276. Hydroboration and Oxymercuration of Some 1-Substituted Norborn-2-enes

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Dedicated to Prof. *Friedhelm Korte* on the occasion of his 60th birthday

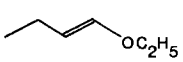
(20.IX.83)

Summary

The 1-substituted norborn-2-enes **11**–**13** and **18** react with electrophiles under kinetic control preferentially in 2-position. The regioselectivity in oxymercuration is higher than in hydroboration and reaction with aqueous palladium chloride.

1. Introduction. – As a part of our search for the preparation of 1,2-substituted norbornanes, which are amenable to elimination [1], the regioselectivity of the reactions of 1-substituted norborn-2-enes with some electrophiles was investigated. Since these norbornes represent conformationally fixed allylic systems, comparison of their reactivity with open-chain counterparts may lead to factors, which control the regioselectivity in these reactions.

BH_3 reacts with olefins and alkynes as an electrophile and its regioselectivity depends on electronic as well as on steric factors. For instance, the π-donating properties of an alkoxy group directs the attack of BH_3 to the terminal C-atom of the π-system of the enol-ether **1** [2]. The σ-acceptor properties of the substituent appear to dominate in case of the olefins **2** and **3**, where attack of BH_3 occurs preferentially, if not exclusively in 2-position [2]. Control of regioselectivity in hydroboration with $BH_3 \cdot THF$ does appear to be hardly dependent of bulky substituents. For instance, the olefins **4** and **5** give the regioisomeric products in a 57 : 43 and a 58 : 42 ratio, respectively. Whereas the substitutents in **2** and **3** are conformationally unrestricted, flexibility is restricted to an antiplanar [1]) conformation in **6** and to a synplanar conformation in **7**. In both compounds, hydroboration of the olefinic double bond with $BH_3 \cdot THF$ occurs preferentially at the C-atom of the double bond closer to the substituent.



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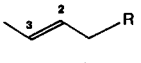
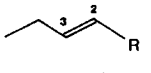
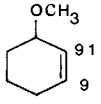


2 R = OC_2H_5
3 R = Cl



4 R = $CH(CH_3)_2$
5 R = $C(CH_3)_3$



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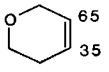

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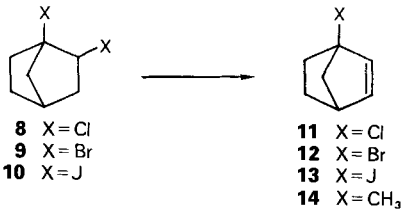
[1]) Antiplanar (ap), synplanar (sp) and orthogonal (o) refer to conformations at the vinylic bond towards the C-center with the substitutent X [3].

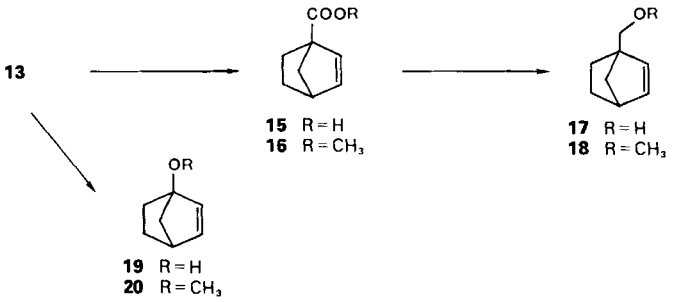
To evaluate the specific electrophilic reactivity of BH_3, oxymercuration and addition of formic acid to the 1-substituted norborn-2-enes **11**–**13**, **18** and **20** were also studied.

2. Synthesis of Precursors and Products. – Base-induced dehydrohalogenation of the dihalides **8**–**10**, which are readily prepared from norcamphor (**8**: [4], **9**: [5], **10**: [6]) gave the 1-halogen-norborn-2-enes **11** [4], **12** and **13** [6] *(Scheme 1)*. 1-(Methoxymethyl)-norborn-2-ene (**18**) and 1-methoxynorborn-2-ene (**20**) were prepared from 1-iodon-orborn-2-ene (**13**). Lithium iodide exchange in **13** with *t*-BuLi [7] followed either by

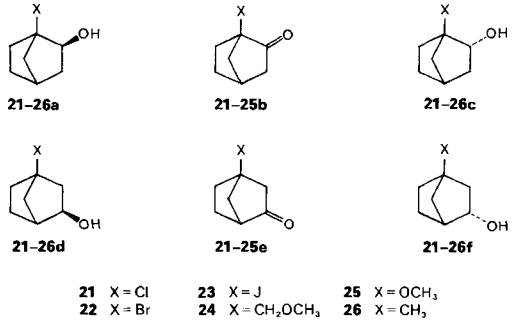
Scheme 1



Scheme 2



reaction with CO_2 or formaldehyde gave products, from which **18** was prepared. 1-Methoxy-norborn-2-ene (**20**) was obtained from norborn-2-en-1-ol (**19**) [7] *(Scheme 2)*. Hydroboration/oxidation of each of the 1-substituted norbornenes **11**–**13**, **18** and **20** gave mixtures of the alcohols **21a**–**25a** and **21d**–**25d**, which were separated by GC and



