119. The Adamantane Rearrangement of 1,2-Trimethylenenorbornanes. III[1]). $AlBr_3$-catalyzed Rearrangement to 2,6-Trimethylenenorbornane

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(30.III.83)

Summary

From treatment of D-labelled 1,2*exo*-, 1,2*endo*- and 2*endo*,6*endo*-trimethylenenorbornane (**1**, **2** and **3**, resp.) with aluminum bromide in carbon disulfide, the evidence is gained that a degenerate rearrangement is involved in the adamantane rearrangement of both **1** and **2** to **3**.

1. Introduction. – 1,2*exo*-Trimethylenenorbornane (**1**)[2]) represents one of the few isomers of the 'adamantaneland'[3]) for which the mechanism of its carbenium ion rearrangement has been the subject of more detailed studies. *Schleyer et al.* [4] were successful to establish that 2,6-trimethylenenorbornane (**3**)[2]) and protoadamantane (**4**) are intermediates in the rearrangement of **1** to adamantane (**5**).

More recently *Schleyer et al.* [6] [7] reported the treatment of $^{13}C(1')$-labelled **1** with $AlBr_3$ in CS_2 at $-15°$. Recovered reactant did not reveal any label scrambling, the product **3** was specifically $^{13}C(1')$-labelled: 'This helps to eliminate all but one pathway for conversion of **1** to **3**, namely the direct *Wagner-Meerwein* shift of C(1),C(2)-bond in **1** to C(6).'

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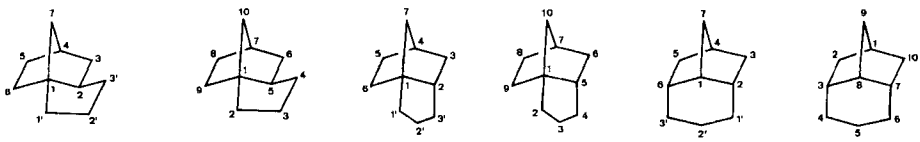
[1]) For part I, see [1]; for part II, see [2].

[2]) Compounds **1**, **2** and **3** are also called as follows: **1**: 1,2*exo*-Trimethylene-8,9,10-trinorbornane, *rel*-(1*R*,5*R*)-tricyclo[5.2.1.$0^{1,5}$]decane (**a**), 3a,6-methano(3aα,6α,7aβ)perhydro-indene; **2**: 1,2-*endo*-trimethylene-8,9,10-trinorbornane, *rel*-(1*R*,5*S*)-tricyclo[5.2.1.$0^{1,5}$]decane (**b**), 3a,6-methano-(3aα,6α,7aα)perhydro-indene; **3**: 2*endo*,6*endo*-trimethylene-8,9,10-trinorbornane, tricyclo[5.2.1.$0^{3,8}$]-decane (**c**), 4-homobrendane, 2,4-methanoperhydro-1*H*-indene. In the present communication the numbering of the C-atoms follows the trimethylenenorbornane nomenclature. The correct IUPAC names are added in parentheses in *Exper. Part.*

