12. The Adamantane Rearrangement of 1,2-Trimethylenenorbornanes

Part IV[1])

Hydride-Ion Abstraction in 1,2-*exo*-Trimethylenenorbornane

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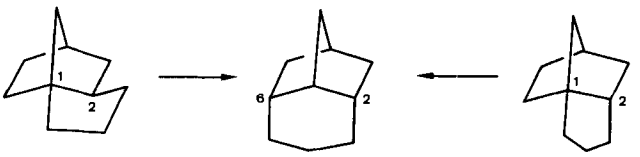
In the $AlBr_3$-catalyzed adamantane rearrangement in CS_2 of 1,2-*exo*-trimethylenenorbornane (**1**) to 2-*endo*,6-*endo*-trimethylenenorbornane (**3**), hydride-ion abstraction occurs at C(6) from the *exo*-side. The k_H/k_D value for competition between **1** and **5** (D_{exo}–C(6)) was 1.58 ± 0.05, whereas no kinetic isotope effect was operative for competition between unlabeled **1** and **4** (D_{endo}–C(5)) and between **1** and **6** (D_{endo}–C(6)).

1,2-*exo*-Trimethylene-8,9,10-trinorbornane (**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.* [3] were successful to establish that 2-*endo*,6-*endo*-trimethylene-8,9,10-trinorbornane (**3**)[2]) is an intermediate in the adamantane rearrangement of **1**.

Scheme 1



1 **3** **2**

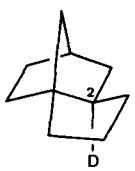
From our recent studies, evidence was gained that a degenerate rearrangement is involved in the $AlBr_3$-catalyzed adamantane rearrangement in CS_2 of both 1,2-*exo*- (**1**)[2]) and 1,2-*endo*-trimethylene-8,9,10-trinorbornane (**2**)[2]) to **3**[2]) [1]. To determine which H-atom in **1** is abstracted as a hydride ion, the three selectively mono-D-labeled 1,2-*exo*-compounds **4**[4]) (D_{endo}–C(2)), **5**[4]) (D_{exo}–C(6)) and **6**[4]) (D_{endo}–C(6)) were prepared, and the kinetic isotope effects in competition experiments explored. Mixtures of

[1]) Part III: [1].

[2]) For nomenclature, see [1].

[3]) 'Adamantaneland': a set of 19 isomeric $C_{10}H_{16}$-hydrocarbons [2–4].

[4]) Compounds **4**–**6** correspond to the general formula **B**–**D** (R^1 = D, R^2 = R^3 = R^4 = H) of Scheme 3 in [1].



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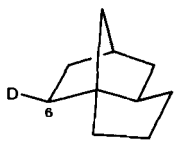

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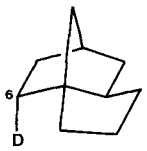


6

1 and **4**, **1** and **5** as well as **1** and **6** were subjected to the usual rearrangement conditions ($AlBr_3$ in CS_2 at −20°C). At various degrees of conversion, the mixtures were worked up, the reactants as well as the products isolated and their D-contents determined by mass spectroscopy. The results are listed in the *Table*.

The k_H/k_D ratios for the disappearance of reactants were then calculated applying the standard procedures[5]). Only for competition between **1** and **5** a distinct kinetic isotope effect could be observed: $k_H/k_D = 1.58 \pm 0.05$. This result provides conclusive evidence that in the $AlBr_3$-catalyzed adamantane rearrangement of **1** to **3**, the hydride ion is abstracted predominantely, from the 6-*exo*-position, if not exclusively.

Synthesis of Compounds 4–6. – Hydroboration of the olefin **7** [6] with 9-borabicyclo[3.3.1]nonan (9-BBN) followed by acetylation of the crude product gave the acetate **8** (87%), which could easily be purified. Base hydrolysis (→84% of **9**) followed by oxidation with pyridinium chlo-rochromate led to the 3-oxo compound **10** (82%) with the 1,2-*endo*-skeleton. A small amount (5%) had already isomerized to the correspond-

