80. The Adamantane Rearrangement of 1,2-Trimethylenenorbornanes

Part V[1])

Rearrangements of 1,2-Trimethylenenorbornanes Initiated by Regioselective Formation of Carbocation Centers at C(2) and C(6)

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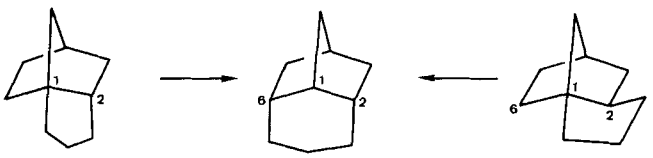
The behaviour of the regioselectively generated carbocation centers at C(2) and C(6) in 1,2-trimethylenenorbornanes was investigated in order to study the occurrence or absence of a degenerate rearrangement **E**⇄**M** in the adamantane rearrangement of both 1,2-*endo*- (**1**) and 1,2-*exo*-trimethylenenorbornane (**2**) to 2-*endo*,6-*endo*-trimethylenenorbornane (**3**). A degenerate rearrangement **E**⇄**M** is inevitably involved inasmuch as a 1,2-trimethylenenorborn-2-yl cation **E** not only is formed directly as manifested by the conversions of the reactants **4** (C(2), C(3)-olefin) and **6** (C(2), C(3')-olefin), but also indirectly (*via* **F**→**E**) if the leaving group at C(6) to be ionized occupies the *endo*-position (6-*endo*-alcohol **8**). No degenerate rearrangement **E**⇄**M** is operative starting from reactants that lead directly to a 2,6-trimethylenenorborn-2-yl cation **G**; this is the case with both the ionization of the 6-*exo*-alcohol **10** having the leaving OH-group in a stereoelectronically favoured configuration to undergo simultaneous C(1),C(2)-bond migration (→**G**) as well as the protonation of the olefin **13** which is followed by the same reaction pathway.

1. Introduction. – In the adamantane rearrangement of both 1,2-*endo*- (**1**)[2]) and 1,2-*exo*-trimethylenenorbornane (**2**)[2]) to 2-*endo*,6-*endo*-trimethylenenorbornane (**3**)[2]), a degenerate rearrangement (**E**⇄**M**[3]); *Scheme 2*) is involved as verified from treatment of D-labelled 1,2-*endo*-, 1,2-*exo*-, and 2-*endo*,6-*endo*-trimethylenenorbornane (D-labelled **1**, **2**, and **3**, resp.) with $AlBr_3$ in CS_2 [2].

Scheme 1



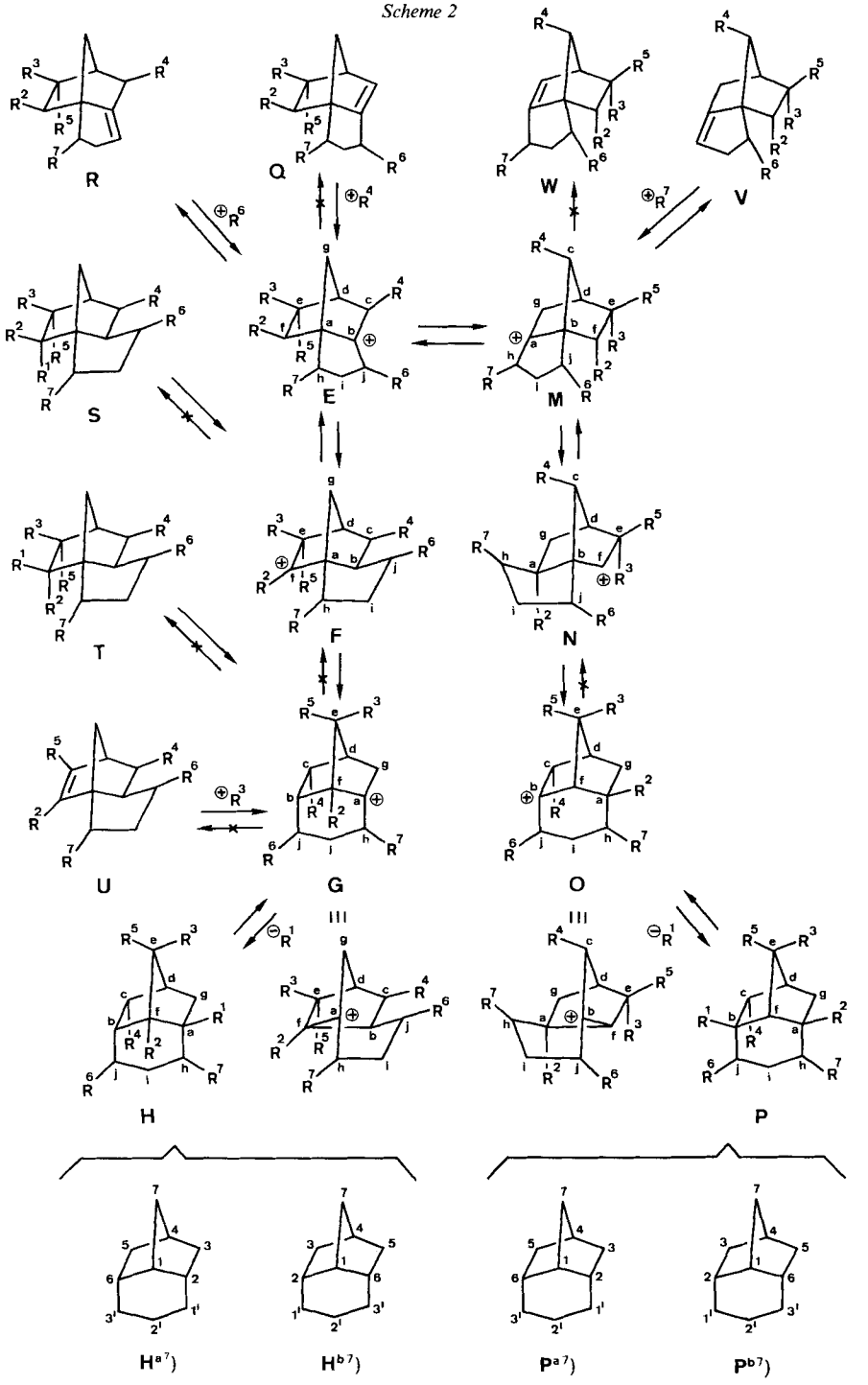
1 **3** **2**

[1]) For Part IV, see [1].

[2]) In the present communication the numbering of the C-atoms follows the trimethylenenorbornane nomenclature. The correct IUPAC names are listed in the *Exper. Part* (see also *Footnote 2* in [2]).

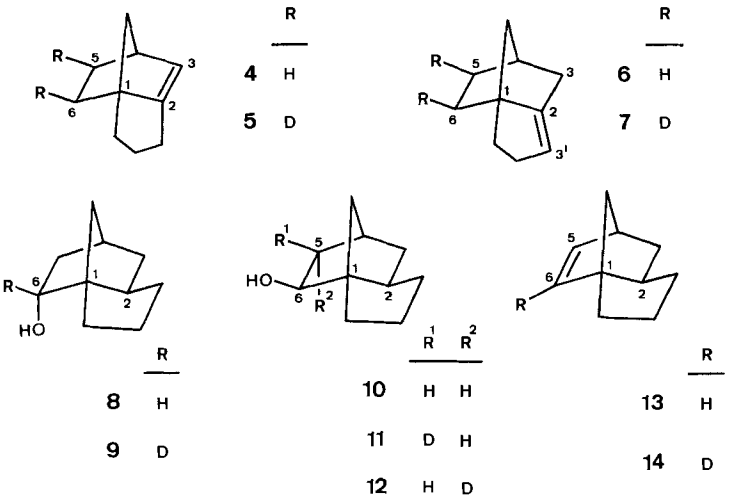
[3]) For the purpose of facilitating the comparison of the present *Scheme 2* with the *Scheme 3* in [2] for the $AlBr_3$-catalyzed adamantane rearrangement of both **1** and **2**, the letters **E**–**H** and **M**–**P** are used again in the present *Scheme 2* for corresponding formulas and by consequence the letters **A**–**D** and **I**–**L** are omitted.