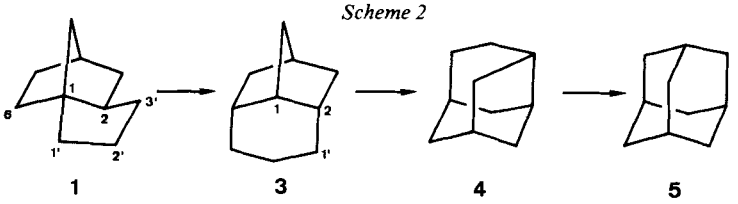
Scheme 1



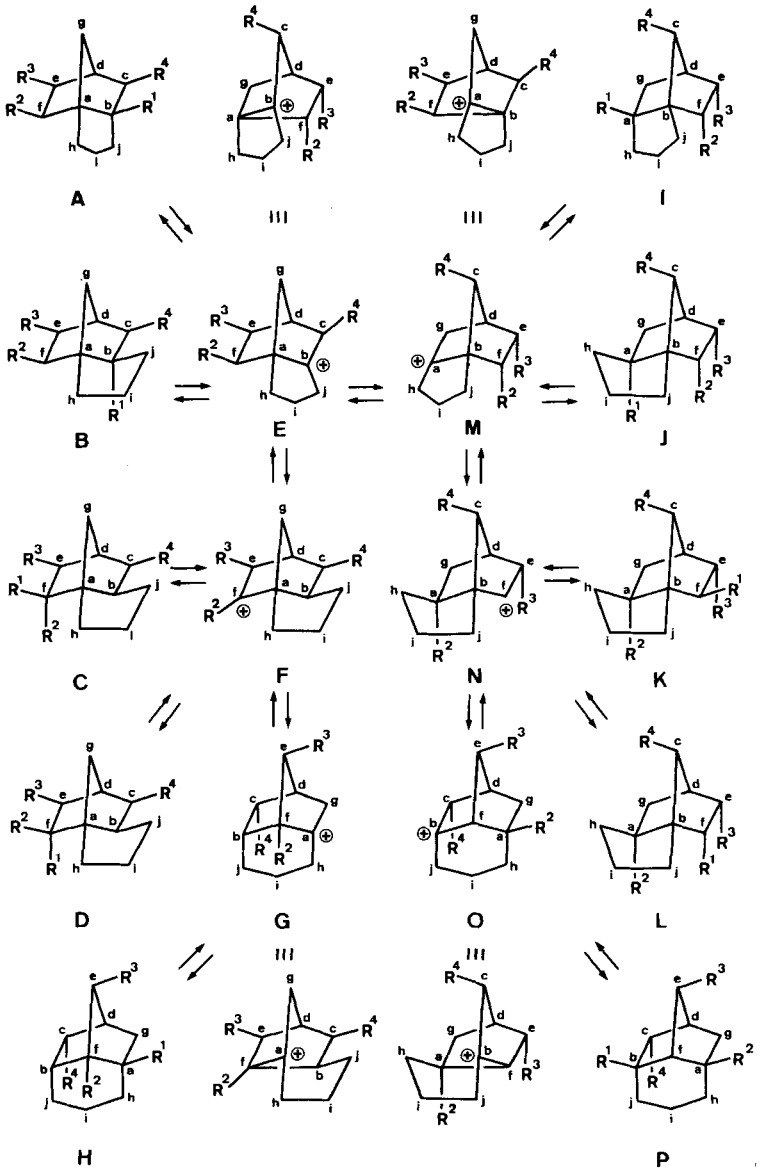
1 **a** **2** **b** **3** **c**

[3]) 'Adamantaneland': a set of 19 isomeric $C_{10}H_{16}$-hydrocarbons [3–5].

Scheme 2



Scheme 3



However, as can easily be seen from *Scheme 3,* the conclusion considering the pathway **C** or **D**[4]) (hydride ion abstraction at C(f))→**F**→**G**→**H**[5]) as the only possibility to explain the results of the ^{13}C-labelling studies, is not relevant. On the one hand, starting from ^{13}C(1′)-labelled **1** (abstraction of R^1 as hydride ion in (h-^{13}C)-**B**, -**C** or -**D**[4]))[5]), no ^{13}C(3′)-labelled **1** ((h-^{13}C)-**J**, -**K**, or -**L**[4]))[5]) is expected, even though a degenerate rearrangement (**E**⇄**M**) and [1,3]-H-shifts (**E**⇄**F** and **M**⇄**N**) are involved, if cation **N** reacts faster to **P** (*via* **O**) than **M** to **J** and **N** to **K** or **L**, respectively. That this is indeed the case, has already been confirmed by the isomerization ($AlBr_3$ in CS_2 at −60°) of the corresponding 1,2*endo*-isomer **2** to **3**, which proceeds not *via* **1** as an intermediate as shown by us recently [2]. One the other hand, ^{13}C-labelling of any one of the ten C-atoms in **1** (**B**, **C** or **D**[5]), C(a)-C(j)) in both cases (with or without **E**⇄**M** and **E**⇄**F**/**M**⇄**N**) causes the same C-atoms to be labelled in **3** (see **H** and **P**[4]))[5]).

Considering different possible pathways *(see Scheme 3),* we reexamined the aluminum bromide-catalyzed rearrangement of the 1,2*exo*-compound **1** to **3**, especially also in view of the rearrangement of the corresponding 1,2*endo*-isomer **2** to **3**. In the latter case, preliminary studies with D-labelled **2**[6]), which yielded **3** with label scrambling, have already manifested **E**⇄**M** being involved in this isomerization[7]).

2. 1,2*endo*-Trimethylenenorbornane. – Treatment of ^{13}C(3)-labelled **2**[8]) *(Scheme 5)* with $AlBr_3$ in CS_2 at −60° gave (3-^{13}C)-**3** without any label scrambling, and the recov-

[4]) The compounds are identical for $R^1 - R^4 = H$.

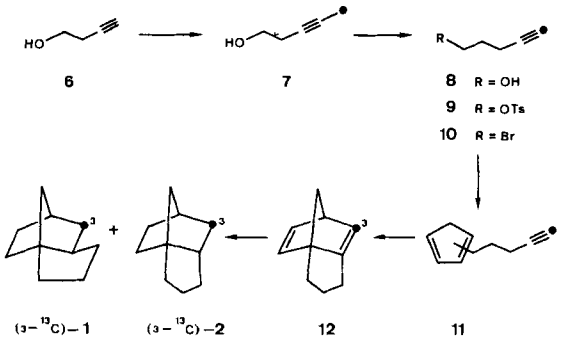
[5]) For the purpose of symplifying the discussions, the latter are based on one enantiomeric form only although racemates were used in all experiments.

[6]) For the synthesis of D-labelled **1** and **2**, see [1].

[7]) Our results not yet published have been discussed in a recent report by *Schleyer et al.* [7] on the basis of our private communications.