Table. *Competition Experiments*

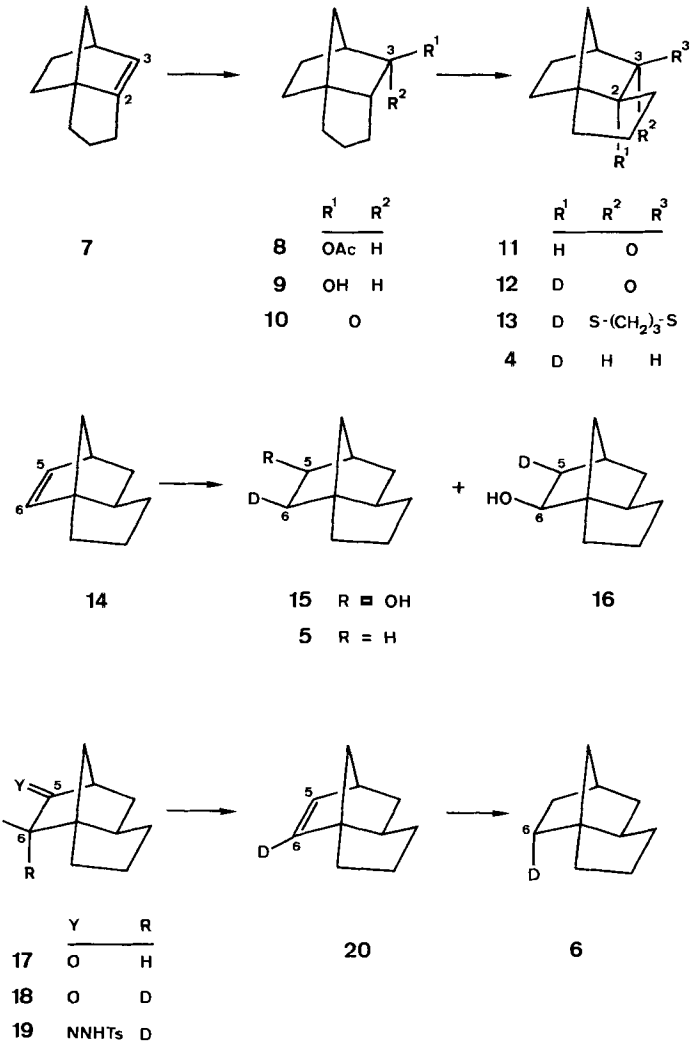
Competition experiment	Conversion [%]	D_1-Compounds [%]		
		Reactants	Products	Reactants + Products
1 + **4**	–	46.0	–	46.0
	27.9	46.4	45.0	46.0
	42.5	46.2	45.1	45.7
	45.3	46.2	45.2	45.7
	52.9	46.4	46.1	46.2
1 + **5**	–	46.5	–	46.5
	47.6	53.9	38.8	46.7
	51.0	54.5	37.6	45.9
	62.4	57.4	39.1	46.0
	69.3	60.0	40.5	46.5
1 + **6**	–	38.3	–	38.3
	49.5	39.1	39.0	39.1
	56.3	38.8	38.1	38.4
	61.5	38.8	38.3	38.5
	65.1	39.0	37.2	37.8

[5]) $k_A/k_B = \log([A]_t/[A]_o)/\log([B]_t/[B]_o)$ or $k_A/k_B = \{\log[(1 - x_t)/(1 - x_o)] + \log(1 - s)\}/\{\log(x_t/x_o) + \log(1 - s)\}$, where x_o and x_t represent percentage of B/100, and s represents percentage of conversion/100 [5].

ing ketone **11** with the 1,2-*exo*-skeleton. The latter was obtained quantitatively on treatment of **10** with base. The D_{endo}–C(2) labeled compound **12** (97%) was prepared from ketone **10** with Na/CH_3OD. Finally the carbonyl function was removed on the one hand *via* the thioacetal **13** (88%) to yield the D_{endo}–C(2) labeled hydrocarbon **4** 17%), or on the other hand directly from ketone **12** by reduction with BF_3/Et_3SiH[6]) (37%).

The synthesis of **5** started from the olefin **14** [8]. In analogy to [8], deuteroboration gave a 2:1 mixture (87%) of the two alcohols **15** and **16**, which can easily be separated.

Scheme 2



[6]) On 'ionic hydrogenation', see [7] and references cited therein.

Subsequent treatment with $SOCl_2$ and reduction of the resulted mixture of chlorides by *Grignard* reaction yielded the D_{exo}–C(6) labeled hydrocarbon **5**.

