8. Interaction between Non-Conjugated Chromophores: 5,6-Dimethylidene-*exo*-2-norborneol, 5,6-Dimethylidene-*exo*, *exo*-2,3-norbornanediol and 5,6-Dimethylidene-2-norbornanone

by **André Chollet, Cyril Mahaim, Christophe Foetisch, Michèle Hardy** and **Pierre Vogel**
Institut de chimie organique de l'Université, 2, rue de la Barre, CH-1005 Lausanne

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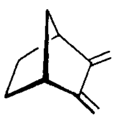
Summary

Preparation of the title compounds **11**, **12** and **13** is described. Preliminary kinetic results indicate that the hydroxyl substituents in **11** and **12** have a very small retardation effect on the *Diels-Alder* reactivity of 2,3-dimethylidene-norbornane. The keto group in **13** exerts a larger retardation effect, although it is much smaller than the retardation effect introduced by an *exo*-5,6-epoxide ring in 2,3-dimethylidene-norbornane.

Introduction. – Chemical and spectroscopic properties of the s-*cis*-butadiene chromophore in 2,3-dimethylidene-norbornane **1** can be modified without direct substitution of the diene moiety. Substitution of an ethereal bridge for the $H_2C(7)$ bridge (**2**, **4**, **6**) and/or introduction of a double bond (**5**, **6**) or of an *exo*-epoxide ring (**3**, **4**) for the $H_2C(5)$–$H_2C(6)$ bridge cause a decrease in the rates of *Diels-Alder* cycloaddition with strong dienophiles [1]. *A priori*, these observations are explicable by: (a) geometry changes of the diene moiety in **1**–**6** due to modification of the ring strain of the bicyclic skeleton or by removal of gauche interactions; (b) changes in steric hindrance due to modified gauche interactions between the cycloaddends in the transition state; (c) variations in the electrostatic interactions between the cycloaddends themselves, between the solvent and the cycloaddends and between the solvent and the transition states; (d) differences in electronic properties of the s-*cis*-butadiene group (energies and shapes of the frontier and extra-frontier MO's) in **1**–**6** due to through-space and/or through bond interactions [2] between the non-conjugated chromophores.

The lack of correlation between ring strain of the bicyclic skeleton and the observed reactivity differences and the non-observation of bridgehead methyl sub-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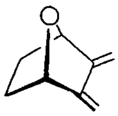
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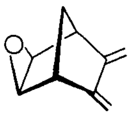
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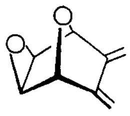
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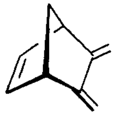
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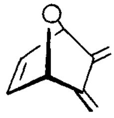
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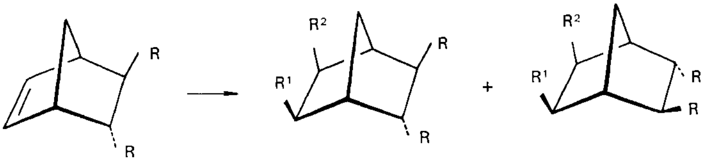
stituent effects on the *Diels-Alder* reactivity of **2** suggested that both strain and geometry effects are not important in differentiating the reactivity of dienes **1–6** toward strong dienophiles. A correlation between spectroscopic parameters ($V \leftarrow N$ transition energies, the ^{13}C chemical shifts of the olefinic carbon atoms) and the reactivity differences of **1–6** indicated that electronic factors dictate the chemical and spectroscopic behaviors of these compounds. The rate retardation observed in the *Diels-Alder* additions of **3** and **4** compared with **1** and **2**, respectively, is likely a consequence of specific electronic features of the oxirane ring which can interact with the s-*cis*-butadiene chromophore by a through bond and/or through space mechanism [3], but it can also be due to pure electrostatic effects arising from the oxygen atom of the epoxide function. In order to better understand the effect of the epoxide ring on the chemical and spectroscopic properties of the dienes **3** and **4** we chose to study 5,6-dimethylidene-*exo*-2-norborneol (**11**), 5,6-dimethylidene-*exo,exo*-2,3-norbornanediol (**12**) and 5,6-dimethylidene-norcamphor (**13**). The facile synthesis of these three new dienes and preliminary results on the kinetics of their *Diels-Alder* cycloadditions to dimethyl acetylenedicarboxylate (DAD) and tetracyanoethylene (TCE) are reported herein.

