53. Selective Hydrogen Chloride Elimination from Primary Chlorides Induced by the Fluoride Anion. Anchimeric Participation of the Chloromethyl Group in the Heterolytic Opening of an Epoxide

Stereospecific Syntheses of 5,6-Bis(methylidene)-*syn*-2-norbornen-7-ol and 5,6-Bis(methylidene)-*endo*-3-chloro-*exo*-2-norbornanol[1])

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Dedicated to Professor *H. Dahn* on his 60th anniversary

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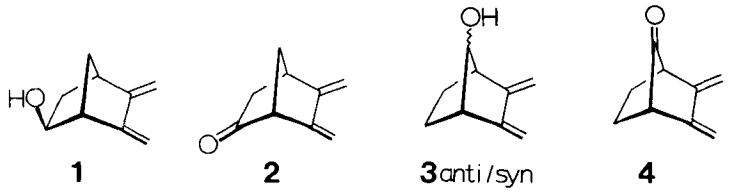
Summary

Syntheses of the alcohols **10** and **18**, and the corresponding ketones **11** and **19** are presented. *Endo*-5, *exo*-6-bis(chloromethyl)-*endo*-3-chloro-*exo*-2-norbornanol (**16**) and *endo*-5-(bromomethyl)-*exo*-6-(chloromethyl)-*endo*-3-chloro-*exo*-2-norbornanol (**17**) were obtained by HCl- and, respectively, HBr-addition to *endo*-5,*exo*-6-bis(chloromethyl)-*exo*-2,3-epoxynorbornane (**5**). The *Wagner-Meerwein* rearrangement was precluded in these reactions probably because of the formation of a relatively stable chloronium ion **15** arising from the participation of the 1,4-chlorine atom of the *endo*-5-chloromethyl group in the heterolytic ring opening of the epoxide **5**.

The 'naked' fluoride anion (excess CsF in DMF or KF in DMF with 18-crown-6-ether) permitted the selective elimination of 2 equivalents of HCl from **16** and yielded the chlorohydrin-diene **18**.

Introduction. – The 5,6-bis(methylidene)norbornanes substituted at C(2,3) or C(7) are interesting compounds for at least 2 reasons: a) these rigid systems lend themselves to study of the interactions between the s-*cis*-butadiene group (or the corresponding transition metal complexes) and a homoconjugated function [1–3]; b) they are reactive towards dienophiles [2] [3] and may be used as synthons. Recently we easily prepared 5,6-bis(methylidene)-*exo*-2-norbornanol (**1**) and 5,6-bis(methylidene)-2-norbornanone (**2**) from dimeric cyclopentadiene and 1,4-dichloro-*trans*-2-butene [3]. The *Diels-Alder* additions of the diene-ketone **2** are regio- and stereo-selective [4]. These characteristics, coupled with the fact that optically pure **2** can be prepared [5], should make this diene a potential synthon in the preparation of polyfunctionalized polycyclic systems.

[1]) Part of this work was presented at the autumn meeting of the «Societé Suisse de Chimie» in Bern, Oct. 7, 1977.



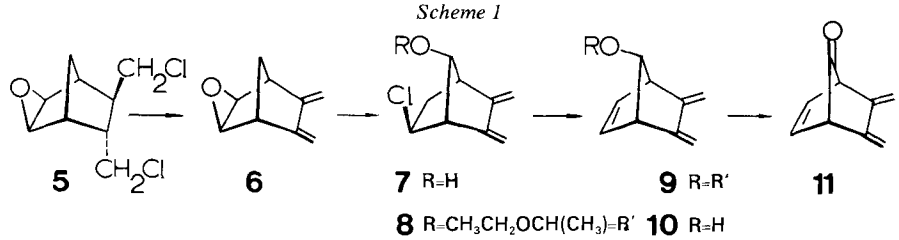
The 2,3-bis(methylidene)-7-norbornanols **3***anti* and **3***syn* were prepared for the first time by *Tanida et al.* [6], starting with an acetal of cyclopentadienone [7] and maleic anhydride. After several steps, the keto-diene **4** was obtained and this was reduced to a mixture of **3***anti*+**3***syn*. We prepared **3***anti* stereospecifically by aluminium hydride reduction of 5,6-bis(methylidene)-*exo*-2,3-epoxynorbornane (**6**) [8]. This depended on the well-known *Wagner-Meerwein* rearrangement involved in the heterolytic opening of the *exo*-2,3-epoxynorbornane [9]; it avoided the tedious preparation of an acetal of cyclopentadienone [7] [10]. We are now showing that it can also be applied to the preparation of 5,6-bis(methylidene)-*syn*-2-norbornen-7-ol (**10**).

Trans-2,3-disubstituted norbornanes are difficult to prepare. Most norbornene derivatives add electrophiles with *syn exo* selectivity and yield *cis exo*-2,3 and/or rearranged 2,7-disubstituted norbornanes [11]. We are showing that *exo*-2,3-epoxynorbornanes can add hydrogen halides without yielding the typical rearranged products provided an *endo*-5-chloromethyl substituent is present. We have exploited this property to develop a stereospecific synthesis of 5,6-bis(methylidene)-*endo*-3-chloro-*exo*-2-norbornanol (**18**).

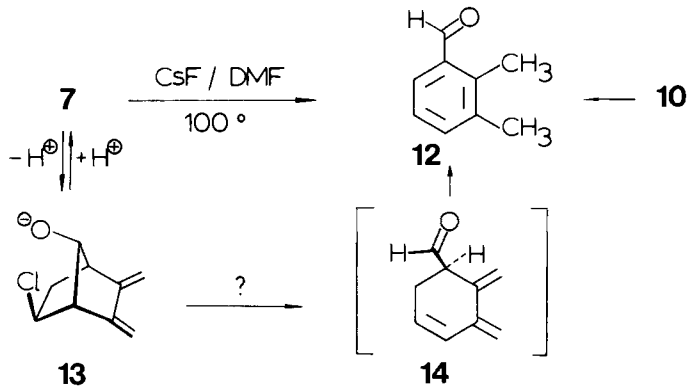
Results and discussion. – a) *5,6-Bis(methylidene)*-syn-2-*norbornen-7-ol* (**10**). The readily available epoxy-diene **6** [8] adds 1 mol HCl (ether, 0°) to give the rearranged *exo*-2-chloro-5,6-bis(methylidene)-*syn*-7-norbornanol (**7**) [8]. All attempts to eliminate 1 mol HCl from **7** to form the trienol **10** in one step failed. After prolonged heating in benzene with an excess of 1,5-diazabicyclo[4.3.0]non-5-ene [12], **7** remained intact. When **7** was treated with strong bases such as potassium *t*-butoxide or KOH in tetrahydrofuran (THF) or dimethylsulfoxide (DMSO), only polymeric material was formed with traces of aromatic compounds. When heated in dimethylformamide (DMF) (100°, 24 h) with a 3-fold excess of anhydrous CsF [13], **7** eliminated 1 mol HCl and yielded 2,3-dimethylbenzaldehyde (**12**) [14].

