92. 1,2*endo*-Trimethylenenorbornane. A Novel Isomer of Adamantane

by **Franz Josef Jäggi** and **Camille Ganter**

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, Universitätstrasse 16, CH-8092 Zürich

(6.II.80)

Summary

An easy approach to the novel adamantane isomer 1,2*endo*-trimethylenenorbornane (**2**) is described. Starting from a mixture of pent-4-ynylcyclopentadienes **3** the tricyclic monosaturated key intermediate **5** was prepared by intramolecular cycloaddition (→**4**) and subsequent regioselective reduction of the C(5),C(6) double bond. The title hydrocarbon **2** was obtained from **5** upon stereoselective hydrogenation by diimide. In addition specifically deuteriated analogues of **2** were prepared applying dideuteriodiimide. Compound **2** rearranged to 2*endo*,6*endo*-trimethylenenorbornane (4-homobrendane, **10**) in sulfuric acid as well as with aluminium bromide in carbon disulfide.

Only two members of the 'adamantaneland'[1]) contain a *trans*-perhydropentalene ring system as a structural element. One of them, 1,7-trimethylenenorbornane (**1**), became known only very recently[2]). The second one, the novel 1,2*endo*-trimethylenenorbornane (**2**)[3]), is subject of the present communication.

Its corresponding ethano-bridged *cis*-perhydropentalene isomer **13**[4]), whose *Lewis*-acid catalyzed isomerisation to adamantane has been studied by *Schleyer et al.* [1b], appears to be 6–7 kcal/mol more stable than **2** [1b] [4]. This difference in thermodynamic stability, which is approximately in the same order of magnitude as determined for other pairs of *cis*- and *trans*-perhydropentalenes [5], has to be

Scheme 1

1 **2**

[1]) 'Adamantaneland': a set of 19 isomeric $C_{10}H_{16}$ hydrocarbons [1].

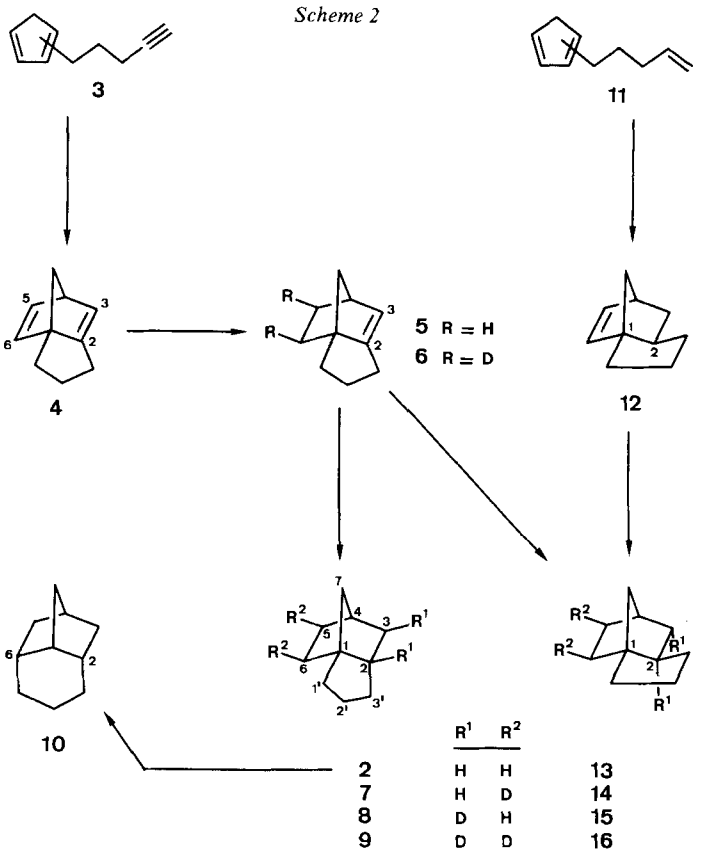
[2]) Two synthetic approaches were described, one by us [2] and a similar one by *Skattebøl & Holm* [3].

[3]) *rel*(1*R*,5*S*)-Tricyclo[5.2.1.$0^{1,5}$]decane, 3a,6-methano (3aα,6α,7aα)perhydro-indene.

[4]) 1,2*exo*-Trimethylenenorbornane, *rel*(1*R*,5*R*)-Tricyclo[5.2.1.$0^{1,5}$]decane, 3a,6-methano(3aα,6α,7aβ)-perhydro-indene.