Synthesis. – Double elimination of *p*-toluenesulfonic acid from the corresponding bis-toluenesulfonates is probably the best method available to prepare very pure dimethylidene hydrocarbons [1] [3] [4] and polymethylidene derivatives [5], but it has the disadvantage, sometimes, to require several steps for reaching the starting polytoluenesulfonates. In the bicyclo[2.2.1]heptane series, *trans*-5,6-bis(chloromethyl)-2-norbornene (**7**) is readily available by *Diels-Alder* addition of cyclopentadiene to 1,4-dichloro-*trans*-2-butene.



7 R=CH_2Cl **8** R^1=OH; R^2=H **9** R^1=OH; R^2=H
10 R^1=R^2=OH

The endocyclic double bond in **7** can be exploited to functionalize the bicyclic skeleton. For example the *exo*-2-norborneols **8** and **9** are easily prepared by hydroboration-oxidation [6] of **7**. Treatment of this mixture in boiling KOH/EtOH (72 h) furnished the hydroxy-diene **11** in good yield[1]).

The alcohol **11** can be oxidized by CrO_3/pyridine [10] to the corresponding 5,6-dimethylidene-norcamphor (**13**)[2]).

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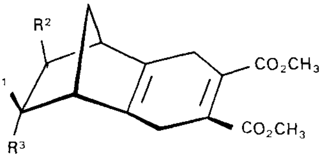
[1]) This method had been applied previously to the preparation of **1**, **5** [7], **3** [8] and other halogenated olefinic derivatives [9].

[2]) The reduction of the 2,3-dimethylidene-*exo*-5,6-epoxy-norbornane **3** by $LiAlH_4$ in THF yielded 5-methylidene-6-methyl-*anti*-3-nortricyclanol (major) together with minor amounts of alcohol **11** and 2,3-dimethylidene-*anti*-7-norborneol [11]. Attempts to hydrate the epoxide in **3** or to isomerize **3** into the ketone **9** by known methods [12] lead to decomposition of the diene.

$KMnO_4$ oxidation [13] of **7** in a two-phase system using tetrabutylammonium hydroxide as phase transfer catalyst [14] yielded the diol **10** which furnished the corresponding dihydroxy-diene **12** after double HCl elimination in boiling KOH/EtOH.

The dienes **11**, **12** and **13** have been characterized spectroscopically, by their elemental analysis and by formation of Diels-Alder adducts with dimethyl acetylenedicarboxylate (**14**, **15**, **16**) and tetracyanoethylene (**17**, **18**, **19**).



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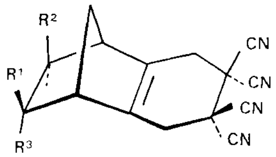


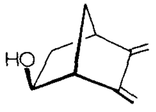
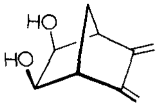
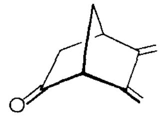
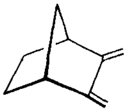
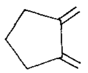
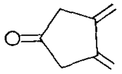
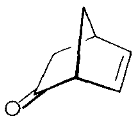
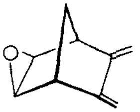
17 $R^1=OH; R^2=R^3=H$
18 $R^1=R^2=OH; R^3=H$
19 $(R^1-R^3)=O; R^2=H$