Scheme 2



Under the applied reaction conditions [2], not only abstraction of the tertiary 2-*exo*- and the secondary 6-*exo*-hydride ion in **1** and **2**, respectively, is observed, but also abstraction of the tertiary 2-*exo*- and/or the 6-*exo*-hydride ion in **3**, which causes an equilibrium between 2,6-trimethylenenorbornanes, *i.e.* **H** and **P** (see *Scheme 2*[3])), again involving a degenerate rearrangement **E**⇄**M**.

To avoid such complications and to gain more detailed information about the adamantane rearrangement of both **1** and **2** to **3**, we studied the behaviour of the regioselectively generated carbocation centers at C(2) and C(6) in 1,2-trimethylenenorbornanes. This could efficiently be accomplished mainly by making use of 'ionic hydrogenation'[4]). As substrates for our studies we have chosen alkenes and alcohols of the types **Q**–**U**[5]) (**4**–**14**; see *Scheme 2* and *Table*).



2. Rearrangements Involving a Degenerate Rearrangement E⇄M. – 2.1. *C(2)-Carbenium Ion.* 2.1.1. *C(2),C(3)-Olefin (Type* **Q***) as Reactant.* In order to test the applicability of the ionic hydrogenation method[4]), first on the one hand the unlabelled olefin **4** [4] of type **Q** was treated with CF_3CO_2H/Et_3SiH *(Table, Run 1)* to yield 2,6-trimethylenenorbornane (**3**). On the other hand, addition of neat CF_3CO_2H[6]) to **4** followed by hydrolysis with aq. KOH *(Run 2)* gave 2,6-trimethylenenorbornan-2-ol (**15**, see below). Although both experiments led to the expected products, they do not allow to decide whether a degenerate rearrangement **E**⇄**M** is involved (→**H** + **P**) or not (**H** only), because of **H** and

[4]) See the review [3] and ref. cit. therein. In the first step, a carbocation is formed by either protonation of an alkene by trifluoroacetic acid or ionization of an alcohol by boron trifluorate, and in the final step, a hydride ion from triethylsilane is transferred to the primarily formed carbenium ion or a rearranged one.

[5]) For the purpose of comprehensive discussions, the latter are based on one enantiomeric form of the reactants **Q**–**U** only although racemates were used in all experiments. For a given product of the types **H** and **P**, its enantiomer is specified by a dash (*e.g.* **15** and **15′**, resp.).

[6]) For adducts of CF_3CO_2H with olefins, see [5] and ref. cit. therein.

[7]) The different numbering in $\mathbf{H}^a$ and $\mathbf{H}^b$, resp., and $\mathbf{P}^a$ and $\mathbf{P}^b$, resp., of the same C-atoms follows from the correct IUPAC nomenclature. In order to ease the comprehension, the substituents R^1 to R^7 are not drawn in $\mathbf{H}^a/\mathbf{H}^b$ and $\mathbf{P}^a/\mathbf{P}^b$; their positions are the same as in *Formulae* **H** and **P**, resp., and are independent of the different numbering.

Table. *Conversions of the Alkenes and Alcohols* **4**–**14** *as well as of Related Compounds*

Section	*Run*	Reactant									Reaction Conditions[a])	Products[5])[7])								
		Compound	Type	R^1	R^2	R^3	R^4	R^5	R^6	R^7		Compound	Type	R^1	R^2	R^3	R^4	R^5	R^6	R^7
2.1.1	*1*	**4**	**Q**	–	H	H	–	H	H	H	*A*	**3**	$\mathbf{H^a{\equiv}P^b}$	H	H	H	H	H	H	H
	2	**4**	**Q**	–	H	H	–	H	H	H	*B*	**15/15′**	$\mathbf{H^a/P^b}$	OH	H	H	H	H	H	H
	3	**5**	**Q**	–	D	D	–	H	H	H	*A*	**16/17**	$\mathbf{H^a/P^a}$	H	D	D	H	H	H	H
	4	**5**	**Q**	–	D	D	–	H	H	H	*B*	**18/19**	$\mathbf{H^a/P^b}$	OH	D	D	H	H	H	H
	5	**18/19**	$\mathbf{H^a/P^b}$	OH	D	D	H	H	H	H	*C*	**16/17**	$\mathbf{H^a/P^a}$	H	D	D	H	H	H	H
	6	**15**	$\mathbf{H^a}$	OH	H	H	H	H	H	H	*D*	**20**	$\mathbf{H^a}$	D	H	H	H	H	H	H
	7	**21**	$\mathbf{H^a}$	OH	H	D	H	H	H	H	*C*	**22**	$\mathbf{H^a}$	H	H	D	H	H	H	H
	8	**23**	H^a	Cl	H	H	H	D	H	H	*E*	**24**	$\mathbf{H^a}$	OH	H	H	H	D	H	H
	9	**4**	**Q**	–	H	H	–	H	H	H	*F*	**25**	$\mathbf{H^b{\equiv}P^b}$	H	H	H	D	H	D	D
	10	**4**	**Q**	–	H	H	–	H	H	H	*G*	**26/27**	$\mathbf{H^a/P^b}$	OH	H	H	D	H	D	D
	11	**4**	**Q**	–	H	H	–	H	H	H	*H*	**28/29**[b])	**R/V**	–	H	H	D	H	–	H
	12	**30/31**	$\mathbf{H^a/P^b}$	OR[c])	H	H	D	H	D	D	*I*	**32/33**	$\mathbf{H^a/P^b}$	OH	H	H	D	H	D	D
2.1.2	*13*	**6**	**R**	–	H	H	H	H	–	H	*A*	**3**	$\mathbf{H^a{\equiv}P^b}$	H	H	H	H	H	H	H
	14	**6**	**R**	–	H	H	H	H	–	H	*B*	**15/15′**	$\mathbf{H^a/P^b}$	OH	H	H	H	H	H	H
	15	**7**	**R**	–	D	D	H	H	–	H	*B*	**18/19**	$\mathbf{H^a/P^b}$	OH	D	D	H	H	H	H
	16	**6**	**R**	–	H	H	H	H	–	H	*F*	**34**	$\mathbf{H^a{\equiv}P^b}$	H	H	H	H	H	D	D
	17	**6**	**R**	–	H	H	H	H	–	H	*G*	**35/35′**	$\mathbf{H^a/P^b}$	OH	H	H	H	H	D	D
	18	**7**	**R**	–	D	D	H	H	–	H	*J*	**7/36**[d])	**R/V**	–	D	D	H	H	–	H
2.2	*19*	**8**	**S**	OH	H	H	H	H	H	H	*C*	**3**	$\mathbf{H^a{\equiv}P^b}$	H	H	H	H	H	H	H
	20	**8**	**S**	OH	H	H	H	H	H	H	*K*	**37/37′**	$\mathbf{H^a/P^b}$	Cl	H	H	H	H	H	H
	21	**9**	**S**	OH	D	H	H	H	H	H	*C*	**38/20**[10])	$\mathbf{H^a/P^a}$	H	D	H	H	H	H	H
	22	**9**	**S**	OH	D	H	H	H	H	H	*K*	**39/40**	$\mathbf{H^a/P^b}$	Cl	D	H	H	H	H	H
	23	**39/40**	$\mathbf{H^a/P^b}$	Cl	D	H	H	H	H	H	*E*	**41/42**	$\mathbf{H^a/P^b}$	OH	D	H	H	H	H	H
3.1	*24*	**10**	**T**	OH	H	H	H	H	H	H	*C*	**3**	$\mathbf{H^a{\equiv}P^b}$	H	H	H	H	H	H	H
	25	**10**	**T**	OH	H	H	H	H	H	H	*K*	**37**	$\mathbf{H^a}$	Cl	H	H	H	H	H	H
	26	**11**	**T**	OH	H	D	H	H	H	H	*L*	**43**	$\mathbf{H^a}$	Cl	H	D	H	H	H	H
	27	**12**	**T**	OH	H	H	H	D	H	H	*K*	**23**	$\mathbf{H^a}$	Cl	H	H	H	D	H	H
3.2	*28*	**13**	**U**	–	H	–	H	H	H	H	*A*	**3**	$\mathbf{H^a{\equiv}P^b}$	H	H	H	H	H	H	H
	29	**13**	**U**	–	H	–	H	H	H	H	*M*	**20**	$\mathbf{H^a}$	D	H	H	H	H	H	H
	30	**13**	**U**	–	H	–	H	H	H	H	*F*	**22**	$\mathbf{H^a}$	H	H	D	H	H	H	H
	31	**14**	**U**	–	D	–	H	H	H	H	*A*	**38**	$\mathbf{H^a}$	H	D	H	H	H	H	H
	32	**13**	**U**	–	H	–	H	H	H	H	*N*	**17**[13])	$\mathbf{H^a}$	D	H	D	H	H	H	H
	33	**13**	**U**	–	H	–	H	H	H	H	*G*	**21**	$\mathbf{H^a}$	OH	H	D	H	H	H	H

