Preparation of Chiral Hydroxy Carbonyl Compounds and Diols by Ozonolysis of Olefinic Isoborneol and Fenchol Derivatives: Characterization of Stable Ozonides by ^{1}H-, ^{13}C-, and ^{17}O-NMR and Electrospray Ionization Mass Spectrometry

by **Kalina Kostova**[a]), **Vladimir Dimitrov**[a])*, **Svetlana Simova**[a]), and **Manfred Hesse**[b])*

[a]) Institute of Organic Chemistry, Bulgarian Academy of Sciences, BG-1113 Sofia
[b]) Organisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich

The allylic and homoallylic alcohols **1**–**8**, prepared from (+)-camphor and (−)-fenchone, were ozonized in Et_2O at −78° and treated with Et_3N or $LiAlH_4$ to give the chiral hydroxy carbonyl compounds **9**–**16** and the diols **17**–**24**, respectively (*Scheme 1*). In the case of the diols **19** and **24**, the formation of new chiral centers proceeded with high diastereoselectivity. These diols were prepared highly diastereoselectively also by $LiAlH_4$ reduction of the hydroxy carbonyl compounds **11** and **16a**, respectively (*Scheme 2*). The absolute configuration of the new chiral centers in **19** and **24** was determined by X-ray and NMR methods. The ozonization of compounds **2**, **3**, **7**, and **8** provided the relatively stable hydroxy-substituted 1,2,4-trioxolane derivatives (ozonides) **37**–**40** (*Scheme 5*) which were characterized by ^{1}H- and ^{13}C-NMR spectra, ESI-MS, and natural-abundance ^{17}O-NMR spectra.

Introduction. – The cleavage of C=C bonds by ozone is a very convenient route for the preparation of carbonyl compounds or alcohols depending on the reducing reagent used in a second step [1]. The ozonolysis of alkenes has been carried out in various solvents, *e.g.*, MeOH [2], CH_2Cl_2 [3], AcOEt [4], as well as other solvents [1]. For the synthesis of alcohols, $LiAlH_4$ and $NaBH_4$ have been usually applied in the second step. Dimethyl sulfide (Me_2S) has been suggested as the most convenient reagent for the preparation of carbonyl compounds [1], although other agents, *e.g.*, Et_3N or Ph_3P, have been reported to provide excellent results [5][6]. The mechanism formulated by *Criegee* (formation of a relatively unstable primary ozonide which is cleaved into a carbonyl compound and a carbonyl oxide, followed by recombination to the more stable normal ozonide) [7] to describe the ozonolysis of alkenes in aprotic solvents has been widely accepted, though some details are not completely understood, thus the object of further investigations [8][9]. Normal ozonides, which have been recognized as 1,2,4-trioxolanes by *Rieche et al.* in 1942 [10] have, in recent years, received increased attention in studies on their stability, reactivity, and structure [6][11].

The addition of vinyl and allyl *Grignard* reagents to (+)-(1*R*)-camphor and (−)-(1*R*)-fenchone provided the corresponding allylic and homoallylic alcohols, which are suitable for ozonolytic cleavage, in high yields on a multigram scale [12]. We have preliminarily communicated about the ozonolysis of four camphor- and fenchone-derived homoallylic alcohols which gave, after reduction with $LiAlH_4$, chiral 1,3-diols in high yields [13]. In continuation of our studies concerning the preparation of functionalized optically active compounds based on transformations of camphor and fenchone derivatives [14], we report here the synthesis of new hydroxy carbonyl

compounds and diols, as well as the isolation of stable 1,2,4-trioxolanes (so-called normal ozonides).

Results and Discussion. – The ozonolysis of the alcohols **1**–**8** (*Scheme 1*) was carried out in Et_2O at $-78°$. The reduction occurred with Et_3N or $LiAlH_4$ to give, in high yields, the hydroxy carbonyl compounds **9**–**16** and the diols **17**–**24**, respectively. It is interesting to note that the hydroxy aldehydes **9** and **14** were also formed without treatment with Et_3N directly after the ozonization of **1** and **6**, respectively; however the Et_3N treatment is highly recommended since in this case, the products obtained are of higher purity.[1])

The crude hydroxy carbonyl compounds **9**–**16** were isolated in very good purities. This is important for further transformations, since the hydroxy aldehydes are unstable on standing – compounds **9** and **12**–**14** decomposed significantly to unidentified compounds within several hours. The aldehydes **10** and **15**, which are more stable (decomposition within 3–4 weeks), were best purified by bulb-to-bulb distillation rather than by flash chromatography (FC) because of the higher yields thus realized. During chromatography and on prolonged contact with silica gel, compound **10** eliminated H_2O to give (1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene)acetaldehyde (**25**; see below, *Scheme 2*)[2]) as a by-product. The ketones **11** and **16a** are stable, but not so the isomer **16b** which decomposed within several weeks. It must be pointed out that the starting alcohols with the fenchone skeleton were *endo*/*exo*-isomeric mixtures 92 : 8 for **6** and **7** and 82 : 18 for **8**. The minor isomers **14b** and **15b** (with an *exo*-OH group) could be observed in the ^{13}C-NMR spectra (content *ca.* 5%) of the isolated hydroxy aldehydes **14** and **15** only. It was not possible to isolate them in pure form by FC. The isomeric hydroxy ketones, **16a** and **16b**, were separated by FC.

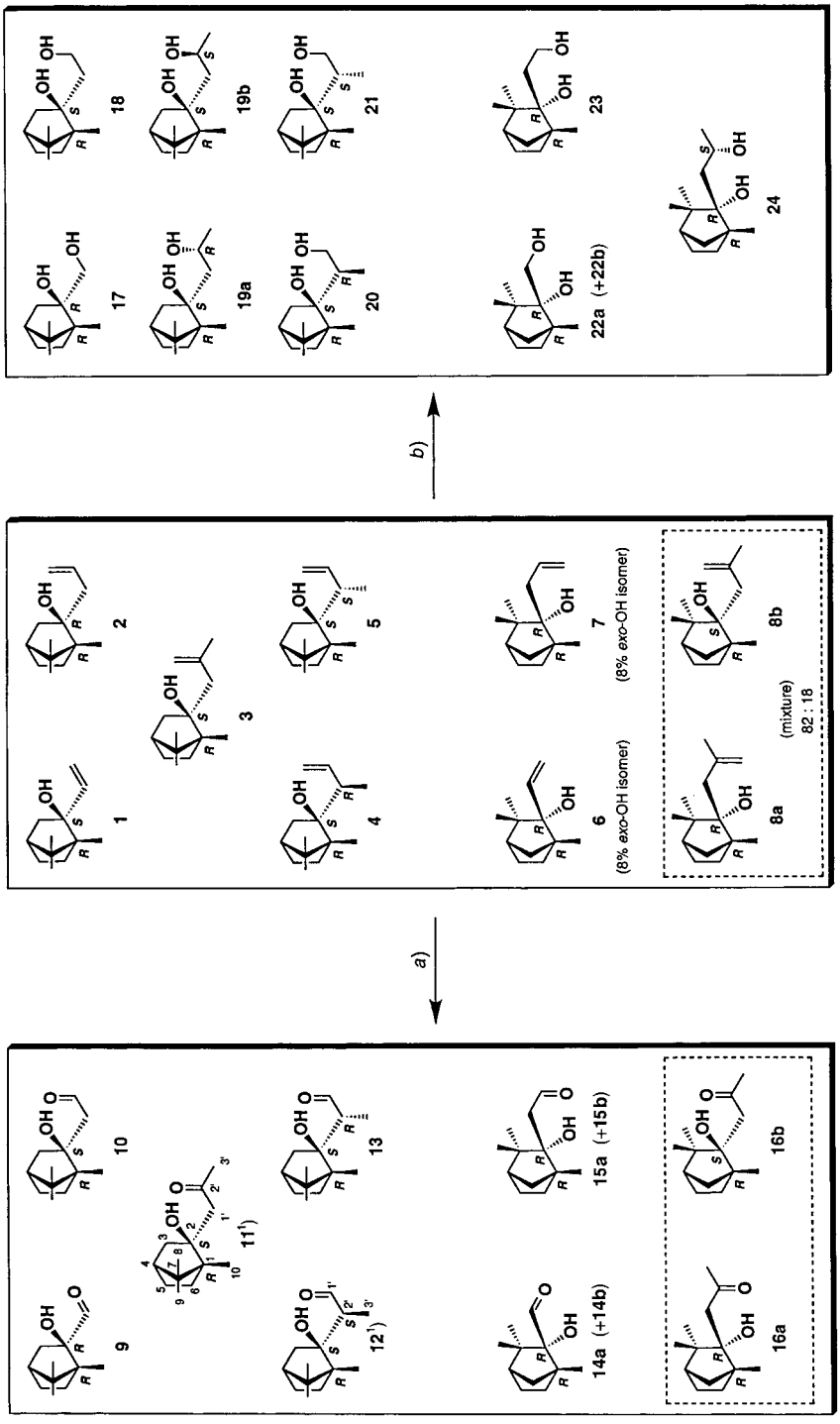
The treatment of the solutions of ozonized compounds **1**–**8** with $LiAlH_4$ at $-78°$, followed by slow warming to room temperature and hydrolytic workup, provided the diols **17**–**24**, which were isolated, after FC or recrystallization, in high yields. Interestingly, in the crude **17** and **22**, significant quantities of isoborneol and *endo*-fenchol, respectively, were observed (**17**/isoborneol 85 : 15, **22**/*endo*-fenchol 85 : 15; by ^{1}H-NMR). A small amount of *endo*-fenchol was also isolated on chromatography of diol **24**. In the case of diols **23** and **24**, the corresponding *exo*-OH isomers were only detected as impurities by ^{13}C-NMR, without quantification. Contrarily, in the ^{13}C-NMR spectrum of **22**, signals of the minor *exo*-OH isomer **22b** (content *ca.* 8%) could be unambigously assigned (*Table 1*). Consequently, the minor *exo*-OH isomers of the diols **23** and **24** are probably not stable and, therefore, could only be detected as impurities. The diols **19** and **24** were obtained diastereoselectively with respect to the newly formed chiral center. Compound **19** (diastereoisomer ratio in the crude product: **19a**/**19b** 75 : 25 by ^{1}H-NMR) was separated into the individual diastereoisomers by chromatography. Moreover, diastereoisomer **19a** could be enriched to a ratio **19a**/**19b** 88 : 12 by a single recrystallization of the crude product from hot hexane. The (2′*R*)-configuration[1]) of **19a** was determined by an X-ray crystal-structure analysis; however, the quality of the crystals of **19a** did not allow an exact structure determination