The assignment of the *exo*-configuration of the hydroxyl groups in dienes **11** and **12**, as well as in the corresponding starting dichlorides **8**, **9** and **10** and in the *Diels-Alder* adducts **14**, **15**, **17** and **18** was based on their mode of formation [6] [15] and ^1H-NMR. analysis. The use of double resonance technique and lanthanide shift reagents [16] permitted unambiguous assignment of NMR. signals. Comparative analysis of the NMR. spectra of **11**, **12** and **13** with those of *exo*-2-norborn-5-enol [17], *exo,exo*-2,3-norborn-5-enediol [18] and dehydronorcamphor [19], respectively, indicates that the s-*cis*-butadiene group affects the ^1H-chemical shift and coupling constants of the bridge hydrogen atoms in the same way as does the endocyclic double bond. In particular, we find H_{7syn} more shielded relatively to H_{7anti} due to anisotropy effect of the diene. The structurally significant coupling constants such as $J_{H_1,H_{7syn}}$ (1.3–1.7 Hz), $J_{H_1,H_{2endo}}$ (0–1 Hz) and $J_{H_{2endo},H_{7syn}}$ (2.0–2.5 Hz) are quite similar to those found for norbornene derivatives [20].

UV. Absorption spectra. – Comparison of the UV. absorption spectra of alcohol **11** and the diol **12** with that of the parent diene **1** shows that the hydroxyl groups at C(2) and C(3) of **11** and **12** introduce a very small blue shift of the $V \leftarrow N$ transition of the butadiene chromophore (see Table 1). That observation suggests that the oxygen atom of the epoxide in **3** and **4** affects the electronic properties of the diene more than the oxygen atom of the hydroxyl substituents in **11** and **12** because it is part of a bent three-membered ring [3].

Homoconjugative interactions are expected between the carbonyl group and the s-*cis*-butadiene chromophore of 5,6-dimethylidene-norcamphor (**13**). The UV. absorption spectrum of **13** shows a red shift and an hyperchromic effect on the $Q \leftarrow N$ ($n \rightarrow \pi^*$) transition of the ketone. Similar observations have been reported for dehydronorcamphor **22** (see Table 1) and analogous rigid β,γ-unsaturated ketones [21]. The $V \leftarrow N$ transition energy of **13** does not change dramatically relative to the parent diene **1**. In the gas phase, a bathochromic shift of about 6 nm is observed in the

Table 1. *UV. absorption characteristics of dienes* **11**, **12**, **13** *and related compounds* **1**, **3**, **20**, **21**, **22** [λ_{max} (ε) in nm]

			
11	**12**	**13**	**1**
245.5 (8900)e) 245.5 (9150)i) 241g)	246.5 (9280)e)	297 (285); 250 (5870)e) 309 (330); 248 (7150)i) 248g)	248e,i) 242g)
			
20	**21**	**22**	**3**
243i) [22]	255 (5500)i) [23]	305 (290); 210 (3000)h) [21] 308 (290); 210 (3000)e)	239e,i) 234.5g)

e) In 95% ethanol.
i) In isooctane.
h) In hexane.
g) In gas phase.

absorption UV. spectrum of **13** (λ_{max}=248 nm) relatively to **1** (λ_{max}=242 nm) (see Table 1). Protic solvent such as 95% ethanol causes a red shift for this transition, whereas a blue shift is observed for the n $\rightarrow \pi^*$ transition of the carbonyl group (compare spectra measured in isooctane and ethanol). These observations are indicative of the existence of a homoconjugative interaction between ketone and diene chromophores in **13**. The fact that the energy of the V $\leftarrow$ N transition of the s-*cis*-butadiene in **13** does not change significantly relatively to **1** suggests that the expected bathochromic effect of 10–15 nm in solution (compare the UV. spectrum of 3,4-dimethylidene-cyclopentanone (**21**) with that of 1,2-dimethylidene-cyclopentane (**20**) [22], or the spectrum of dehydronorcamphor (**22**) with that of norbornene [21]) is compensated partially by an hypsochromic effect3).

Table 2 summarizes the relative rates of *Diels-Alder* additions of DAD to **1**, **11**, **12**, **13** and **3** measured by ^{1}H-NMR. technique [1]. It is found that the hydroxyl substituents in **11** and **12** have an unsignificant effect on the reactivity of 2,3-dimethylidene-norbornane toward DAD. The carbonyl group in **13** causes a rate retar-

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3) The $V \leftarrow N$ transition of most 2,3-dimethylidene-norbornane derivatives is split into three bands due to vibrational coupling. The central band is generally the highest in intensity; it is reported here and is assumed to represent the $V \leftarrow N$ transition energies in all the dienes. This hypothesis has to be tested before any qualitative or quantitative interpretation of the factors which affect the electronic properties of the investigated compounds can be presented.