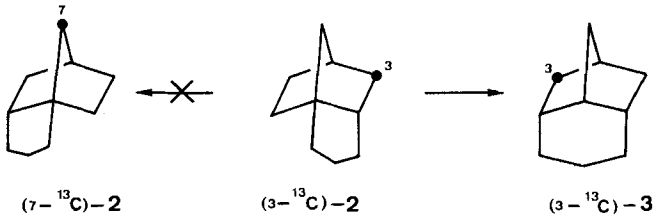
[8]) Compound (3-^{13}C)-**2** was prepared starting from 3-butyn-1-ol (**6**). The required ^{13}C-atom was introduced by reaction of **6** with $^{13}CH_3I$ to yield **7**, which was isomerized to the terminal acetylene **8**.

Scheme 4



The subsequent steps (→**9**→**10**→**11**→**12**) were carried out in analogy to the synthesis of unlabelled **2** [1].

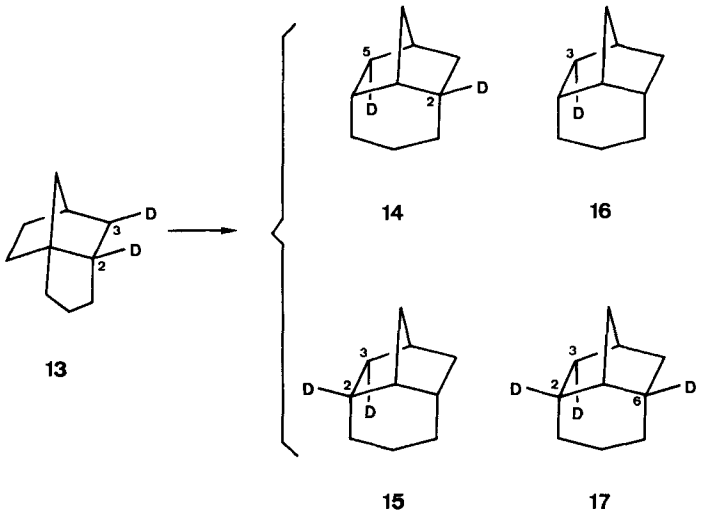
Scheme 5



ered reactant did not contain (7-^{13}C)-**2**. Formation of the latter would have required and proven the equilibria **A** ⇄ **E** ⇄ **M** ⇄ **I** (*Scheme 3*, ^{13}C(c), $R^1-R^4=H$). The result with (3-^{13}C)-**2** is analogous to the one with ^{13}C(1')-labelled **1** (see discussion above) and neither excludes nor proves a degenerate rearrangement **E** ⇄ **M** being involved in the isomerization **2** → **3**.

Rearrangement ($AlBr_3$, CS_2, −60°, 5–15 min) of the (2*exo*,3*exo*-D_2)-compound **13**[6])[9]) yielded a product mixture[10]) mainly containing compounds with 2 D-atoms

Scheme 6



[9]) It should be mentioned that no label scrambling in the recovered reactant, *i.e.* no D–C(7) (see *Scheme 3*: **I**: $R^1=R^4=D$) was observed. This result is complementary to that of the corresponding experiment with ^{13}C(3)-labelled **2** (see above).

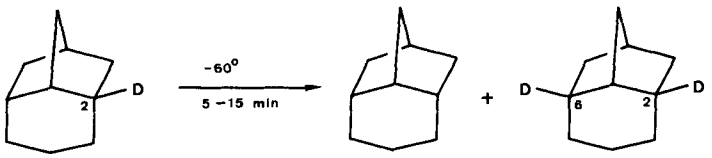
[10]) Recovered reactants and product mixtures were analyzed spectroscopically (^{13}C-NMR., ^{1}H-NMR., MS.). The following characteristic features are observed in the ^{13}C-NMR. spectra of D-labelled compounds [8]: a) D-labelled C-atoms: $t(^1J(C,D)\approx 20$ Hz), shifted by *ca.* 0.4 ppm to higher field; b) C-atoms *α* to D-labelled C-atoms: $t(^2J(C,D)<1$ Hz), shifted by *ca.* 0.1 ppm to higher field; c) C-atoms *β* to D-labelled C-atoms: $t(^3J(C,D)<1$ Hz), shifted by *ca.* 0,02 ppm to higher field.

In the 300-MHz-^{1}H-NMR. spectra of **3**, the signals for H–C(1), H–C(2) and H–C(6) as well as for H_{endo}–C(3) and H_{endo}–C(5) are well-separated and hence allow unambiguous assignments in the various D-labelled compounds **3**.