---

[1]) Arbitrary or trivial numbering; for systematic names, see *Exper. Part.*

[2]) For spectral data of **25**, see *Table 1* and *Exper. Part.*

Scheme 1



a) O_3/Et_2O, $-78°$; Et_3N, $-78°$ to r.t. *b*) O_3/Et_2O, $-78°$; $LiAlH_4$, $-78°$ to r.t.

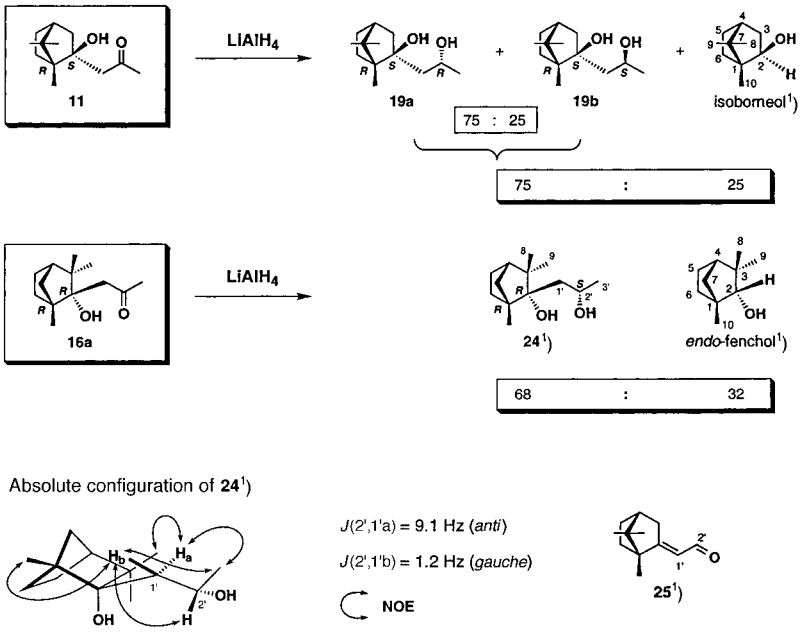
concerning bond lengths and angles. The diol **24** was isolated as a single diastereoisomer demonstrating an extraordinarily high diastereoselectivity of the $LiAlH_4$ reduction of the ozonized **8**.

Table 1. *^{13}C-NMR Chemical Shifts* ($CDCl_3$, 300 K, δ in ppm from $SiMe_4$) *of Compounds* **9**–**25** *and* **31**. Tentative assignments are marked with asterisks; for the numbering (arbitrary or trivial[1])) of the C-atoms, see *Schemes 1*, *2*, and *4*

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(1′)	C(2′)	C(3′)
9	53.00	84.42	41.54	45.08	27.05	29.74	50.07	20.30	18.91	10.34	205.58	–	–
10	52.36	80.00	46.24	44.96	26.65	30.59	48.53	21.20	20.83	10.18	52.64	204.07	–
11	52.22	79.30	47.20	45.03	26.84	30.47	48.73	21.46	20.96	10.52	50.81	211.39	31.49
12	52.68	80.69	47.80	44.78	27.39	30.03	49.86	21.34	20.86	10.04	206.10	56.32	11.98
13	52.67	83.29	46.07	44.03	27.04	30.14	49.91	21.16	20.95	10.45	206.78	53.69	11.68
14a	52.07	85.81	44.95	47.89	25.28	29.06	40.34	26.58	22.65	15.75	205.95	–	–
14b	54.01	84.98	47.24	45.20	24.78	31.70	41.50	23.16	21.51	14.43	207.87	–	–
15a	52.01	81.82	43.81	49.23	25.02	28.73	40.46	28.40	21.97	17.60	48.99	205.35	–
15b	53.91	79.84	47.15	45.14	24.75	31.64	41.44	23.13	21.48	14.42	45.48	204.83	–
16a	52.05	81.55	44.32	49.76	25.35	28.83	40.65	27.97	22.29	17.80	48.02	213.65	31.12
16b	52.76	81.95	45.34	49.44	25.76	30.50	41.03	25.79	24.13	16.62	43.89	213.12	31.51
17	51.04	80.63	44.70	43.52	26.90	29.98	49.53	21.07	20.22	11.16	68.65	–	–
18	52.35	82.87	46.16	44.94	26.84	30.40	49.23	21.37	20.95	10.63	39.81	60.81	–
19a	52.11	81.74	48.99*	44.74	27.00	30.44	49.98	21.26	20.88	11.77	48.49*	66.85	24.80
19b	52.63	83.04	44.87*	45.08	26.82	30.36	48.92	21.52	21.02	10.20	45.60*	66.37	24.68
20	52.62	84.20	47.31	44.61	27.56	29.76	50.27	21.44	21.04	12.23	67.22	43.42	13.72
21	52.64	84.23	47.16	44.43	27.64	29.53	50.51	21.48	21.27	12.22	66.17	41.35	13.86
22a	50.92	80.13	43.40	49.26	25.06	30.13	41.15	26.04	22.38	17.37	65.55	–	–
22b	51.28	81.11	44.81	48.97	25.45	30.27	41.81	25.67	22.66	16.88	63.13	–	–
23	52.72	82.60	44.25	49.86	24.86	29.98	40.88	28.01	22.61	17.95	36.93	61.26	–
24	53.34	81.31	45.32	48.77	25.19	29.86	41.28	27.65	21.87	18.63	42.66	65.63	23.96
25	53.76	179.61	35.42	44.21	27.21	33.99	47.84	19.48	18.53	12.04	119.10	191.76	–
31	52.17	79.07	47.09	44.90	26.97	30.36	49.40	21.28	20.97	11.02	41.13	103.25	52.72

The diols **19** and **24** were prepared also by $LiAlH_4$ reduction of the ketones **11** and **16a**, respectively (*Scheme 2*), with reproduction of the diastereoselectivities observed on application of the ozonization/reduction procedure described above. Thus, the ratio **19a**/**19b** was 75:25, and diol **24** was obtained as a single diastereoisomer. Surprisingly, the $LiAlH_4$ reduction of compounds **11** and **16a** provided significant quantities of isoborneol and *endo*-fenchol, respectively (**19**/isoborneol 75:25, **24**/*endo*-fenchol 68:32; by ^{1}H-NMR). For the newly formed chiral center in diol **24**, we have previously proposed (2′*R*)-configuration[1]) [13]; however, this assumption was incorrect. The (2′*S*)-configuration[1]) could now be established on the basis of the measured vicinal ^{1}H,^{1}H-coupling constants, distance constraints (NOE measurements), and force-field calculations, taking into account the known (1*R*)-configuration of the fenchone skeleton. Only the diastereoisomer with (2′*S*)-configuration[1]) is compatible with the experimental evidence, as illustrated in *Scheme 2*.