21 X = Cl
22 X = Br
23 X = J
24 X = CH_2OCH_3
25 X = OCH_3
26 X = CH_3

oxidized to the corresponding ketones **21b–25b** and **21e–25e**. The structures of the isomeric ketones **21b–23b** and **21e–23e** were determined by ^{13}C-NMR spectroscopy. The ^{13}C-shifts of all C-atoms of the isomeric pairs were compared with calculated values [6]. As already noted for the iodoketones **23b** and **23e** the experimental and calculated values for the individual chemical shifts show good agreement, except for the substituted bridgehead C-atom and the carbonyl-C-atom, respectively *(Table 1* and *2)*. The large differences between experimental and calculated values, which amount up to 20 ppm, do, however, not affect the structural assignments, because of the fact that additional evidence supporting the structures of **21b/e** and of **23b/e** is available.

Chloroketone **21e** had been prepared by a different route [8]; reaction of iodoketone **23b** with aqueous base gave bicyclo[2.1.1]hexane-1-carboxylic acid, whereas the isomeric

Table 1. *Experimental and Calculated δ-Values for the ^{13}C-NMR Shifts in* **21b** *and* **22b** *Relative to TMS as Internal Standard*

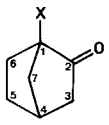
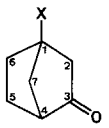
C-Atom		X = Cl		X = Br	
		21b		**22b**	
		Exper.	Calc.	Exper.	Calc.
1		73.9	82.8	66.4	75.1
2		207.9	225.4	207.5	227.0
3		45.6	45.8	43.6	46.5
4		32.5	33.2	33.6	33.2
5		29.9	27.7	29.4	28.5
6		33.0	32.3	34.4	33.9
7		44.1	45.5	46.7	46.9

Table 2. *Experimental and Calculated δ-Values for the ^{13}C-NMR Shifts in* **21e** *and* **22e** *Relative to TMS as Internal Standard*

C-Atom		X = Cl		X = Br	
		21e		**22e**	
		Exper.	Calc.	Exper.	Calc.
1		64.1	68.3	53.9	60.6
2		53.1	53.3	54.0	54.9
3		208.5	217.9	210.8	218.6
4		49.8	47.7	49.5	47.7
5		24.6	24.8	25.5	26.0
6		36.2	35.3	37.5	36.9
7		45.7	45.5	46.8	46.9

23e gave 3-methylidenecyclopentanecarboxylic acid, both characterized as their methyl-esters [9]. The methoxymethyl-alcohols **24a** and **24d** show different IR spectra: only in **24a** is the relative intensity of the absorption band at 3465 cm^{-1} independent of the

concentration. Furthermore, in the ^{1}H-NMR spectrum of **24a** the methoxy substituted methylene group appears as an *AB*-system, whereas in **24d** it is a singlet. The structure of the isomeric methoxyalcohols **25a** and **25d** could be assigned because **25d** had been prepared by a different route [7]. The *exo*/*endo*-pairs of the alcohols **21a–25a**/**21c–25c** and **21d–25d**/**21f–25f** invariably show the expected relative ^{1}H-NMR shifts of the proton, bonded to the same C-atom as the OH-group [10].

3. Results and Discussion. – *Oxymercuration.* Even in sterically hindered cases, norbornenes are oxymercurated in a *cis,exo*-fashion [11]. In the 1-substituted norbornenes **11–13** and **18** attack of the electrophilic reagent occurs preferentially at 2-position, yielding after reduction and workup the alcohols **21d–24d** *(Table 3)*. Only in case of 1-bromonorbornene (**12**), formation of the *endo*-alcohol **22c** as a minor product has been observed. 1-Methylnorbornene (**14**) and 1-methoxymethylnorbornene (**18**) show significant differences in their regioselectivity. Whereas **14** yields the two *exo*-alcohols **26a** and

Table 3. *Oxymercuration of 1-Substituted Norbornenes in H_2O at r.t.*

1-Substituted Norbornene	Products **21–26** (**a**, **c**, **d**, **f**)[a]		
	Yield [%]	Ratio	Unidentified Products [%]
	21–26 (**a** + **c** + **d** + **f**)	(**a** + **c**) : (**d** + **f**) (**a** : **c** : **d** : **f**)	
11	86.2	1.4 : 98.6 (1.4 : 0 : 98.6 : 0)	0
12	68.3	11 : 89 (1 : 10 : 89 : 0)	2.4
13	85	1 : 99 (1 : 0 : 99 : 0)	3.5
14 [12]		50 : 50	
18	54.2	4.4 : 95.6 (4.4 : 0 : 95.6 : 0)	0.8
20	32.3	4.2[b])	0.7

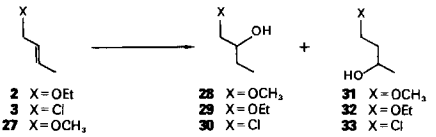
[a]) Yields refer to crude products isolated, and ratios have been determined by GC, using a *Varian CDS-111* integrator. Values not corrected for response factors.