0018-019X/80/4/0866-06$01.00/0

Scheme 2



taken into account planning a synthesis of **2**. We therefore envisaged the intermediate **5** with a C(2),C(3) double bond though opening the possibility of preparing the title compound **2** by a kinetically controlled attack of hydrogen from the actually more favoured *exo*-side of the norbornene skeleton[5]).

The starting material **3**, a mixture of pent-4-ynylcyclopentadienes, was prepared in analogy to *Corey*'s procedure for **11** [4]. Cyclopentadienylsodium was alkalyted in ammonia [6] by 5-bromo-1-pentyne. Thermolysis of **3** in tributylamine led to the 1,2-trimethylenenorborna-2,5-diene (**4**) in good yield. As expected, hydrogenation of **4** in pentane with 5% $Pd/CaCO_3$ as catalyst yielded exclusively the already known 1,2*exo*-trimethylenenorbornane **13** [1b][6]). However, the target hydro-

[5]) According to the energy difference between **2** and **13**, thermolysis of the triene mixture **11**, as described by *Corey & Glass* [4], yielded the expected tricyclic 2*exo*-compound **12** and none of the corresponding product with 2*endo*-configuration.

[6]) Compounds **4** and **5** can also be described as derivatives of bicyclo[3.3.0]-1-octene, which upon reduction of the double bond in the presence of a catalyst such as supported Pd or Pt as well as by alkali metals are known to form the more stable *cis*-perhydropentalenes despite of steric hindrance, see *e.g.* the platinum catalyzed hydrogenation of bicyclo[3.3.0]-1-octene [7] and a reaction sequence in the synthesis of cedrol [8].

Table 1. *Results of diimide reductions*

Run	Starting material	Amount of olefin mmol	PADA equiv.	N_2R_2 R	Isolated yield %	Composition (%)		Determination method
1	**4**	6.0	1.00	H	88	**5** (86)	**4** (14)	^{1}H-NMR.
2	**4**	6.3	1.16	H	96	**5** (90)	**2**+**13** (10)	^{1}H-NMR.
3	**4**	1.8	3.74	H	Not isolated	**2** (67)	**5**+**13** (33)	GLC.
4a	**4**	5.3	7.84	H	[a])	**2** (87.5)	**5**+**13** (12.5)	GLC.
4b	[b])	0.7	19.4	H	91.5	**2** (92)	**13** (8)	GLC.
5	**4**	6.3	1.05	D	[c])	**6** (90)	**4** (10)	^{1}H-NMR.
6	[d])	3.15	6.31	H	76.6	**7** (87)	**6**+**14** (13)	GLC.
7	[d])	3.15	6.38	D	78	**9** (55)	**6**+**16** (45)	GLC.
8a	**5**	5.5	7.58	D	[e])	**8** (54)	**5**+**15** (46)	GLC.
8b	[f])	2.5	16.0	D	80	**8** (74)	**5**+**15** (26)	GLC.
9	**5**+**15**[g])	0.4	30	H	Isolated by prep. GLC.	**2** (57)	**13**+**15** (43)	GLC.
10	**12**	4.5	1.34	D	88	**14** (100)		^{1}H-NMR.

[a]) Directly used for run 4b; [b]) Crude mixture from run 4a; [c]) Divided into two equal amounts and used for run 6 and 7; [d]) Half amount of crude mixture from run 5; [e]) Directly used for run 8b; [f]) Crude mixture from run 8a; [g]) Separated from the mixture of run 8b.

Table 2. ^{13}*C-NMR. data of 1,2-trimethylenenorbornanes*[a])