($D_1 : D_2 : D_3$ *ca.* 1 : 2 : 1). The D-atoms were localized at C(2), C(3) (and C(5), resp.[11])) and C(6): **14**[11])–**17**. *(Scheme 6).*

To determine the origin of the latter two products **16** and **17** the monodeuterated compound **18**[12]) was independently subjected to the same conditions ($AlBr_3$, CS_2, −60°, 5–15 min) as **13**. A mixture of **3** and the dideuterated analog **19** was obtained *(Scheme 7), i.e.* a direct intermolecular H/D-exchange at C(2) and C(6) occurred, but definitively not *via* **E** ⇄ **M**, otherwise D-atom would also have been found at

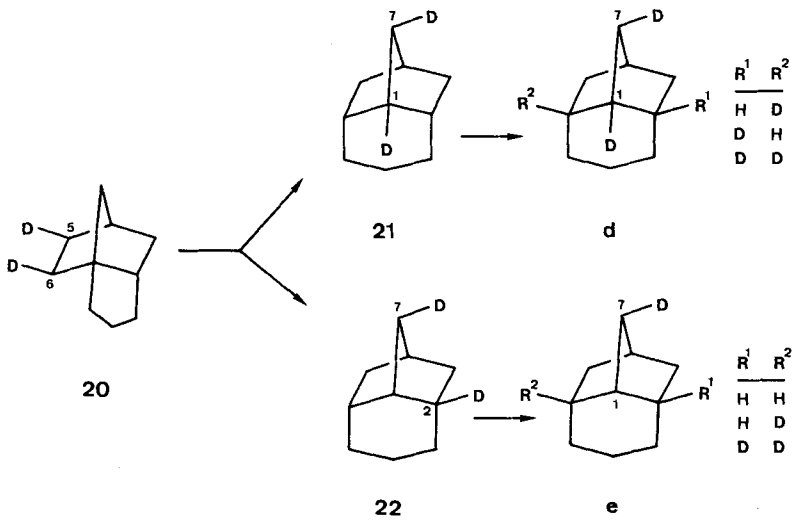
Scheme 7



18 **3** **19**

but definitively not *via* **E** ⇄ **M**, otherwise D-atom would also have been found at C(1)[13]). On the basis of this result, one cannot distinguish whether, starting from the 1,2 *endo*-compound **13** (**A**: $R^1 = R^4 = D$), the formation of **15** (**P**: $R^1 = R^4 = D$) proceeds *via* **E** ⇄ **M** and/or a simple H/D-exchange in the 2,6-isomer.

Scheme 8



[11]) It should be noted that D_{endo}–C(5) in **14** corresponds to D_{endo}–C(3) in **15**–**17**. The different numbering of the same C-atoms follows from the correct IUPAC nomenclature.

[12]) The syntheses of **18** and **19** will be described in a forthcoming communication.

[13]) ^{1}H-NMR.: > 95% H at C(1) (error limit: ± 5%).

From treatment ($AlBr_3$, CS_2, $-60°$, 5–10 min) of the (5*exo*,6*exo*-D_2)-**20**[14]), a product mixture was isolated mainly containing compounds with 2 D-atoms (D_1: D_2: D_3 *ca.* 1:2:1) *(Scheme 8)*. The D-atoms were localized at C(1), C(2), C(6) and C(7): **21**, **22**, **d** and **e**. Isomerization of **20** (**A**: $R^2=R^3=D$) without participation of **E** ⇄ **M** would have resulted in **21** (**H**: $R^2=R^3=D$) as the sole product with D-atom only at C(1) and C(7). However, the formation of products bearing D-atom at C(2) conclusively proves that a rearrangement **E** ⇄ **M** and a subsequent [1,3]-D-shift from C(f) to C(a) (**M** ⇄ **N**[15]) are involved. The primary product **22** (**P**: $R^2=R^3=D$) with D-atom at C(2) and C(7) is then responsible for the secondary compounds of the types **d** and **e** in the reaction mixture. As must be deduced from the experiment with **18** (→**3**+**19**), direct intermolecular H/D-exchange in **22** (→**e**) and by consequence also in **21** (→**d**) could only occur at C(2) and/or C(6) but not at C(1).

3. 1,2*exo*-Trimethylenenorbornane. – Three different possibilities have *a priori* to be considered for abstraction of a hydride ion in 1,2*exo*-trimethylenenorbornane (**1**): Abstraction of the tertiary 2*endo*-, the secondary 6*exo*- and the secondary 6*endo*-hydride ion.

Converting selectively D_{exo}–C(6)-labelled **1** (**B**: $R^2=D$; **C**: $R^1=D$; **D**: $R^2=D$), the following D-contents in the products and product mixtures, respectively, should result, regardless if **E** ⇄ **M** is involved (→**H**+**P**) or not (→**H**) in the isomerization: On the one hand, no D–C(1) starting from **C** (→**H** or **H**+**P**; $R^1=D$), on the other hand, ⩾50% D–C(1) starting from **B** as well as from **D** (→**H** or **H**+**P**: $R^2=D$).