[a]) *A:* CF_3CO_2H/Et_3SiH; *B:* 1) CF_3CO_2H, 2) aq. KOH; *C:* BF_3/Et_3SiH; *D:* BF_3/Et_3SiD; *E:* aq. K_2CO_3; *F:* CF_3CO_2D/Et_3SiH; *G:* 1) CF_3CO_2D, 2) aq. KOH; *H:* ⩽ 0.5 mol-equiv. CF_3CO_2D; *I:* $LiAlH_4$ or aq. KOH; *J:* ⩽ 0.5 mol-equiv. CF_3CO_2H; *K:* $SOCl_2$, r.t.; *L:* $SOCl_2$, −20°; *M:* CF_3CO_2H/Et_3SiD; *N:* CF_3CO_2D/Et_3SiD.

[b]) In addition: a mixture of the esters **30/31** (type $\mathbf{H^a/P^b}$: $R^1 = OCOCF_3$, $R^4 = D$)[9]).

[c]) $R = COCF_3$.

[d]) In addition: a mixture of esters (not isolated).

P being identical in the first case and $\mathbf{H}^{a}$[7]) (**15**) and $\mathbf{P}^{b}$[7]) (**15'**) being enantiomeric[5]) in the second case for R^1 to R^7 = H. However, the D-labelled C(2),C(3)-olefin **5** [4] (*Run 3:* CF_3CO_2H/Et_3SiH) yielded a mixture of the 2 constitutional isomers **16** and **17**, which in fact proves indirectly that a C(2)-carbenium ion **E** of a 1,2-trimethylenenorbornane, once formed, ultimately undergoes a degenerate rearrangement **E**⇄**M** as happens in the $AlBr_3$-catalyzed rearrangements of both **1** and **2** [2]. The same conclusion has to be drawn from the conversion of **5** to the constitutionally isomeric alcohols **18** and **19** (*Run 4:* 1) CF_3CO_2H; 2) aq. KOH), which on further reduction (*Run 5:* BF_3/Et_3SiH) again afforded a mixture of **16** and **17**.

As basis for the interpretation of the above experiments served the reductions of the unlabelled alcohol **15** to **20** (*Run 6:* BF_3/Et_3SiD) and of the monodeuterated analogue **21** to **22** (*Run 7:* BF_3/Et_3SiH) as well as the hydrolysis of the chloride **23** to **24** (*Run 8:* aq. K_2CO_3) as the only alcohol.

A most remarkable result was obtained from the treatment of the undeuterated olefin **4** with deuterated trifluoroacetic acid *(Run 9)*. Deuterium was not only incorporated at C(3) but in addition also at C(1') and C(3') as established by the partial (*ca.* 15%) formation of **25**[8]). Analogously, D-incorporation was observed when the olefin **4** was reacted with CF_3CO_2D followed by base hydrolysis (*Run 10:* →*ca.* 15% of the alcohols **26**[8]) and **27**[8])). An attractive explanation for this result would be an equilibrium **R**⇄**E**⇄**M**⇄**V**. To prove this proposal, the olefin **4** was treated with only 0.5 mol-equiv. of CF_3CO_2D *(Run 11)*. The reisolated olefins (48%) consisted, in addition to unlabelled **4**, of *ca.* 40% of a 1:1 mixture of **28** (type **R**, R^4 = D–C(3)) and **29** (type **V**, R^4 = D–C(7))[9]).

This provides conclusive evidence for a degenerate rearrangement **E**⇄**M** being involved. It has to be noted that, starting neither from **4** nor **5**, D-incorporation or scrambling in the recovered reactants were detected as it is the case by the $AlBr_3$-treatment [2] of **1** and **2**.

2.1.2. *C(2),C(3')-Olefin (Type* **R***) as Reactant.* As a consequence of the indirect evidence for an equilibrium **R**⇄**E**⇄**M**⇄**V** (see *2.1.1: Runs 10* and *11*), we studied independently the behaviour of C(2),C(3')-olefins (type **R**) themselves. Treatment of unlabelled **6** with CF_3CO_2H/Et_3SiH *(Run 13)* and CF_3CO_2H followed by base hydrolysis *(Run 14)* yielded 2,6-trimethylenenorbornane (**3**) and the corresponding C(2)-alcohols **15**/**15'**[5]), respectively. That a degenerate rearrangement **E**⇄**M** is involved also in these conversions is confirmed by the *ca.* 1:1 mixture of the constitutionally isomeric dideuterated alcohols **18** (type $\mathbf{H}^{a}$) and **19** (type $\mathbf{P}^{b}$), which resulted from the D-labelled olefin **7** (*Run 15:* 1) CF_3CO_2H; 2) aq. KOH).

To gain conclusive direct proof for the equilibrium **R**⇄**E**⇄**M**⇄**V**, the following experiments were carried out: As a prerequisite it was first certified that the unlabelled olefin **6** on CF_3CO_2D treatment gave 2,6-trimethylenenorbornanes with D-incorporation at C(1') as well as at C(3'). Indeed partial (*ca.* 15%) formation of the dideuterated products **34** (*Run 16:* CF_3CO_2D/Et_3SiH) and **35**/**35'**[5]) (*Run 17:* 1) CF_3CO_2D; 2) aq. KOH) were observed. Finally, when exposing the 5-*exo*,6-*exo*-dideuterated olefin **7** to only 0.5

[8]) In addition to the listed compound (see *Table*), the ones with lower D-contents were also present.

[9]) In addition, *ca.* 23% of a mixture of esters containing *ca.* 15% of a 1:1 mixture of trideuterated **30**[8]) and **31**[8]) (see *Table*) was isolated. Reduction or hydrolysis of **30**/**31** *(Run 12)* gave the corresponding alcohols **32**[8]) and **33**[8]).

mol-equiv. of CF_3CO_2H *(Run 18)*, the reisolated reactant consisted of a *ca.* 1:1 mixture of **7** (type **R**, $R^2 = R^3 = D$) and the 5-*endo*,6-*endo*-dideuterated analogue **36** (type **V**, $R^2 = R^3 = D$).