Compound	C(1)	C(2)	C(3)	C(4)	C(5)[b])	C(6)[b])	C(7)	C(1′)	C(2′)	C(3′)
4	70.05	165.69	126.79	54.36	142.74[f])	145.78[f])	79.39	25.78[i])	28.02[i])	30.26[i])
5	60.75	158.77	121.11	46.83	28.15[g])	29.24[g])	53.53	24.67[j])	28.89[j])	29.89[j])
6	60.66	158.96	121.04	46.70	27.67[c,h])	28.82[c,h])	53.46	24.64[k])	28.82[k])	29.86[k])
2	55.86	53.62	29.87	43.48	32.26	27.54	40.41	27.68[l])	28.23[l])	23.26
7	55.69	53.55	29.81	43.32	31.72[c])	26.93[c])	40.34	27.60[m])	28.18[m])	23.21
8	55.70	52.92[c])	29.37[c])	43.33	32.20	27.48	40.35	27.63[n])	28.22[n])	23.11
9	55.59	52.88[c])	29.31[c])	43.18	31.69[c])	26.92[c])	40.29	27.57[o])	28.17[o])	23.09
13	56.49	48.14	40.04	39.29	29.61	33.74	41.13	28.76[p])	26.58[p])	33.74
14	56.35	48.03	39.95	39.11	29.07[c])	33.16[c])	41.07	28.68[q])	26.54[q])	33.68
13+**15**	56.44[d])	48.04[e])	39.96 39.49	39.20 39.11	29.56	33.68[d])	41.09	28.71[r])	26.53[r])	33.68[d])

[a]) 25% $CDCl_3$-Solutions were used; [b]) In saturated compounds the assignment is made in analogy with 1,2*endo*-dimethylnorbornane and 1,2*exo*-dimethylnorbornane, respectively [14]; [c]) Multiplet in compounds containing deuterium; [d]) Signal markedly broadened towards higher field; [e]) The percentage of **15** in the mixture was too small to observe the multiplet of C(2); [f-r]) The assignment may be interchanged.

carbon **2** was obtained in high yield by diimide reduction[7]) of **4** in a stepwise process, first reducing **4** regio- (C(5), C(6) double bond) as well as stereoselectively (*exo* attack) to **5** and subsequently the remaining C(2), C(3) double bond in the latter almost stereoselectively from the *exo*-side. The results starting from **4** as well as from **5** are summarized in *Table 1.*

The stereochemistry of each hydrogen addition was assigned on the basis of ^{13}C-NMR. spectra (see *Table 2*) of the dideuteriodiimide reduction products **7**

[7]) Diimide was generated *in situ* from potassium azodicarboxylate in methanol/acetic acid at room temperature [9a] [9b].

and **8**[8]): in **7** the C(2) and C(3) signals showed the characteristic broadening caused by vicinal coupling with the *exo*-deuterium [10] at C(6) and C(5), respectively, as in **8** the C(5) and C(6) signals due to the vicinal coupling with the *exo*-deuterium at C(3) and C(2), respectively. For the two 1,2-trimethylenenorbornanes **2** (2*endo*) and **13** (2*exo*) an unambigous assignment of the signals in the ^{13}C-NMR.-*(Table 2)* and ^{1}H-NMR.-spectra (exper. part) followed from the spectra of the specifically deuteriated analogues **7** and **8** as well as **14** and **15**, respectively.

The transfer of the two H-atoms from diimide to a C,C double bond is believed to proceed by a synchronous *cis* addition [11] [12]. For norbornene and particularly derivatives thereof the addition is in general strictly *exo-cis* [9][9]). *Garbisch et al.* [12] showed that the major factors that contribute to the reactivity of an olefin are torsional strain, bond angle bending strain and α-alkyl substituent effects. Furthermore, they found that calculated and observed values in reaction rates are in best agreement assuming the transition state in this single elementary process at about one third of the distance along the reaction coordinate (χ)[10]). Norbornene was the most reactive compound among nearly 40 cyclic, *exo*-cyclic and acyclic olefins studied [12]. Strain is released during the reaction with diimide. So it is also for compound **5**.

The availability of **2** allows to study the rearrangement of a further member of the 'Adamantaneland'. As preliminary results we found that **2** in conc. sulfuric acid is converted to 2*endo*,6*endo*-trimethylenenorbornane (4-homobrendane, **10**) [13] [1b] like **13**, however, much more rapidly. Furthermore with $AlBr_3$ in CS_2 at low temperatures (*e.g.* at $-60°$) where we observed no reaction at all of **13**[11]), **2** rearranged exclusively and quantitatively to **10**. Further studies on the rearrangement of **2** as well as of specifically labeled analogues (see *e.g.* **7**–**9**) are in progress and are subject of a forthcoming communication.

Financial support by the *Swiss National Science Foundation* and *Ciba-Geigy AG*, Basel, is gratefully acknowledged.