On the basis of this analysis we treated the (5*exo*,6*exo*-D_2)-compound **23**[16]) with aluminum bromide in carbon disulfide. In comparison to 1,2*endo*-compounds, higher temperature (−20°, 15 min) or longer reaction time (−60°, 3 h) had to be applied with 1,2*exo*-compounds to realize conversions of >50% (see also [2]). Under both conditions, a product mixture similar to the one starting from the 1,2*endo*-isomer **20** was obtained. The compounds contained mainly 2 D-atoms (D_1: D_2: D_3 *ca.* 1:**2**:1) localized at C(1), C(2), C(6) and C(7): **21**, **22**, **24** and **f** *(Scheme 9)*. However, the main difference was the ratio D–C(2) and –C(6)/D–C(1) of ca. 2:1 *versus* 2:3 in the experiment with **20**.

Finding significantly <50% D–C(1) in the product mixture clearly manifests that none of the above discussed pathways can be operating alone. To rationalize the experimental result, one possibility would be a competitive R^1-deuteride abstraction in **C** and R^1-hydride abstraction in **B** and/or **D**. However, a more convincing interpretation would be an equilibrium between **H** and **P** involving **E** ⇄ **M**. To verify this proposition, we treated the (2-D)-compound **18** (−20°, 15 min and −60°, 3 h) as well as the (2,6-D_2)-compound **19**[12]) (−20°, 15 min) with $AlBr_3$ *(Scheme 10)*.

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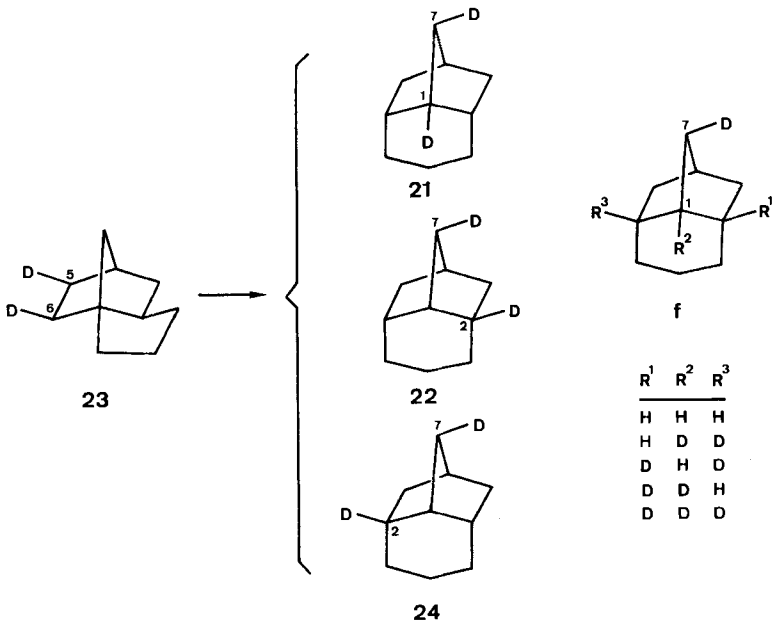
[14]) D-labelling at C(5) is not necessary. However, it is easier to synthesize **20**[6]) than the corresponding analog with only D_{exo}–C(6). D_{exo}–C(5) in **20** will always turn up as D–C(7) in the products.

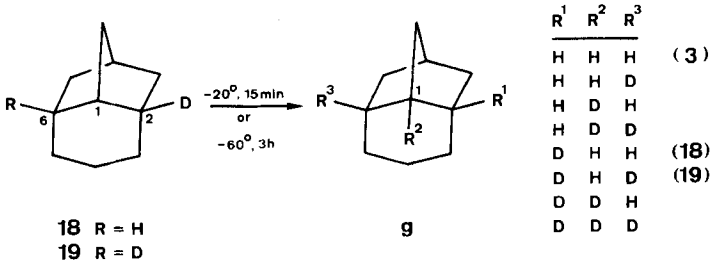
[15]) The [1,3]-D-shift **M** ⇄ **N** (isotope effect) compared to the [1,3]-H-shift **E** ⇄ **F** might be responsible for the 2:3 ratio of D–C(2) and –C(6)/D–C(1) (determined by ^{1}H-NMR.) found in the product mixture.

[16]) D-labelling at C(5) is not required. However, it is easier to synthesize **23**[6]) than the corresponding analog with only D_{exo}–C(6). D_{exo}–C(5) in **23** will always turn up as D–C(7) in the products.

Scheme 9



Scheme 10



In both cases a statistical D-distribution at the 3 C-atoms C(1), C(2) and C(6) was obtained, *i.e.* D–C(2) and –C(6)/D–C(1) *ca.* 2:1[17]).

On the basis of the highly plausible assumption that an energetically most unfavourable bridgehead carbenium ion at C(1) in 2,6-trimethylenenorbornanes has not to be considered as an alternative candidate responsible for the observed D-scrambling at C(1), C(2) and C(6), one has to conclude that in the $AlBr_3$-catalyzed adamantane rearrangement in CS_2 of 1,2*exo*-(**1**) to 2,6-trimethylenenorbornane (**3**) a degenerate rearrangement (**E** ⇄ **M**) and by consequence [1,3]-H-shifts (**E** ⇄ **F** and **M** ⇄ **N**) are always involved.