[b]) 95% *endo*-norbornanol.

26d in a 1 : 1 ratio [12], **18** reacts with the electrophile predominantly in 2-position to give the alcohols **24a** and **24d** in a 4.4 : 95.6 ratio. 1-Methoxynorbornene (**20**) gives only a small amount of the expected *exo*-alcohol **25d**, the major product being 2-*endo*-hydroxynorbornane, formed by rearrangement and subsequent reduction during workup. The regioselective oxymercuration of the 1-(methoxymethyl)norbornene **18** is very similar to that of the methoxymethylolefin **27** [13] *(Table 4)*. The high regioselectivity observed in both cases, however, needs further interpretation (see below).

Reaction with Formic Acid. Reaction of the 1-substituted norbornenes **11–13** and **18** with formic acid leads exclusively to a mixture of *exo*-alcohols *(Table 5)*. The regioselectivity of the reaction of this electrophile with the 1-halogen-norbornenes **11–13** is comparable to that of oxymercuration, whereas in 1-(methoxymethyl)norborn-2-ene (**18**) it is slightly reduced. These results indicate that the selectivity is controlled by the same factors. In contrast to the oxymercuration of 1-methoxynorborn-2-ene (**20**) where the

Table 4. *Hydroboration of* **2** *and* **3** *and Oxymercuration of* **27**



Substituted Olefin	Reagent	Products			
			[%]		[%]
2	$BH_3 \cdot THF$	**29**	83.7	**32**	15.2 [2a]
3	$BH_3 \cdot THF$	**30**	100	**33**	0 [2a]
27	$Hg(OAc)_2$	**28**	2.3	**31**	97.7 [14]

Table 5. *Reaction of 1-Substituted Norbornenes with Formic Acid*

1-Substituted Norbornene	Products **21–26** (**a**, **c**, **d**, **f**)[a]		
	Yield [%]	Ratio	Unidentified Products [%]
	21–26 (**a** + **c** + **d** + **f**)	(**a** + **c**) : (**d** + **f**) (**a** : **c** : **d** : **f**)	
11	17.2	0 : 100 (0 : 0 : 100 : 0)	1.8
12	17.5	1 : 99 (1 : 0 : 99 : 0)	0.5
13	65	3 : 97 (3 : 0 : 97 : 0)	3
14 [14]		50 : 50	
18	75.2	34.2 : 65.8 (34.2 : 0 : 65.8 : 0)	4.7
20	16	5 : 71.5 (5 : 0 : 71.5 : 0)[b]	2

[a] See *Footnote a, Table 3.*
[b] 23.5% of norcamphor has been formed.

rearrangement is faster than the reaction with the nucleophile, the addition of formic acid is faster than proton-induced rearrangement *(Table 5)*.

Hydroboration. Regioselectivity in hydroboration/oxidation of **11–13**, **18** and **20** is smaller than in oxymercuration or in addition of formic acid *(Table 6)*, but attack of the electrophilic BH_3 still occurs preferentially in the 2-position. In addition to the isomeric *exo*-alcohols **21a–23a** and **21d–23d**, the formation of the *endo*-alcohols has been observed with **14** [2b] and **20** as the precursors.

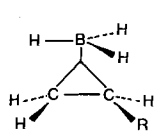
Hydroboration of **11** and **20** occurs with a regioselectivity, which is similar to that of the conformationally mobile systems **2** and **3**. Regardless of the possible orientation of the substituents, their contribution to the factors which control the regioselectivity in these systems cannot be dominant. Concerning the mechanism of hydroboration [15–19], it has been pointed out that reaction of an olefin with $BH_3 \cdot THF$ occurs *via* interaction of the π-system with the 2p-AO of BH_3, which itself might be in contact with complexing solvent molecule. Ignoring such solvent effects, *Lipscomb et al.* in a theoretical study have pointed out that hydroboration occurs *via* a π-complex **34** and that the cluster (three-center-2-electron)-bond can essentially be constructed from the π-system of

Table 6. *Hydroboration/Oxidation of 1-Substituted Norbornenes, in THF at 0°*

1-Substituted Norbornene	Products **21**–**26** (**a**, **c**, **d**, **f**)[a]		
	Yield [%]	Ratio	Unidentified Products [%]
	21–**26** (**a** + **c** + **d** + **f**)	(**a** + **c**) : (**d** + **f**) (**a** : **c** : **d** : **f**)	
11	70.1	74 : 26 (74 : 0 : 26 : 0)	0.5
12	78.5	68 : 32 (64 : 4 : 32 : 0)	0.2
13	82.5[b])	65 : 35 (64 : 1 : 35 : 0)	0.2
14 [2b]		51.8 : 48.2 (49.9 : 1.9 : 47 : 1.2)	
18	87.5	54 : 46 (54 : 0 : 21 : 24.4)	3.6
20	53.5	74.6 : 25.4 (50 : 24.6 : 25.4 : 0)	16.1