To avoid this base-induced rearrangement, the alcohol **7** was protected as the acetal **8** by reaction with ethyl vinyl ether in presence of *p*-toluenesulfonic acid *(Scheme 1)*. Now **8** smoothly eliminated HCl on treatment with potassium

Scheme 1



Scheme 2



t-butoxide in boiling THF and gave the triene **9**. Finally, acid catalyzed methanolysis of **9** yielded the 5,6-bis(methylidene)-*syn*-2-norbornen-7-ol (**10**) (overall yield: 42% from **7**).

The structure of the trienol **10** was deduced from its mode of formation and from its spectra. The stereochemistry of the hydroxyl group was confirmed by the $Eu(dpm)_3$-induced shifts on the δ(H) of the olefinic hydrogen atoms (see exper. part). Hydrogen bonding [15] between the endocyclic double bond C(2,3) and the *syn*-7-hydroxyl group is indicated by comparison of the OH-stretching frequency in the IR. spectrum of **10** with that of related systems *(Table 1)* and by the observation of a relatively large ^3J(H,H) coupling constant (11 Hz) between the H–C(7) and OH protons in the ^{1}H-NMR. spectrum of **10** (these vicinal hydrogen atoms are blocked in an antiperiplanar conformation [16]).

Oxidation of **10** with chromium trioxide-pyridine complex [17] was a very slow reaction as expected for a 7-norbornanol derivative [18]; it furnished the 5,6-bis-

Table 1. *(OH)-Stretching frequencies [cm^{-1}] of selected norbornanols in CCl_4*

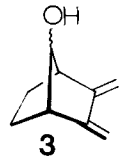
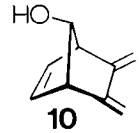
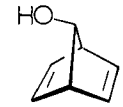
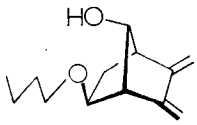
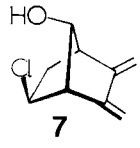
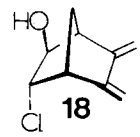
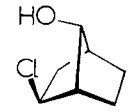
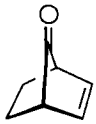
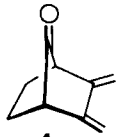
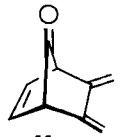
			
syn : 3572 [37] *anti:* 3628 [37]	*syn :* 3582 [6] *anti:* 3640	3585	3551 [37]
			
3500 [8]	3595 [8]	3630	3595

Table 2. *(C=O)-Stretching frequencies [cm^{-1}] of selected norbornanones*

		 **4**	 **11**
1782[a]) [38]	1792[a]) [38]	1787[b]) [6]	1795[c])

[a]) Solvent not reported. [b]) In CCl_4. [c]) In CH_2Cl_2.

(methylidene)-2-norbornen-7-one (**11**) [1] in low yield because of competitive dimerization and polymerization of trienes **10** and **11**. The trienone **11** is a strained ketone as indicated by the relatively high energy of its carbonyl stretching frequency *(Table 2)*.

The trienol **10** polymerized in presence of strong bases such as potassium *t*-butoxide. When heated in DMF (100°, 18 h) in the presence of 3 equivalents of CsF, **10** isomerized smoothly into the benzaldehyde **12** *(Scheme 2)* (isolated yield: 52%). The trienol **10** might therefore be an intermediate in the elimination-rearrangement reaction **7** → **12**. An alternative path could, however, be a fragmentation [19] of the conjugate base **13** (of **7**) into the triene **14** that is expected to aromatize easily *(Scheme 2)*. Such a process cannot be excluded although the C(1)–C(7) and the C(2)–Cl σ-bonds are not aligned favourably for a concerted fragmentation. Control experiments with deuteriated alcohols **7**-OD and **10**-OD did not allow a distinction between these 2 mechanistic limits because of further scrambling under the reaction conditions. No systematic study of base-induced rearrangement of *exo*-2-halogeno-*syn*-7-norbornanols has been reported. *Winstein* [20] has prepared 7-norbornadienol, and *Bartlett* [9a] benzo-7-norbornadienol by HBr elimination of the corresponding protected *exo*-2-bromo-*syn*-5-norbornen-7-ols. 2,5-Norbornadien-7-ol rearranges to cycloheptatrienol when treated by strong bases [21].

b) *5,6-Bis(methylidene)*-endo-*3-chloro*-exo-*2-norbornanol* (**18**). Preparation of 2,3-bis-substituted norbornanes by hydrogen halide additions to the corresponding *exo*-2,3-epoxynorbornanes requires prevention of the *Wagner-Meerwein* rearrangement involved in the acid-catalyzed opening of the epoxides[2]). We expected participation of the *endo*-5-chloromethyl group in *endo*-5,*exo*-6-bis(chloromethyl)-*exo*-2,3-epoxynorbornane (**5**) [8] in the heterolytic ring opening of the protonated epoxide leading to a 5-membered ring chloronium ion **15** [22] probably more stable than the corresponding *exo*-3-hydroxy-2-norbornyl cation intermediate. The chloride anion would attack either the *exo*-3 position or the primary methylene group yielding respectively the *exo*- or *endo*-3-chloro-*exo*-2-norbornanol derivative *(Scheme 3)*.

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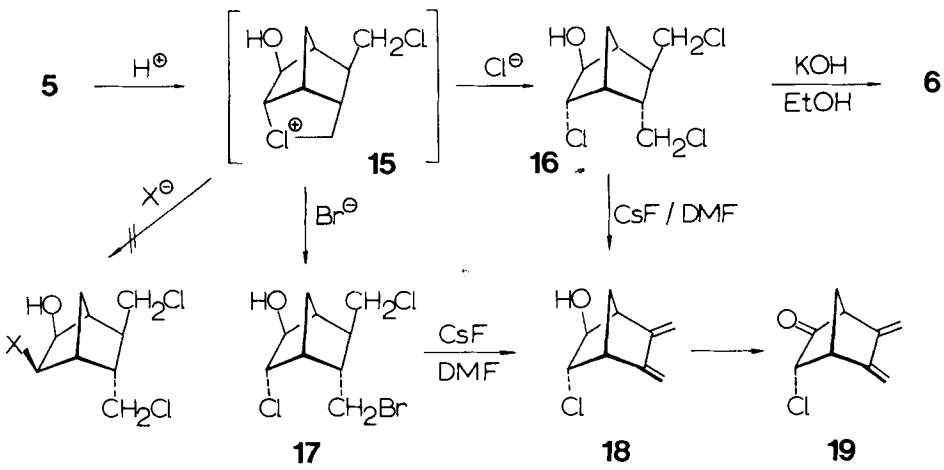
[2]) We found that nortricyclanol (26%), *exo*-5-chloro-2-norbornanols (7%) and 3 products (23%) of undetermined structure were formed beside *exo*-2-chloro-*syn*-7-norbornanol (44%) by addition of HCl (ether, 0°) to *exo*-2,3-epoxynorbornane; 2,3-disubstituted products were not detected (see also [9]).