Scheme 2



Absolute configuration of **24**[1])

We tried further to use **16a** synthetically for reaction with lithiated ferrocene[3]), expecting that the addition to the carbonyl moiety would occur smoothly, resulting in the formation of the ferrocene derivatives **26** and **27** (*Scheme 3*). Surprisingly, after the reaction with the ferrocenyllithium reagent, which proceeded with quantitative conversion of **16a**, only the ferrocene derivatives **28** and **29** were isolated (27 and 14% yield, resp., after FC). The compounds **28** and **29** have been previously prepared by the addition of lithiated ferrocene to cerium(III) chloride-activated fenchone [14a].

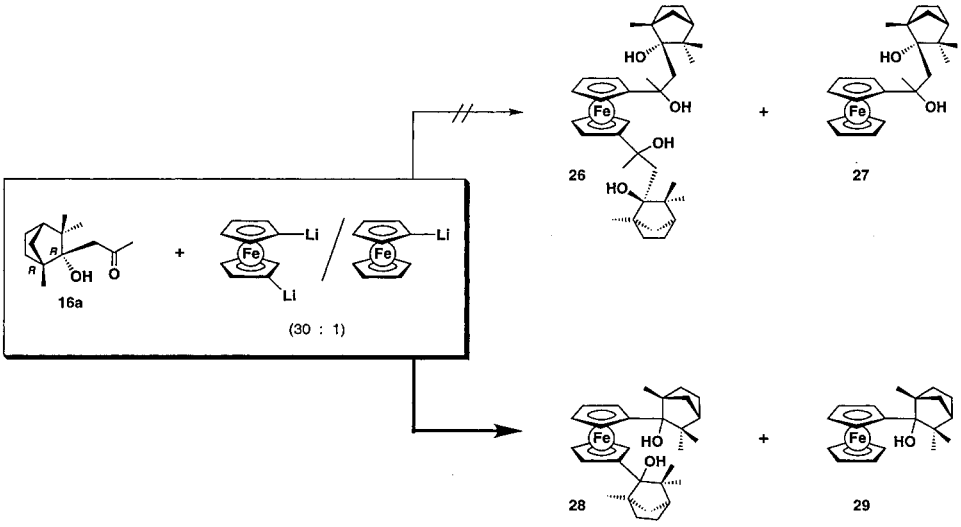
The formation of isoborneol and *endo*-fenchol from **11** and **16a** (*Scheme 2*) and the ferrocene derivatives **28** and **29** from **16a** (*Scheme 3*) leads to the assumption that during the reduction with $LiAlH_4$ or the addition of the ferrocenyllithium reagent, respectively, the ketones camphor and fenchone were probably formed *in situ*. Therefore, we submitted (+)-camphor and (−)-fenchone to reduction with $LiAlH_4$ and obtained, indeed quantitatively, isoborneol (containing 5% borneol) and *endo*-fenchol (containing 10% *exo*-fenchol). However, (+)-camphor and (−)-fenchone did not react with the ferrocenyllithium reagent without the assistance of anhydrous $CeCl_3$ [14a]. Moreover, it is not clear in which way the cleavage of the side chain in **11** or **16a** with formation of camphor and fenchone would occur. The investigation of these problems is planned in further experiments.

The choice of Et_2O as solvent for the ozonolysis of **1**–**8** and the reagents Et_3N or $LiAlH_4$ for the preparation of compounds **9**–**16** and **17**–**24**, respectively, presented in

---

[3]) The ferrocenyllithium reagent was prepared by lithiation of ferrocene with BuLi · TMEDA (Cp_2Fe/BuLi/TMEDA 1 : 2.2 : 1.2; TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine); the ratio $(LiCp)_2Fe$/Li(Cp)-Fe(Cp) 30 : 1 was determined by the procedure described in [14a].

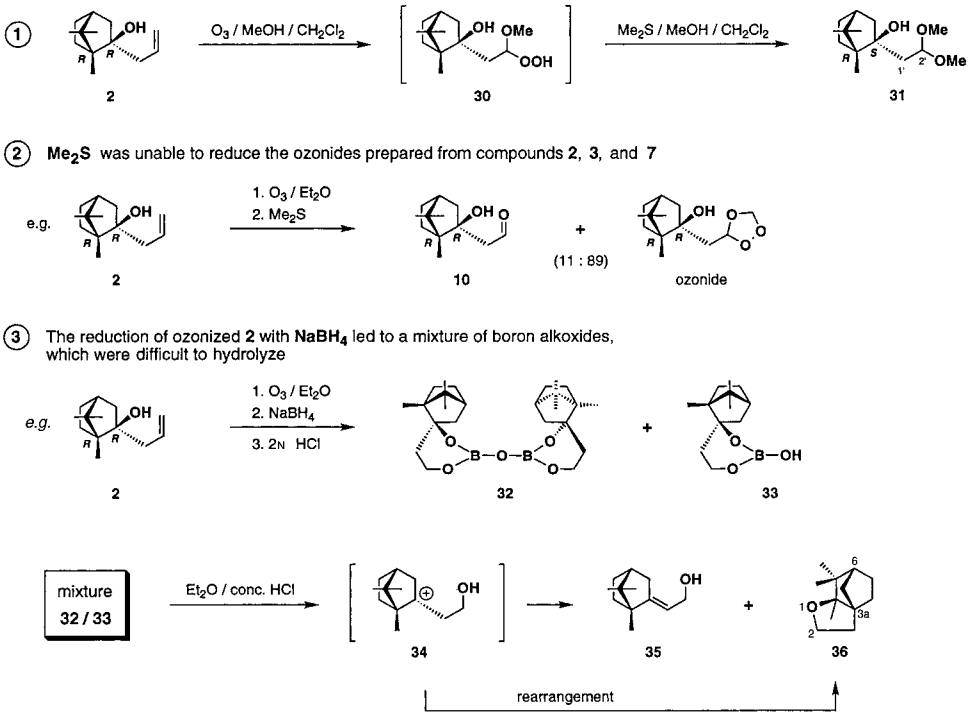
Scheme 3



Scheme 1, was caused by interesting observations (see *Scheme 4*). We found that the ozonolysis of **2** in the presence of MeOH, followed by treatment with Me_2S, produced only the dimethyl acetal **31** (*Scheme 4*, *Entry 1*). It has previously been described [6e][7][15–17] that the ozonolysis of olefins in MeOH generate α-methoxyalkyl hydroperoxides as intermediates like **30**, which afford, after suitable workup, aldehydes or their dimethyl acetals, depending on the propensity towards acetalization. We found further that Me_2S was unable to react completely with the ozonized **2**, **3**, and **7**, giving only small amounts of the hydroxy carbonyl compounds **10**, **11**, and **15**, respectively, even after extended reaction times (up to 48 h); the unreacted ozonides remained as main products after workup of the reaction mixtures (*Entry 2*, *Scheme 4*). A similar observation has been reported [6a]. The third surprising aspect was observed with $NaBH_4$ as reducing reagent (*Entry 3*): instead of the diol **18**, we isolated, after ozonolysis of **2** followed by $NaBH_4$ reduction and hydrolytic workup (2N HCl), a mixture of two boron-containing compounds **32** and **33** (1:2 ratio; by ^{1}H-NMR). The presence of B-atoms was established by standard chemical analysis. Moreover, in the mass spectra (EI-MS, CI-MS, and ESI-MS; see *Exper. Part*) of the mixture, the molecular-ion peaks for compounds **32** and **33** with the corresponding isotope patterns could be identified. The ^{1}H-NMR spectra are rather complicated and change with temperature. They indicate the presence of O–B–O six-membered rings. It is important to note that the NMR spectra of **32**/**33** were recorded in C_6D_6; indeed, when using $CDCl_3$ solutions, especially the ^{1}H signals rather then the ^{13}C signals of the two different bicyclic moieties were heavily overlapped.