Table 2. *Summary of preliminary kinetic data of cycloadditions of dienes* **1**, **11**, **12**, **13** *and* **3** *to dimethyl acetylenedicarboxylate* (DAD) *in CCl_4 and to tetracyanoethylene* (TCE) *in CH_2Cl_2*

Dienophile	Diene				
	1	**11**	**12**	**13**	**3**
DAD[a])					
k^{II} [10^5 l/mol · s]	7.5 ± 0.15[b])	4.4 ± 0.1	6.1 ± 0.1	1.3 ± 0.05	0.41[c])
temperature of the measurement above	12°	11°	11°	11°	11°
k^{II} at 11°; relative	(1.0)	~0.6	~0.84	~0.18	~0.056
TCE[d])					
k^{II} at 25° relative	(1.0)	0.25 ± 0.02	0.054 ± 0.013	0.034 ± 0.014	0.005 ± 0.002

[a]) For experimental details of the kinetic measurements and the errors on the temperature, see [1].

[b]) Values taken from [1].

[c]) Value extrapolated from data obtained at higher temperatures, see [1].

[d]) Average values of at least three runs; the concentrations of the dienes mixed with various amounts of the reference compound **1** are measured by GC. (*Hewlett Packard*, glass injector and glass columns) before and after complete reaction with various amounts of TCE in CH_2Cl_2. The cycloaddition of TCE to **12** was also compared with that to **11**, to **13** and to **3**.

dation by a factor of 5–6 (at 11°). This is about one third of the magnitude of the rate retardation observed for the *exo*-5,6-epoxy derivative **3** relative to the parent diene **1** [1]. Relative rate constants for the cycloadditions of TCE to dienes **11**, **12** and **13** (Table 2) were obtained by a competitive technique using GC. analysis. The hydroxyl substituents show a small retardation effect which seems to be multiplicative on the rate constants. Again this effect is smaller than the retardation effect observed in the cycloaddition of TCE to the ketone derivative **13** relative to **1**. The reactivity difference of **1** and **3** in the *Diels-Alder* additions is much larger with TCE as dienophile than with DAD. This observation is in agreement with the hypothesis [1] that electronic factors modify the *Diels-Alder* reactivity of the epoxy-diene **3** relative to the parent diene **1**.

Conclusion. – Three new oxygenated derivatives (**11**, **12**, **13**) of 2,3-dimethylidene norbornane have been prepared by very simple methods. Their UV. absorption spectra and their *Diels-Alder* reactivity do not differ very much from those of the parent diene **1**. This is in sharp contrast with the relatively large effects introduced by the *exo*-5,6-epoxide ring in **3** and **4** on the properties of the s-*cis*-butadiene chromophore of the 2,3-dimethylidene-norbornane derivatives. The observed effects caused by the epoxide function in **3** and **4** on the chemical and spectroscopic behaviours of the exocyclic diene systems are likely the manifestations of strain introduced to the bicyclic skeleton and/or specific electronic features (*i. e.*, low-lying empty orbitals) of the oxirane [1].

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Experimental Part[4])

The melting points (m.p.) are not corrected. IR. spectra were measured on a *Beckmann* IR-20A spectrophotometer ($\tilde{\nu}$ [cm^{-1}]). UV. spectra were recorded with a *Carl Zeiss* RPQ 20 A/C instrument (λ_{max} [nm]; (ε)). MS. were taken at 70 eV with a *CEC* 21-490 *Bell-Howell* spectrometer (m^+/e [amu] (% base peak)). ^{1}H-NMR. spectra were recorded on a *Varian* A60A instrument (δ [ppm] (multiplicity, apparent coupling constant J [Hz], number of protons)); internal TMS was used as reference δ_{TMS} = 0.00 ppm (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br. = broad). Microanalysis were performed by the 'Microlabor' of the Institute of Organic Chemistry of Basle (Dr. *Thommen*). Abbreviations: *i. V.* = in vacuo, RT. = room temperature.