Base-catalyzed H/D-exchange in ketone **17** [8] afforded the (6-*endo*,6-*exo*-D_2)-compound **18** (80%). Conversion to the *p*-toluenesulfonylhydrazone **19** (94%) followed by reaction with CH_3Li gave the D–C(6)-olefin **20** (35%) which was reduced to the D_{endo}–C(6) labeled hydrocarbon **6** (76%) by diimide.

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Experimental. – *General*. See [1]. For nomenclature *cf*. Footnote 2 in [1].

1,2-endo-*Trimethylene-8,9,10-trinorbornane-3*-exo-*yl acetate* (**8**). To a soln. of 1.3 g (9.7 mmol) of **7** [6] in 30 ml of THF (distilled over $LiAlH_4$), 3.5 g (28.7 mmol) of 9-**BBN** were added and the mixture refluxed for 1.5 h. After cooling to r.t., 7 ml of 3N NaOH and 7 ml of 30% H_2O_2 were added and the mixture refluxed for 1 h. Workup with Et_2O and chromatography in Et_2O/pentane 1:1 afforded the alcohol **9**, which immediately was treated with 12.3 ml of Ac_2O/pyridine 1:1 for 2 h at 60°. Workup with Et_2O and bulb-to-bulb distillation (110°/0.2 Torr) gave 1.64 g (87%) of **8**. IR: 1732*s*, 1475*w*, 1458*m*, 1362*w*, 1291*m*, 1242*s*, 1197*w*, 1115*m*, 1038*m*, 1018*m*, 980*w*, 970*w*, 912*w*. ^{1}H-NMR (100 MHz): 1.0–2.2 (*m*, 14H); 1.93 (*s*, CH_3COO_{exo}–C(3)); 2.39 (*m*, $w_{½} \approx 8$, among others $J(4,5exo) = 4$, H–C(4)); 4.09 (*d*, $J(2,3endo) = 5$, H_{endo}–C(3)). MS: 194 (1, M^+, $C_{12}H_{18}O_2$), 152 (4), 151 (6), 134 (98), 133 (28), 124 (16), 119 (40), 106 (72), 105 (30), 93 (38), 92 (62), 91 (48), 79 (38), 67 (36), 43 (100), 41 (20).

1,2-endo-*Trimethylene-8,9,10-norbornan-3*-exo-*ol* (**9**). A soln. of 1.197 g (6.17 mmol) of **8** in 70 ml of a potash soln. (K_2CO_3 (15 g), H_2O (150 ml), CH_3OH (750 ml)) was refluxed for 2 h. Workup with Et_2O yielded 792 mg (84%) of **9**. IR: 3610*m*, 3340 br., 1460*m*, 1322*m*, 1291*m*, 1275*m*, 1209*w*, 1190*w*, 1115*m*, 1050*s*, 1021*m*, 1003*s*, 970*w*, 952*w*, 931*w*, 915*w*, 902*w*, 890*w*. ^{1}H-NMR (100 MHz): 0.9–2.2 (*m*, 14H); 2.23 (*m*, $w_{½} \approx 8$, among others $J(4,5exo) = 4$, H–C(4)); 2.77 (*s*, HO_{exo}–C(3)); 3.25 (*d*, $J(3endo,4) = 4$, H_{endo}–C(3)). ^{13}C-NMR (25 MHz): 21.04 (C(1')); 27.31, 27.46 (C(2'), C(3')); 27.21, 27.51 (C(5), C(6)); 37.20 (C(7)); 51.92 (C(4)); 55.88 (C(1)); 64.92 (C(2)); 75.30 (C(3)). MS: 152 (5, M^+, $C_{10}H_{16}O$), 134 (55), 121 (87), 119 (55), 110 (21), 108 (26), 106 (34), 105 (26), 95 (42), 93 (74), 92 (55), 91 (47), 80 (84), 70 (63), 67 (100), 55 (32), 41 (43), 39 (24).