The attempts to hydrolyze the mixture **32**/**33** with conc. HCl solution were successful, yielding the products **35** and **36**, which were isolated and analyzed (see *Exper. Part*). Thus, under acidic conditions and in the presence of boron as a *Lewis* acid, the elimination of H_2O to **35** and the rearrangement to **36**, obviously *via* the carbonium ion

Scheme 4



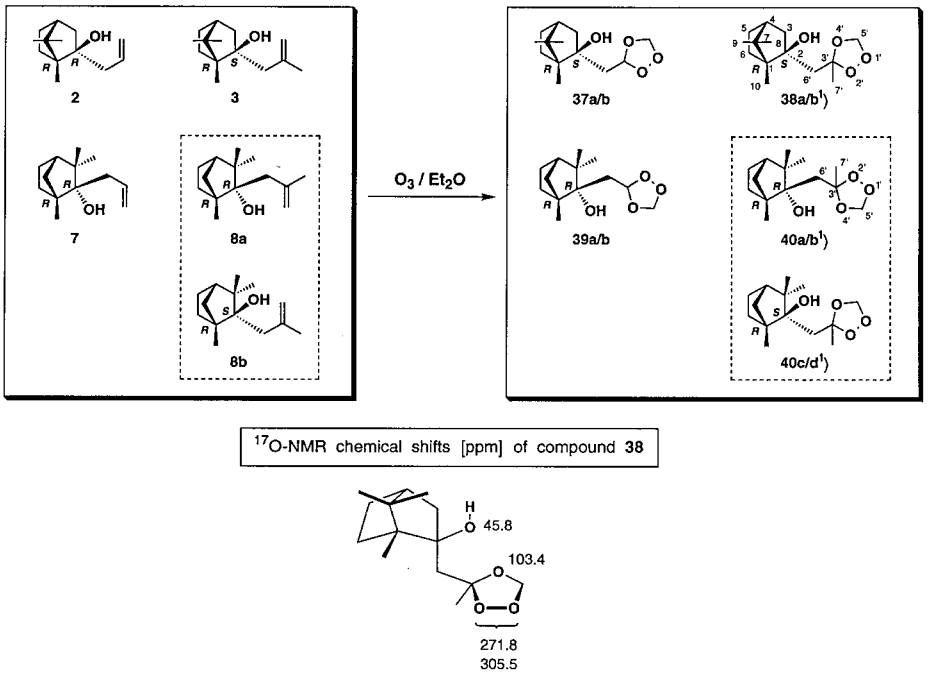
34, is preferred. We have recently reported [14c,d] a similar behavior of compounds containing the camphor skeleton.

In view of the observation described in *Entry 2* (*Scheme 4*), we ozonized compounds **2**, **3**, **7**, and **8** and worked the reaction mixtures up without prior treatment by the reduction reagent (*Scheme 5*). In the case of the unsubstituted homoallylic alcohols **2** and **7**, the crude reaction mixtures after ozonolysis contained the corresponding ozonides **37** (diastereoisomer mixture **37a**/**37b** 71:29) and **39** (diastereoisomer mixture **39a**/**39b** 47:53), besides the hydroxy aldehydes **10** (4%) and **15** (10%) respectively. The diastereoisomeric ozonide resulting from the *exo*-OH isomer of **7** could not be observed. The ozonides **37a**, **37b**, **39a**, and **39b** could be isolated as individual diastereoisomers by FC. Compounds **37** and **39** decomposed slowly over several days giving a mixture of unidentified products and small amounts of aldehydes **10** and **15**, respectively.

The ozonolysis of compound **3** gave nearly pure ozonide **38** as crude product. The ratio of the diastereoisomers **38a**/**38b**, concerning the newly formed chiral center of the trioxolane ring, was 75:25. This ratio corresponds to that observed for the diols **19a**/**19b** prepared after reduction of ozonized **3** with $LiAlH_4$. The diastereoisomers **38a** and **38b** could not be separated by column chromatography. The ozonide **38** is quite stable, remaining unchanged after several months at room temperature.

After the ozonolysis of the homoallylic alcohol **8** without reductive workup, the crude reaction mixture was rather complicated. The following compounds could be

Scheme 5



isolated by FC: a mixture of the ozonides **40b**/**40c** (ratio 66:34; yield 8%), a mixture of the ozonides **40b**/**40c**/**40d** (ratio 29:11:60; 8%), ozonide **40a** as a single diastereoisomer (16%), ketone **16b** (5%), and ketone **16a** (29%). Therefore, in this case, we could observe all four diastereoisomeric ozonides resulting from *endo*-OH isomer **8a** and *exo*-OH-isomer **8b**. A significant amount of the ozonides decomposed during the reaction, giving the hydroxy ketones **16a** and **16b**, similarly to the observations made in the case of the ozonolysis of compounds **1** and **6**, as described above. The isolation of only one diastereoisomeric diol **24** (*Scheme 1*) after $LiAlH_4$ reduction of ozonized **8** means that the formation of **24** proceeds in two steps *via* primary generation of the hydroxy ketone **16a** from ozonides **40a**/**b**. Actually, we demonstrated in *Scheme 2* that **16a** was reduced with $LiAlH_4$ completely diastereoselectively to diol **24**.

The ozonides **37**–**40** were characterized by NMR and ESI mass spectra (see *Table 2* and *Exper. Part*). For ozonide **38**, it was possible to obtain the natural-abundance ^{17}O-NMR spectrum (see *Scheme 5*). The chemical shifts for the ether O-atom and for the peroxide O-atoms are comparable with the data observed recently for several different ozonides [11c]. The chemical nonequivalence of the two peroxide O-atoms in the unsymmetrically substituted trioxolane, confirmed the observation by *Griesbaum et al.* [11c] that this nonequivalence can be caused also by hydrocarbon substituents and not only by electron-withdrawing heteroatom substituents. It was not possible to differentiate between the diastereoisomers **38a**/**b** because of the considerable linewidth of the ^{17}O-signals (2000 Hz for the peroxide and 1300 Hz for the ether signals). Comparing the ^{17}O-chemical shifts with literature data for cyclic

Table 2. *^{13}C-NMR Chemical Shifts* ($CDCl_3$, 300 K, δ in ppm relative to $SiMe_4$) *of Ozonides* **37**–**40**. Tentative assignments are marked with asterisks; for the numbering (arbitrary or trivial[1])) of the C-atoms, see *Scheme 5*.

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(3′)	C(5′)	C(6′)	C(7′)
37a	52.44	79.65	46.33	44.99	26.90	30.54	49.23	21.36	21.06	10.60	102.59	93.76	41.00	–
37b	52.63	79.57	45.88	45.12	26.87	30.51	49.01	21.45	21.09	10.32	102.76	93.86	40.20	–
38a	53.35	78.85	47.11	45.23	26.85	29.72	48.15	23.58	21.31	9.91	110.53	93.67	43.89	20.92
38b	53.09	79.00	47.11	45.23	26.80	29.84	48.23	23.90	21.36	9.91	110.53	93.17	44.50	20.92
39a	52.57	79.36	44.30	49.63	24.97	29.83	40.89	27.88	22.17	17.75	102.71	93.56	37.96	–
39b	52.68	79.64	44.30	49.91	24.91	29.79	40.78	27.94	22.13	17.67	102.77	93.73	37.30	–
40a	53.05	80.78	44.60	50.07	25.13	29.87	40.51	28.75	21.16	18.53	110.38	93.01	39.78	26.23
40b	53.31	80.49	44.43	50.03	25.05	29.85	40.54	28.58	21.33	18.22	110.30	94.20	38.75	26.14
40c	54.13	80.38	45.19	49.31	25.67	29.65	40.59	25.40*	25.10*	15.93	110.25	93.95	36.02	25.00*
40d	53.88	80.51	45.37	49.35	25.73	29.64	40.61	25.40*	25.12*	15.97	110.34	93.26	37.19	24.80*

peroxides [18], it is possible to propose a relatively low C–O–O–C dihedral angle in the trioxolane ring, because of the relatively high δ values for the peroxide O-atoms of **38**.

In conclusion, we demonstrated a very convenient way to prepare of new chiral, diastereoisomerically pure hydroxy carbonyl compounds and diols *via* ozonolysis of allylic and homoallylic alcohols having camphor and fenchone skeletons. These chiral compounds can be prepared on a multigram scale, being thus of practical interest for further transformations and applications.

