 ml of anh. THF at 0° and under N_2. The mixture was heated at 60° for 4½ days and then cooled to 0°. 20 ml of a 20% aq. sol. of KOH and 200 ml of H_2O were added in succession. The white precipitate was filtered off and the solution extracted 5 times with 10 ml of ether. The ethereal extract was dried over anh. $MgSO_4$. After evacuation of the solvent, the tricyclic alcohol **4** was distilled under reduced pressure (bulb to bulb): 0.6 g (54%), colourless oil. – UV.(ethanol 96%): 205.5 (8000). – IR.($CHCl_3$): 3380, 2940, 2880, 1680, 1390, 1300, 1160, 1040, 880, 840. – ^{1}H-NMR. and – ^{13}C-NMR., see *Table 2*. – MS.(EI.): 137 (12), 136 (96), 121 (63), 108 (75), 105 (45), 92 (96), 91 (100), 77 (45).

$C_9H_{12}O$ (136.19) Calc. C 79.37 H 8.88% Found C 78.93 H 9.13%

3,5-Dinitrobenzoate of **4**. M.p.: 96–97°. – UV.(ethanol 96%): 208 (32600). – IR.(KBr): 3120, 2960, 2880, 1730, 1690, 1640, 1550, 1470, 1350, 1300, 1280, 1180, 1080, 1000, 880. – ^{1}H-NMR.($CDCl_3$): 9.3–9.0 (*m*, 3 H); 5.07 (*m*, 1 H); 4.87 (br. *s*, 1 H); 4.63 (br. *s*, 1 H); 2.60 (br. *s*, 1 H); 2.2–1.5 (*m*, 4 H). – MS.(EI.): 331 (21), 330 (100), 195 (66), 165 (10), 149 (39), 135 (94), 119 (20), 118 (70), 117 (29), 107 (37), 105 (18), 103 (17), 92 (21), 91 (57), 90 (51).

$C_{16}H_{14}N_2O_6$ (330.3) Calc. C 58.18 H 4.27 Found C 57.82 H 4.45%

exo-*2-Butoxy-5,6-dimethylidene*-syn-*7-norbornanol* (**5**). The first fraction obtained by column chromatography of the mixture isolated in the AlH_3/THF reduction of **1** (see preparation of **3**, here-above) was composed of the ether-alcohol **5**; the second fraction contained **3**, a third fraction contained **2** and **4**. After evacuation of the solvent, **5** was purified by bulb to bulb distillation i.V.: 2–3% (based on **1**), colourless oil. – UV.(isooctane): 258 (sh, 6470), 250 (9650), 244 (sh, 8660). – UV.(ethanol 96%): 257 (sh, 5660), 248.5 (8320), 243 (sh, 7700). – IR.(CCl_4): 3500, 3080, 2980, 2930, 1780, 1660, 1630, 1420, 1340, 1235, 1200, 1080, 890. – ^{1}H-NMR.(CCl_4): 5.22 (br. *s*, 1 H); 5.08 (br. *s*, 1 H); 4.88 (br. *s*, 1 H); 4.77 (br. *s*, 1 H); 3.8 (*m*, 2 H, H–C(2), H–C(7)); 3.5 (*m*, 2 H); 2.92 (*m*, 1 H, H–C(1)); 2.83 (*m*, 1 H, H–C(4)); 2.00 (*m*, 2 H, H*exo* –C(3), H*endo* –C(3)); 1.45 (*m*, 4 H); 0.93 (*m*, 3 H). Eu(dpm)$_3$ induced shifts on δ(H) confirmed the assignments given here and the structure of **5**. – MS.(EI.): 208 (<0.1), 190 (2), 134 (85), 119 (26), 117 (28), 106 (50), 105 (100), 91 (53).