Scheme 3



When **5** was treated with dry gaseous HCl (ether, 0°) *endo*-5,*exo*-6-bis(chloromethyl)-*endo*-3-chloro-*exo*-2-norbornanol (**16**) was formed (70% yield) whose structure was established by 360-MHz-^{1}H-NMR. *(Table 3).*

The assignments were confirmed by the use of Eu(dpm)$_3$ [23] and double irradiation experiments. The signal at 3.85 ppm assigned to H(*endo*-2) couples with that of H(*anti*-7) with a typical *W*-coupling constant of 2.2 Hz [24]; it also couples with the signal of H(*exo*-3) with a typical '*trans*' coupling constant of 3 Hz [24] [25]. No coupling is observed between H–C(2) and the bridgehead protons H–C(1) and H–C(4). This confirms the *endo* position for H–C(2) [3] [24] [25]. The signal at 2.36 ppm attributed to H–C(1) does not couple with that of H–C(6), whereas

Table 3. ^{1}*H-NMR. (360 MHz, $CDCl_3$) characteristics of the HCl and HBr adducts to the epoxide* **5** ($\delta_{TMS}=0$ ppm)[a])

δ_H[ppm]	in **16**	in **17**	J_{app}[Hz]	in **16**	in **17**		in **16**	in **17**
H–C(1)	2.36	2.37	$J_{1,2}$	~0	~0	$J_{3,4}$	3.8	3.5
Hendo-C(2)	3.85	3.89	$J_{1,3}$	<1	<1	$J_{3,5}$	1.5	1.5
H*exo*-C(3)	3.97	3.99	$J_{1,4}$	<1	<1	$J_{4,5}$	4	3.5
H–C(4)	2.74	2.76	$J_{1,6}$	~0	~0	$J_{5,6}$	6	6.3
H*exo*-C(5)	2.02	2.13	$J_{1,7s}\simeq J_{4,7s}$	1.8	1.8	$J_{5,CH_2Cl(5)}$	6–7	–
H*endo*-C(6)	1.71	1.69	$J_{1,7a}\simeq J_{4,7a}$	1.5	1.5	$J_{5,CH_2Br(6)}$	–	6–7
H*syn*-C(7)	1.77	1.78	$J_{2,3}$	3.	3.	$J_{6,CH_2Cl(6)}$	5.5 9.5	5.5 9.
H*anti*-C(7)	1.55	1.52	$J_{2,7a}$	2.2	2.2	$J^{AB}_{CH_2Cl(6)}$	10.5	11.
(Cl–H_2C)–C(5) *endo*	3.98	–						
(Br–H_2C)–C(5) *endo*	–	3.86						
(Cl–H_2C)	3.75 3.41	3.78 3.42						
OH	2.78	2.46						

[a]) Signal assignments were confirmed by using Eu(dpm)$_3$ and by double irradiation experiments.

the signal of H–C(4) couples with those of H–C(3) and H–C(5) with typical coupling constants of 3.5–4 Hz [3] [24] [26]. This establishes unambigously the *exo*-substitution for the Cl–H_2C(6) group and the *endo*-substitution of the Cl–H_2C(5) group and excludes all other possible configurations for **16**. There is a *W*-coupling constant between H*exo*-C(3) and H*exo*-Cl(5) of 1.5 Hz [27]. The H–C(6) couples with the protons at 3.75 ppm (J = 5.5 Hz) and 3.41 ppm (J = 9.5 Hz) attributed to the *exo*-CH_2Cl group. The signal at 2.02 ppm attributed to H*exo*-C(5) couples with the multiplet at 3.98 ppm, (J = 6–7 Hz) of the Cl–H_2C(5) substituent.

When heated in KOH/EtOH, **16** rapidly eliminated 3 equivalents of HCl and yielded the epoxy-diene **6** (this observation confirms the *exo*-2-hydroxy and *endo*-3-chloro substitution of **16**). 1,2-Eliminations from the CH_2Cl groups were competing with 1,3-elimination of HCl from the chlorohydrin **16**. In contrast to this, when heated in DMF in the presence of a 6-fold excess of CsF (or excess of KF + 1 equivalent of 18-crown-6 ether) at 105° (24 h), **16** gave our synthetic goal, 5,6-bis(methylidene)-*endo*-3-chloro-*exo*-2-norbornanol (**18**) in good yield (76%). Under these conditions the 1,3-elimination of HCl from the chlorohydrin was a slow reaction[3]); it occurred only after prolonged heating in boiling DMF/CsF.

The structure of the diene **18** was deduced from its spectra (see exper. part) and from its reactivity. The UV. absorption spectrum was analogous to those of other 2,3-bis(methylidene)norbornanes [2] [3] [6] [13] [28]; the IR. spectrum showed the typical bands at 3620 cm^{-1} (OH) and 3090 cm^{-1} (CH stretching of the methylidene groups). The ^{1}H-NMR. signals were assigned readily using Eu(dpm)$_3$ (see exper. part). The *exo*-2-hydroxy and *endo*-3-chloro substitution was confirmed by measuring typical coupling constants between the bridgehead protons H–C(1), H–C(4) and the adjacent H–C(2) and H–C(3) ($J_{Hexo\text{-}C(3),H\text{-}C(4)}$ = 3,5–4 Hz; $J_{Hendo\text{-}C(2),H\text{-}C(1)} \simeq 0$ Hz [3] [24] [26]). Chromium trioxide oxidation of **18** gave the expected chloroketone **19** whose ^{1}H-NMR. spectrum (with decoupling experiments) showed a typical coupling constant $J_{Hexo\text{-}C(3),H\text{-}C(4)}$ = 4 Hz, confirming the *endo*-position of the chlorine atom. The UV. absorption spectrum of **19** was similar to that of 5,6-bis(methylidene)-2-norbornanone [3] for the $V \rightarrow N$ transition (λ_{max} = 246 nm, isooctane); an expected shift of 10 nm [29] is observed for the $Q \rightarrow N$ transition when comparing the spectrum of the latter diene-ketone (λ_{max} = 309 nm, isooctane) with that of **19** (λ_{max} = 319 nm, isooctane). The IR. spectrum is also consistent with the α-chloroketone ($\tilde{\nu}_{CO}$ = 1770 cm^{-1} in **19**).

The double elimination **16** → **18**, and the smooth elimination-fragmentation **7** → **12** are two further examples of the fluoride anion as a base [13] [30]. The thermal stability in aprotic media of CsF or KF + 18-crown-6 ether constitutes an advantage over the commonly used tetraalkylammonium halides for HI and HBr eliminations [31], higher temperatures being required for the more difficult elimination of HCl [32].

The difference in behaviour of **16** towards different bases can be rationalized as follows: the 1,3-elimination yielding the epoxide **1** probably follows an ElcB type mechanism favoured by strong bases in protic solvents such as ethanol (increase of

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[3]) The epoxy-diene **6** did not add HCl or HBr under the conditions used for the elimination **16** → **18** and **17** → **18**.

the concentration of the conjugate base of **16**); the 1,2-elimination of HCl from **16** leading to the diene **18** more likely follows concerted E2 mechanisms that are less influenced by the medium.

c) *The chloronium ion intermediate hypothesis.* When the epoxide **5** was treated with gaseous HBr (ether, 0°), *endo*-5-(bromomethyl)-*exo*-6-(chloromethyl)-*endo*-3-chloro-*exo*-2-norbornanol (**17**) was obtained (76% yield); its structure was established spectroscopically and chemically.