We thank Dr. *A. Linden*, Dr. *D. Rentsch*, Dr. *L. Bigler*, and *N. Bild*, Organisch-chemisches Institut der Universität Zürich, for X-ray analysis of compound **19a**, for the ^{17}O-NMR spectra, for the ESI-MS, and for EI- and CI-MS, respectively. Support of the *Bulgarian National Fund for Scientific Research* (project X-711) and of the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. The alcohols *(1*R,*2*S*)-2-ethenyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol*, (**1**), *(1*R,*2*R*)-1,7,7-trimethyl-2-(prop-2-enyl)bicyclo[2.2.1]heptan-2-ol* (**2**), *(1*R,*2*S*)-1,7,7-trimethyl-2-(2-methylprop-2-enyl)bicyclo-[2.2.1]heptan-2-ol* (**3**), *(1*R,*2*S*)-1,7,7-trimethyl-2-[(1*R*)- and (1*S*)-1-methylprop-2-enyl]bicyclo[2.2.1]heptan-2-ol* (**4** and **5**, resp.), *(1*R,*2*R*)-2-ethenyl-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol* (**6**), *(1*R,*2*R*)-1,3,3-trimethyl-2-(prop-2-enyl)bicyclo[2.2.1]heptan-2-ol* (**7**), and *(1*R,*2*R)- and *(1*R,*2*S*)-1,3,3-trimethyl-2-(2-methylprop-2-enyl)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol* (**8a** and **8b**, resp.; ratio 82 : 18) were prepared according to [12]. The org. solvents were distilled prior to use. Ozonolysis: ozone generator *502 Fischer* (3–5 g O_3/h). TLC: precoated silica gel *60 F_{254}* plates (*Merck*); visualization by irradiation with UV light or by $Ce(SO_4)_2$/phosphomolybdic acid soln. Flash chromatography (FC): silica gel *Merck 60* (0.040–0.063 mm). M.p.: *Mettler FP-5/FP-52*. Optical rotation: *Perkin-Elmer-241* polarimeter. IR Spectra ($CHCl_3$): *Perkin-Elmer 781*; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra (300 K): *Bruker-AC-300*, *Bruker-ARX-300*, *Bruker DRX-250*, *Bruker AM-400*, or *Varian XL-200* spectrometer; δ in ppm rel. to Me_4Si (= 0 ppm), J in Hz; unless stated otherwise, $CDCl_3$ soln.; C-multiplicities were assigned by DEPT techniques. ^{17}O-NMR Spectra: *Bruker AMX-600*, 81.37 MHz, δ in ppm rel. to external water, number of scans 102 400, pulse angle 13 µs, relaxation delay 20 ms, spectral width 62.5 kHz, 4 *K* time-domain points, transformed to spectrum size 32 *K*, exponential multiplication with a broadening factor of 400 Hz. EI- (70 eV) and CI-MS (NH_3 as reactant gas): *Finnigan MAT 90* or *Finnigan SSQ 700*; fragment ions in *m*/*z* with rel. intensities (%) in parenthesis. ESI-MS: *Finnigan MAT TSQ 700*.

General Procedure (GP) for the Ozonolysis of Alcohols **1**–**8**. A flow of ozonized oxygen was bubbled (*G2* frit) through a soln. of the corresponding alcohol at −78° until appearance of blue color indicated an excess of O_3. After blowing out the excess of O_3 with dry N_2, the corresponding reducing reagent (Et_3N or $LiAlH_4$) was introduced at −78° and the mixture allowed to warm to r.t. and stirred for 1 h at r.t. Workup: *a*) when treated with Et_3N, the reaction mixture was washed with 1N HCl, 5% aq. $NaHCO_3$ soln., and H_2O, dried ($MgSO_4$), and

evaporated; *b*) when treated with $LiAlH_4$, the reaction mixture was hydrolyzed (2N HCl), washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated. For removing the last traces of the solvent, the isolated compounds were properly dried under high vacuum (oil pump).

*(1*R*,2*R*)-2-Hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane-2-carbaldehyde* (**9**). Following the *GP*, **1** (0.16 g, 0.89 mmol) in Et_2O (20 ml) was ozonized and then treated with Et_3N (0.20 g, 1.98 mmol): 0.16 g (quant.) of pure (by TLC and NMR) **9**. Colorless oil. IR: 3500 br. (OH), 2960, 2870, 2740 (CHO), 1715 (C=O), 1490, 1450, 1390, 1355, 1315, 1245, 1145, 1120, 1080, 980, 940. ^{1}H-NMR (*ARX-300*)[1]): 9.66 (*s*, H–C(1′)); 3.56 (*s*, OH); 2.00 (*dt*, *J* = 13.4, 3.6, H_{exo}–C(3)); 1.93–1.81 (*m*, H_{endo}–C(3), H–C(4), H_{exo}–C(5)); 1.63–1.53 (*m*, H_{exo}–C(6)); 1.46–1.42 (*m*, H_{endo}–C(6)); 1.39–1.28 (*m*, H_{endo}–C(5)); 1.11 (*s*, Me(8)); 0.87 (*s*, Me(9)); 0.82 (*s*, Me(10)). CI-MS: 200 (28, $[M+18]^+$), 183 (11, $[M+1]^+$), 170 (40), 108 (31), 95 (100).

*(1*R*,2*S*)-2-Hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptane-2-acetaldehyde* (**10**). Following the *GP*, **2** (2.01 g, 10.34 mmol) in Et_2O (35 ml) was ozonized and then treated with Et_3N (2.10 g, 20.75 mmol): crude **10** (1.91 g) of satisfactory purity (by TLC and NMR). The crude product was chromatographed (1.7 × 49 cm column, silica gel (49 g), hexane/Et_2O 5 : 1) to give 0.11 g of **25** (as a result of H_2O elimination on silica gel) and 1.57 g (77%) of **10** as colorless oil. After bulb-to-bulb distillation of the crude **10** at $3 \cdot 10^{-2}$ Torr/110°, the yield was 86%.

Data of **10**: $[\alpha]_{21}^{D} = -1.4$ (*c* = 4.41, $CHCl_3$). IR: 3640 (free, OH), 3520 (br., OH), 2960, 2880, 2740 (CHO), 1715 (C=O), 1490, 1455, 1390, 1370, 1315, 1245, 1145, 1120, 1085, 985, 940, 905. ^{1}H-NMR (*AC-300*)[1]): 9.90 (*dd*, *J* = 2.6, 1.1, H–C(2′)); 2.71 (*dd*, *J* = 16.1, 2.6, H_a–C(1′)); 2.59 (*dd*, *J* = 16.1, 1.1, H_b–C(1′)); 2.38 (*s*, OH); 2.20 (*dt*, *J* = 13.4, 3.8, H_{exo}–C(3)); 1.79 (*t*, *J* = 4.2, H–C(4)); 1.78–1.67 (*m*, H_{exo}–C(5)); 1.56 (*d*, *J* = 13.4, H_{endo}–C(3)); 1.52–1.22 (*m*, 2 H–C(6)); 1.12 (*s*, Me(8)); 1.12–0.95 (*m*, H_{endo}–C(5)); 0.87 (*s*, Me(9)); 0.86 (*s*, Me(10)). CI-MS: 214 (49, $[M+18]^+$), 196 (12, $M^{+\cdot}$), 179 (100, $[M-OH]^+$). Anal. calc. for $C_{12}H_{20}O_2$ (196.29): C 73.43, H 10.27; found: C 73.21, H 10.19.

*Data of [(1*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene]acetaldehyde* (**25**): ^{1}H-NMR (*AC-300*)[1]): 9.79 (*d*, *J* = 7.7, H–C(2′)); 5.74 (*dt*, *J* = 7.9, 2.2, H–C(1′)); 2.81 (br. *d*, *J* = 18.0, H_{exo}–C(3)); 2.39 (*dd*, *J* = 18.0, 2.1, H_{endo}–C(3)); 1.88 (*t*, *J* = 4.1, H–C(4)); 1.81–1.65 (*m*, H_{exo}–C(5), H_{exo}–C(6)); 1.27–1.14 (*m*, H_{endo}–C(6)); 0.92 (*s*, Me(8)); 0.92–0.76 (*m*, H_{endo}–C(5)); 0.89 (*s*, Me(9)); 0.71 (*s*, Me(10)). EI-MS: 178 (79, $M^{+\cdot}$), 163 (44, $[M-Me]^+$), 135 (100, $[M-CH_2CHO]^+$).