Experimental Part

General. The products were isolated from etheral solutions removing the solvent by careful distillation through a *Vigreux* column. The residue was transferred in a kugelrohr and distilled under the conditions described in the text. IR. spectra were recorded on a *Perkin-Elmer* 257 spectrometer, bands are given in cm^{-1}, CCl_4-solutions were used. Abbreviations: *s* = strong, *m* = medium, *w* = weak. If not specified, ^{1}H-NMR. spectra (100 MHz) were measured on a *Varian*-HA-100 and ^{13}C-NMR. spectra (25.5 MHz) on a *Varian*-XL-100 using $CDCl_3$ as solvent and TMS ($\delta = 0.00$) as internal standard. Chemical shifts are given in ppm, spin-spin coupling constants *J* in Hz. Abbreviations: *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, $w_{1/2}$ = half width at half hight. Mass spectra (MS.) were recorded on a *Perkin-Elmer* RMU-6M, electron source energy: 70 eV (180°), inlet temperature 200°; the molecular ions (M^+) and fragment ions are given as *m/z* with relative intensities in % of the most abundant fragment.

---

[8]) A kinetic isotope effect can be observed comparing the runs 4a and 8 or the runs 6 and 7 (see *Table 1*).

[9]) It is noteworthy that in the case of **5** to a small extend (8%) also *endo* attack was observed (→ **13**, see *Table 1*, run 4b).

[10]) χ indicates the fractional progress of conversion of alkene to alkane (*i.e.* change of sp^2 to sp^3 hybridization of the olefinic C-atoms) taken from zero to unity.

[11]) The rearrangement of **13** in $AlBr_3/CS_2$ at $-10°$ was already studied by *Schleyer et al.* [1b].

Mixture of pent-4-ynylcyclopentadienes (**3**). Maintaining an inert atmosphere, cooling in a dry ice/2-propanol bath and stirring, freshly distilled cyclopentadiene (6.75 ml, 81 mmol) was added to a solution of 1.25 g sodium metal (54 mmol) in ammonia distilled from sodium. As soon as the mixture became colorless 7.5 g 5-bromo-1-pentyne (51 mmol) was added over a 10 min period. Stirring was continued for 2½ h. After allowing the ammonia to evaporate, ether and water were added. The organic layer was washed 3 times with water. Distillation (60°/12 Torr) yielded 3.37 g (50%) of **3**. – IR.: 3310*s*, 3125*w*, 3060*m*, 2735*w*, 2120*m*, 1612*m*, 1603*m*, 1454*m*, 1433*s*, 1368*s*, 1347*m*, 1329*m*, 1247*s*, 977*w*, 950*m*, 941*m*, 900*s*, 893*s*, 678*s*, 630*s*. – ^{1}H-NMR. (CCl_4, 60 MHz): 1.5–2.7 (*m*, 2 H–C(1′), 2 H–C(2′), 2 H–C(3′) and H–C(5′)); 2.80 and 2.88 (2 *m*, $w½$ each ≈ 4, 2 H–C(5)); 5.8–6.4 (*m*, H–C(1) or H–C(2), H–C(3) and H–C(4)).

1,2-Trimethylenenorborna-2,5-diene (**4**). – a) *From the distilled mixture* **3**. To 30 ml tributylamine maintained at 200° a solution of 4.40 g **3** in 20 ml of tributylamine was added dropwise with stirring over a period of 35 min. After further 10 min the solution was cooled, diluted with ether, washed with 2N HCl and water. Distillation (70°/12 Torr) of the residual yellow oil from 160 mg of lithium aluminum hydride yielded 3.70 g (80%) diene **4** as a colorless oil. – IR.: 3110*w*, 3065*m*, 1640*w*, 1550*w*, 1445*m*, 1433*m*, 1314*m*, 1306*s*, 1280*w*, 1250*w*, 1203*w*, 1187*w*, 1157*w*, 1146*w*, 1055*w*, 977*w*, 908*m*, 890*m*, 842*w*, 693*s*, 663*w*, 652*w*, 618*w*. – ^{1}H-NMR. (CCl_4): 1.5–2.6 (*m*, 2 H–C(7), 2 H–C(1′), 2 H–C(2′) and 2 H–C(3′)); 3.55 (*m*, $w½ \approx 7$, H–C(4)); 5.92 (*m*, $w½ \approx 7$, H–C(3)); 6.40 (*d*, $J_{5,6} = 5$, H–C(6)); 6.60 (*d* × *d*, $J_{5,6} = 5$, $J_{4,5} = 3$, H–C(5)). – MS.: 132 (M^+, 74), 131 (54), 118 (13), 117 (100), 116 (14), 115 (21), 106 (13), 105 (10), 104 (45), 103 (12), 92 (10), 91 (47), 79 (15), 78 (20), 77 (18), 65 (9), 53 (6), 51 (11), 39 (12), 27 (5); $C_{10}H_{12} = 132$.