[a]) See *Footnote a, Table 3.*
[b]) At *r.t.*

the olefin and the 2p-AO of BH_3 (**35**) [18]. In terms of localized bond orbitals, he has found that the bond between the B- and the C-atom, which carries a π-acceptor substituent (R = CN in **34**) is stronger whereas it is weaker than the adjacent B–C bond, if R is a σ-donating substituent (R = CH_3 in **34**). If regioselectivity is controlled by such π-complexes, in which deformation of the olefin towards the structure of the product of hydroboration is still insignificant, we may use the coefficients in HOMO of the substi-



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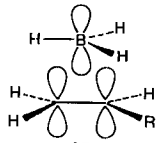

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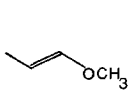
tuted olefin as mechanistic model of regioselectivity. For this purpose, MNDO-calculations have been performed, which provide heats of formation as well as coefficients of frontier orbitals of the substituted olefins under investigation. To test this procedure the coefficients of the HOMO in (*E*)-1-methoxy-1-propene (**36**) – serving as a model of the enol-ether **1** – have been determined. As expected for the HOMO of **36**, c_2 at the C-atom adjacent to the CH_3O-group is smaller than c_3 (c_2(HOMO) = 0.528; c_3(HOMO) = 0.667). The difference $(c_3^2 - c_2^2)_{HOMO}$ is then a measure of the regioselectivity in a kinetically controlled hydroboration reaction[2]).

The MNDO-results for the olefins **2** and **3** as well as for the 1-substituted norbornenes **11** and **20** clearly indicate that substituents like chloride and methoxygroups, which



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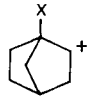
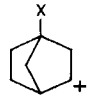


37 X = Cl
39 X = CH_3



38 X = Cl
40 X = CH_3

[2]) Details will be discussed in the planned Ph.d. Thesis of *W. Luef.*

Table 7. *Reaction of 1-Substituted Norbornenes with $PdCl_2$ in $HClO_4$ at 80°*

1-Substituted Norbornene	Products **21–24** (**b**, **e**)[a]			
	Yield [%] **21–24** (**b** + **e**)	Ratio (**b**:**e**)	Yield [%] **21d–24d**	Unidentified Products [%]
11	54.3	21:79	10.3	1.7
12	37.3	26.5:73.5	0.8	7.2
13	18.3	22.6:77.4	4.7	2.0
18	46.4	6.5:93.5	19.9	1.7

[a]) See *Footnote a, Table 3.*

are separated from the double bond by at least one CH_2-group have a minor contribution to regioselectivity of hydroboration. In numerical terms, this contribution is at least one order of magnitude smaller than in **36** and it is also independent of conformational arrangements.

The regioselectivity of reactions of the 1-substituted norbornenes **11–13** and **18** with mercuric acetate and formic acid, respectively, is higher than of hydroborations. In view of the concepts about the mechanistic pathways of the oxymercuration [11], it is hardly surprising that the HOMO-coefficients of the olefins show no correlation with the product ratios. Oxymercuration of strained olefins like norbornene, which occurs in a *syn*-fashion, has been taken as evidence that 'open' ions are involved. MNDO-results for the carbenium ions **37**/**38** and **39**/**40**, used as models for unbridged intermediates in oxymercuration reactions suggest a slightly higher stability for ion **37** over **38** but a lower stability for **39** relative to **40**. These computational results are in variance with the observed regioselectivities.

The high regioselectivity of the oxymercuration of **11–13** and **18**, particularly compared with that of 1-methylnorborn-2-ene (**14**) is remarkable and remains to be explained.

Our results clearly indicate that the 1-substituted norbornenes **11–13** and **18** react with electrophiles under kinetically controlled conditions preferentially in the 2-*exo*-position. Under the same conditions the oxymercuration of 1-methoxynorborn-2-ene (**20**) yields mainly a product, which can be explained by a reaction of the electrophile at the 3-position followed by a rearrangement. Based upon the observed differences in regioselectivity of oxymercuration, hydroboration and addition of formic acid, other electrophilic reagents may be classified, even if the mechanistic details of their reactions may be different. This is illustrated by the reaction of $PdCl_2$ with the norbornenes **11–13** and **18** *(Table 7)*. It is apparent that the regioselectivity in formation of the ketones **21b–23b** and **21e–23e** is similar to that of the alcohols **21a–24a** and **21d–24d** in hydroboration. The yield, however, is only moderate with **11–13**. As shown by a control experiment with **13**, the formation of **23d** is due to competing addition of H_2O, catalyzed by $HClO_4$.