1,2-endo-*Trimethylene-8,9,10-trinorbornan-3-one* (**10**). A soln. of 1.5 g (6.98 mmol) of pyridinium chlorochromate in 50 ml of CH_2Cl_2 (filtered through *Alox B*) was treated under Ar at 0° with 295 mg (1.94 mmol) of **9** and stirred at r.t. for 2 h. Workup with Et_2O afforded a mixture of 239 mg (82%) of **10** and 12 mg (5%) of **11**. An analytical sample of **10** was obtained by prep. GLC (A: 150°). IR: 1742*s*, 1458*m*, 1338*m*, 1282*m*, 1210*m*, 1189*m*, 1168*m*, 1122*w*, 1102*w*, 1062*m*, 1032*w*, 1005*m*, 970*m*, 950*w*, 928*w*, 910*w*, 885*m*, 695*m*. ^{1}H-NMR (300 MHz): 1.3–2.1 (*m*, 12H); 2.28 (*dd*, $J(2,3'a) \approx 11$, $J(2,3'b) \approx 8$, H–C(2)); 2.81 (*d*, $J(4,5exo) = 5$, H–C(4)). MS: 150 (35, M^+, $C_{10}H_{14}O$), 132 (4), 122 (6), 121 (6), 119 (10), 107 (6), 94 (33), 93 (100), 81 (65), 80 (35), 79 (38), 67 (17), 55 (8), 53 (9), 41 (15), 39 (14).

1,2-exo-*Trimethylene-8,9,10-trinorbornan-3-one* (**11**). A soln. of 42 mg (0.28 mmol) of a ~ 10:1 mixture of **10** and **11** (see *above*) in 2 ml of $CH_3OH/NaOCH_3$ (15 mg of Na in 2 ml of MeOH) was stirred at r.t. for 10 min. Workup with Et_2O gave 42 mg (quant.) of **11**. IR: 1740*s*, 1448*m*, 1322*m*, 1300*w*, 1270*w*, 1202*w*, 1172*m*, 1072*m*, 940*m*, 922*w*. ^{1}H-NMR (100 MHz): 1.2–2.1 (*m*, 13H); 2.44 (*m*, $w_{½} \approx 8$, among others $J(4,5exo) = 3$, H–C(4)). MS: 150 (28, M^+, $C_{10}H_{14}O$), 132 (4), 122 (7), 121 (6), 119 (10), 107 (8), 94 (32), 93 (100), 81 (39), 80 (25), 79 (26), 67 (11), 55 (4), 53 (7), 41 (10), 39 (10).

1,2-exo-*Trimethylene-[2*-endo-$^2H_1$]-*8,9,10-trinorbornan-3-one* (**12**). A soln. of 210 mg (1.4 mmol) of a ~ 10:1 mixture of **10** and **11** (see *above*) in 6 ml of CH_3OD was treated with 50 mg of Na and stirred at r.t. for 30 min. Workup with Et_2O yielded 203 mg (97%) of **12**. IR: among others 2160*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.2–2.3 (*m*, 12H); 2.65 (*m*, $w_{½} \approx 8$, among others $J(4,5exo) = 3$, H–C(4)). MS: 151 (33, M^+, $C_{10}H_{13}DO$), 150 (10), 133 (4), 123 (6), 122 (7), 120 (8), 108 (6), 106 (10), 95 (14), 94 (35), 93 (100), 82 (33), 81 (35), 80 (35), 79 (23), 67 (10), 41 (10), 39 (9).

3,3(Trimethylenedithio)-1,2-exo-*trimethylene-[2*-endo-$^2H_1$]-*8,9,10-trinorbornan-3-one* (**13**). To a soln. of 189 mg (1.25 mmol) of **12** in 4 ml of dry $CHCl_3$, 0.13 ml (140 mg, 1.3 mmol) of freshly distilled 1,3-propanedithiol were added and the mixture stirred at r.t. for 1 h. After cooling to 0°, 0.7 ml of $BF_3 \cdot Et_2O$ were added and

stirring continued for additional 16 h at 0°. Workup with Et_2O yielded 267 mg (88%) of **13**. IR: 1452*m*, 1432*m*, 1422*m*, 1415*m*, 1375*w*, 1295*w*, 1270*m*, 1235*w*, 1157*w*, 1130*w*, 945*w*, 930*w*, 904*s*, 872*w*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.1–2.4 and 2.4–3.2 (2*m*, 13H and 6H). MS: 242 (21), 241 (100, M^+, $C_{13}H_{19}DS_2$), 240 (31), 194 (48), 167 (40), 166 (32), 165 (45), 145 (25), 134 (26), 119 (25), 106 (20), 93 (31), 86 (22), 84 (31), 43 (15), 41 (26).