[17]) It has to be noted that with **18** at low temperature (–60°) for a short time (5–15 min), no D-incorporation at C(1) was observed (see above).

Studies to determine which hydride ion in **1** (*Scheme 3:* **B**, **C** or **D**) is abstracted are in progress and are subject of a forthcoming communication.

Financial support by *Schweizerischer Nationalfonds zur Förderung wissenschaftlicher Forschung* and by *Ciba-Geigy AG*, Basel, is gratefully acknowledged.

Experimental Part

General remarks. IR. spectra (CCl_4) were recorded on a *Perkin-Elmer 297* spectrometer, bands are given in cm^{-1}. – ^{1}H-NMR. spectra were measured on a *Varian HA-100* (CCl_4) or *Bruker WM-300* ($CDCl_3$) and ^{13}C-NMR. spectra ($CDCl_3$) on a *Varian XL-100* (25.2 MHz) or *Bruker WM-300* (75.4 MHz) spectrometer. Chemical shifts (δ) are given in ppm relative to TMS as internal standard; J = spin coupling constant (Hz), $W_{1/2}$ = half width at half height (Hz). – Mass spectra (MS.) were recorded on a *Hitachi-Perkin-Elmer RMU-6M* or *RMU-6D* instrument at 70 eV ionizing electron energy, source temp. 180°, inlet temp. 200°. The most important ions are listed as *m/z* values with relative intensities (% of base peak) in parenthesis. Capillary GLC. was performed on a *Carlo Erba Fractovap 4160* gas chromatograph using a *SE 52* glass capillary column, length 25 m, diameter 0.33 mm; prep. GLC. on a *Varian A-90-P* gas chromatograph using metal columns (10′ × 3.8″): 10% *NPGS* on *Chromosorb GHP 80/100* (method A) or 5% *SE 30* on *Chromosorb W 80/100 AW-DMCS* (method B); column chromatography on silica gel *60 Merck* (70–230 mesh ASTM). – Workup: the org. layer was washed with 2N HCl, sat. $NaHCO_3$ and NaCl solution, dried over $MgSO_4$, filtered and the solvent removed by distillation through a *Vigreux* column.

(5-^{13}C)-3-Pentyn-1-ol (**7**). To a solution of 361 mg (52 mmol) of Li in 300 ml of liq. NH_3, 50 mg of $Fe(NO_3)_3 \cdot 9\,H_2O$ were added. To the white suspension formed after 1 h of stirring, 1.76 g (25.17 mmol) of 3-butyn-1-ol (**6**), and 30 min later, 3.6 g (25.17 mmol) of $^{13}CH_3I$ were added dropwise under cooling. Stirring was continued for 1 h and subsequently the NH_3 allowed to evaporate. Then, 500 ml of Et_2O and 10 ml of H_2O were added. Workup and distillation 80°/12 Torr) yielded 1.81 g (85%) of **7**. – IR.: 3680*w*, 3630*w*, 3500*w*, 3360*s* br., 1435*m*, 1390*m*, 1330*m*, 1215*w*, 1185*m*, 1140*w*, 1040*s*, 922*w*, 850*m*. – ^{1}H-NMR. (100 MHz): 1.74 (*d* × *t*, $J(^{13}C,H) = 130$, $J(2,5) = J(2',5) = 3$, 3 H–C(5)); 2.28 (*m*, $w_{1/2} \approx 14$, 2 H–C(2)); 3.31 (*s*, HO–C(1)); 3.54 (*t*, $J(1,2) = J(1,2') = 7$, 2 H–C(1)). – MS.: 85 (22, M^+, $C_4{}^{13}CH_8O$), 67 (5), 55 (100), 54 (50), 53 (11), 52 (11), 40 (22), 39 (15), 31 (20), 28 (15).

(5-^{13}C)-4-Pentyn-1-ol (**8**). To 100 ml of 1,3-propanediamine (distilled over BaO at 45°/16 Torr), 10 ml of KH suspension (22.5% in oil) were added. After stirring for 1 h, the mixture was cooled to 0°, treated with 1.108 g (13.04 mmol) of **7**, stirred at 0° for 30 min and at r.t. for 1 h. Cooling to 0°, addition of 30 ml of H_2O and 750 ml of Et_2O, workup and distillation (80°/15 Torr) gave 697 mg (63%) of **8**. – IR.: 3638*m*, 3350*m* br., 3312*m*, 3298*s*, 2120*w*, 2100*w*, 1470*w*, 1432*m*, 1387*w*, 1348*w*, 1322*w*, 1240*m*, 1055*s*, 940*m*, 903*w*. – ^{1}H-NMR. (100 MHz): 1.76 (*s*, HO–C(1)); 1.76 (*qi*, $J(1,2) = J(1',2) = J(2,3) = J(2,3') = 6$, 2 H–C(2)); 1.95 (*d* × *t*, $J(^{13}C,H) = 246$, $J(3,5) = J(3',5) = 3$, H–C(5)); 2.32 (*m*, $w_{1/2} = 12$, 2 H–C(3)); 3.74 (*t*, $J(1,2) = J(1,2') = 6$, 2 H–C(1)). – MS.: 85 (11, M^+, $C_4{}^{13}CH_8O$), 84 (31), 83 (16), 69 (49), 67 (100), 66 (58), 56 (38), 55 (27), 54 (38), 44 (38), 43 (29), 42 (24), 41 (38), 40 (58), 39 (44), 31 (36), 27 (38).