Mixture of trans-*5,6-bis(chloromethyl)*-exo-*2-norborneols* **8** *and* **9**. Under N_2, a freshly distilled solution of $Et_2O \cdot BF_3$ (12 g, 0.085 mol) was added dropwise to a vigorously stirred suspension of $NaBH_4$ (2.6 g, 0.069 mol) and *trans*-5,6-bis(chloromethyl)-2-norbornene (10 g, 0.052 mol) in 30 ml of anhydrous tetrahydrofuran cooled to 0°. The mixture was stirred for 3 h at 20° and then cooled to 0° by an ice bath. Water (10 ml), aqueous 3 N KOH (15 ml) and finally 30% H_2O_2 (12 ml, 0.118 mol) were added dropwise in succession. The mixture was stirred for 24 h at 20° and then extracted several times with ether and dried over anhydrous $MgSO_4$. The solvent was removed *i. V.* affording a mixture of *trans*-5,6-bis(chloromethyl)-*exo*-2-norborneols (**8** + **9**) as a colourless liquid. Yield: 8.6 g (79,4%); b.p. 100°/0.01 Torr. – IR. (CCl_4): 3320, 2940, 1440, 1290, 1025, 700. – UV. (95% EtOH): end absorption. – ^{1}H-NMR. (CCl_4): 4.05 (m, 1H); 4.0–3.0 (m, 4H); 2.5–1.0 (m, 8H). – MS.: 210 (< 1), 208 (1), 192 (10), 190 (14), 143 (65), 141 (100), 93 (78), 79 (85), 67 (77).

5,6-Dimethylidene-exo-*2-norborneol* (**11**). A mixture of alcohols **8** + **9** (5.0 g, 0.024 mol) and KOH (4.0 g, 0.071 mol) in 15 ml of abs. ethanol was heated under N_2 and under reflux for 72 h. After addition of water (20–30 ml) the mixture was extracted 5 to 6 times with 30 ml portions of CH_2Cl_2. The organic extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed *i. V.* and the residue distilled affording 2.35 g (72%) of 5,6-dimethylidene-*exo*-2-norborneol (**11**) as a colourless liquid; b.p. 50°/0.01 Torr. – IR. (film): 3300, 2960, 1625, 1045, 970, 875. – UV. (isooctane): 254 (sh, 6030), 245.5 (9150), 240 (sh, 8500). – MS.: 137 (3), 136 (21), 118 (53), 117 (29),

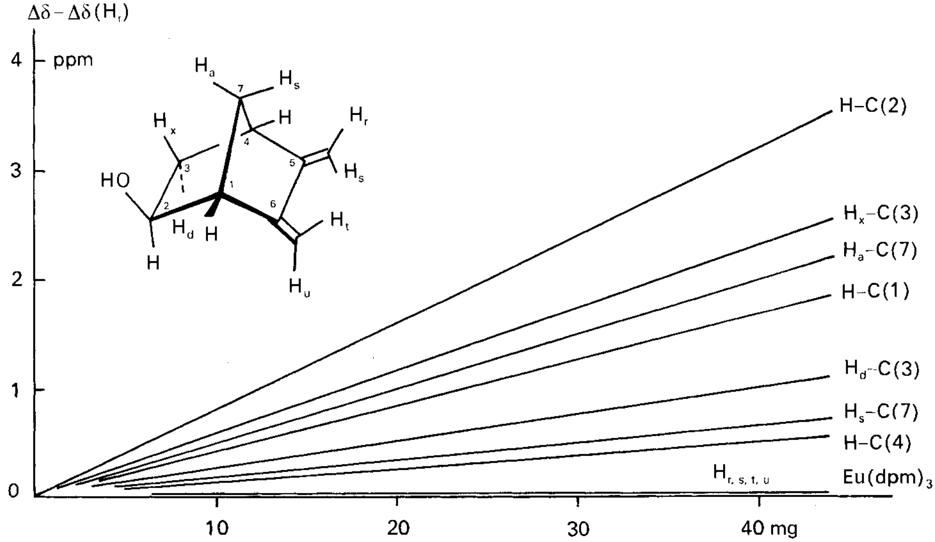

Fig. 1. *Eu(dpm)$_3$ induced shifts on the ^{1}H-NMR. signals of alcohol* **11** (30 mg in approx. 0.5 ml of $CDCl_3$; 40°)

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[4]) We wish to thank Mr *H. Serra* and Mr *D. Quarroz* for their technical assistance.