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Experimental Part

General Remarks. See [20]. If not stated otherwise, GC analyses and separations were performed on a *Carlo-Erba*-instrument *Fractovap 2450* with 10% *Carbowax 20M* on *Chromosorb A*, non-acid washed, in glas columns. In some cases, relative GC retention times have been estimated from injections, run with a temperature program.

1-Bromonorborn-2-ene (**12**)[3]. A solution of 94.18 g (0.37 mol) of 1,2-*exo*-dibromonorbornane (**9**) [20] in 300 ml DMSO was slowly added at 50° to a solution of 124.6 g (1.1 mol) *t*-BuOK in 700 ml DMSO. After 12 h, the mixture was worked up and the org. phase (pentane) concentrated *i.v.* After distillation (40°/11 Torr) the colorless oil was chromatographed over silica gel with CH_2Cl_2 to give 39.13 g (61%) of **12**. An analytically pure sample was obtained by GC, R_f (CH_2Cl_2) 0.78. IR: 2980, 1330, 991, 952. ^{1}H-NMR: 1.0–2.3 (stack, 6H); 2.76 (*m*, 1H); 5.85–6.15 (*AB*-system of *ABX*, 2H). MS: 174 (2), 172 (2), 146 (97), 144 (100), 91 (29), 65 (77).

C_7H_9Br (173.1) Calc. C 48.59 H 5.24% Found C 48.56 H 5.22%

Preparation of the Bromoalcohols **22a** *and* **22d**. Hydroboration/oxidation [21] of 0.32 g (1.82 mmol) **12** gave an oil, which was chromatographed over silica gel with CH_2Cl_2 giving 0.7 g (50.6%) of a 94.4:2.8 mixture of **22a** and **22c** and 0.12 g (33.7%) of crude **22d**.

22a: R_f (CH_2Cl_2) 0.46. IR: 3560, 2975, 1083, 1012, 991. ^{1}H-NMR: 0.7–2.5 (stack, 9H); 2.75 (*m*, 1H); 3.67 (*m*, 1H); impurities at 3.25 and 4.15.

22d: R_f (CH_2Cl_2) 0.29. IR: 3605, 3450, 2980, 2950, 1305, 975. ^{1}H-NMR: 0.7–2.4 (stack, 9H); 2.5 (*s*, 1H); 3.85 (*m*, 1H).

1-Bromonorbornan-2-one (**22b**). Oxidation of 0.20 g (1.05 mmol) **22a** with 0.52 g (2.39 mmol) pyridinium chlorochromate in CH_2Cl_2 [22] gave after chromatography with CH_2Cl_2 0.128 (1.0 mmol) of **22b** of 95% purity. An analytically pure sample was obtained by GC, R_f (CH_2Cl_2) 0.58. IR: 2980, 2960, 1753, 951. ^{1}H-NMR: 1.1–2.5 (stack, 8H); 2.5–2.95 (*m*, 1H). ^{13}C-NMR: see *Table 1*. MS: 190 (20), 188 (20), 146 (100), 144 (100), 109 (44), 81 (50), 79 (50), 65 (46).

C_7H_9BrO (189.1) Calc. C 44.47 H 4.80 Br 42.27% Found C 44.58 H 5.05 Br 42.44%

1-Bromonorbornan-3-one (**22e**). The bromoalcohol **22d** was oxidized as described above giving 68% of **22e** as white crystals. An analytically pure sample was obtained by GC, m.p. 67°, R_f (CH_2Cl_2) 0.55. IR: 2980, 2960, 1751, 1289, 1069. ^{1}H-NMR: 0.9–2.45 (stack, 6H); 2.52 (*s*, 3H). ^{13}C-NMR: see *Table 2*. MS: 190 (7), 188 (7), 109 (78), 81 (100), 79 (45), 53 (12).

C_7H_9BrO (189.1) Calc. C 44.57 H 4.80 Br 42.27% Found C 44.40 H 4.83 Br 41.86%

1-Bromo-2-endo-*norbornanol* (**22c**). Reaction of **22b** with $LiAlH_4$ gave a 91:7.6 mixture of **22c** and **22a** GC-separation gave pure **22c**, m.p. 51°, t_R (200°) 9.8 min; R_f (CH_2Cl_2) 0.50. IR: 2970, 1090, 1035, 1026, 989, 850. ^{1}H-NMR: 0.7–3.0 (stack, 9H); 3.2 (*s*, 1H); 4.28 (*m*, 1H). MS: 192 (2), 190 (3), 174 (75), 172 (69), 111 (92), *93* (100), 67 (63).

$C_7H_{11}BrO$ (191.1) Calc. C 44.0 H 5.80 Br 41.82% Found C 43.92 H 5.68 Br 41.65%

1-Bromo-3-endo-*norbornanol* (**22f**). The bromoalcohol **22f** was prepared by reduction of **22e** with $LiAlH_4$ in THF. GC-separation gave pure **22f**, m.p. 83°; t_R (200°) 17.7 min, R_f (CH_2Cl_2) 0.18. IR: 3615, 1290, 1130, 1120, 1031, 1012, 1005, 981, 935, 849. ^{1}H-NMR: 0.95–2.7 (stack, 9H); 2.83 (*s*, 1H); 4.35 (*m*, 1H). MS: 112 (9, M^+–Br), 111 (100), 93 (76), 67 (43), 43 (32).