1,2-exo-*Trimethylene-[2*-endo-$^2H_1$*]-8,9,10-trinorbornane* (**4**). – a) *From* **13**. A soln. of 183 mg (0.76 mmol) of **13** in 10 ml of EtOH was treated with 3 g of *Raney*-Ni and stirred at r.t. for 16 h. Filtration through *Celite*, workup with pentane and bulb-to-bulb distillation (100°/20 Torr) led to 18 mg (17%) of **4**. ^{1}H-NMR (300 MHz): ~ 1.5–1.55, signal for H_{endo}–C(2) missing, ^{13}C–NMR (25.2 MHz)[7]: 26.50 (C(2')); 28.72 (C(1')); 29.51 (C(5)); 33.54 (C(3')); 33.61 (C(6)); 39.17 (C(4)); 39.93[8] (C(3)); 41.09 (C(7)); 48.00 (unlabeled C(2)[8])); 56.34[8]) (C(1)). MS: 138 (12), 137 (87, M^+, $C_{10}H_{15}D$), 136 (31), 122 (49), 121 (46), 109 (31), 108 (46), 107 (33), 96 (31), 95 (67), 94 (100), 93 (41), 83 (38), 82 (37), 81 (54), 80 (82), 79 (62), 68 (43), 67 (45), 55 (13), 53 (13), 41 (23), 39 (21).

b) *From* **12** *Directly*. During 5 min BF_3 gas was passed through a soln. of 300 mg (1.99 mmol) of **12** in 5 ml of abs. CH_2Cl_2 and 900 µl of Et_3SiH. The mixture was washed with H_2O, concentrated by distilling off the solvent through a *Vigreux* column and **4** (101 mg, 37%) isolated by prep. GLC (B: 120°).

Deuteroboration of **14**. In analogy to [8] 10 ml of 0.57M BD_3/THF was added at 0° to 2.001 g (14.9 mmol) of **14** in 5 ml of THF. After stirring at r.t. for 24 h 10 ml of 3N NaOH and 10 ml of 33% H_2O_2 were added and the mixture refluxed for 1 h. Workup with Et_2O afforded 1.988 g (87%) of a 2:1 mixture of the alcohols **15** and **16**. Analytical samples were obtained by prep. GLC (20% *Carbowax M 2000*, 180°).

1,2-exo-*Trimethylene-[6*-exo-$^2H_1$*]-8,9,10-trinorbornan-5*-exo-*ol* (**15**). ^{1}H-NMR (300 MHz): 1.1–2.0 (*m*, 13H); 2.12 (*d*, J = 4, $w_{½} \approx 2$ each, H–C(4)); 3.90 (*d*, J(5*endo*,6*endo*) = 6.8, $w_{½} \approx 3$ each, H_{endo}–C(5)). MS: 154 (3.1), 153 (22.7, M^+, $C_{10}H_{15}DO$), 152 (1.6), 135 (65), 134 (11), 124 (14), 122 (48), 120 (25), 119 (14), 109 (17), 108 (98), 107 (100), 106 (47), 97 (17), 96 (30), 95 (15), 94 (23), 93 (34), 92 (28), 91 (22), 82 (26), 81 (26), 80 (73), 79 (62), 78 (17), 77 (17), 68 (13), 67 (14), 66 (14), 41 (28).

1,2-exo-*Trimethylene-[5*-exo-$^2H_1$*]-8,9,10-trinorbornan-6*-exo-*ol* (**16**). ^{1}H-NMR (300 MHz): 1.1-2.0 (*m*, 13H); 2.23 (*m*, $w_{½} \approx 7$, H–C(4)); 3.62 (*dd*, J(5*endo*,6*endo*) = 6.7, J = 1.4 H_{endo}–C(6)). MS: 154 (7.5), 153 (56.7, M^+, $C_{10}H_{15}DO$), 152 (4.6), 135 (26), 124 (13), 122 (14), 120 (12), 108 (24), 107 (100), 106 (62), 105 (12), 94 (13), 93 (20), 92 (16), 91 (19), 82 (17), 81 (19), 80 (36), 79 (55), 77 (16), 67 (35), 55 (13), 41 (26).