*1-[(1*R*,2*S*)-2-Hydroxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-yl]propan-2-one* (**11**). Following the *GP*, **3** (12.21 g, 58.62 mmol) in Et_2O (140 ml) was ozonized and then treated with Et_3N (12 g, 118.58 mmol): 12.27 g of crude **11** (pure by NMR). Bulb-to-bulb distillation at $3 \cdot 10^{-2}$ Torr/100° provided 10.73 g (87%) of **11**. Colorless crystals. M.p. 46.2–47.5°. $[\alpha]_{21}^{D} = -47.0$ (*c* = 3.95, $CHCl_3$). IR: 3500 (br., OH), 2980, 2950, 2880, 1700 (C=O), 1490, 1455, 1390, 1365, 1330, 1300, 1240, 1165, 1120, 1080, 995. ^{1}H-NMR (*AC-300*)[1]): 3.73 (*s*, OH); 2.72 (*d*, *J* = 17.1, H_a–C(1′)); 2.54 (*d*, *J* = 17.1, H_b–C(1′)); 2.14 (*s*, Me(3′)); 2.09 (*dt*, *J* = 13.3, 3.7, H_{exo}–C(3)); 1.68–1.58 (*m*, H–C(4), H_{exo}–C(5)); 1.48–1.15 (*m*, 2 H–C(6)); 1.29 (*d*, *J* = 13.3, H_{endo}–C(3)); 1.06 (*s*, Me(8)); 0.96–0.84 (*m*, H_{endo}–C(5)); 0.78 (*s*, Me(9), Me(10)). CI-MS: 193 (23, $[(M-OH]^+$), 95 (100). Anal. calc. for $C_{13}H_{22}O_2$ (210.32): C 74.24, H 10.54; found: C 74.39, H 10.54.

*(*S*)-2-[(1*R*,2*S*)-2-Hydroxy-1,7,7-trimethylbicyclo[2.1.1]hept-2-yl]propanal* (**12**). Following the *GP*, **4** (0.15 g, 0.72 mmol) in Et_2O (15 ml) was ozonized and then treated with Et_3N (0.16 g, 1.58 mmol): 0.15 g (quant.) of **12**. Colorless oil (pure by TLC and NMR). On standing, **12** decomposed significantly within 3–4 h (hence no elemental analysis and optical rotation). IR: 3510 (br., OH), 2960, 2880, 2740 (CHO), 1715 (C=O), 1480, 1455, 1390, 1360, 1310, 1240, 1140, 1120, 1085, 980, 940, 905. ^{1}H-NMR (*ARX-300*)[1]): 9.77 (*d*, *J* = 1.4, H–C(1′)); 2.57 (*q*, *J* = 7.3, H–C(2′)); 2.29 (*s*, OH); 2.27 (*dt*, *J* = 13.2, 3.8, H_{exo}–C(3)); 1.82–1.71 (*m*, H–C(4), H_{exo}–C(5)); 1.60 (*d*, *J* = 13.2, H_{endo}–C(3)); 1.56–1.45 (*m*, H_{exo}–C(6)); 1.39–1.31 (*m*, H_{endo}–C(6)); 1.20 (*d*, *J* = 7.3, Me(3′)); 1.10 (*s*, Me(8)); 1.10–1.01 (*m*, H_{endo}–C(5)); 0.96 (*s*, Me(10)); 0.85 (*s*, Me(9)). EI-MS: 210 (3, $M^{+\cdot}$), 192 (3, $[M-H_2O]^{+\cdot}$), 153 (10), 122 (8), 110 (16), 109 (15), 108 (17), 96 (9), 95 (100), 81 (8), 69 (18), 67 (7), 55 (11), 41 (20).

*(*R*)-2-[(1*R*,2*S*)-2-Hydroxy-1,7,7-trimethylbicyclo[2.1.1]hept-2-yl]propanal* (**13**). Following the *GP*, **5** (0.09 g, 0.43 mmol) in Et_2O (15 ml) was ozonized and then treated with Et_3N (0.10 g, 0.99 mmol): 0.09 g (quant.) of **13**. Colorless oil (pure by TLC and NMR). On standing, **13** decomposed significantly within 3–4 h (hence no elemental analysis and optical rotation). IR: 3520 (br., OH), 2960, 2880, 2740 (CHO), 1715 (C=O), 1480, 1450, 1380, 1360, 1315, 1230, 1145, 1120, 1085, 980, 930, 905. ^{1}H-NMR (*ARX-300*)[1]): 9.91 (*d*, *J* = 2.8, H–C(1′)); 2.69–2.60 (*m*, H–C(2′)); 1.96 (*dt*, *J* = 13.2, 3.7, H_{exo}–C(3)); 1.81–1.69 (*m*, H–C(4), H_{exo}–C(5)); 1.55–1.39 (*m*, 2 H–C(6)); 1.43 (*d*, *J* = 13.2, H_{endo}–C(3)); 1.18 (*d*, *J* = 7.4, Me(3′)); 1.12–0.97 (*m*, H_{endo}–C(5)); 1.08 (*s*, Me(8)); 0.85 (*s*, Me(9)); 0.82 (*s*, Me(10)). EI-MS: 210 (3, $M^{+\cdot}$), 192 (2, $[M-H_2O]^{+\cdot}$), 153 (12), 151 (9), 110 (16), 109 (17), 108 (21), 107 (7), 96 (9), 95 (100), 93 (8), 81 (10), 69 (21), 55 (11), 43 (9), 41 (19).

*(1*R*,2*R*)- and (1*R*,2*S*)-2-Hydroxy-1,3,3-trimethylbicyclo[2.2.1]heptane-2-carbaldehyde* (**14a** and **14b**, resp.). Following the *GP*, **6** (0.17 g, 0.94 mmol) in Et_2O (15 ml) was ozonized and then treated with Et_3N (0.21 g, 2.08 mmol): 0.17 g (quant.) of pure (by TLC and NMR) **14a** as colorless oil (containing 5% of **14b**). IR: 3520 (br., OH), 2960, 2880, 2735 (CHO), 1715 (C=O), 1480, 1455, 1380, 1365, 1310, 1255, 1110, 1080, 1010, 990. ^{1}H-NMR (*ARX-300*)[1]: 9.70 (*s*, H–C(1′)); 3.39 (br. *s*, OH); 2.11–2.07 (*m*, H_{syn}–C(7)); 2.01–1.92 (*m*, H_{endo}–C(6)); 1.82–1.71 (*m*, H–C(4), H_{endo}–C(5)); 1.53–1.39 (*m*, H_{exo}–C(5)); 1.36–1.32 (*m*, H_{anti}–C(7)); 1.03–0.80 (*m*, H_{exo}–C(6)); 0.97 (*s*, Me(10)); 0.86 (*s*, Me(8)); 0.85 (*s*, Me(9)). CI-MS: 183 (5, $[M+1]^+$), 153 (17), 109 (7), 81 (100). Anal. calc. for $C_{11}H_{18}O_2$ (182.26): C 72.49, H 9.95; found: C 72.57, H 9.82.

*(1*R*,2*R*)- and (1*R*,2*S*)-2-Hydroxy-1,3,3-trimethylbicyclo[2.2.1]heptane-2-acetaldehyde* (**15a** and **15b**, resp.). Following the *GP*, **7** (2.01 g, 10.34 mmol) in Et_2O (35 ml) was ozonized and then treated with Et_3N (2.10 g, 20.75 mmol): 1.93 g of crude **15** with satisfactory purity (by TLC and NMR). Bulb-to-bulb distillation ($3\cdot10^{-2}$ Torr/90°) gave 1.80 g (88%) of **15a** as colorless oil (containing 5% **15b**). $[\alpha]_{21}^{D} = -4.6$ ($c = 3.84$, $CHCl_3$). IR: 3520 (br., OH), 2960, 2880, 2840, 2735 (CHO), 1715 (C=O), 1475, 1465, 1390, 1375, 1310, 1270, 1240, 1115, 1085, 1060, 1010, 990. ^{1}H-NMR (*ARX-300*)[1]: 10.03 (*d*, $J = 1.5$, H–C(2′)); 3.36 (*s*, OH); 2.81 (*dd*, $J = 18.0, 1.5$, H_a–C(1′)); 2.52 (*d*, $J = 17.6$, H_b–C(1′)); 2.06–2.00 (*m*, H_{endo}–C(6)); 1.77–1.66 (*m*, H–C(4), H_{endo}–C(5)); 1.52–1.38 (*m*, H_{exo}–C(5), H_{syn}–C(7)); 1.15–0.92 (*m*, H_{exo}–C(6), H_{anti}–C(7)); 1.01 (*s*, Me(10)); 1.00 (*s*, Me(8)); 0.92 (*s*, Me(9)). EI-MS: 196 (20, $M^{+\cdot}$), 181 (15), 178 (25, $[M-H_2O]^{+\cdot}$), 153 (6), 125 (8), 114 (29), 113 (11), 83 (6), 82 (11), 81 (100), 70 (20), 69 (41), 55 (12), 41 (32). Anal. calc. for $C_{12}H_{20}O_2$ (196.29): C 73.43, H 10.27; found: C 73.15, H 10.38.