2.2. *C(6)-Carbenium Ion: 6*-endo-*Alcohol (Type* **S***) as Reactant.* Two different reaction conditions were applied to convert the 6-*endo*-alcohol **8** (type **S**) to 2,6-trimethylenenorbornanes. Ionic hydrogenation (*Run 19:* BF_3/Et_3SiH) led to unsubstituted **3**, whereas treatment with $SOCl_2$ *(Run 20)* yielded the 2-chloro compounds **37**/**37'**[5]). Analogous treatment of the corresponding D_{exo}–C(6)-labelled alcohol **9** with BF_3/Et_3SiH *(Run 21)* gave a *ca.* 3:1 mixture of **38** (D–C(1)) and **20**[10]) (D–C(2)) and with $SOCl_2$ *(Run 22)* a *ca.* 10:1 mixture of the chlorides **39** (D–C(1)) and **40** (D–C(2))[11]). The formations of the above mixtures conclusively prove a degenerate rearrangement **E**⇄**M**, and by consequence [1,3]-H-shifts (**E**⇄**F** and **M**⇄**N**[12])) are always involved as soon as a C(6)-carbenium ion **F** of an 1,2-*exo*-trimethylenenorbornane is an intermediate. Isomerizations without participation of **E**⇄**M** would have resulted in compounds of type $\mathbf{H}^a$ (**38** and **39**, resp.) as the sole products with a D-atom (R^2) at C(1) only.

3. Rearrangements Not Involving a Degenerate Rearrangement E⇄M. – 3.1. *6*-exo-*Alcohol (Type* **T***) as Reactant.* The 6-*exo*-alcohol **10** [6] of type **T** was first treated under reaction conditions which verified that the rearrangements to 2,6-trimethylenenorbornanes can be accomplished smoothly. Normal ionic hydrogenation (*Run 24:* BF_3/Et_3SiH) yielded **3**. Reaction of **10** with $SOCl_2$ *(Run 25)* gave the expected 2-chloro compound **37**.

Interestingly enough, treatment of the D_{exo}–C(5)-labelled alcohol **11** [1] with $SOCl_2$ *(Run 26)* led only to the monodeuterated chloride **43** of the general type $\mathbf{H}^a$. No product of type $\mathbf{P}^b$ ($R^1 = Cl$, $R^3 = D$), *i.e.* the enantiomer of the C(7)-diastereoisomer **23**[5]), could be detected. Equivalent to this result was the conversion of the D_{endo}–C(5)-labelled alcohol **12** with $SOCl_2$ *(Run 27)*, which gave rise to the monodeuterated chloride **23** (type $\mathbf{H}^a$) as the sole product. Again no compound of type $\mathbf{P}^b$ ($R^1 = Cl$, $R^5 = D$), *i.e.* the enantiomer of the C(7)-diastereoisomer **43**[5]), was observable.

These results clearly demonstrate that in **10** the 6-*exo*-hydroxy group occupies a stereoelectronically favoured configuration so that on its leaving simultaneous C(1),C(2)-bond migration occurs to generate directly the carbenium ion **G**. The latter does not undergo a [1,2]-C-shift to **F**, but is instantaneously trapped by a hydride ion to yield the product of type $\mathbf{H}^a$.

3.2. *C(5),C(6)-Olefin (Type* **U***) as Reactant.* The ionic hydrogenation was finally applied to the C(5),C(6)-olefin **13** [6] of type **U**. Indeed 2,6-trimethylenenorbornane (**3**) was obtained quantitatively (*Run 28:* CF_3CO_2H/Et_3SiH). Analogously, experiments either with Et_3SiD *(Run 29)* or CF_3CO_2D *(Run 30)* gave the expected monodeuterated products **20** and **22**, respectively[5]). Further information about the reaction pathway was gained as follows. The D-labelled olefin **14** [1] was transformed to the D–C(1) compound **38** of type $\mathbf{H}^a$ as the sole product (*Run 31:* CF_3CO_2H/Et_3SiH), and none of its constitutional isomer of type $\mathbf{P}^a$ ($R^2 = D$) which corresponds to **20** ($\mathbf{H}^a$, $R^1 = D$) was observed.

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[10]) It has to be noted that for **20**, type $\mathbf{P}^a$ with $R^2 = D$ is identical to type $\mathbf{H}^a$ with $R^1 = D$.

[11]) For further identification, **39**/**40** was hydrolyzed to the corresponding mixture of the alcohols **41** and **42** *(Run 23)*.

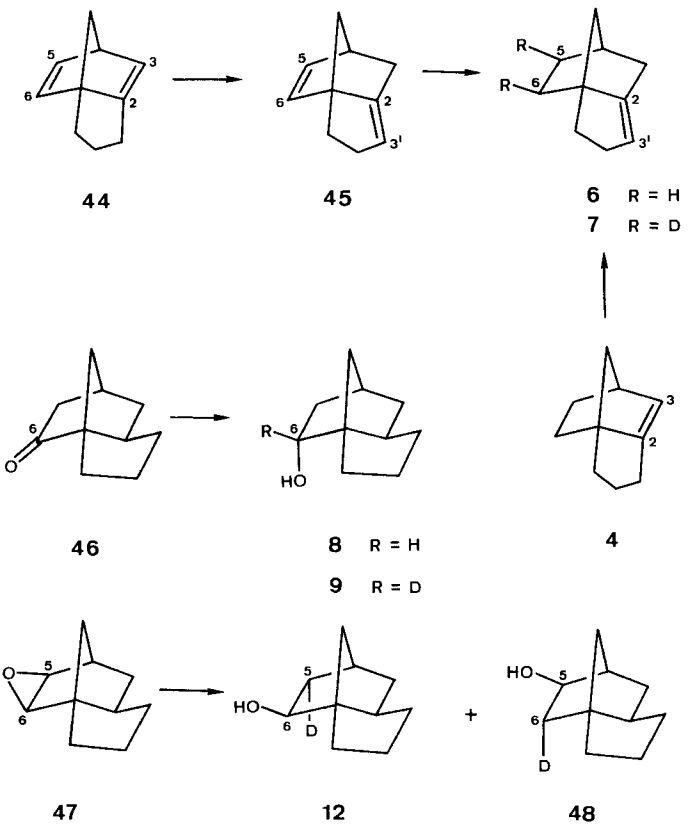
[12]) The [1,3]-D-shift **M**⇄**N** (isotope effect) compared to the [1,3]-H-shift **E**⇄**F** might in part be responsible for the 3:1 ratio of **38** and **20**[10]) and the 10:1 ratio of **39** and **40** (determined by ^{1}H-NMR).

Again only a type-$\mathbf{H}^a$ compound and none of a type-$\mathbf{P}^b$ one, *i.e.* the C(7)-diastereoisomer of its enantiomer, was obtained by converting the undeuterated olefin **13** to the dideuterated product **17**[13]) (*Run 32:* CF_3CO_2D/Et_3SiD) and to the monodeuterated alcohol **21** (*Run 33:* 1) CF_3CO_2D; 2) aq. KOH), respectively. Obviously protonation of the C(5),C(6)-double bond is accompanied by simultaneous C(1),C(2)-bond migration. Thus, starting from the C(5),C(6)-olefin **13**, as in the case of the 6-*exo*-alcohol **10** (see *3.1*), the carbenium ion **G** is formed directly and does not undergo a [1,2]-C-shift to **F**. By consequence no degenerate rearrangement **E**⇄**M** is involved in the transformation of olefin **13** to 2,6-trimethylenenorbornane (**3**).

4. Reactants and Products: Syntheses and Structure Assignments[5][7]). – The following reactants and products have already been described earlier: **3** [2] [7][14]), **4** [4], **5** [4], **10** [6], **11** [1], **13** [6], **14** [1], **15** [6] [8][14]), **16** [2], **17** [2] and **20** [2][14]).