1,2-exo-*Trimethylene-[6*-exo-$^2H_1$*]-8,9,10-trinorbornane* (**5**). To 1200 g (7.84 mmol) of a 2:1 mixture of **15** and **16** (see *above*) 5 ml (190 mmol) of $SOCl_2$ were dropped at –70°. After 4 h at r.t. the mixture was poured on ice/H_2O and extracted with pentane. The org. layer was washed with H_2O. Bulb-to-bulb distillation (160°/28 Torr) yielded 915 mg (68%) of a mixture of chlorides.

To 805 mg (33.1 mmol) of Mg in 55 ml of THF (distilled over $LiAlH_4$), 3.1 ml (36 mmol) of 1,2-dibromoethane were added and the mixture warmed to 90° for 2 h. After cooling to r.t., addition of 6.85 g (41.3 mmol) of KI, followed by 2.7 g of K (69.5 mmol), refluxing for 2 h, again cooling to r.t., 915 mg of the above chloride mixture in 3 ml of THF were added dropwise. Stirring for 12 h at r.t. and subsequent refluxing for 15 min, cooling to 0°, hydrolyzing with sat. NH_4Cl soln., extraction with pentane, washing with H_2O and bulb-to-bulb distillation (120°/24 Torr) gave 604 mg (83%) of a 2:1 mixture of two hydrocarbons, from which **5** was isolated by prep. GLC (B: 120°)[9]). ^{1}H-NMR (300 MHz): ~ 1.55–1.6, signal for H_{exo}–C(6) missing. ^{13}C-NMR (25.2 MHz)[7]: 26.50 (C(2')); 28.65 (C(1')); 29.41[8]) (C(5)); 33.25[8]) (C(6)); 33.66 (C(3')); 39.16 (C(4)); 39.93 (C(3)); 41.07 (C(7)); 47.99 (C(2)); ~ 56.4[8]) (C(1)). MS: 138 (11.9), 137 (100, M^+, $C_{10}H_{15}D$), 136 (9.6), 123 (6), 122 (59), 121 (15), 109 (30), 108 (43), 107 (35), 96 (49), 95 (93), 94 (68), 93 (33), 92 (15), 83 (18), 82 (53), 81 (61), 80 (84), 79 (63), 68 (31), 67 (63), 66 (18), 55 (16), 53 (16), 41 (31).

1,2-exo-*Trimethylene-[6*-endo,*6*-exo-$^2H_2$*]-8,9,10-trinorbornan-5-one* (**18**). A mixture of 1.397 g (9.313 mmol) of **17** [8], 10 ml of CH_3OD and 3 g (55.6 mmol) of $NaOCH_3$ was refluxed for 1 h and subsequently stirred at r.t. for 12 h. Et_2O (80 ml) was added and the org. layer washed twice with 2N HCl and H_2O to give 1.173 g (80%) of **18**. IR: among others 2115*w*, 2130*w*, 2208*w*. MS: 153 (1.8), 152 (14.1, M^+, $C_{10}H_{12}D_2O$), 151 (3.5), 123 (9), 107 (19), 106 (100), 83 (15), 81 (21), 80 (23), 79 (22), 41 (11).

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[7]) For the ^{13}C-NMR of unlabeled **1**, see [6].

[8]) The following characteristic features are observed in the ^{13}C-NMR spectra of D-labeled compounds [9] compared to unlabeled ones: a) D-labeled C-atoms: *t* (^1J(C,D) ≈ 20 Hz), shifted by ~ 0.4 ppm to higher field, whereby the signals become very small for tertiary C-atoms; b) C-atoms α to D-labeled C-atoms: *t* (^2J(C,D) < 1 Hz), shifted by ~ 0.1 ppm to higher field; c) C-atoms β to D-labeled C-atoms: *t* (^3J(C,D) < 1 Hz), shifted by ~ 0.02 ppm to higher field.

[9]) The second hydrocarbon is a D-labeled 2-*endo*,6-*endo*-trimethylene-8,9,10-trinorbornane.