(5-^{13}C)-4-Pentyn-1-yl p-*toluenesulfonate* (**9**). To a solution of 670 mg (3.53 mmol) of *p*-TsCl in 3 ml of dry pyridine, 300 mg (3.53 mmol) of **8** were added under Ar at 0°. Stirring for 2 h at 0° and 30 min at r.t., workup with Et_2O and chromatography on 40 g of SiO_2 in benzene yielded 818 mg (97%) of **9**. – IR.: 3310*m*, 3295*s*, 3070*w*, 3030*w*, 2120*w*, 2100*w*, 1598*s*, 1490*m*, 1465*m*, 1440*m*, 1432*m*, 1365*s*, 1305*m*, 1288*m*, 1214*m*, 1187*s*, 1175*s*, 1095*s*, 1010*s*, 980*s*, 940*s*, 922*s*, 684*w*, 660*s*, 630*s*. – ^{1}H-NMR. (100 MHz): 1.74 (*d* × *t*, $J(^{13}C,H) = 246$, $J(3,5) = J(3,5') = 3$, H–C(5)); 1.84 (*qi*, $J(1,2) = J(1',2) = J(2,3) = J(2,3') = 6$, 2 H–C(2)); 2.23 (*m*, $w_{1/2} \approx 14$, 2 H–C(3)); 2.42 (*s*, $CH_3C_6H_4$)); 4.06 (*t*, $J(1,2) = J(1,2') = 6$, 2 H–C(1)); 7.2–7.4, 7.65–7.8 (2 *m*, each 2 H, arom. H)). – MS.: 239 (1, M^+, $C_{11}{}^{13}CH_{14}O_3S$), 238 (1), 175 (14), 155 (35), 92 (15), 91 (100), 85 (12), 83 (20), 67 (39), 66 (22), 65 (29), 39 (11).

(1-^{13}C)-5-Bromo-pentyne (**10**). A solution of 1.2 g (5.02 mmol)of **9** in 30 ml of DMSO (freshly distilled over CaH_2) was treated with 2.3 g (26.75 mmol) of LiBr and stirred. The mixture was warmed up and **10** (651 mg, 88%) obtained by distillation at 28° through a *Vigreux* column. – IR.: 3310*s*, 3297*s*, 2120*w*, 2100*w*, 1450*w*, 1430*s*, 1350*m*, 1330*w*, 1322*w*, 1295*w*, 1272*m*, 1245*s*, 1205*w*, 1195*w*, 1170*w*, 1130*w*, 1070*w*, 978*m*, 962*m*, 880*m*, 840*m*. – ^{1}H-NMR. (100 MHz): 1.84 (*d* × *t*, $J(^{13}C,H) = 246$, $J(1,3) = J(1,3') = 3$,

H–C(1)); 2.02 (*qi*, $J(3,4)=J(3',4)=J(4,5)=J(4,5')=6$, 2 H–C(4)); 2.36 (*m*, $w_{1/2}\approx 14$, 2 H–C(3)); 3.44 (*t*, $J(4,5)=J(4',5)=6$, 2 H–C(5)). – MS.: 109 (7), 107 (7), 68 (100), 67 (53), 66 (18), 41 (26), 40 (34), 39 (25), 27 (18).

(3-^{13}C)-1,2-Trimethylenenorborna-2,5-diene (=(6-^{13}C)-tricyclo[5.2.1.0^{1,5}]deca-5,8-diene; **12**). Freshly destilled cyclopentadiene was added under Ar to a stirred solution of 150 mg (6.5 mmol) of Na in 30 ml of NH_3 at −70° until the solution lost the color. After 30 min, the mixture was dropwise treated with 650 mg (4.42 mmol) of **10** and stirred for further 30 min. After allowing the NH_3 to evaporate, Et_2O and H_2O were added. Workup and distillation (80°/12 Torr) yielded a mixture **11** of alkylated cyclopentadienes, which was dissolved in 5 ml of tributylamine and slowly dropped into 10 ml of tributylamine preheated to 200°. Dilution with Et_2O, workup and distillation (75°/12 Torr) gave 280 mg (46% with respect to **10**) of **12**. – IR.: 3105*w*, 3060*w*, 1440*w*, 1112*w*, 1102*w*, 708*m*. – ^{1}H-NMR. (300 MHz): 1.8, 1.85–2.15, 2.4 (3 *m*, 1 H($w_{1/2}\approx 20$), 6 H, and 1 H($w_{1/2}\approx 30$), resp.); 3.64 (*m*, $w_{1/2}\approx 8$, H–C(4)); 6.05 (*d*, $J(^{13}C,H)=174$, $w_{1/2}$ each ≈8, H–C(3)); 6.57 (*d*, $J(5,6)=5$, H–C(6)); 6.75 (*d*×*d*, $J(5,6)=5$, $J(4,5)=3$, H–C(5)). – ^{13}C-NMR. (25.2 MHz): 126.79 (C(3), see also [1]). – MS.: 133 (68, M^+, $C_9{}^{13}CH_{12}$), 132 (87), 131 (32), 118 (100), 117 (81), 116 (32), 105 (45), 104 (32), 92 (50), 91 (48), 78 (45), 77 (30), 76 (30), 65 (13), 51 (16), 39 (18), 27 (10).