$C_{13}H_{20}O_2$ (208,30) Calc C 74.96 H 9.68% Found C 75.51 H 9.42%

Reduction of **1** *by LiAlD$_4$/THF*. 1.1 g (0.0082 mol) of **1** in 15 ml of anh. THF were added under N_2 to a stirred suspension of 2.5 g (0.060 mol) of $LiAlD_4$ (>99% atom D) in 70 ml of anh. THF maintained at 0°. After heating at 60° for 3 days, the mixture was cooled to 0°. 20 ml of a 20% aq. sol. of KOH and 200 ml of H_2O were added in succession. The precipitate was filtered off and the solution extracted 5 times with 20 ml of ether. The organic extract was dried over anh. $MgSO_4$. The solvent was evacuated by distillation and the residue distilled i.V.: 0.8 g (71%), mixture of 9% of **1**, 37% of **2**-d, 12% of **3**-d, 38% of **4**-d and 4% of an unknown material. The deuterated alcohols were separated by preparative GC. (Carbowax 20M 10% on Chromosorb WAW 60/80 mesh; 3 m pyrex column, int. diameter: 8 mm; 120°; 60 ml/min H_2).

Analysis of the deuterated alcohols **2**-d, **3**-d *and* **4**-d. – **2**-d. – ^{1}H-NMR.($CDCl_3$) [4]: 5.34 (br. *s*, 1 H); 5.20 (br. *s*, 1 H); 5.04 (br. *s*, 1 H); 4.90 (br. *s*, 1 H); 4.06 (*m*, J=2, 1 H; H–C(2)); 2.85 (*m*, J=3.5 and 1.5, 2 H, H–C(1) and H–C(4)); 1.72 (*m*, J=9.5 and 1.5, 1 H, H*syn* –C(7)); 1.52 (*m*,J=3.5, 1 H, H*exo* –C(3)); 1.43 (*m*, J=9.5 and 1.5, 1 H, H*anti* –C(7)); – MS.(EI.).: 138 (2), 137 (21), 118 (12), 108 (25), 94 (30), 93 (23), 92 (100), 91 (81). The signal at 1.92 (*m*, J= 12.5, 6.0 and 2.5; 1 H, H*endo* –C(3)) of **2**. that could be well separated from the other peaks by adding $Eu(dpm)_3$, had completely disappeared.

3-d. – ^{1}H-NMR. ($CDCl_3/CCl_4$ 1:1)[proton assignments; relative slope of the effect of added $Eu(dpm)_3$ on δ(H)]: 5.15 (br. *s*, 2 H ['internal olefinic H', 1.62]); 4.73 (br. *s*, 2 H, ['external olefinic H', 2.13]); 3.81 (*m*, 1 H [H–C(7), 17.8]); 2.56 (*m*, 2 H [H–C(1) and H–C(4), 8.76]); 1.95 (*m*, 1 H, [H*exo* –C(6), 11.3]; 1.38 (*m*, 2 H [H*endo* –C(5) and H*endo* –C(6), 5.54]). – MS.(EI.): 138 (4), 137 (39), 122 (18), 118 (18), 109 (22), 108 (100), 107 (28), 106 (32), 105 (14), 94 (44), 93 (22), 92 (56), 91 (30).

4-d. ^{1}H-NMR.($CDCl_3$): same spectrum as that of **4** except for the 6-methyl group: an apparent *t* (J(D,H)≅2 Hz) was found at δ= 1.20 ppm that integrates for 2 H only. – MS.(EI.): 138 (11), 137 (100), 121 (45), 108 (58), 106 (37), 94 (42), 93 (95), 92 (58), 91 (47), 77 (32).