107 (24), 105 (13), 103 (16), 92 (58), 91 (100), 79 (29), 78 (16), 77 (24), 66 (63). – ^{1}H-NMR. ($CDCl_3$): 5.34 (br. *s*, 1 H, H_t); 5.20 (br. *s*, 1 H, H_s); 5.04 (br. *s*, 1 H, H_u); 4.90 (br. *s*, 1 H, H_r)⁵); 4.06 (*m*, $J_{app}=6.0$, 2.5, 1 H, H–C(2)); 2.85 (*m*, $J=3.5$, 1.5, 2 H, H–C(1) and H–C(4)); 1.92 (*m*, $J=12.5$, 6.0, 2.5, 1 H, H_d–C(3)); 1.72 (*m*, $J=9.5$, 1.5, 1 H, H_a–C(7)); 1.52 (*m*, $J=12.5$, 3.5, 1 H, H_x–C(3)); 1.43 (*m*, $J=9.5$, 2.5, 1.5, 1 H, H_s–C(7)).

$C_9H_{12}O$ (136.19) Calc. C 79.37 H 8.88% Found C 79.04 H 8.85%

Adduct of **11** *with Tetracyanothylene* (*TCE*) (**17**). 5,6-Dimethylidene-*exo*-2-norborneol (80 mg, 0.59 mmol) and TCE (75 mg, 0.59 mmol) were stirred in 3 ml of anhydrous benzene for 24 h at RT. The precipitate was recrystallized from CH_2Cl_2/pentane affording 130 mg (83%) of **17**. M.p. 173–173.5°. – IR. (KBr): 3540, 3420, 2920, 2860, 2250, 1435, 1405. – UV. (95% EtOH): 210 (3000). – MS.: 264 (11), 221 (11), 220 (66), 105 (9), 92 (100), 91 (27), 77 (7), 65 (4), 51 (6). – ^{1}H-NMR. (pyridine): 4.25 (*m*, 1 H); 3.47 (*m*, 4 H); 2.88 (br. *s*, 1 H); 2.72 (br. *s*, 1 H); 2.3–1.4 (*m*, 4 H).

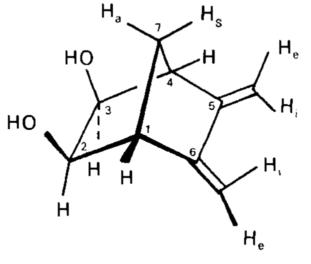
$C_{15}H_{12}N_4O$ (264.28) Calc. C 68.57 H 4.58% Found C 68.16 H 4.80%

trans-*5,6-bis(chloromethyl)*-exo,exo-*2,3-norbornanediol* (**10**). A saturated aqueous solution of $KMnO_4$ (38 g, 0.24 mol) was added dropwise to a stirred mixture of *trans*-5,6-bis(chloromethyl)-2-norbornene (46 g, 0.24 mol) and tetrabutylammonium hydroxyde (40% in H_2O) (7.4 g, 0.011 mol) in 200 ml of CH_2Cl_2 and 200 ml of 40% NaOH in H_2O cooled to 0°. After the addition was complete, the reaction was allowed to reach RT. and stirred for 24 h. A saturated aqueous solution of $NaHSO_3$ was then added slowly to destroy the MnO_2 formed. The mixture was extracted several times with CH_2Cl_2, and after decolouring with charcoal, the organic extracts were dried over anhydrous $MgSO_4$. The solvent was removed *i. V.* and the solid residue recrystallized from CH_2Cl_2/pentane affording 20 g (37%) of *trans*-5,6-bis(chloromethyl)-*exo,exo*-2,3-norbornanediol (**10**) as white crystals. M.p. 76–76.5°. – IR. (KBr): 3300, 2960, 2920, 1300, 1090, 720. – UV. (95% EtOH): final absorption. – MS.: 226 (3), 224 (5), 208 (5), 206 (8), 195 (29), 193 (43), 129 (100). – ^{1}H-NMR. ($CDCl_3$): 4.15–3.2 (*m*, 6 H); 2.5–1.1 (*m*, 6 H).