b) *From the crude mixture* **3**. Thermolysis of undistilled crude mixture **3** under conditions as described above (see a)) yielded 3.75 g (55.5% with respect to 5-bromo-1-pentyne) diene **4**.

Diimide Reductions. – General procedure. A 50–60% methanolic solution of acetic acid (3.0 mol-equiv. with respect to potassium azodicarboxylate PADA) was added over a 10–25 min period to a stirred suspension of PADA in methanol (ratio: 0.4 g/ml) containing the olefin. After further stirring for 20 min, water was added and the product was extracted with ether. The organic layer was washed twice with dilute hydrochloric acid and once with 5% Na_2CO_3-solution. After distillation (80°/25 Torr) the product was analyzed by GLC. (10% NPGS)[12]).

Dideuteriodiimide Reductions. Under dry conditions, dideuteriodiimide was generated from PADA, methanol-d_1, and acetic acid-d_1, analogously to the description above[12]).

*1,2-*endo*-Trimethylenenorbornane* (**2**). – IR.: 2700*w*, 1453*s*, 1360*w*, 1328*m*, 1316*m*, 1300*w*, 1288*m*, 1248*m*, 1233*w*, 1208*m*, 1145*w*, 1073*w*, 1040*w*, 985*w*, 960*w*, 912*m*, 874*w*. – ^{1}H-NMR.: 0.70 (*d* × *d*, $J_{3endo,3exo} = 11.5$, $J_{2,3endo} = 7.5$, H*endo*–C(3)); 0.9–2.2 (*m*, 2 H–C(5), 2 H–C(6), 2 H–C(7), 2 H–C(1′), 2 H–C(2′), 2 H–C(3′), H–C(2) and H*exo*–C(3)); 2.38 (*m*, $w½ \approx 10$, H–C(4)). – MS.: 137 (5), 136 (41, M^+), 121 (42), 108 (26), 107 (100), 95 (20), 94 (46), 93 (34), 91 (13), 82 (11), 81 (18), 80 (33), 79 (70), 77 (15), 67 (37), 53 (12), 41 (20), 39 (17), 27 (9); $C_{10}H_{16} = 136$.

1,2-Trimethylenenorborn-2-ene (**5**). – IR.: 3055*m*, 1637*w*, 1446*s*, 1432*m*, 1313*s*, 1298*m*, 1290*m*, 1230*w*, 1208*w*, 1182*w*, 1125*w*, 1096*w*, 917*w*, 863*w*, 843*w*. – ^{1}H-NMR. (CCl_4): 0.9–2.3 (*m*, 2 H–C(5), 2 H–C(6), 2 H–C(7), 2 H–C(1′), 2 H–C(2′) and 2 H–C(3′)); 2.85 (*m*, $w½ \approx 8$, H–C(4)); 5.49 (*m*, $w½ \approx 7$, H–C(3)). – MS.: 134 (14, M^+), 119 (5), 107 (12), 106 (100), 105 (15), 91 (35), 79 (13), 78 (22), 77 (12), 65 (6), 51 (7), 41 (8), 39 (13), 27 (8); $C_{10}H_{14} = 134$.

5exo,6exo-*Dideuterio-trimethylenenorborn-2-ene* (**6**). – IR.: 3055*m*, 2175*s*, 1637*w*, 1450*s*, 1432*s*, 1300*s*, 1278*m*, 1272*m*, 1220*w*, 1208*w*, 1183*w*, 993*m*, 902*m*, 840*m*. – ^{1}H-NMR.: 0.9–1.3 and 1.3–2.3 (2 *m*, 4 H and 6 H, 2 H–C(7), 2 H–C(1′), 2 H–C(2′), 2 H–C(3′), H*endo*–C(5) and H*endo*–C(6)); 2.85 (*m*, $w½ \approx 7$, H–C(4)); 5.44 (*m*, $w½ \approx 7$, H–C(3)). – MS.: 136 (10, M^+), 135 (2), 107 (11), 106 (100), 92 (9), 91 (22), 78 (18), 65 (3), 51 (4), 41 (3), 39 (6), 27 (3); $C_{10}H_{12}D_2 = 136$.