$C_7H_{11}BrO$ (191.1) Calc. C 44.0 H 5.80 Br 41.82% Found C 43.6 H 5.71 Br 41.46%

1-Iodo-3-endo-*norbornanol* (**23f**). The iodoalcohol **23f** was prepared by reduction of **23e** [6] with $LiAlH_4$ in THF. GC separation from 2-*endo*-norbornanol, formed as by-product, gave pure **23f**, m.p. 82°, R_f (CH_2Cl) 0.22. IR: 3615, 3007, 2970, 1287, 1125, 1030, 1009, 1000, 842. ^{1}H-NMR: 0.8–2.82 (stack, 10H); 4.32 (*m*, 1H). MS: 238 (21, M^+), 111 (100), 93 (65), 81 (34), 43 (28).

$C_7H_{11}IO$ (238.1) Calc. C 35.32 H 4.66 I 53.31% Found C 35.22 H 4.81 I 53.07%

1-Chloro-3-endo-*norbornanol* (**21f**). The chloroalcohol **21f** was prepared as described above for **22f** and purified by GC, m.p. 88.5°, R_f (CH_2Cl_2) 0.22. IR: 3615, 2970, 1291, 1249, 1129, 1033, 1012, 990. ^{1}H-NMR:

[3] The IUPAC-conform name of 'norbornane' is *8,9,10-trinorbornane*.

1.0–2.55 (stack, 10H); 4.36 (*m*, 1H). MS: 146 (2, M^+), 11 (57), 110 (100), 93 (64), 81 (60), 67 (70), 66 (71), 57 (67).

$C_7H_{11}ClO$ (146.6) Calc. C 57.34 H 7.56 Cl 24.18% Found C 57.31 H 7.68 Cl 24.42%

1-Methoxynorborn-2-ene (**20**). *Norborn-2-en-1-ol* (**19**) [7] (4.0 g, 36.4 mmol) was methylated with dimethylsulfate according to [23] giving after chromatography over silica gel with CH_2Cl_2 and a bulb-to-bulb distillation (80°/100 Torr) 72% of **20**. R_f (CH_2Cl_2) 0.5. IR (neat): 2975, 2950, 1338, 1996, 1221, 1187, 1151, 1070, 716, 611. ^{1}H-NMR: 1.0–2.25 (stack, 6H); 2.8 (*m*, 1H); 3.4 (*s*, 3H); 6.02–6.22 (*AB*-system of *ABX*, 2H). MS: 124 (9), 109 (33), 96 (100), 81 (24), 53 (41).

Preparation of the Methoxyalcohols **25a** *and* **25d.** Hydroboration/oxidation [21] of **20** gave **25a** and **25d** in a ratio of 3:1 with a crude yield of 60–80%. GC separation gave pure **25a** and **25d**.

25a: t_R (160°) 9.4 min, R_f (Et_2O) 0.44. IR: 3558, 2960, 2910, 2876, 1350, 1309, 1275, 1164, 1125, 1101, 1083, 1010. ^{1}H-NMR: 0.9–2.2 (stack, 9H); 2.9 (*m*, 1H); 3.3 (*s*, 3H); 3.7 (*m*, 1H). MS: 142 (2, M^+), 97 (100).

25d: t_R (180°) > 20 min, R_f (Et_2O) 0.35. IR: 3605, 3435, 2965, 2880, 1318, 1293, 1130, 1101, 1039, 1021, 999, 982. ^{1}H-NMR: 1.0–2.2 (stack, 9H); 2.53 (*s*, 1H); 3.3 (*s*, 3H); 3.9 (*m*, 1H). MS: 142 (3, M^+), 113 (42), 109 (31), 97 (100), 81 (18).

Photolysis of **23d** [24]. A solution of 0,5 g (2.08 mmol) of **23d** in 25 ml anh. MeOH was irradiated with a 125-W high-pressure Hg-lamp in the presence of 1 g of Na_2CO_3. After 4.5 h, Et_2O was added and the org. phase extracted with H_2O. Evaporation of the solvents gave a brownish oil, which was purified by GC. Besides 3-*exo*-norbornanol (54%) 0.048 g (16%) of **25d** was obtained. IR and ^{1}H-NMR data were identical with **25d** prepared by the route described above.

1-Methoxynorbornan-2-one (**25b**) *and 1-Methoxynorbornan-3-one* (**25e**). Methoxyalcohol **25a** was oxidized as described for the preparation of **22b** giving after GC purification 27% of **25b**. IR and ^{1}H-NMR data corresponded to those reported in [25]. R_f (Et_2O) 0.59. In an analogous manner, **25e** was prepared from **25d** in a yield of 41% after GC purification. R_f Et_2O 0.53. IR: 2970, 1742, 1314, 1301, 1128. ^{1}H-NMR: 0.8–2.1 (stack, 6H); 2.3 (*m*, 2H); 2.52 (*m*, 1H); 3.35 (*s*, 3H). MS: 140 (23, M^+), 112 (25), 97 (100), 83 (17), 67 (26), 43 (22).