The novel 1,2-trimethylenenorbornanes **6–9** and **12** were synthesized according to *Scheme 3*. The C(2),C(3)-olefin **4** [4], on treatment with a catalytic amount (*ca.* 0.15

Scheme 3



[13]) It has to be noted that for **17**, type $\mathbf{H}^a$ with $R^1 = R^3 = D$ is identical to type $\mathbf{P}^a$ with $R^2 = R^3 = D$.
[14]) See also *Exper. Part.*

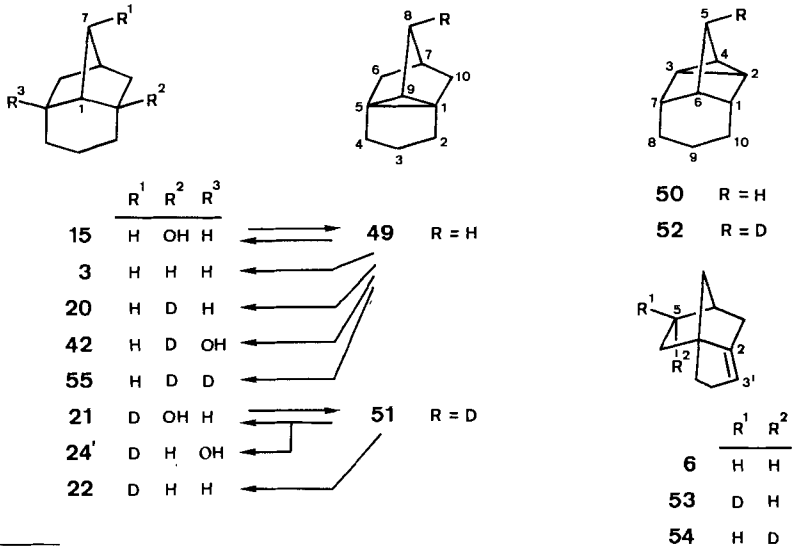
mol-equiv.) of CF_3CO_2H at r.t., was readily converted to the C(2),C(3')-olefin **6**. The latter could also be prepared from the diene **44** [4]. Heating for 4 h at 150° in the presence of *t*-BuOK yielded almost quantitatively the isomerized diene **45**, which on diimide reduction[15]) gave **6**. Analogous treatment of **45** with dideuterated diimide[15]) resulted in **7**.

Reduction of the C(6)-ketone **46** [6] with $LiAlH_4$ or $LiAlD_4$ led to the unlabelled 6-*endo*-alcohol **8** and the 6-*exo*-deuterio analogue **9**, respectively.

Reaction of the epoxide **47** [6] with $LiEt_3BD$ gave a 6:1 mixture (80%) of the desired 5-*endo*-deuterated 6-*exo*-alcohol **12** and its isomer **48**, from which the former was easily separated.

Unambiguous structural assignments to the various D-labelled compounds (see *Table*) are based on spectral analyses (^{1}H-NMR, ^{13}C-NMR, MS)[16]) of products and recovered reactants as well as of the following compounds, specifically prepared by independent routes: **20–22**, **24**, **42**, and **53–55**. Their syntheses are summarized in *Scheme 4*. The unlabelled alcohol **15** [6] [8] was dehydrated in refluxing hexamethylphosphoric triamide (HMPT)[17]). A mixture of compounds was formed, from which the tetracyclic hydrocarbons **49** [6] (*ca.* 50%) and **50** [10] (*ca.* 5%) as well as the olefins **6** (*ca.* 15%) and **13** [6] (*ca.* 15%) were isolated. Analogous treatment of the D–C(7)-alcohol **21**[18]) yielded **51** as the main product. Minor amounts of the tetracyclic compound **52** and a 1:1 mixture of the D–C(5)-olefins **53**/**54** were collected too.

Scheme 4



[15]) Diimide or dideuterated diimide was generated *in situ* at r.t. from dipotassium azodicarboxylate (PADA) in CH_3OH/AcOH and CH_3OD/AcOD, respectively.

[16]) The ^{1}H-NMR and ^{13}C-NMR data of the 4 unlabelled compounds **3**, **6**, **15**, and **37** are listed in the *Exper. Part.* 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), *ca.* 0.4 ppm shifted to higher field; b) C-atoms α to D-labelled C-atoms: t (^2J(C, D) < 1 Hz), *ca.* 0.1 ppm shifted to higher field; c) C-atoms β to D-labelled C-atoms: t (^3J(C, D) < 1 Hz), *ca.* 0.02 ppm shifted to higher field.

[17]) For earlier studies on dehydration of alcohols in HMPT, see [9].

[18]) For the synthesis of **21**, see below and *Table (Run 33)*.

Reaction of **49** with CF_3CO_2H/Et_3SiH led to 2-*endo*,6-*endo*-trimethylenenorbornane (**3**), whereas the application of CF_3CO_2H followed by basic hydrolysis (aq. KOH) gave the corresponding C(2)-alcohol **15**. These transformations by ionic hydrogenation[4]) opened the possibility to prepare various D-labelled analogues of **3** and **15**, just by choosing a specific combination of reactant (**49** or **51**) and reagents. Thus the following compounds were synthesized specifically: **20** (**49** + CF_3CO_2H/Et_3SiD or CF_3CO_2D/Et_3SiH), **21/24'** (**51** + CF_3CO_2H followed by aq. KOH), **22** (**51** + CF_3CO_2H/Et_3SiH), **42** (**49** + CF_3CO_2D followed by aq. KOH), **55** (**49** + CF_3CO_2D/Et_3SiD).

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Experimental Part

General Remarks. See [2].

1. NMR Data of 3, 6, 15, and 37. – *2*-endo,*6*-endo-*Trimethylene-8,9,10-trinorbornane* (**3**). ^{1}H-NMR (300 MHz): 0.95 (*dd*, J_{gem} = 11, $J_{2,3endo}$ and $J_{5endo,6}$, resp., = 4, H_{endo}–C(3), H_{endo}–C(5)); 1.25–1.65 (*m*, 10H); 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 (75.5 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)).

1,2-Trimethylene-8,9,10-trinorborn-2(3')-ene (= 10,2-(1'-Ethanyl-2'-ylidene)-8,9-dinorbornane; **6**). ^{1}H-NMR (300 MHz)[19]): 1.44 (*dq*, J_{gem} = 9, *J* = 2, 2, 2, H–C(7)$^{C(2)}$); 1.25–1.35 (*m*, among others *J* = 9, H_{endo}–C(5)); 1.39 (*dt*, J_{gem} = 9, *J* = 3.5, 3.5, H–C(7)$^{C(5)}$); 1.4–1.65 (*m*, 2H–C(6)); 1.71 (*m*, $w_{1/2} \approx 35$, H_{exo}–C(5)); 1.76 (*ddd*, J_{gem} = 13.5, $J_{1'a,2'b}$ = 8, $J_{1'a,2'a}$ = 2, H–C(1'a)); 1.84 (*d*, J_{gem} = 16, $w_{1/2} \approx 8$, H_{endo}–C(3)); 1.91 (*dt*, J_{gem} = 13.5, $J_{1'b,2'a} = J_{1'b,2'b}$ = 9, H–C(1'b)); 2.18 (*d*, J_{gem} = 16, $w_{1/2} \approx 11$ each, H_{exo}–C(3)); 2.46 (*m*, $w_{1/2} \approx 11$, H–C(4)); 2.5–2.6 (*m*, H–C(2'a)); 2.65–2.8 (*m*, H–C(2'b)); 4.96 (*m*, $w_{1/2} \approx 6$, H–C(3')). ^{13}C-NMR (75.5 MHz): 27.64 (*t*, C(1')); 29.96 (*t*, C(5)); 32.29 (*t*, C(6)); 32.71, 36.95 (2*t*, C(3), C(2')); 43.39 (*t*, C(7)); 40.83 (*d*, C(4)); 61.54 (*s*, C(1)); 112.81 (*s*, C(3')); 155.14 (*d*, C(2)).