The ^{1}H-NMR. (360 MHz) spectrum of **17** was almost identical to that of **16**, except for the signals attributed to the H*exo*-C(5) and to the 2 H of the CH_2Br-group at C(5) *(Table 3)*. The replacement of a Cl by a Br on a methyl group shifts the NMR. signals of the α-hydrogen atoms to higher field and the β-hydrogen atoms to lower field [33]; this is observed on comparing **17** with **16**. The ^{13}C-NMR. spectrum of **17** was almost identical to that of **16** (see exper. part) except for the signal of the $BrCH_2$ group in **17** ($\delta_C = 34.5$ ppm) which was at higher field than the corresponding $ClCH_2$ group in **16** ($\delta_C = 46.4$ or 46.1 ppm), as expected [34]. The distinction between the (ClH_2C)*exo*-C(6) or *endo*-C(5) and (BrH_2C)*endo*-C(5) or *exo*-C(6) signals of **17** was made by virtue of the long-range carbon-proton couplings that differentiate the multiplicity of the $ClCH_2$ and $BrCH_2$ carbon atom signals (see *Fig.*). Correlations between vicinal $^3J_{C,H}$ and $^3J_{H,H}$ coupling constants for geometrically equivalent couplings within homologous saturated molecules have been demonstrated [35]. The (BrH_2C)*endo*-C(5) carbon atom in **17** is expected to couple with H*exo*-C(5) ($^2J_{C,H} = -4$ to -5 Hz) and with H*endo*-C(6) ($^3J_{C,H} =$ 6–8 Hz [35]. No coupling is expected with the bridgehead hydrogen H–C(4) if the BrH_2C–C(5) group is *endo*, so each line of the $BrCH_2$ triplet ($^1J_{C,H} = 152$ Hz) in the proton-coupled ^{13}C-NMR. spectrum of **17** must be split into a doublet of a doublet or, as observed, an apparent triplet. The (ClH_2C)*exo*-C(6) carbon signal is expected to couple with H–C(6) ($^2J_{C,H} = -4$ to -5 Hz), with H*exo*-C(5)

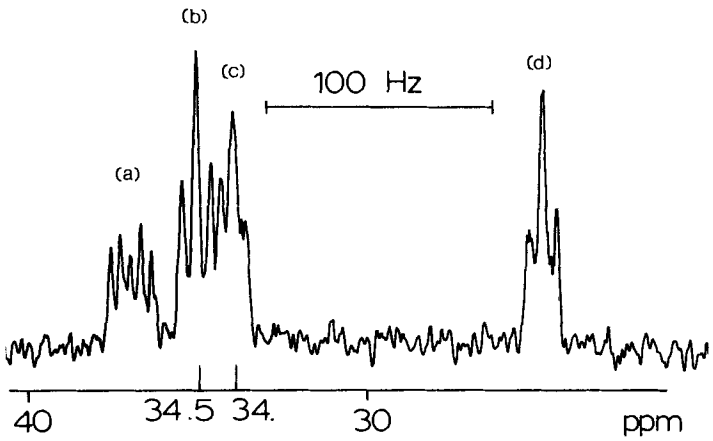
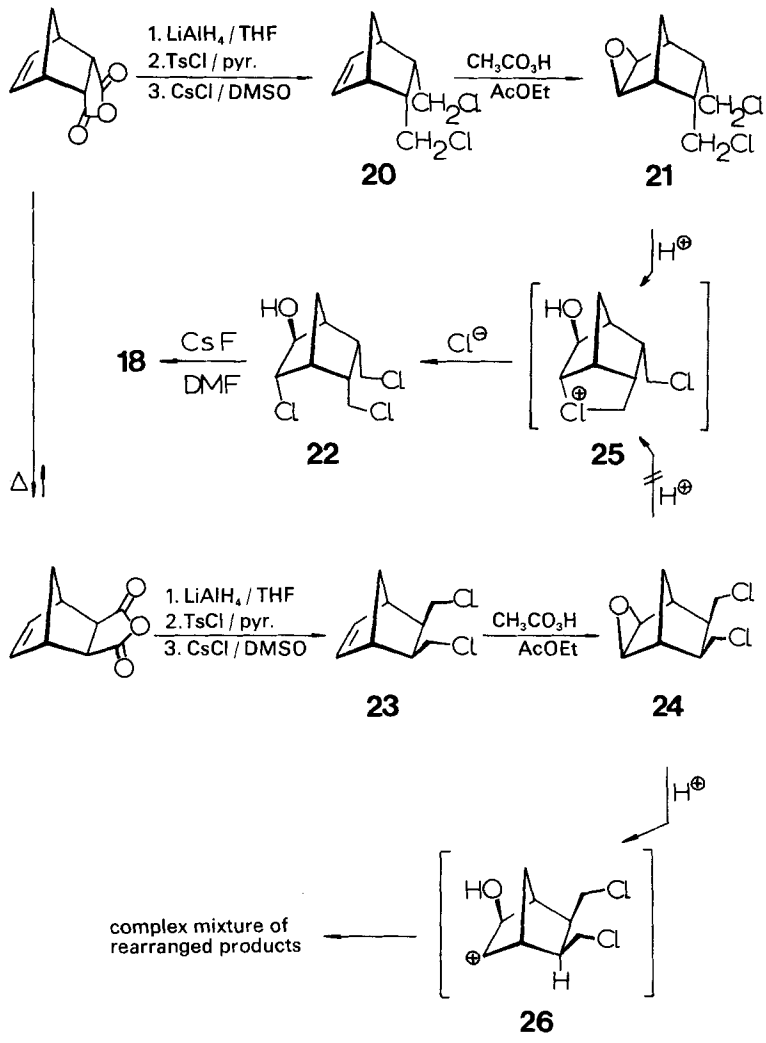


Fig. *Part of the* $^{13}C\{^1H\}$ *NMR. spectrum* (15.08 MHz, FT mode, CD_3OD, 40°) *of* **17**. (a): *m* (high field lateral band of the (ClH_2C *exo*-C(6)); (b): *m* (central band of the (BrH_2C) *endo*-C(5)); (c): *m* (central band of the H_2C(7)); (d): *m* (superposed high field lateral bands of the H_2C(7) and (BrH_2C) *endo*-C(5))

($^3J_{C,H}$ = 5–10 Hz) and with H–C(1) ($^3J_{C,H}$ = 2–4 Hz), so each line of the $ClCH_2$ triplet ($^1J_{CH}$ = 150 Hz) must be split into a multiplet corresponding to a 'doublet × doublet × doublet' or to an observed apparent 'triplet × doublet', (see *Fig.*). Proton and carbon atom chemical shifts, as well as the long range $J_{C,H}$ of **17** compared with those of **16**, are only consistent with the (Br-H_2C)*endo*-C(5) and (Cl–H_2C)*exo*-C(6) position in **17**. Single frequency proton decoupling of the ^{13}C-NMR. (15.08 MHz) spectrum confirmed the structure of **17**. Irradiation of the signal at δ_H = 3.86 ppm (H adjacent to the H*exo*-C(5) leads to decoupling of the multiplet at δ_C = 34.5 ppm attributed to the $BrCH_2$ group and maintained residual couplings (function of the irradiating power) at the signal at δ_C = 46.5 ppm of the

Scheme 4



CH_2Cl group. When treated in DMF (105°, 24 h) with an excess of CsF, **17** selectively eliminated 1 equivalent of HBr and 1 equivalent of HCl and yielded the chlorohydrin-diene **18** *(Scheme 3)*, confirming the structure **17** (no Br at C(3)).