Reduction of **1** *with* AlD_3*/THF.* 1.75 g (0.013 mol) of **1** in 75 ml of anh. THF were added under N_2 to a solution of AlD_3 (0.012 mol) in 30 ml of anh. THF prepared from $LiAlD_4$ according to [17]. After heating under reflux for 22 h, the mixture was cooled to 0°. 5 ml of THF/H_2O 9:1 were added dropwise and the mixture stirred for 1 h at RT. The precipitate was filtered off and the solution dried over anh. $MgSO_4$. The solvent was evacuated under reduced pressure. The residue was transferred on a vacuum line and the deuterated alcohols were separated by preparative GC. (same conditions as above). The alcohols **3**-d, **4**-d and **5**-d were found to have incorporated only one deuterium atom (by ^{1}H-NMR., MS.(EI.), and MS.(CI.)). **3**-d and **4**-d were found identical to the deuterated alcohols obtained by reduction of **1** by $LiAlD_4$/THF. The ^{1}H-NMR.(CCl_4) spectrum of **5**-d was the same as that of **5** except for the terminal methyl group of the *n*-butoxy chain which showed a multiplet at δ=0.93 ppm that integrated for 2 H only. – MS. (Cl./CH_4) of **5**-d: 210 ([M+H]$^+$), 208 ([M–H]$^+$). – MS.(CI./CH_4) of **5**: 209 ([M+H]$^+$), 207 ([M–H]$^+$).

Addition of HCl to **1**. Gaseous HCl was bubbled slowly into a solution of 1.5 g (0.0119 mol) of **1** in 100 ml of anh. ether under N_2 and at 0°. The reaction was monitored by TLC. When the starting material **1** had completely disappeared, 20 ml of an aq. solution of $NaHCO_3$ were added slowly and the mixture was extracted twice with 10 ml of ether. The extract was dried over anh. $MgSO_4$. Removal of the solvent under reduced pressure afforded a colourless oil: 1.25 g (61%), 75±5: 25±5 mixture of *exo*-2-chloro-5,6-dimethylidene-*syn*-7-norbornanol (**6**) and 6-chloromethyl-5-methylidene-*anti*-3-nortricyclanol (**7**). **6** and **7** were isolated by preparative column chromatography on SiO_2 ($CHCl_3$); the first fraction was composed of **6**, the second one contained **7**.

6. – White solid, purified by sublimation i.V., m.p.: 60–61°. – UV.(isooctane): 256 (sh, 6900), 249 (9450), 242 (sh, 8200). – UV.(ethanol 96%): 256 (sh, 6850), 248.5 (9400), 242 (sh, 8330). – IR.(CH_2Cl_2): 3580, 2940, 1640, 1400, 1180, 1080, 990, 890. – ^{1}H-NMR.($CDCl_3$): 5.35 (br. *s*, 1 H); 5.25 (br. *s*, 1 H); 5.05 (br. *s*, 1 H); 4.92 (br. *s*, 1 H); 4.15 (*m*, 2 H); 3.03 (*m*, 1 H); 2.93 (*m*, 1 H); 2.43 (*m*, 2 H). – MS.(EI.): 172 (0.3), 170 (1), 135 (28), 134 (15), 133 (9), 121 (8), 117 (18), 115 (8), 108 (13), 107 (20), 106 (70), 105 (100), 104 (19), 103 (14), 92 (9), 91 (93), 79 (27), 78 (12), 77 (23).

$C_9H_{11}ClO$ (170.64) Calc C 63.35 H 6.50% Found C 63.46 H 6.50%

7. – Colourless liquid purified by distillation i.V. – UV.(isooctane): 208 (8080). – UV.(ethanol 96%): 209 (8200). – IR.(film): 3360, 2950, 1680, 1300, 1060, 880, 820, 670, 650. – ^{1}H-NMR. and ^{13}C-NMR.: see *Table 2*. – MS.(EI.): 172 (3), 170 (8), 135 (22), 121 (40), 119 (95), 117 (100), 105 (16), 91 (19), 84 (15), 82 (21).

$C_9H_{11}ClO$ (170.64) Calc C 63.35 H 6.50% Found C 62.64 H 6.80%

A 40±3: 60±3 mixture of **6**:**7** was obtained by treating **1** with an equiv. of $ZnCl_2$ and an equiv. of HCl in ether at 0° (followed by treatment with water and extraction).

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