1-Methoxy-2-endo-*norbornanol* (**25c**) *and 1-Methoxy*-3-endo-*norbornanol* (**25f**). Reaction of **25b** with $LiAlH_4$ in THF gave a mixture of two methoxyalcohols in a ratio of 33:62. The minor isomer had a t_R identical with that of the *exo*-alcohol **25a**. The ^{1}H-NMR spectrum of the major alcohol **25c** showed signals at 3.35 (*s*, 3H) and 4.20 (*m*, 1H). Similarly, reduction of **25e** gave a 86:7 mixture of two methoxyalcohols, of which the minor had a t_R identical with that of **25d**. The ^{1}H-NMR spectrum of the major isomer **25f** showed signals at 3.25 (*s*, 3H), and 4.39 (*m*, 1H).

Methyl bicyclo[2.2.1]hept-2-ene-1-carboxylate (**16**). To a solution of 2.03 g (9.24 mmol) **13** in 20 ml anh. Et_2O was slowly added 15 ml of *t*-BuLi (0.93 N in hexane) at −75° [7]. After 90 min dry CO_2 was bubbled through the reaction mixture. After workup the crude acid was esterified with CH_2N_2 in the usual manner. Chromatography over silica gel with CH_2Cl_2 yielded after a bulb-to-bulb distillation (85°/20 Torr) 1.2 g (85%) ester **16**. R_f (CH_2Cl_2) 0.58. IR, ^{1}H-NMR and MS were identical with those reported [26a, b].

(2-Norbornen-1-yl)methanol (**17**). This alcohol was prepared according to [26a]. Alternatively **17** was obtained by reaction of 1-lithiumnorbornene, prepared as described above, with gaseous formaldehyde, in a yield of 80% on a 30-mmol scale.

(2-Norbornen-1-yl) methyl ether (**18**). A solution of 2.02 g (16.3 mmol) **17** in 15 ml anh. THF was treated with NaH at 0° for 3 h. Reaction with 2 ml CH_3I over night at 20° gave after workup a brownish oil. After flash chromatography [27] and bulb-to-bulb distillation (75°/11 Torr) 1.77 g (79%) **18** as a colorless oil was obtained. R_f (pentane) 0.64. IR: 2968, 2898, 2870, 2817, 1100. ^{1}H-NMR: 0.75–2.0 (stack, 6H). 2.8 (*m*, 1H); 3.35 (*s*, 3H); 3.6 (*s*, 2H); 5.78–6.2 (*AB*-system of *ABX*, 2H). MS: 138 (4, M^+), 110 (100), 99 (22), 95 (22), 79 (23), 45 (22).

$C_9H_{14}O$ (138.1) Calc. C 78.21 H 10.21% Found C 78.12 H 10.22%

Preparation of the Methoxymethyl-alcohols **24a** *and* **24d**. Hydroboration/oxidation [21] of 1.49 g (10.9 mmol) **18** with 13 ml of 0.87 M $BH_3 \cdot$ THF gave an oil, which was separated by GC giving 0.71 g (42%) **24a** and 0.64 g (40%) **24d.**

24a: t_R (90°) 9.6 min, R_f (CH_2Cl_2) 0.34. IR: 3000, 2952, 2875, 1388, 1200, 1135, 1095, 1059, 1012. ^{1}H-NMR: 0.7–1.9 (stack, 8H); 2.2 (*m*, 1H); 3.15 (*m*, 1H) 3.35 (*s*, 3H); 3.45–3.85 (*AB*- and *X*-part of *ABX*-system, 3H). MS: 124 (4, $M^+ - CH_3OH$), 109 (5), 81 (12), 80 (100), 79 (23).

24d: t_R (90°) > 20 min; R_f (CH_2Cl_2) 0.23. IR: 2950, 2870, 2830, 1195, 1139, 1095, 1038, 1000. ^{1}H-NMR: 0.75–1.9 (stack, 8H); 2.14 (*m*, 1H); 2.75 (*s*, 1H); 3.35 (*s*, 3H); 3.47 (*s*, 2H); 3.73–3.95 (*m*, 1H). MS: 111 (100), 110 (24), 93 (29), 91 (23), 80 (44), 79 (30), 67 (32), 45 (21).

1-(Methoxymethyl)-norbornan-2-one (**24b**) *and 1-Methoxymethylnorbornan-3-one* (**24e**). Alcohols **24a** and **24d** were each oxidized as described above for the preparation of **22b** and **22e** and purified by GC.