The isolation of the adduct **17** strongly supports the intermediacy of the chloronium ion **15** in the addition of HBr to the epoxide **5**. Intervention of this intermediate is also reasonable in the addition of HCl to **5** yielding the tris-chloride **16** in high yield (absence of rearranged products). The nucleophile Br^- preferentially attacks the primary carbon atom adjacent to the chloronium ion of **15** *(Scheme 3)*. In methanol, HCl and HBr additions to **5** gave only the adducts **16** and **17**, and no methoxy-substituted derivatives. This is in agreement with the expected high stability and, consequently, relative high selectivity of the chloronium ion intermediate **15** toward strong nucleophiles (Cl^-, Br^- *vs.* MeOH).

Similarly chloronium ion might also intervene in the addition of HCl to *endo*-5,6-bis(chloromethyl)-*exo*-2,3-epoxynorbornane (**21**). This epoxide and its isomer **24** (*exo*-5,6-bis(chloromethyl)-*exo*-2,3-epoxynorbornane) have been prepared following *Scheme 4* (see exper. part). When treated with gaseous HCl (ether, 0°), the 'all-*exo*' epoxide **24** furnished a complex mixture of HCl adducts (GC., ^{13}C-NMR., *etc.*). In contrast, **21** yielded, under the same conditions, a single adduct whose spectra were consistent with *endo*-5,6-bis(chloromethyl)-*endo*-3-chloro-*exo*-2-norbornanol (**22**). When treated in DMF in presence of an excess of CsF (105°, 24 h), **22** gave selectively the diene **18** in good yield. The high selectivity in the addition **21** + HCl → **22** compared with the absence of selectivity in the addition of HCl to **24** could be explained by formation of a chloronium ion **25** *(Scheme 4)* precluded with **24** + HCl; this leaves the hypothetical 3-hydroxy-2-norbornyl cation **26** to undergo all the possible rearrangements [36] expected for such an intermediate.

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Experimental Part

General Apparatus. Melting points (m.p.) and boiling points (b.p.) (not corrected), *Tottoli* apparatus; IR. spectra ($\tilde{\nu}$[cm^{-1}]), *Beckman* IR-20A and *Beckman* IR-4230 spectrometers; UV. spectra, *Carl Zeiss* RPQ 20 A/C instrument (λ_{max}[nm] (ε)); Mass spectra (MS.(EI)) at 70 eV, CEC 21-490 *Bell-Howell* spectrometer (*m/e*[amu] (% base peak)); MS. in chemical ionization mode (MS.(CI/ionizing gas) 1 Torr), GC./MS. system HP 5980 A *(Hewlett-Packard)*; ^{1}H-NMR. spectra, *Varian* EM 360, *Bruker* WP 80 CW or *Bruker* WH-360 (only for **16**, **17**) spectrometers (δ[ppm] (multiplicity, coupling constant J (Hz); number of protons)); s = singlet, br. = broad, d = doublet, t = triplet, qa = quartet, m = multiplet, $\delta_{TMS} = 0.0$ ppm. ^{13}C-NMR. spectra, *Bruker* WP 60 spectrometer (15.08 MHz, spectrum width: 3750 Hz, 4096 points, FT mode). The lanthanide chelates (LIS reagents) were from *Willow Brook Labs*, Waukesha, Wis., USA. Linear induced shifts of the δ(H) were observed for concentration ratios: 0.05 < [LIS reagent]/[alcohol or ketone] < 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 compound under investigation. Analytical gas chromatography (GC.) was carried out with a HP 5710A chromatograph *(Hewlett-Packard)*. Elementary analysis were performed by the 'Microlabor' of the University of Geneva (Dr. *K. Eder*). Abbreviations: i.V. = *in vacuo*, RT. = room temperature, TLC. = thin layer

chromatography on SiO_2, anh. = anhydrous, potassium *t*-butoxide = *t*BuOK, *p*-toluenesulfonic acid = TsOH, sh. = shoulder, aq. = aqueous, sat. = saturated.

Mixture of syn-*7-(1-ethoxyethoxy)*-exo-*2-chloro-5,6-bis(methylidene)norbornanes* (**8**). A mixture of *exo*-2-chloro-5,6-bis(methylidene)-*syn*-7-norbornanol [8] (1.07 g, 0.00627 mol), ethyl vinyl ether (0.46 g, 0.00638 mol) and anh. ether (10 ml) was stirred in presence of TsOH (5 mg) at RT. for 20 min. Anh. Na_2CO_3 (50 mg) was added, the solution was filtered and the solvent was distilled i.V.; yield: 1.38 g (90.7%), colourless liquid. - IR. ($CHCl_3$): 2980, 1730, 1700, 1600, 1445, 1380, 1350, 1130, 1080, 1010, 900. - ^{1}H-NMR. ($CDCl_3$): 5.27 (br. *s*, 1 H); 5.19 (br. *s*, 1 H); 4.99 (br. *s*, 1 H); 4.87 (br. *s*, 1 H); 4.82 (*qa*×*d*, *J* = 6, 1 H); 4.1–3.9 (*m*, 2 H); 3.6 (*qa*×*d*, *J* = 7, 2 H); 3.1–2.8 (*m*, 2 H); 2.5–2.0 (*m*, 2 H); 1.35 (*d*×*d*, *J* = 6, 3 H); 1.18 (*t*, *J* = 7, 3 H). - MS. (CI/CH_4): 245, 243 [M + 1], 241.

$C_{13}H_{19}ClO_2$ (242.75) Calc. C 64.32 H 7.88% Found C 64.63 H 7.88%

syn-*7-(1-Ethoxyethoxy)-5,6-bis(methylidene)-norborn-2-ene* (**9**). A mixture of **8** (0.86 g, 0.00354 mol), *t*BuOK (1.2 g, 0.0107 mol) and anh. THF was heated under N_2 and under reflux for 24 h. After cooling to RT. water (40 ml) was added and the solution was extracted with ether (3 × 10 ml). The ethereal extract was washed with a sat. solution of NaCl (2 × 20 ml) and water (3 × 20 ml) and finally dried ($MgSO_4$). The solvent was removed i.V.; the residue was distilled i.V.; yield: 0.396 g (54%), b.p. 45–50°/0.01 Torr. - UV. (isooctane): 243 (9010). - UV. (ethanol/water 96:4): 243 (9370). - IR. (film): 3070, 2980, 2900, 1635, 1435, 1370, 1335, 1245, 1175, 1135, 1090, 950, 870, 780. - ^{1}H-NMR. ($CDCl_3$): 6.2 (*m*, 2 H); 5.24 (br. *s*, 2 H); 5.0 (br. *s*, 2 H); 4.7 (*qa*, *J* = 6, 1 H); 4.0 (*m*, 1 H); 3.59 (*qa*×*d*, *J* = 7, 2 H); 3.4 (*m*, 2 H); 1.3 (*d*, *J* = 6, 3 H); 1.2 (*t*, *J* = 7, 3 H). - MS.: 206 (0.1), 161 (7), 149 (6), 133 (8), 117 (14), 115 (27), 105 (12), 103 (9), 91 (18), 77 (11), 73 (100).