2-endo,*6*-endo-*Trimethylene-8,9,10-trinorbornan-2-ol* (**15**). ^{1}H-NMR (300 MHz)[19]): 0.83 (*ddd*, J_{gem} = 12, *J* = 4.5, $J_{5endo,7}^{C(2)}$ = 3, H_{endo}–C(5)); 1.22 (*dd*, J_{gem} = 10, *J* = 1, $w_{1/2} \approx 4$ each, H–C(7)$^{C(5)}$); 1.26 (*m*, $w_{1/2} \approx 5$, HO–C(2)); 1.3–1.7 (*m*, 8H); 1.70 (*m*, $w_{1/2} \approx 8$, H–C(1)); 1.75–1.8 (*m*, H–C(7)$^{C(2)}$ and 1H)); 2.13 (*m*, $w_{1/2} \approx 20$, H–C(6)); 2.21 (*m*, $w_{1/2} \approx 9$, H–C(4)). ^{13}C-NMR (25.2 MHz): 18.64 (*t*, C(2')); 26.47 (*t*, C(3')); 31.90 (*t*, C(5)); 34.13 (*d*, C(6)); 35.87 (*t*, C(1')); 37.16 (*d*, C(4)); 38.68 (*t*, C(7)); 44.87 (*t*, C(3)); 50.08 (*d*, C(1)); 77.15 (*s*, C(2)).

*2-Chloro-2-*endo,*6*-endo-*trimethylene-8,9,10-trinorbornane* (**37**). ^{1}H-NMR (300 MHz)[19]): 1.19 (*ddd*, J_{gem} = 12.5, *J* = 4.5, $J_{5endo,7}^{C(2)}$ = 2.5, H_{endo}–C(5)); 1.35 (*dm*, J_{gem} = 10, $w_{1/2} \approx 5$ each, H–C(7)$^{C(5)}$); 1.37–1.57 (*m*, 4H); 1.63 (*tdd*, *J* = 12, 12, 4, 3, 1H); 1.77 (*dd*, J_{gem} = 14, $J_{3endo,7}^{C(5)}$ = 2.5, H_{endo}–C(3)); 2.03 (*dtd*, J_{gem} = 10, *J* = 2, 2, $J_{1,7}^{C(2)}$ = 1.5, H–C(7)$^{C(2)}$); 2.1–2.25 (*m*, 3H, among others H–C(1)); 2.27 (*m*, $w_{1/2} \approx 9$, H–C(4)). ^{13}C-NMR (25.2 MHz): 18.76 (*t*, C(2')); 26.08 (*t*, C(3')); 31.80 (*t*, C(5)); 35.26 (*d*, C(6)); 37.95 (*d*, C(4)); 38.60 (*t*, C(1')); 39.76 (*t*, C(7)); 46.29 (*t*, C(3)); 52.15 (*d*, C(1)); 76.86 (*s*, C(2)).

2. Experiments of *Table 1*. – As a representative example for each type of reaction conditions, the experiment of the unlabelled reactant with unlabelled reagents is described.

Method A *(CF_3CO_2H/Et_3SiH): Conversion* **13**→**3** *(and Analogously Methods* F, M, *and* N*).* To a soln. of 170 mg (1.269 mmol) of olefin **13** [6] in 4 ml of dry CH_2Cl_2, 210 µl (1.322 mmol) of Et_3SiH followed by 720 µl (9.411 mmol) of CF_3CO_2H were added. After stirring for 1 h at r.t., the solv. was removed by distillation through a *Vigreux* column. From the residue, 134 mg (78%) of **3** [2] [7] were isolated by prep. GLC (A: 140°).

Method B *(CF_3CO_2H Followed by aq. KOH): Conversion* **13**→**15** *(and Analogously Method* G*).* To 2.00 g (14.95 mmol) of olefin **13** [6], 5 ml (7.45 g, 64.8 mmol) of CF_3CO_2H were added with stirring at r.t. After 1 h, Et_2O (30 ml) and 20 ml of a 10% aq. KOH soln. were added and the mixture stirred for further 12 h. Usual workup and bulb-to-bulb distillation (130°/12 Torr) afforded 2.09 g (92%) of **15** [6] [8].

Method C *(BF_3/Et_3SiH): Conversion* **15**→**3** *(and Analogously Method* D*).* A soln. of 102 mg (0.67 mmol) of alcohol **15** [6] [8] in 3 ml of dry CH_2Cl_2 was treated with 200 µl (1.259 mmol) of Et_3SiH. BF_3-gas was bubbled through the mixture for 5 min. The solv. was distilled off through a *Vigreux* column. From the residue, 71 mg (70%) of **3** [2] [7] were isolated by prep. GLC (B: 120°).

Method J *(≤ 0.5 mol-equiv. CF_3CO_2H): Conversion* **4**→**6** *(and Analogously Method* H*).* A soln. of 245 mg (1.828 mmol) of the olefin **4** [4] in 1 ml of dry CH_2Cl_2 was treated with 20 µl (0.261 mmol) of CF_3CO_2H. After

[19]) The superscripts indicate toward which C-atom a substituent is orientated.

stirring for 5 min, the soln. was concentrated by distillation through a *Vigreux* column, and **6** (137 mg, 56%) was isolated by prep. GLC (B: 110°).

Method K *($SOCl_2$): Conversion* **10→37** *(and Analogously Method* L*).* To 22 mg (0.145 mmol) of alcohol **10** [6], 100 µl (1.378 mmol) of $SOCl_2$ were added at −70°. The mixture was allowed to warm up and stirred for 1 h at r.t., worked up in pentane, and the org. layer washed 3 times with H_2O and once with sat. $NaHCO_3$. Bulb-to-bulb distillation (150°/20 Torr) yielded 22 mg (89%) of **37**. M.p. 69–71°. IR: 1472*w*, 1455*m*, 1445*s*, 1335*w*, 1325*m*, 1300*m*, 1291*m*, 1265*m*, 1212*m*, 1110*m*, 1068*s*, 1048*s*, 948*w*, 932*w*, 917*s*, 905*m*. ^{1}H-NMR and ^{13}C-NMR: see above. MS: 172 (0.6), 170 (2.1, M^+, $C_{10}H_{15}Cl$), 136 (11), 135 (100), 107 (11), 93 (17), 91 (11), 79 (20), 77 (11), 67 (18).

3. Syntheses of 6–9 and 12 *(Scheme 3). – 1,2-Trimethylene-8,9,10-trinorborna-2(3'),5-diene* (= *10,6-(1'-Ethanyl-2'-ylidene)-8,9-dinorborn-2-ene;* **45**). A soln. of 240 mg (1.82 mmol) of **44** [4] in 3 ml of *t*-BuOH and 1 g of *t*-BuOK was heated in a sealed tube for 4 h to 150°. Workup and bulb-to-bulb distillation (110°/12 Torr) gave 225 mg (94%) of **45**. IR: 3120*w*, 3050*m*, 1670*w*, 1608*w*, 1452*w*, 1440*w*, 1431*m*, 1332*m*, 1309*w*, 1288*w*, 1150*w*, 1127*m*, 1068*w*, 973*w*, 900*m*. ^{1}H-NMR (300 MHz)[19]: 1.24 (*d*, J_{gem} = 7.5, $w_{½} \approx 3$ each, H–C(7)$^{C(2)}$); 1.60 (*dt*, J_{gem} = 7.5, J = 4, 4, H–C(7)$^{C(5)}$); 1.68 (*d*, J_{gem} = 15, $w_{½} \approx 7$ each, H_{endo}–C(3)); 1.85 (*ddd*, J_{gem} = 13.5, $J_{1'a,2'a}$ = 9.5, $J_{1'a,2'b}$ = 9, H–C(1'a)); 2.12 (*ddd*, J_{gem} = 13.5, $J_{1'b,2'b}$ = 8, $J_{1'b,2'a}$ = 2, H–C(1'b)); 2.27 (*d*, J_{gem} = 15, $w_{½} \approx 8$ each, H_{exo}–C(3)); 2.6–2.75 (*m*, among others J_{gem} = 15.5, $J_{1'a,2'a}$ = 9.5, H–C(2'a)); 2.75–2.9 (*m*, among others J_{gem} = 15.5, $J_{1'b,2'b}$ = 8, H–C(2'b)); 3.10 (*m*, $w_{½} \approx 8$, H–C(4)); 5.12 (*m*, $w_{½} \approx 7$, H–C(3')); 6.05–6.15 (*m*, H–C(5), H–C(6)). ^{13}C-NMR (25.2 MHz): 25.71, 29.33, 38.01 (3*t*, C(3), C(1'), C(2')); 46.45 (*d*, C(4)); 55.10 (*t*, C(7)); 68.17 (*s*, C(1)); 113.68 (*d*, C(3')); 135.74, 138.42 (2*d*, C(5), C(6)); 150.69 (*s*, C(2)). MS: 132 (41, M^+, $C_{10}H_{12}$), 131 (38), 117 (100), 115 (22), 104 (31), 91 (52), 79 (18), 78 (16), 77 (24), 65 (11), 63 (8), 53 (8), 51 (14), 39 (18).