*1-[(1*R*,2*R*)- and (1*R*,2*R*)-2-Hydroxy-1,3,3-trimethylbicyclo[2.2.1]hept-2-yl]propan-2-one* (**16a** and **16b**, resp.). Following the *GP*, **8** (13.05 g, 62.65 mmol) in Et_2O (150 ml) was ozonized and then treated with Et_3N (12.68 g, 125.30 mmol): 13.12 g of crude **16**. The crude product was chromatographed (3.5×100 cm column, silica gel (310 g) hexane/Et_2O 30:1 → 15:1): 0.24 g of **16b** (oil), 3.24 g of mixed fractions, and 8.28 g of **16a** (oil). Total yield of **16**: 11.76 g (89%).

Data of **16a**: $[\alpha]_{21}^{D} = +11.2$ ($c = 4.04$, $CHCl_3$). IR: 3480 (br., OH), 2980, 2880, 1703 (C=O), 1465, 1406, 1375, 1362, 1326, 1171, 1080, 995. ^{1}H-NMR (*ARX-300*)[1]: 4.52 (*s*, OH); 2.82 (*d*, $J = 17.8$, H_a–C(1′)); 2.43 (*d*, $J = 17.8$, H_b–C(1′)); 2.21 (*s*, Me(3′)); 2.20–2.07 (*m*, H_{endo}–C(6)); 1.76–1.61 (*m*, H–C(4), H_{endo}–C(5)); 1.54–1.32 (*m*, H_{exo}–C(5), H_{syn}–C(7)); 1.11–1.07 (*m*, H_{anti}–C(7)); 1.02–0.85 (*m*, H_{exo}–C(6)); 0.99 (*s*, Me(10)); 0.99 (*s*, Me(8)); 0.86 (*s*, Me(9)). EI-MS: 210 (13, $M^{+\cdot}$), 195 (12), 192 (24, $[M-H_2O]^{+\cdot}$), 152 (9), 128 (35), 127 (10), 109 (9), 85 (24), 82 (10), 81 (100), 80 (15), 70 (9), 69 (47), 67 (9), 55 (9), 43 (39), 41 (23). Anal. calc. for $C_{13}H_{22}O_2$ (210.32): C 74.24, H 10.54; found: C 74.30, H 10.40.

Data of **16b**: $[\alpha]_{21}^{D} = -0.7$ ($c = 1.84$, $CHCl_3$). IR: 3720 (OH, free), 3580 (br., OH), 3070, 2980, 1750 (C=O), 1525, 1455, 1435, 1425, 1380, 1365, 1265, 1220, 1140, 1105, 930. ^{1}H-NMR (*ARX-300*)[1]: 4.37 (*s*, OH); 2.92 (*d*, $J = 18.2$, H_a–C(1′)); 2.46 (*d*, $J = 18.2$, H_b–C(1′)); 2.20 (*s*, Me(3′)); 2.09–2.04 (*m*, H_{syn}–C(7)); 1.61–1.52 (*m*, H–C(4), H_{endo}–C(5)); 1.42–1.18 (*m*, H_{exo}–C(5), 2 H–C(6)); 1.06 (*s*, Me(10)); 1.02 (*s*, Me(8)); 0.99–0.96 (*m*, H_{anti}–C(7)); 0.84 (*s*, Me(9)).

*(1*R*,2*R*)-2-(Hydroxymethyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol* (**17**). Following the *GP*, **1** (0.36 g, 2.00 mmol) in Et_2O (15 ml) was ozonized and then treated with $LiAlH_4$ (0.35 g, 9.22 mmol): 0.34 g of crude **17** (**17**/isoborneol 85:15; by NMR). The crude product was chromatographed (1.3×43 cm column, silica gel (19 g), hexane/Et_2O 2:1): 0.06 g of isoborneol and 0.27 g (74%) of **17** as colorless crystals.

*Data of Isoborneol (=(1*R*,2*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ol):* ^{1}H-NMR (*ARX-300*)[1]: 3.55 (*dd*, $J = 6.4, 3.9$, H–C(2)); 1.68–1.53 (*m*, 2 H–C(3), H–C(4), H_{exo}–C(5), OH); 1.45–1.39 (*m*, H_{exo}–C(6)); 0.96–0.87 (*m*, H_{endo}–C(5), H_{endo}–C(6)); 0.95 (*s*, Me(8)); 0.83 (*s*, Me(10)); 0.75 (*s*, Me(9)). ^{13}C-NMR (75 MHz): 79.51 (C(2)); 48.76 (C(1)); 46.14 (C(7)); 44.87 (C(4)); 40.22 (C(3)); 33.82 (C(6)); 27.09 (C(5)); 20.35 (Me(8)); 20.01 (Me(9)); 11.27 (Me(10)).

Data of **17**: M.p. 191–192° (hexane/Et_2O). $[\alpha]_{21}^{D} = -3.0$ ($c = 4.05$, $CHCl_3$). IR (CCl_4): 3620 (OH, free), 3450 (br., OH), 2940, 2866, 1450, 1390, 1370, 1350, 1276, 1120, 1083, 1066, 1050, 976. ^{1}H-NMR (*ARX-300*)[1]: 3.59 (*dd*, $J = 10.6, 3.5$, H_a–C(1′)); 3.44 (*dd*, $J = 10.6, 5.6$, H_b–C(1′)); 2.13 (*s*, OH); 1.87 (*dt*, $J = 13.1, 3.7$, H_{exo}–C(3)); 1.85 (*s*, OH); 1.73–1.61 (*m*, H–C(4), H_{exo}–C(5)); 1.43–1.20 (*m*, 2 H–C(6)); 1.28 (*d*, $J = 13.1$, H_{endo}–C(3)); 1.05 (*s*, Me(8)); 1.00–0.89 (*m*, H_{endo}–C(5)); 0.86 (*s*, Me(10)); 0.78 (*s*, Me(9)). EI-MS: 184 (5, $M^{+\cdot}$), 153 (47), 135 (7), 110 (16), 109 (13), 108 (18), 97 (9), 96 (9), 95 (100), 93 (13), 69 (20), 67 (7), 55 (13), 43 (10), 41 (16). Anal. calc. for $C_{11}H_{20}O_2$ (184.28): C 71.70, H 10.94; found: C 71.82, H 10.87.

*(1*R*,2*S*)-(2-Hydroxyethyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol* (**18**). Following the *GP*, **2** (1.53 g, 7.87 mmol) in Et_2O (40 ml) was ozonized and then treated with $LiAlH_4$ (1.37 g, 36.05 mmol): 1.52 g of crude **18**. Recrystallization from hexane gave 1.28 g (82%) of **18**. Colorless crystals. M.p. 55.0–55.2°. $[\alpha]_{21}^{D} = +10.1$ ($c = 3.65$, $CHCl_3$). IR: 3600 (OH, free), 3440 (br., OH), 2990, 2950, 2880, 1490, 1455, 1430, 1390, 1375, 1275,

1145, 1115, 1080, 1025, 1000, 940. ^{1}H-NMR (*ARX-300*)[1]): 4.00–3.83 (*m*, 2 H–C(2′)); 2.66 (*s*, OH); 2.41 (*s*, OH); 2.07 (*dt*, *J* = 13.2, 3.7, H_{exo}–C(3)); 1.92–1.83 (*m*, H_a–C(1′)); 1.76–1.61 (*m*, H–C(4), H_{exo}–C(5), H_b–C(1′)); 1.46 (*d*, *J* = 13.2, H_{endo}–C(3)); 1.43–1.37 (*m*, 2 H–C(6)); 1.10 (*s*, Me(8)); 1.01–0.93 (*m*, H_{endo}–C(5)); 0.90 (*s*, Me(10)); 0.86 (*s*, Me(9)). CI-MS: 216 (3, $[M+18]^+$), 198 (11, $M^{+\bullet}$). 181 (100, $[M-OH]^{+\bullet}$). Anal. calc. for $C_{12}H_{22}O_2$ (198.31): C 72.68, H 11.18; found: C 72.73, H 11.00.

*(1*R,2S*)-2-[(2*R*)- and (2*S*)-2-Hydroxypropyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol* (**19a** and **19b**, resp.). Following the *GP*, **3** (5.12 g, 24.58 mmol) in Et_2O (100 ml) was ozonized and then treated with $LiAlH_4$ (3.74 g, 98.42 mmol): 5.11 g of crude **19a**/**19b** 3 : 1 (by NMR). The crude product was chromatographed (4.2 × 72 cm column, silica gel (430 g), hexane/Et_2O 4 : 1): 0.93 g of **19b**, 1.42 g of mixed fractions, and 2.45 g of **19a**. Yield of **19**: 4.80 g (92%).