$C_{13}H_{18}O_2$ (206.3) Calc. C 75.69 H 8.80% Found C 75.67 H 8.86%

5,6-Bis(methylidene)-syn-*2-norbornen-7-ol* (**10**). A solution of the acetal **9** (0.152 g, 0.737 mmol) and TsOH (1 mg) in methanol (2 ml) was stirred at RT. for 5 min. After addition of anh. Na_2CO_3 (10 mg) the solution was filtered, the solvent evaporated and the residue distilled i.V.; yield: 0.085 g (86%), b.p. 35–40°/0.01 Torr. - UV. (isooctane): 245.5 (10720), 232 (10020). - UV. (96% ethanol): 243.5 (11070). - IR. ($CHCl_3$): 3580, 3000, 1670, 1660, 1415, 1330, 1270, 1170, 1080, 900. - IR. (CCl_4): 3585 (OH). - ^{1}H-NMR. [relative induced shifts by Eu(dpm)$_3$] ($CDCl_3$, 25°): 6.18 (*m*, 2 H, H (2,3) [30.9]); 5.23 (br. *s*, 2 H, H_2=C(5′ *Z*, 6′ *Z*) [11.8]; 4.97 (br. *s*, 2 H, H_2=C(5′ *E*, 6′ *E*) [9.4]); 4.02 (*m*, 1 H, H(7) [100]); 3.33 (*m*, 2 H, H(1,4) [46.8]). - MS.: 134 (5), 133 (16), 115 (16), 106 (45), 105 (86), 103 (38), 91 (100), 77 (52).

$C_9H_{10}O$ (134.2) Calc. C 80.56 H 7.51% Found C 80.47 H 7.67%

5,6-Bis(methylidene)-2-norbornen-7-one (**11**). Small portions of CrO_3 (1.8 g, 0.018 mol) were added under N_2 to a solution at 0° of anh. pyridine (2.85 g, 0.036 mol) in CH_2Cl_2 (15 ml). The mixture was stirred at RT. for 10 min, then a solution of **10** (0.39 g, 0.0029 mol) in CH_2Cl_2 (5 ml) was added. The mixture was stirred at RT. for 3 days. The precipitate was filtered off and washed with ether (2 × 10 ml). The solution was concentrated to 5 ml and 15 ml of ether were added. After filtration, the etheral solution was washed successively with NaOH-solution 5% (3 × 10 ml), hydrochloric acid 5% (3 × 10 ml) and saturated $NaHCO_3$-solution (10 ml). The organic extract was dried ($MgSO_4$) and concentrated i.V.; The residue was chromatographed on a column of SiO_2 ($CHCl_3$). The first fraction contained the ketone **11**; yield: 20 mg (5%), colourless oil. - UV. (isooctane): 239.5; 297. - UV. (96% ethanol): 239; 286. - IR. (CH_2Cl_2): 2940, 2860, 1795, 1190, 1060, 890. - ^{1}H-NMR. ($CDCl_3$): 6.69 (*m*, 2 H); 5.4 (br. *s*, 2 H); 5.1 (br. *s*, 2 H); 3.56 (*m*, 2 H). - MS.: 104 (86), 103 (60), 78 (100), 77 (49). - MS. (CI/CH_4): 133 (48), 105 (100).

2,3-Dimethylbenzaldehyde (**12**). A mixture of *exo*-2-chloro-5,6-bis(methylidene)-*syn*-7-norbornanol [8] (0.72 g, 0.0042 mol) and anh. CsF (1.9 g, 0.0125 mol) in 5 ml of anh. DMF was heated to 100° under N_2 for 24 h. After cooling to RT., 15 ml of water were added and the mixture was extracted with ether (3 × 5 ml). The ethereal extract was washed (sat. aq. NaCl-solution (3 × 20 ml) and water (20 ml)) then dried ($MgSO_4$). The solvent was removed i.V. and the residue transferred on a vacuum line; yield: 0.185 g (33%), colourless liquid. - IR. (CH_2Cl_2): 2950, 2750, 1700, 1600, 1460, 1390, 1240, 1220, 1080, 1000, 900, 880, 790. - ^{1}H-NMR. (CCl_4): 10.1 (*s*, 1 H); 7.6–6.9 (*m*, 3 H); 2.5 (*s*, 3 H); 2.25 (*s*, 3 H). - MS.: 134 (100), 133 (99), 119 (4), 105 (83), 91 (38), 79 (26), 77 (35).

Semicarbazone of **12**: white solid, m.p. 220–221° ([14] 221–221.5°).

$C_{10}H_{13}N_3O$ (191.23) Calc. C 62.81 H 6.85% Found C 62.95 H 6.77%

endo-*3-Chloro*-endo-*5*,exo-*6-bis(chloromethyl)*-exo-*2-norbornanol* (**16**). Dry HCl was bubbled through a solution of *endo*-5,*exo*-6-bis(chloromethyl)-*exo*-2,3-epoxynorbornane (**5**) [8] (5 g, 0.024 mol) in anh. ether (50 ml) at 0° until complete disappearance of **5** (by TLC.) A sat. solution of $NaHCO_3$ was added dropwise to effect neutralization. The ethereal solution was washed with water (2 × 20 ml) and dried ($MgSO_4$). The solvent was removed i.V. and the residue crystallized in CCl_4; yield: 4.1 g (70%), white crystals, m.p. 95–96°. – UV. (isooctane): end absorption. – IR. (KBr): 3400, 3000, 2960, 1460, 1320, 1110, 1050, 930, 820, 720. – ^{1}H-NMR. ($CDCl_3$): see *Table 3*. – ^{13}C-NMR. ($CDCl_3$): 82.8 ($^1J_{CH}$ = 160; C(2)); 67.8 ($^1J_{CH}$ = 154; C(3)); 49.3 (*d*); 48.2 (*d*); 47.6 (*d*); 46.7 (*d*); 46.4 (*t*); 46.1 (*t*); 33.8 (*t*; *J* = 136 Hz; C(7)). – MS.: 246 (0.6), 244 (2), 242 (2), 211 (2), 210 (3), 209 (12), 208 (19), 207 (17), 206 (26), 195 (52), 193 (81), 177 (38), 175 (24), 169 (24), 157 (29), 142 (38), 141 (40), 139 (33), 134 (48), 129 (79), 119 (45), 117 (52), 105 (55), 93 (64), 91 (74), 83 (100), 79 (52), 77 (45).