$C_9H_{14}Cl_2O_2$ (225.1) Calc. C 48.02 H 6.27% Found C 48.22 H 6.38%

5,6-Dimethylidene-exo,exo-*2,3-norbornanediol* (**12**). A mixture of diol **10** (220 mg, 0.98 mmol) and KOH (220 mg, 3.92 mmol) in 2 ml of abs. ethanol was heated under N_2 and under reflux for 80 h. Water (5 ml) was then added and the mixture extracted 4–5 times with ether. The organic layers were washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the solid residue recrystallized form ether/light petroleum affording 85 mg (57%) of 5,6-dimethylidene-*exo*, *exo*-2,3-norbornanediol as white crystals. M.p.: 97–98°. – IR. (KBr): 3300, 2970, 1640, 1470, 1440, 1330, 1090, 900. – UV. (95% EtOH): 255 (sh, 6390), 246.5 (9280), 241 (sh, 8520). – MS.: 153 (1), 152 (9), 134 (11), 105 (22), 93 (97), 91 (100), 79 (22), 77 (28), 65 (14). – ^{1}H-NMR. ($CDCl_3$): 5.26 (br. *s*, 2 H, H_i); 4.96 (br. *s*, 2 H, H_e)⁵); 3.86 (*d*, $J_{app}=1.5$, 2 H, H–C(2) and H–C(3)); 2.80 (*t*, $J=1.3$, 2 H, H–C(1) and H–C(4)); 1.95 (*m*, $J=10.2$, 1.3, 1 H, H_a–C(7)); 1.45 (*m*, $J=10.2$, 1.5, 1.3, 1 H, H_s–C(7)).

$C_9H_{12}O_2$ (152.19) Calc. C 71.02 H 7.95% Found C 70.76 H 8.24%



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⁵) The assignments of this ^{1}H-NMR. signal is tentative.

Adduct of **12** *with dimethyl acetylenedicarboxylate* (**15**). **12** (20 mg, 0.13 mmol) was mixed with freshly distilled DAD (20 mg, 0.14 mmol) in 2 ml of anhydrous ether. The mixture was stirred for 3 days at RT. under N_2. The white crystalline product formed was filtered off and recrystallized from CH_2Cl_2/pentane affording 30 mg (77%) of adduct **15**. – M.p. 154–154.5°. – IR. (KBr): 3420, 2940, 1705, 1635, 1435, 1285, 1060. – UV. (95% EtOH): 250 (sh, 1000), 207 (8000). – MS.: 294 (1), 263 (14), 235 (32), 203 (100), 202 (47), 201 (37), 175 (13), 143 (18), 131 (10), 115 (18), 105 (8), 91 (7), 77 (5). – ^{1}H-NMR. ($CDCl_3$): 3.80 (*s*, 6H); 3.70 (*m*, 2H); 3.05 (*d–m*, *J*=2.5, 4H); 2.58 (*m*, 2H); 1.89 (*d–m*, *J*=9.5, 1H); 1.68 (*d–m*, *J*=9.5, 1H).