5exo,6exo-*Dideuterio-1,2-*endo*-trimethylenenorbornane* (**7**). – IR.: 2700*w*, 2175*s*, 1452*s*, 1360*w*, 1324*m*, 1288*m*, 1267*m*, 1135*w*, 1052*w*, 908*w*, 876*w*. – ^{1}H-NMR.: 0.70 (*d* × *d*, $J_{3endo,3exo} = 11.5$, H*endo*–C(3)); 0.9–2.2 (*m*, 2 H–C(7), 2 H–C(1′), 2 H–C(2′), 2 H–C(3′), H–C(2), H*exo*–C(3), H*endo*–C(5) and H*endo*–C(6)); 2.38 (*d*, $J_{4,5exo} = 4.5$, $w½ \approx 5$, H–C(4)). – MS.: 138 (30, M^+), 137 (5),

---

[12]) For results consult *Table 1*.

136 (3), 123 (26), 110 (11), 109 (25), 108 (19), 107 (100), 97 (10), 96 (23), 95 (39), 94 (19), 93 (14), 92 (7), 82 (17), 81 (28), 80 (39), 79 (45), 77 (11), 69 (11), 68 (14), 67 (24), 55 (9), 42 (9), 41 (16), 39 (14); $C_{10}H_{14}D_2$ = 138.

2exo,3exo-Dideuterio-1,2endo-trimethylenenorbornane (**8**). – IR.: 2175*s*, 2130*m*, 2115*m*, 1457*s*, 1323*m*, 1293*m*, 1247*m*, 1227*m*, 1208*m*, 1156*w*, 1128*w*, 1074*w*, 1028*w*, 984*w*, 963*w*, 915*m*, 903*w*, 876*w*. – ^{1}H-NMR.: 0.67 (*m*, $w^1/_2 \approx 6$, H*endo*–C(3)); 0.9–1.8 and 1.7–2.2 (2 *m*, 10 H und 2 H, 2 H–C(5), 2 H–C(6), 2 H–C(7), 2 H–C(1′), 2 H–C(2′) und 2 H–C(3′)); 2.38 (*m*, $w^1/_2 \approx 7$, H–C(4)). – MS.: 138 (32, M^+), 137 (7), 136 (5), 123 (14), 122 (22), 121 (10), 110 (24), 109 (100), 108 (31), 107 (20), 97 (12), 96 (22), 95 (48), 94 (31), 93 (18), 83 (14), 82 (25), 81 (48), 80 (45), 79 (30), 77 (11), 69 (10), 68 (27), 67 (24), 55 (10), 42 (10), 41 (18), 39 (16), 28 (11), 27 (10); $C_{10}H_{14}D_2$ = 138.

2exo,3exo,5exo,6exo-Tetradeuterio-1,2endo-trimethylenenorbornane (**9**). – IR.: 2175*s*, 2120*m*, 1453*s*, 1328*m*, 1320*m*, 1303*w*, 1292*m*, 1280*w*, 1268*m*, 1249*w*, 1232*w*, 1213*w*, 1143*w*, 1058*w*, 907*m*. – ^{1}H-NMR.: 0.68 (*m*, $w^1/_2 \approx 6$, H*endo*–C(3)); 1.0–1.8 and 1.7–2.2 (2 *m*, 8 H and 2 H, 2 H–C(7), 2 H–C(1′), 2 H–C(2′), 2 H–C(3′), H*endo*–C(5) and H*endo*–C(6)); 2.38 (*m*, $w^1/_2 \approx 5$, H–C(4)). – MS.: 140 (34, M^+), 139 (12), 138 (2), 124 (28), 112 (10), 111 (22), 110 (33), 109 (100), 108 (24), 98 (19), 97 (27), 96 (47), 95 (29), 94 (14), 93 (10), 84 (14), 83 (22), 82 (37), 81 (53), 80 (38), 79 (17), 78 (11), 69 (24), 68 (28), 67 (12), 56 (8), 55 (8), 54 (9), 43 (12), 42 (15), 41 (12), 39 (10), 28 (10); $C_{10}H_{12}D_4$ = 140.