24b: t_R (200°) 6.1 min; R_f (Et_2O) 0.63. IR: 2963, 2880, 1735, 1200, 1102, 1060. ^{1}H-NMR: 1.1–2.4 (stack, 8H); 2.6 (*m*, 1H); 3.34 (*s*, 3H); 3.45 (*A*-part of *AB*, J_{AB} = 10, 1H), 3.68 (*B*-part of *AB*, 1H). ^{13}C-NMR: 26.4 (*m*); 27.7 (*m*); 33.8 (*d*); 29.8 (*t*); 45.5 (*t*); 51.1 (*s*); 59.0 (*q*); 70.3 (*t*); 215.6 (*s*). MS: 154 (7, M^+), 125 (25), 122 (29), 94 (25), 81 (83), 80 (100), 79 (57), 71 (22), 45 (24).

$C_9H_{14}O_2$ (154.2) Calc. C 70.10 H 9.15% Found C 70.22 H 9.25%

24e: t_R (200°) 9.7 min. R_f (Et_2O) 0.52. IR: 2990, 2950, 2925, 2878, 1742, 1132, 1100. ^{1}H-NMR: 1.25–2.45 (stack, 8H); 2.58 (*m*, 1H); 3.35 (*s*, 3H), 3.49 (*s*, 2H). ^{13}C-NMR: 24.6 (*m*); 29.7 (*m*); 39.5 (*t*); 47.7 (*s*); 50.5 (*d*); 59.0 (*q*); 75.5 (*t*); 216.1 (*s*). MS: 154 (48, M^+), 110 (34), 109 (100), 81 (94), 80 (99), 67 (33), 66 (34), 45 (43).

$C_9H_{14}O_2$ (154.2) Calc. C 70.10 H 9.15% Found C 70.06 H 9.15%

1-(Methoxymethyl)-2-endo-*norbornanol* (**24c**) *and 1-(Methoxymethyl)*-3-endo-*norbornanol* (**24f**). Ketone **24b** was reduced with $LiAlH_4$ in THF as described above for the preparation of **22c** giving 90% of **24c** in ≥ 99.5% purity. R_f (Et_2O) 0.61. IR: 3000, 2950, 2900, 2872, 1100, 1085, 1035. ^{1}H-NMR: 0.7–2.4 (stack, 9H); 2.57 (*m*, 1H); 3.33 (*s*, 3H); 3.51 (*s*, 2H); 4.10 (*m*, 1H). MS: 80 (27), 79 (7), 67 (3), 32 (19), 28 (100).

Similarly, reduction of ketone **24e** gave the *endo*-alcohol **24f** and the *exo*-alcohol **24d** in a ratio of 91 : 6. R_f (Et_2O) 0.55. IR: 3000, 2950, 2898, 2870, 1200, 1099, 1028. ^{1}H-NMR: 0.75–2.4 (stack, 10H); 3.2–3.5 (stack, 5H); 4.2 (*dt*, *J* = 10,3, 1H). MS: 111 (100), 93 (35), 80 (47), 67 (41), 45 (26).

General Procedures. – *Oxymercuration* [28]. A solution of the 1-substituted norbornene in THF was slowly added at r.t. to 1.5 mol-equiv. of $Hg(OAc)_2$, dissolved in H_2O. After stirring for 4 h, the yellow solution was treated with 6M NaOH and 4.3 mol-equiv. $NaBH_4$ in 3M NaOH. The dark mixture was stirred over night, filtered over *Celite* and worked up. Products were determined by GC comparison with reference compounds. In case of **13**, a 47 fold extension of reaction time before reduction did not alter the product distribution.

When oxymercuration was performed in AcOH at r.t., the olefins **11**–**13**, **18** and **20** gave the products, described in *Table 3*, in similar ratios. However, when **12** was reacted under these conditions for 10 days, 2-*endo*-norbornanol (85%) **22a** (0.5%) and **22d** (10.74%) were obtained.

Hydroboration [21]. One mol-equiv. of a solution of $BH_3 \cdot THF$ (1.05M) was slowly added at 0° to the 1-substituted norbornene dissolved in THF. After stirring for 90 min, 0.5 mol-equiv. of 3M NaOH and excess H_2O_2 (30%) was added. After 3 h, the mixture was worked up. Products were determined by GC comparison as described above. The ratio of products was unchanged, when **11**–**13** dissolved in THF, were added to $BH_3 \cdot THF$ at 0°.

Addition of Formic Acid. A 0.56M solution of the 1-substituted norbornene in a 1 : 4 mixture of THF and HCOOH was refluxed for 5 h. After cooling, pentane was added and HCOOH extracted with H_2O. The solvent was removed and the mixture was stirred with MeOH and a trace of TsOH for 2 h. After workup, the mixture was analyzed by GC as described above.

Reaction with $PdCl_2$ [29]. A suspension of 1.1 mol-equiv. $PdCl_2$ in 1M $HClO_4$ was heated to 80° for 15 min. After addition of the 1-substituted norbornene in monoglyme, heating was continued for 25 h. The dark solution was filtered over *Celite*, worked up and the products were analyzed by GC.

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