$C_9H_{13}Cl_3O$ (243.56) Calc. C 44.38 H 5.38% Found C 44.64 H 5.18%

endo-*3-Chloro-5,6-bis(methylidene)*-exo-*2-norbornanol* (**18**). A mixture of *endo*-3-chloro-*endo*-5,*exo*-6-bis(chloromethyl)-*exo*-2-norbornanol (**16**) (2.5 g, 0.0103 mol) and anh. CsF (9.35 g, 0.0616 mol) in 20 ml of anh. DMF was heated to 105° for 24 h under N_2. After cooling to RT., 50 ml of water were added and the mixture was extracted with ether (3 × 20 ml). The ethereal extract was washed successively with a sat. solution of NaCl (3 × 20 ml) and with water (20 ml) and dried ($MgSO_4$). The solvent was removed i.V. and the viscous residue was filtered on a column of Florisil ($CHCl_3$). After removal of the $CHCl_3$, a colourless oil was obtained that crystallized at 0°; yield: 1.34 g (76%), white crystals, m.p. 44–45° (hexane). – UV. (isooctane): 251 (sh., 6840), 243 (9910), 237 (sh., 8980). – UV. (96% ethanol): 252 (sh., 6305), 243.5 (9105), 238 (sh., 8350). – IR. ($CHCl_3$): 3620, 3410, 3090, 2980, 1650, 1480, 1400, 1270, 1140, 1120, 1050, 1000, 980, 960, 930, 910, 830. – IR. (CCl_4): 3630 (OH). – ^{1}H-NMR. [relative induced shift by Eu(dpm)$_3$](CCl_4, 25°): 5.33 (br. *s*, 1 H, H_2=C(6′ *Z*) [13.4]); 5.20 (br. *s*, 1 H, H_2=C(5′ *Z*) [13.2]); 4.92 (br. *s*, 2 H, H_2=C(5′ *E*) [11.7], H_2=C(6′ *E*) [14.5]); 3.8 (*m*, 1 H, H(3) [80.0]); 3.7 (*m*, 1 H, H–C(2) [100]); 2.9 (*m*, 1 H, H–C(4) [24.8]); 2.7 (*m*, 1 H, H–C(1) [63.6]); 1.97 (*m* × *d*, J_{app} = 10, 1 H, H_{syn}-C(7) [61.4]); 1.62 (*m* × *d*, J_{app} = 10, 1 H, H*anti*-C(7) [24.6]). – MS. 172 (17), 170 (52), 135 (93), 134 (37), 119 (28), 117 (63), 107 (27), 105 (58), 94 (26), 93 (37), 92 (87), 91 (100), 79 (34), 77 (33).

$C_9H_{11}ClO$ (170.64) Calc. C 63.35 H 6.50% Found C 63.40 H 6.58%

endo-*3-Chloro-5,6-bis(methylidene)-2-norbornanone* (**19**). Chromium trioxide (4.6 g, 0.046 mol) was added portionwise under N_2 to a solution of anh. pyridine (7.27 g, 0.092 mol) in anh. CH_2Cl_2 (30 ml) at 0°. The mixture was stirred for 10 min while warming to RT. A solution of *endo*-3-chloro-5,6-bis(methylidene)-*exo*-2-norbornanol (**18**) (1.3 g, 0.0076 mol) in anh. CH_2Cl_2 (10 ml) was added portionwise. The mixture was stirred at RT. under N_2 for 8 h. The precipitate was filtered off and washed with ether (2 × 20 ml). The organic solution was concentrated i.V. to *ca.* 10 ml and 20 ml of ether were added. Another precipitate was formed; it was filtered off and washed with ether (20 ml). The ethereal extract was washed successively with aq. 5% NaOH-solution (3 × 20 ml), aq.5%hydrochloric acid (5 × 30 ml) and sat. solution of $NaHCO_3$ (3 × 20 ml) and dried ($MgSO_4$). The solvent was removed i.V. and the residue recrystallized in ether/petroleum ether; yield: 0.74 g (58%), white crystals, m.p. 59–60°. – UV. (96% ethanol): 306 (308). – UV. (isooctane): 330 (sh., 185), 319 (330), 308 (340), 299 (sh., 260), 246 (6990). – IR. ($CHCl_3$): 2960, 1770, 1140, 1010, 960, 900. – ^{1}H-NMR. ($CDCl_3$): 5.54 (br. *s*, 1 H); 5.44 (br. *s*, 1 H); 5.16 (br. *s*, 2 H); 4.30 (*d*, *J* = 4, 1 H); 3.36 (*m*, 2 H); 2.05 (*m*, 2 H). – MS.: 170 (19), 168 (56), 133 (51), 105 (100), 91 (82), 79 (32), 77 (35).

C_9H_9ClO (168.62) Calc. C 64.11 H 5.38% Found C 63.93 H 5.26%

endo-*5-(Bromomethyl)*-endo-*3-chloro*-exo-*6-(chloromethyl)*-exo-*2-norbornanol* (**17**). Gaseous HBr (prepared by adding dropwise 40 ml of HBr 48% to a solution of 300 ml of H_2SO_4 98% and dried by passing through H_2SO_4 98%) was bubbled through a solution of **5** (7.0 g, 0.0338 mol) in anh. and degassed ether (100 ml) cooled to 0°. After disappearance of the epoxide **5** (by TLC.), the ethereal solution was washed with water (3 × 100 ml) and a sat. aq. solution of $NaHCO_3$ (5 × 100 ml). The organic extract was decolorized with active charcoal. After filtration and evaporation of the solvent i.V. a

yellowish oil was obtained, which was chromatographed on SiO_2 (light petroleum/ethyl acetate 4:1) affording 7.4 g (76%) of colourless oil which crystallized. White solid, m.p. 105–106° (from $CHCl_3$). – IR. (film): 3390, 2900, 1720, 1450, 1310, 1105, 1045, 930, 730, 640. – ^{1}H-NMR. ($CDCl_3$), see *Table 3.* – ^{13}C-NMR. ($CDCl_3$): 83.0 (*d*, $^1J_{CH}$ = 152 Hz); 67.9 (*d*, $^1J_{CH}$ = 154 Hz); 49.6 (*d*); 48.6 (*d*); 48.3 (*d*); 47.0 (*d*); 46.5 (*t*, $^1J_{CH}$ = 150 Hz); 34.5 (*t*, $^1J_{CH}$ = 152 Hz); 34.0 (*t*, $^1J_{CH}$ = 136 Hz), see *Figure.* – MS.: 292 (1), 290 (4.5), 288 (M^+, 9), 286 (6), 274 (0.5), 272 (3), 270 ($M^+ - H_2O$, 6), 268 (4), 255 (9), 254 (12), 253 ($M^+ - Cl$, 39), 252 ($M^+ - HCl$, 50), 251 (30), 250 (36), 241 (13), 239 ($M^+ - CH_2Cl$, 54), 237 (40), 211 (12), 209 (60), 207 ($M^+ - Br$, 100), 193 (10), 191 (58), 189 ($M^+ - Br - H_2O$, 93), 173 (33), 171 ($M^+ - BrCl$, 78).