Olefin **6**. a) *From* **45**. To a suspension of 200 mg (1.515 mmol) of **45** in 1.5 ml of CH_3OH and 295 mg (1.521 mmol) of PADA, a mixture of 260 µl (4.55 mmol) of CH_3CO_2H and 0.5 ml of CH_3OH was added dropwise. Workup and bulb-to-bulb distillation (110°/12 Torr) gave 135 mg (67%) of **6**. IR: 3047*m*, 1665*w*, 1452*m*, 1445*m*, 1430*m*, 1312*m*, 1298*m*, 1285*m*, 1252*w*, 1215*w*, 1165*m*, 1160*m*, 1080*m*, 1050*w*, 975*m*, 940*m*, 905*m*. ^{1}H-NMR and ^{13}C-NMR: see above. MS: 134 (47, M^+, $C_{10}H_{14}$), 133 (7), 119 (56), 105 (100), 93 (13), 92 (33), 91 (61), 80 (11), 79 (29), 78 (16), 77 (29), 65 (11), 51 (11), 41 (14).

b) *From* **4** *with HMPT.* A soln. of 5 mg (0.037 mmol) **4** in 1 ml of HMPT was refluxed (240°). Capill. GLC (60°) showed the ratio of **4**/**6** to be 1:1 after 2 h and 2:3 after 12 h.

c) *From* **4** *with* CF_3CO_2H. See above *(Chap. 2).*

*1,2-Trimethylene(5-*exo*,6-*exo-$^2H_2$*)-8,9,10-trinorborn-2(3')-ene* (= *10,2-(1'-Ethanyl-2'-ylidene)(5-*exo*,6-*exo-$^2H_2$*)-8,9-dinorbornane;* **7**). To a suspension of 380 mg (2.879 mmol) of **45** in 2.0 ml of CH_3OD and 570 mg (2.938 mmol) of PADA, a mixture of 520 µl (8.951 mmol) of CH_3CO_2D and 0.7 ml of CH_3OD was added dropwise. Workup, distillation (110°/12 Torr) and prep. GLC (100°, *Carbowax M 20* on *Chromosorb W 60/80*) yielded 211 mg (54%) of **7**. ^{1}H-NMR (300 MHz): 1.5–1.7, signals for H_{exo}–C(5) and H_{exo}–C(6) missing. ^{13}C-NMR (25.2 MHz, ^{1}H-decoupled): characteristic signals[16]) at 29.51 (*t*, J = 20, C(5)); 31.81 (*t*, J = 20, C(6)). MS: 137 (4.2), 136 (37.7, M^+, $C_{10}H_{12}D_2$), 135 (10.5), 121 (25), 120 (26), 108 (12), 107 (15), 106 (23), 105 (100), 94 (11), 93 (25), 92 (33), 91 (20), 80 (11), 79 (19), 78 (16), 77 (14).

*1,2-*exo*-Trimethylene-8,9,10-trinorbornan-6-*endo*-ol* (= *6-*exo*,10-(1',2'-Ethanediyl)-8,9-dinorbornan-2-*endo*-ol;* **8**). A mixture of 60 mg (0.40 mmol) **46** [6] in 60 ml of Et_2O and 123 mg (3.24 mmol) of $LiAlH_4$ was stirred at r.t. over night. Workup and chromatography on 7.5 g of silica gel in pentane/Et_2O 3:1 yielded 42 mg (69%) of **8**. IR: 3630*m*, 3380 br., 1475*m*, 1450*m*, 1304*m*, 1097*w*, 1077*s*, 1060*m*, 1045*m*, 1019*w*, 993*w*, 952*w*, 904*w*, 870*w*. ^{1}H-NMR (300 MHz)[19]): 0.95 (*dt*, J_{gem} = 12.5, $J_{5endo,6exo}$ = 4, $J_{5endo,7}^{C(2)}$ = 4, H_{endo}–C(5)); 1.30 (*dm*, J_{gem} = 10, $w_{½} \approx 8$ each, among others $J_{2endo,7}^{C(5)} = J_{4,7}C(5) \leqslant 1$, H–C(7)$^{C(5)}$); 1.15–1.32 (*m*, 1H); 1.37 (*ddd*, J_{gem} = 10, $J_{5endo,7}^{C(2)}$ = 4, $J_{4,7}^{C(2)}$) = 1.5, H–C(7)$^{C(2)}$); 1.42 (*dddd*, J_{gem} = 11.5, $J_{3exo,4}$ = 5.5, $J_{2endo,3exo}$ = 3.5, $J_{3exo,5exo}$ = 2.5, H_{exo}–C(3)); 1.49 (*m*, $w_{½} \approx 5$, HO_{endo}–C(6)); 1.5–1.8 (*m*, 4H); 1.8–2.0 (*m*, 2H); 2.07 (*ddd*, J_{gem} = 12.5, $J_{5exo,6exo}$ = 10, $J_{4,5exo}$ = 5, $J_{3exo,5exo}$ = 2.5, H_{exo}–C(5)); 2.17 (*dddd*, $J_{3exo,4}$ = 5.5, $J_{4,5exo}$ = 5, $J_{4,7}^{C(2)}$ = 1.5, $J_{4,7}^{C(5)} \leqslant 1$, H–C(4)); 2.26 (*dddd*, J = 16.5, 8.5, 5, $J_{2endo,7}^{C(5)} \leqslant 1$, H_{endo}–C(2)); 4.06 (*dd*, $J_{5exo,6exo}$ = 10, $J_{5endo,6exo}$ = 4, H_{exo}–C(6)). MS: 152 (67, M^+, $C_{10}H_{16}O$), 134 (35), 121 (19), 119 (15), 108 (28), 107 (100), 106 (90), 105 (24), 93 (26), 91 (34), 81 (24), 80 (32), 79 (66), 77 (23), 67 (39), 55 (16), 53 (12), 43 (14), 41 (27), 39 (19).

*1,2-*exo*-Trimethylene(6-*exo*-^2H)-8,9,10-trinorbornan-6-*endo*-ol* (= *6-*exo*,10-(1',2'-Ethanediyl)(2-*exo*-^2H)-8,9-dinorbornan-2-*endo*-ol;* **9**). A soln. of 261 mg (1.74 mmol) of **8** in 35 ml of Et_2O and 164 mg (3.9 mmol) of $LiAlD_4$ was stirred at r.t. for 18 h. Addition of 0.3 ml of H_2O and workup gave 146 mg (55%) of **9**. IR: 3620*m*, 3400 br., 2140*w*, 1465*w*, 1450*m*, 1307*s*, 1245*w*, 1200*w*, 1172*s*, 1150*m*, 1095*s*, 1050*m*, 1010*m*, 958*w*, 948*w*, 907*w*, 898*w*, 868*w*. ^{1}H-NMR (300 MHz): 4.06, signal for H_{exo}–C(6) missing. MS: 154 (4.9), 153 (37.1, M^+, $C_{10}H_{15}OD$), 152 (1.3), 135 (23), 121 (15), 120 (13), 119 (12), 108 (24), 107 (100), 106 (58), 105 (12), 94 (12), 93 (22), 92 (16), 91 (20), 82 (13), 81 (20), 80 (35), 79 (61), 77 (14), 67 (35), 41 (22).