$C_{15}H_{18}O_6$ (294.3) Calc. C 61.22 H 6.16% Found C 61.14 H 6.34%

5,6-Dimethylidene-2-norbornanone (**13**). To a stirred suspension of CrO_3 (1.5 g, 0.015 mol) in 12 ml of anhydrous pyridine, a solution of 5,6-dimethylidene-*exo*-2-norborneol (**11**, 0.7 g, 0.005 mol) in 3 ml of pyridine was added dropwise. The mixture was stirred for 48 h at 20°. The dark-brown mixture was extracted 5–6 times with ether. The ethereal extracts were combined, washed with 0.01 N HCl and dried over $MgSO_4$. The solvent was removed *i. V.* and the residue transferred on vac-line at 10^{-5} Torr affording 0.3 g (44%) of 5,6-dimethylidene-2-norbornanone (**13**) as a colourless liquid. – IR. (film): 2960, 1750, 1630, 1410, 1150, 1000, 890. – UV. (isooctane): 309 (330); 248 (7150). – UV. (95% EtOH): 297 (285), 250 (5870). – UV. (gas phase): 248, 202. – MS.: 135 (4), 134 (40), 106 (18), 105 (28), 92 (35), 91 (100), 86 (16), 84 (23). – ^{1}H-NMR. ($CDCl_3$): 5.45 (br.*s*, 1H, H_t); 5.33 (br.*s*, 1H, H_s); 5.18 (br.*s*, 1H, H_u); 5.08 (br.*s*, 1H, H_r); 3.26 (*m*, 2H, H–C(1) and H–C(4)); 2.15 (*m*, 2H, H_x- and H_d-C(3)); 1.92 (*m*, 2H, H_a- and H_s-C(7)).

$C_9H_{10}O$ (134.18) Calc. C 80.56 H 7.51% Found C 80.42 H 7.66%

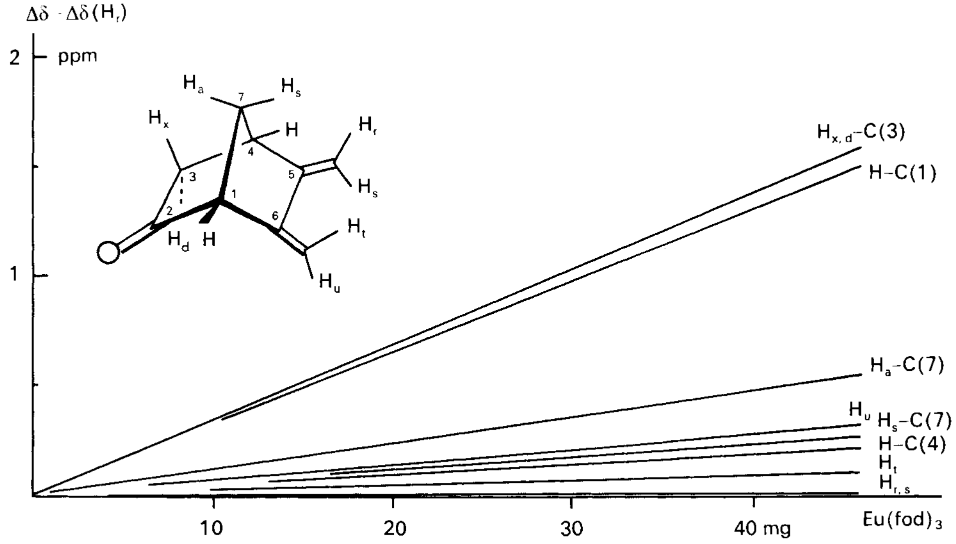

Fig. 2. *Eu(fod)$_3$ induced shifts on the ^{1}H-NMR. signals of ketone* **13** (46 mg in approx. 0.5 ml $CDCl_3$; 40°)

Adduct of **13** *with TCE* (**19**). Same method as for **17**. Recrystallize from CH_2Cl_2/pentane. Yield: 69%, colourless powder. M.p. 215–216°. – IR. (KBr): 2940, 2220, 1730, 1420, 1250, 1220, 1140, 1100, 980. – UV. (95% EtOH): 302 (500), 213 (6000). – MS.: 263 (4), 262 (16), 220 (68), 92 (100), 91 (36). – ^{1}H-NMR. (pyridine): 3.70 (*m*, 4H); 3.12 (br.*s*, 1H); 3.03 (*m*, 1H); 2.2–1.7 (*m*, 4H).

$C_{15}H_{10}N_4O$ (262.28) Calc. C 68.69 H 3.84% Found C 68.61 H 3.91%

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