$C_9H_{13}BrCl_2O$ (288.02) Calc. C 37.53 H 4.55% Found C 37.67 H 4.64%

When **17** (2.9 g, 0.01 mol) was heated to 105° in anh. DMF (20 ml) in presence of an excess of anh. CsF (9.1 g, 0.06 mol) for 24 h under N_2, the diene **18** (72%) was obtained by the method described for the preparation of **18** from **16** (see above).

endo-*5,6-Bis(chloromethyl)-2-norbornene* (**20**). A mixture of *endo*-5,6-bis(*p*-toluenesulfonyloxymethyl)-2-norbornene [39] (2.5 g, 0.0054 mol) and anh. CsCl (3.6 g, 0.0214 mol) in anh. DMSO (50 ml) was heated to 100° for 12 h under N_2. After cooling to RT., water was added (50 ml) and the mixture was extracted with ether (3 × 20 ml). The ethereal extract was washed successively with a sat. solution of NaCl (3 × 20 ml) and water (20 ml), then dried ($MgSO_4$). The residue, after evaporation, was distilled i.V., yield: 0.52 g (50%), colourless liquid, b.p. 104–106°/2 Torr. – UV. (isooctane): end absorption. – IR. (CH_2Cl_2): 2960, 2880, 1450, 1340, 1305, 1280, 1170, 1100, 1060, 1030, 950, 920, 900, 880, 860, 800, 650. – ^{1}H-NMR. ($CDCl_3$): 6.27 (*m*, 2 H); 3.7–2.4 (*m*, 8 H); 1.57 (*m* × *d*, J_{app} = 10, 1 H); 1.40 (*m* × *d*, J_{app} = 10, 1 H). – MS.: 194 (4), 192 (15), 190 (25), 157 (2), 155 (6), 143 (4), 141 (12), 129 (5), 127 (13), 119 (11), 117 (13), 115 (15), 105 (53), 103 (29), 91 (100), 79 (56), 77 (90).

$C_9H_{12}Cl_2$ (191.1) Calc. C 56.57 H 6.33% Found C 56.69 H 6.46%

endo-*5,6-Bis(chloromethyl)*-exo-*2,3-epoxynorbornane* (**21**). A solution of peracetic acid (40% in acetic acid) (3.4 g, 0.031 mol) in ethyl acetate (2 ml) was added to a solution of *endo*-5,6-bis(chloromethyl)-2-norbornene (**20**) (1.6 g, 0.0083 mol) in ethyl acetate (6 ml). After stirring at RT. for 15 h, water was added (20 ml) and the mixture was extracted with CH_2Cl_2 (3 × 20 ml). The organic extract was washed successively with sat. $NaHCO_3$-solution (3 × 20 ml) and water (20 ml) and dried ($MgSO_4$). The solvent was removed and the residue distilled i.V.; yield: 1.38 g (79%), colourless oil. – UV. (isooctane): end absorption. – IR. ($CHCl_3$): 2980, 1470, 1380, 1335, 1300, 1260, 1060, 1010, 855. – ^{1}H-NMR. ($CDCl_3$): 3.9–3.5 (*m*, 4 H); 3.3 (*m*, 2 H); 2.8 (*m*, 2 H); 2.6 (*m*, 2 H); 1.4 (*m* × *d*, J_{app} = 10, 1 H); 0.9 (*m* × *d*, J_{app} = 10, 1 H). – MS.: 210 (0.1), 208 (0.5), 206 (1), 173 (2), 171 (7), 105 (14), 91 (54), 82 (100), 81 (89).

$C_9H_{12}Cl_2O$ (207.1) Calc. C 52.20 H 5.84% Found C 52.42 H 6.08%

exo-*5,6-Bis(chloromethyl)-2-norbornene* (**23**) was prepared as described for **20**, from *exo*-5,6-bis(*p*-toluenesulfonyloxymethyl)-2-norbornene (2.5 g, 0.0054 mol) [39]; yield: 0.78 g (76%), colourless oil, b.p. 70–75°/1 Torr. – UV. (isooctane): end absorption. – IR. (film): 3080, 2970, 2890, 1465, 1445, 1330, 1300, 1290, 1270, 710. – ^{1}H-NMR. (CCl_4): 6.18 (*m*, 2 H); 3.95–3.05 (*m*, 4 H); 2.92 (*m*, 2 H); 1.97 (*m*, 2 H); 1.42 (*m*, 2 H). – MS.: 194 (0.2), 192 (1), 190 (1.5), 156 (4), 154 (11), 136 (10), 119 (19), 105 (35), 91 (25), 79 (10), 77 (10), 69 (63), 66 (100).

$C_9H_{12}Cl_2$ (191.1) Calc. C 56.57 H 6.33% Found C 56.64 H 6.29%

exo-*5,6-Bis(chloromethyl)*-exo-*2,3-epoxynorbornane* (**24**) was prepared as described for **21**, from **23** (1.6 g, 0.0083 mol); yield: 1.36 g (78%), colourless oil, b.p. 115°/0.2 Torr. – UV. (isooctane): end absorption. – IR. (film): 2980, 1640, 1470, 1400, 1300, 860, 800. – ^{1}H-NMR. (CCl_4): 4.0–3.2 (*m*, 4 H); 3.1 (*m*, 2 H); 2.6 (*m*, 2 H); 2.1 (*m*, 2 H); 1.3 (*m* × *d*, J_{app} = 9.5, 1 H); 0.95 (*m* × *d*, J_{app} = 9.5, 1 H). – MS.: 210 (0.2), 208 (1), 206 (2), 173 (1), 171 (3), 121 (31), 105 (21), 91 (41), 88 (86), 82 (100).

$C_9H_{12}Cl_2O$ (207.1) Calc. C 52.20 H 5.84% Found C 52.17 H 5.90%

endo-*3-Chloro*-endo-*5,6-bis(chloromethyl)*-exo-*2-norbornanol* (**22**). Same procedure as for the preparation of **16**, the starting material being **21** (0.79 g; 0.0038 mol); yield: 0.67 g (72%). White solid purified by

filtration through SiO_2($CHCl_3$), m.p. 67–68° (CCl_4). – UV. (isooctane): end absorption. – IR. (CH_2Cl_2): 3600, 2980, 1740, 1470, 1380, 1330, 1240, 1205, 1100, 1060, 935, 810. – ^{1}H-NMR. ($CDCl_3$): 4.5–3.3 (*m*, 6 H); 2.95 (*m*, 1 H); 2.7 (*m*, 1 H); 2.6–2.4 (*m*, 2 H); 1.9 (*m* × *d*, J_{app} = 10, 1 H); 1.45 (*m* × *d*, J_{app} = 10, 1 H). – ^{13}C-NMR. ($CDCl_3$): 76.6 (*d*, $^1J_{CH}$ = 158 C(2)); 68.2 (*d*, $^1J_{CH}$ = 152 C(3)); 48.0 (*d*); 47.5 (*d*); 45.7 (*d*); 43.2 (*t*; CH_2Cl); 41.8 (*t*; CH_2Cl); 40.3 (*d*); 35.7 (*t*, $^1J_{CH}$ = 137; C(7)). – MS.: 246 (0.5), 244 (1), 242 (1), 223 (9), 211 (1), 209 (7), 207 (10), 195 (26), 193 (39), 177 (21), 175 (17), 149 (99), 141 (23), 139 (22), 129 (44), 105 (17), 93 (40), 91 (50), 86 (74), 84 (100), 83 (57), 79 (33), 77 (37).

$C_9H_{13}Cl_3O$ (243.56) Calc. C 44.38 H 5.38% Found C 44.10 H 5.33%

When **22** (0.29 g, 0.0012 mol) was heated to 105° in anh. DMF (5 ml) in presence of an excess of anh. CsF (1 g, 0.0066 mol) for 24 h under N_2, it yielded the diene **18** (73%). The method described for the preparation of **18** from **16** (see above) was used.

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