1,2-exo-Trimethylene(5-endo-^2H)-8,9,10-norbornan-6-exo-ol (= *6-exo,10-(1',2'-Ethanediyl)(3-endo-^2H)-8,9-dinorbornan-2-exo-ol;* **12**). A soln. of 2.820 g (18.8 mmol) of **47** [6] in 21 ml of 1M $LiEt_3BD$ in THF was refluxed for 12 h. Further 1.5 ml of 1M $LiEt_3BD$ in THF were added and refluxing continued for additional 6 h. The mixture was cooled to 0°, treated with 15 ml of 2N NaOH, 15 ml of 30% H_2O_2, and refluxed for 1 h. Workup in Et_2O afforded 2.310 g (80%) of a *ca.* 6:1 mixture of **12** and **48**, from which **12** was separated by prep. GLC (170°, 20% *Carbowax M 20* on *Chromosorb W 60/80*). ^{1}H-NMR (300 MHz)[19]: 1.17 (*dm*, J_{gem} = 10, $w_{½} \approx 4$ each, H–C(7)$^{C(2)}$); 1.2–1.35 (*m*, 2H); 1.35–1.5 (*m*, 4H, among others H_{exo}–C(5)); 1.55–1.85 (*m*, 3H, among others H_{endo}–C(5) missing); 1.85–1.95 (*m*, 2H); 2.24 (*m*, $w_{½} \approx 10$, H–C(4)); 3.62 (*m*, $w_{½} \approx 4$, H_{endo}–C(6)). MS: 154 (5.2), 153 (47.5, M^+, $C_{10}H_{15}OD$), 152 (2.7), 135 (26), 124 (13), 122 (14), 120 (13), 110 (13), 108 (25), 107 (100), 106 (60), 105 (11), 97 (13), 94 (13), 93 (20), 92 (16), 91 (18), 82 (18), 81 (18), 80 (37), 79 (57), 77 (16), 67 (36), 41 (26).

4. Syntheses of 20–22, 24, and 53–55 *(Scheme 4).* – *Dehydration of* **15**. A soln. of 600 mg (3.95 mmol) of **15** in 10 ml of HMPT was refluxed (240°) for 1 h. Workup with pentane and bulb-to-bulb distillation (120°/12 Torr) gave 473 mg (*ca.* 90%) of a mixture of hydrocarbons (capill. GLC at 60°: 53% **49**, 13% **13** [6], 16% **6**, 5% **50** [10], and further compounds), which was stirred for 4 h in 10 ml of EtOH in the presence of 10% Pd/C under H_2. After filtration, addition of 25 ml of pentane, and washing the org. layer with H_2O, the solv. was distilled through a *Vigreux* column. From the residue, 227 mg (48%) of *tetracyclo[5.2.1.0^{1,5}.0^{5,9}]decane* (**49**) [6] was collected by prep. GLC (100°, 10% *Apiezon L* on *Chromosorb P 80/100 AW-DMCS*). IR: 3040*m*, 1448*s*, 1380*w*, 1345*w*, 1278*s*, 1262*m*, 1215*w*, 1170*w*, 1165*w*, 1120*s*, 1000*w*, 915*m*, 905*m*, 890*m*, 875*w*. ^{1}H-NMR (300 MHz): 1.03 (*m*, $w_{½} \approx 3$, H–C(9)); 1.17, 1.34 (*2'd'*, *AB*, J_{gem} = 10, further J = 1, 2H–C(6), 2H–C(10)); 1.38 (*m*, $w_{½} \approx 4$, 2H–C(8)); 1.4–1.8 (*m*, 2H–C(2), 2H–C(4), H–C(3)); 1.87 (*m*, $w_{½} \approx 25$, H–C(3')); 2.06 (*m*, $w_{½} \approx 6$, H–C(7)). ^{13}C-NMR (75.5 MHz): 18.51 (*d*, C(9)); 26.15 (*t*, C(2), C(4)); 28.69 (*t*, C(3)); 31.99 (*s*, C(1), C(5)); 34.87 (*t*, C(8)); 36.29 (*d*, C(7)); 36.29 (*t*, C(6), C(10)). MS: 134 (71, M^+, $C_{10}H_{14}$), 119 (65), 106 (46), 105 (46), 93 (21), 92 (46), 91 (100), 80 (27), 79 (43), 78 (20), 77 (34), 65 (14), 53 (11), 51 (13), 41 (18).

Dehydration of **21**. A soln. of 880 mg (5.752 mmol) of **21** in 10 ml of HMPT was refluxed (240°) for 1 h. Workup with pentane, bulb-to-bulb distillation (120°/12 Torr) and prep. GLC (100°, 20% *Carbowax M 20* on *Chromosorb W 60/80*) gave 240 mg (31%) of **51**, 60 mg (8%) of a 1:1 mixture **53/54** and 16 mg (2%) of **52**. *(8-^2H)Tetracyclo[5.2.1.0^{1,5}.0^{5,9}]decane* (**51**): ^{13}C-NMR (25.2 MHz, ^{1}H-decoupled): characteristic signals[16]) at 18.39 (C(9)); 36.20 (C(7)); 34.50 (*t*, J = 20, C(8)). MS: 136 (11), 135 (100, M^+, $C_{10}H_{13}D$), 134 (22), 120 (66), 119 (36), 107 (45), 106 (54), 93 (32), 92 (75), 91 (48).

(5-^2H)Tetracyclo[4.4.0.0^{2,4}.0^{3,7}]decane (**52**). ^{13}C-NMR (25.2 MHz, ^{1}H-decoupled): characteristic signal[16]) at 33.67 (*t*, J = 20, C(5)). MS: 136 (11), 135 (100, M^+, $C_{10}H_{13}D$), 134 (10), 120 (25), 119 (8), 107 (12), 106 (26), 105 (12), 94 (13), 93 (23), 92 (48), 91 (22).

1,2-Trimethylene(5-exo-^2H)- and 1,2-Trimethylene(5-endo-^2H)-8,9,10-trinorborn-2(3')-ene (= *10,2-(1'-Ethanyl-2'-ylidene)(5-exo-^2H)- and 10,2-(1'-Ethanyl-2'-ylidene)(5-endo-^2H)-8,9-dinorbornane;* **53/54**). ^{1}H-NMR (300 MHz): integrals for H_{endo}–C(5) (1.25–1.35) and H_{exo}–C(5) (1.71): 50% of 1H each. ^{13}C-NMR (25.2 MHz, ^{1}H-decoupled); characteristic signal[16]) at 29.61 (*t*, J = 20, C(5)). MS: 136 (2.7), 135 (27, M^+, $C_{10}H_{13}D$), 120 (5), 107 (15), 106 (100), 105 (12), 92 (11), 91 (20), 78 (18).

5. Ring Opening in 49 and 51 *(Scheme 4).* – The experiments were carried out like the ones ot the *Table. Method* A *(CF_3CO_2H/Et_3SiH):* Conversions **49**→**3** and **51**→**22** (and analogously method *M* and/or *F* for **49**→**20** and method *N* for **49**→**55**).

Method B *(CF_3CO_2H followed by aq. KOH):* Conversions **49**→**15** and **51**→**21/24'** (and analogously method *G* for **49**→**42**).

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