5exo,6exo-Dideuterio-1,2exo-trimethylenenorbornane (**14**). – IR.: 2165*s*, 1468*s*, 1448*s*, 1325*m*, 1300*m*, 1276*w*, 1248*w*, 1223*w*, 1205*w*, 1182*w*, 1083*w*, 933*w*, 918*w*, 903*w*, 890*w*. – ^{1}H-NMR.: 0.8–2.2 (*m*, 13 H); 2.17 (*m*, $w^1/_2 \approx 7$, H–C(4)). – MS.: 139 (13), 138 (100, M^+), 137 (16), 123 (42), 122 (29), 110 (25), 109 (27), 108 (27), 107 (25), 97 (18), 96 (53), 95 (89), 94 (39), 93 (23), 83 (28), 82 (40), 81 (58), 80 (53), 79 (44), 78 (16), 77 (13), 69 (19), 68 (22), 67 (41), 66 (13), 56 (12), 55 (13), 54 (11), 53 (12), 43 (11), 42 (17), 41 (24), 40 (11), 39 (21), 28 (14), 27 (11); $C_{10}H_{14}D_2$ = 138.

Catalytic Reduction of **4**. Hydrogenation of 204 mg (1.54 mmol) **4** in pentane (8 ml) for 2 h using 5% Pd/$CaCO_3$ as catalyst, filtration on silicagel and distillation (80°/20 Torr) yielded 196 mg (93%) **13** [1b].

REFERENCES

[1] a) *H.W. Whitlock, jr. & M.W. Siefken*, J. Amer. chem. Soc. *90*, 4929 (1968); b) *E.M. Engler, M. Farcasiu, A. Sevin, J.M. Cense & P.v.R. Schleyer*, J. Amer. chem. Soc. *95*, 5769 (1973); see also *R.C. Fort, jr.*, 'Adamantanes. The Chemistry of Diamond Molecules', M. Dekker Inc., New York, N.Y. 1976.

[2] *F.J. Jäggi & C. Ganter*, Helv. *63*, 832 (1980).

[3] *P.v.R. Schleyer, P. Grubmüller, W.F. Maier, L. Skattebøl & K.H. Holm*, Tetrahedron Letters, in print.

[4] *E.J. Corey & R.S. Glass*, J. Amer. chem. Soc. *89*, 2600 (1967).

[5] a) *S. Chang, D. McNally, S. Shary-Tehrany, M.J. Hickey & R.H. Boyd*, J. Amer. chem. Soc. *92*, 3109 (1970); b) *J.W. Barrett & R.P. Linstead*, J. chem. Soc. *1935*, 436; *1936*, 611.

[6] *K. Alder & H.J. Ache*, Ber. deutsch. chem. Ges. *95*, 503 (1962).

[7] *A.D. Ketley & J.C. McClanahan*, J. org. Chemistry *30*, 940 (1965).

[8] *G. Stork & F.H. Clarke, jr.*, J. Amer. chem. Soc. *83*, 3114 (1961).

[9] a) *H.C. Brown, J.H. Kawakami & K.T. Liu*, J. Amer. chem. Soc. *95*, 2209 (1973); b) *W.C. Baird, jr., B. Franzus & J.H. Surridge*, J. Amer. chem. Soc. *89*, 410 (1967); c) *R.G. Weiss & E.I. Snyder*, J. org. Chemistry *35*, 1627 (1970); d) *L.A. Kheifits, A.E. Gol'dovskii, I.S. Kolomikov & M.E. Volpin*, Izv. Akad. Nauk SSSR, Ser. chim. *1970*, 2078.

[10] *J.B. Stothers, C.T. Tan & K.C. Teo*, Canad. J. Chemistry *51*, 2893 (1973).

[11] *S. Hünig & R. Müller*, Angew. Chemie Int. Ed. *1*, 213 (1962).

[12] *E.W. Garbisch, jr., S.M. Schildcrout, D.B. Patterson & C.M. Sprecher*, J. Amer. chem. Soc. *87*, 2932 (1965).

[13] *N. Takaishi, Y. Fujikura, Y. Inamoto & K. Aigami*, J. org. Chemistry *42*, 1737 (1977).

[14] *E. Lipmaa, T. Pehk, J. Paasivirta, N. Belikova & A. Platé*, Org. magn. Res. *2*, 581 (1970).