1,2-exo-Trimethylene-[6-endo,6-exo-$^2H_2$]-8,9,10-trinorbornan-5-one p-*Toluenesulfonylhydrazone* (**19**). A mixture of 876 mg (5.76 mmol) of **18** and 1100 g (5.9 mmol) of $TsNHNH_2$ in 5 ml of AcOH was refluxed for 15 min. AcOH was distilled off under reduced pressure (20 Torr) and the residue chromatographed (220 g SiO_2) in Et_2O/hexane 3:1 to yield 1.738 g (94%) of **19**. M.p. 145–146°. MS: 320 (2.3, M^+, $C_{17}H_{20}D_2N_2O_2S$), 319 (5.2), 318 (1), 165 (41), 164 (89), 163 (59), 137 (17), 136 (32), 135 (22), 122 (19), 121 (34), 120 (32), 119 (18), 107 (41), 106 (43), 105 (44), 94 (20), 93 (38), 92 (72), 91 (100), 81 (34), 80 (36), 79 (55), 78 (23), 77 (26), 67 (28), 66 (15), 65 (39), 41 (45).

1,2-exo-Trimethylene-[6-$^2H_1$]-8,9,10-trinorborn-5-ene (**20**). A soln. of 1.605 g (5.02 mmol) of **19** in 150 ml of abs. Et_2O was treated at 0° with 10 ml of 1.6N CH_3Li in ether (16 mmol). After stirring at r.t. for 24 h, 1 ml of H_2O was added and stirring continued for 15 min. The mixture was dried ($MgSO_4$) and the solvent carefully distilled off through a *Vigreux* column. Bulb-to-bulb distillation (120°, 20 Torr) afforded 237 mg (35%) of **20**. ^{1}H-NMR (300 MHz): 1.13 (*dq*, J_{gem} = 7, J = 2, $H^{C(5)}$–C(7))[10]; 1.17–1.33 (*m*, 3H); 1.44 (*dt*, J = 12, J = 3.5, 1H); 1.45–1.6 (*m*, 1H); 1.67–2.0 (*m*, 5H); 2.88 (*m*, $w_{1/2} \approx 7$, H–C(4)); 5.98 (*d*, $J_{4,5}$ = 2.9, H–C(5)). MS: 136 (4.2), 135 (32, M^+, $C_{10}H_{13}D$), 134 (7.8), 120 (18), 106 (15), 94 (18), 93 (100), 92 (53), 91 (18), 81 (89), 80 (68), 79 (25), 78 (25), 77 (16), 67 (13), 41 (10).

1,2-exo-Trimethylene-[6-endo-$^2H_1$]-8,9,10-trinorbornane (**6**). A soln. of 61 mg (0.45 mmol) of **20** in 600 µl of AcOH/CH_3OH 1:1 was slowly added dropwise to a stirred suspension of 300 mg (1.55 mmol) of potassium azodicarboxylate: the decolorized solution was poured into pentane and the org. layer washed 3 times with H_2O and once with sat. $NaHCO_3$ solution. Bulb-to-bulb distillation (120°, 20 Torr) yielded 47 mg (76%) of **6**. ^{1}H-NMR (300 MHz): *ca.* 1.1–1.2, signal for H_{endo}–C(6) missing. MS: 138 (12), 137 (100, M^+, $C_{10}H_{15}D$), 136 (10), 122 (59), 121 (15), 109 (30), 108 (43), 107 (35), 96 (50), 95 (93), 94 (68), 93 (33), 92 (15), 83 (18), 82 (53), 81 (61), 80 (84), 79 (63), 68 (31), 67 (63), 66 (18), 55 (16), 54 (14), 53 (16), 42 (15), 41 (31).

Rearrangements with $AlBr_3$ in CS_2. – General Procedure. To 120 µl of $AlBr_3$ solution under Ar (prepared from 60 mg of $AlBr_3$ and 600 µl of CS_2), precooled to −20°, 60 µl of a solution of 80 mg of **4**, **5** and **6**, resp., 80 mg of **1** and 160 mg of dodecane (internal standard) in 320 µl of CS_2 (also precooled to −20°) was added under stirring. The reaction was quenched by adding 5 ml of a 3:1 mixture of Et_2O and pyridine (precooled to −100°) and worked up: 10 ml of Et_2O were added and the org. layer washed with 2N HCl. From this solution on the one hand by further dilution with Et_2O, the rate of conversion was determined by capillary GLC (3 measurements in each case). On the other hand the solvent was removed by distillation through a *Vigreux* column. Reactants and products were separated by prep. GLC to determine their D-contents by MS with correction for natural abundance of ^{13}C. The results are listed in the *Table*.

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[10] The index indicates toward which C-atom the H-atom is orientated.