*(3-^{13}C)-1,2*exo-*Trimethylenenorbornane(=(6-^{13}C)*-rel-(*1R,5R)-tricyclo[5.2.1.0^{1,5}]decane; (3-^{13}C)-***1***) and (3-^{13}C)-1,2*endo-*trimethylenenorbornane (=(6-^{13}C)*-rel-(*1R,5S)-tricyclo[5.2.1.0^{1,5}]decane; (3-^{13}C)-***2***).* To a suspension of 60 mg (0.45 mmol) of **12** and 160 mg (1.33 mmol) of dipotassium azodicarboxylate, a 50% solution of AcOH in CH_3OH was added over 10 min until the solution lost the colorless. The mixture was poured into pentane. Workup, distillation (70°/12 Torr) and separation by prep. GLC. (method A, 140°) yielded 4 mg (6.5%) of (3-^{13}C)-**1** (^{13}C-NMR. (25.2 MHz): 40.04 (C(3)), see also [1]) and 43 mg (72%) of (3-^{13}C)-**2** (^{13}C-NMR. (25.2 MHz): 29.87 (C(3)), see also [1]).

Rearrangements with $AlBr_3$ in CS_2. General procedure. To 10·n µl of $AlBr_3$ solution under Ar (prepared from 100 mg of $AlBr_3$ and 0.9 ml of CS_2), precooled to the appropriate temp., a solution of n mg of reactant in n µl of CS_2 (also precooled to the same temp.) was added under stirring. The reactions were quenched by adding a mixture of 5 ml of Et_2O and 2 ml of pyridine (cooled to −100°). Usual workup and distillation at 70–100°/12 Torr yielded the product mixtures, which were separated from unchanged reactant by prep. GLC. Some representative experiments[10]) are summarized in the *Table*.

*Data of 2*endo,*6*endo-*trimethylenenorbornane(=tricyclo[5.2.1.0^{3,8}]decane;* **3**). – ^{1}H-NMR. (300 MHz): 0.95 (*d*×*d*, *J(gem)*=11, $J(2,3endo)$ and $J(5endo,6)=4$, resp., H_{endo}–C(3), H_{endo}–C(5)); 1.25–1.65 (*m*, 10 H); 1.73 (*m*, $w_{1/2}\approx 8$, H–C(1)); 2.00 (*m*, $w_{1/2}\approx 20$, H–C(2), H–C(6)); 2.12 (*m*, $w_{1/2}\approx 10$, H–C(4)). – ^{13}C-NMR. (75.4 MHz): 14.33 (*t*, C(2')); 27.09 (*t*, C(1'), C(3')); 33.67 (*t*, C(3), C(5)); 33.90 (*d*, C(2), C(6)); 37.82 (*d*, C(4)); 41.88 (*d*, C(1)); 41.88 (*t*, C(7)).

Table. *$AlBr_3$-catalyzed rearrangements*

Starting material		Reaction conditions		Total yield		Product distribution[10])					
						Separation method prep. GLC.	Starting material		Product mixture		
	[mg]	Temp. [°C]	Time [min]	[mg]	[%]		[mg]	[%]		[mg]	[%]
(3-^{13}C)-**2**	20	−60	2	18	90	A(145°)	8	40	(3-^{13}C)-**3**	7	35
13	30	−63	20	25	83	B(110°)	0.3	1	**14–17**	20	67
18	108	−60	5	91	84	–			**3, 18, 19**		
18	20	−60	15	12	60	–			**3, 18, 19**		
18	50	−60	180	44	88	–			**g**		
18	100	−20	15	77	77	–			**g**		
19	35	−20	15	28	80	–			**g**		
20	130	−52	2	121	93	A(130°)	13	10	**21, 22, d, e**	80	62
23	200	−9	9	177	90	A(140°)	36	18	**21, 22, 24, f**	83	43
23	100	−20	15	80	80	–	–		**21, 22, 24, f**		
23	50	−60	180	42	84	B(130°)	17	34	**21, 22, 24, f**	18	36

We thank for their assitance: Miss *B. Brandenberg*, Mr. *F. Fehr*, *K. Hiltbrunner* and *M. Langenauer* (NMR.), Mrs. *L. Golgowsky* and Prof. *J. Seibl* (MS.) of our analytical department.

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