Data of **19a**: Colorless crystals from hexane/Et_2O. M.p. 104.0–104.5°. $[\alpha]_{21}^{D} = -0.8$ (*c* = 3.92, $CHCl_3$). IR: 3600 (OH, free), 3460 (br., OH), 2960, 2880, 1490, 1455, 1430, 1390, 1375, 1295, 1240, 1150, 1115, 1085, 940, 910. ^{1}H-NMR (*ARX-300*)[1]): 4.28–4.17 (*m*, H–C(2′)); 3.03 (*s*, OH); 2.51 (*s*, OH); 2.01 (*dt*, *J* = 13.2, 3.8, H_{exo}–C(3)); 1.78–1.57 (*m*, H–C(4), H_{exo}–C(5), 2 H–C(1′)); 1.49–1.26 (*m*, H_{endo}–C(3), 2 H–C(6)); 1.18 (*d*, *J* = 6.2, Me(3′)); 1.07 (*s*, Me(8)); 1.03–0.95 (*m*, H_{endo}–C(5)); 0.98 (*s*, Me(10)); 0.83 (*s*, Me(9)). CI-MS: 230 (48, $[M+18]^+$), 212 (88, $M^{+\bullet}$), 195 (100, $[M-OH)^+$). Anal. calc. for $C_{13}H_{24}O_2$ (212.33): C 73.54, H 11.39; found: C 73.81, H 11.31.

Data of **19b**: Colorless crystals from hexane/Et_2O. M.p. 57.2–57.8°. $[\alpha]_{21}^{D} = +16.2$ (*c* = 4.02, $CHCl_3$). ^{1}H-NMR (*ARX-300*)[1]): 4.19–4.10 (*m*, H–C(2′)); 3.72 (*s*, OH); 2.81 (*s*, OH); 2.06 (*dt*, *J* = 13.3, 3.3, H_{exo}–C(3)); 1.75–1.56 (*m*, H–C(4), H_{exo}–C(5), H_a–C(1′)); 1.46–1.33 (*m*, H_{endo}–C(3), 2 H–C(6), H_b–C(1′)); 1.18 (*d*, *J* = 6.2, Me(3′)); 1.08 (*s*, Me(8)); 0.98–0.87 (*m*, H_{endo}–C(5)); 0.83 (*s*, Me(9), Me(10)).

*(1*R,2S*)-2-[(1*R*)-2-Hydroxy-1-methylethyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol* (**20**). Following the *GP*, **4** (0.21 g, 1.01 mmol) in Et_2O (15 ml) was ozonized and then treated with $LiAlH_4$ (0.16 g, 4.21 mmol). The crude product was chromatographed (1.3 × 22 cm column, silica gel (8 g), hexane/Et_2O 5 : 1): 0.15 g (71%) of **20**. Colorless solid. M.p. 59–61° (hexane/Et_2O). $[\alpha]_{21}^{D} = -1.4$ (*c* = 4.00, $CHCl_3$). IR: 3626 (OH, free), 3466 (br., OH); 2940, 2873, 1480, 1450, 1383, 1150, 1106, 1073, 980, 960. ^{1}H-NMR (*DRX-250*)[1]): 4.05 (*dd*, *J* = 11.0, 3.3, H_a–C(1′)); 3.65 (*dd*, *J* = 11.0, 3.5, H_b–C(1′)); 2.57 (br. *s*, OH); 2.35 (*s*, OH); 2.14 (*dt*, *J* = 13.2, 3.8, H_{exo}–C(3)); 1.77–1.57 (*m*, H–C(4), H_{exo}–C(5), H–C(2′)); 1.54 (*d*, *J* = 13.2, H_{endo}–C(3)); 1.48–1.41 (*m*, 2 H–C(6)); 1.15 (*d*, *J* = 7.0, Me(3′)); 1.07 (*s*, Me(8)); 1.07–0.98 (*m*, H_{endo}–C(5)); 0.96 (*s*, Me(10)); 0.83 (*s*, Me(9)). EI-MS: 212 (3, $M^{+\bullet}$), 194 (0.6, $[M-H_2O]^{+\bullet}$), 180 (3), 171 (4), 153 (12), 121 (10), 110 (16), 109 (24), 108 (41), 96 (10), 95 (100), 93 (12), 83 (12), 81 (15), 69 (33), 67 (12), 59 (11), 55 (17), 43 (13), 41 (28). Anal. calc. for $C_{13}H_{24}O_2$ (212.33): C 73.54, H 11.39; found: C 73.69, H 11.18.

*(1*R,2S*)-2-[(1*S*)-2-Hydroxy-1-methylethyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol* (**21**). Following the *GP*, **5** (0.18 g, 0.86 mmol) in Et_2O (15 ml) was ozonized and then treated with $LiAlH_4$ (0.13 g, 3.42 mmol). The crude product was chromatographed (1.3 × 22 cm column, silica gel (8 g), hexane/Et_2O 5 : 1): 0.12 g (67%) of **21**. Colorless solid. M.p. 89–90° (hexane/Et_2O). $[\alpha]_{21}^{D} = +24.0$ (*c* = 4.00, $CHCl_3$). IR: 3627 (OH, free), 3463 (br., OH), 2933, 2876, 1480, 1450, 1390, 1366, 1106, 1076, 963. ^{1}H-NMR (*DRX-250*)[1]): 4.13 (*dt*, *J* = 10.6, 3.4, H_a–C(1′)); 3.63 (*ddd*, *J* = 10.6, 5.3, 2.3, H_b–C(1′)); 2.72 (*s*, OH–C(2)); 2.22 (*dd*, *J* = 5.3, 4.1, OH–C(1′)); 1.89 (*dt*, *J* = 13.2, 4.2, H_{exo}–C(3)); 1.80–1.64 (*m*, H–C(4), H_{exo}–C(5), H–C(2′)); 1.54–1.37 (*m*, 2 H–C(6)); 1.42 (*d*, *J* = 13.2, H_{endo}–C(3)); 1.17 (*d*, *J* = 7.0, Me(3′)); 1.06 (*s*, Me(8)); 1.03 (*s*, Me(10)); 1.04–0.95 (*m*, H_{endo}–C(5)); 0.84 (*s*, Me(9)). EI-MS: 212 (8, $M^{+\bullet}$), 194 (2, $[M-H_2O]^{+\bullet}$), 153 (17), 110 (15), 109 (17), 108 (43), 102 (9), 96 (8), 95 (100), 93 (12), 83 (9), 81 (11), 69 (20), 67 (9), 55 (14), 43 (12), 41 (23). Anal. calc. for $C_{13}H_{24}O_2$ (212.33): C 73.54, H 11.39; found: C 73.68, H 11.22.

*(1*R,2R*)- and (1*R,2S*)-2-(Hydroxymethyl)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol* (**22a** and **22b**, resp.). Following the *GP*, **6** (0.30 g, 1.66 mmol) in Et_2O (15 ml) was ozonized and then treated with $LiAlH_4$ (0.30 g; 7.89 mmol): 0.31 g of crude **22**/*endo*-fenchol 85 : 15 (by NMR). The crude product was chromatographed (1.3 × 43 cm column, silica gel (25 g), hexane/Et_2O 2 : 1): 0.05 g of *endo*-fenchol and 0.23 g (74%) of **22a** as colorless crystals (containing 8% of the *exo*-OH isomer **22b**). Recrystallization from hexane gave 0.07 g of pure *endo*-OH isomer **22a**.

Data of endo-*Fenchol (=(1*R,2R*)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-ol):* ^{1}H-NMR (300 MHz)[1]): 3.27 (*s*, H_{exo}–C(2)); 1.70–1.60 (*m*, H–C(4), H_{endo}–C(6), OH); 1.49–1.37 (*m*, 2 H–C(5), H_{syn}–C(7)); 1.15–1.07 (*m*, H_{anti}–C(7)); 1.09 (*s*, Me(10)); 1.05–0.98 (*m*, H_{exo}–C(6)); 0.99 (*s*, Me(8)); 0.86 (*s*, Me(9)). ^{13}C-NMR (75 MHz): 84.98 (C(2)); 49.05 (C(1)); 47.85 (C(4)); 40.90 (C(7)); 38.98 (C(3)); 30.61 (Me(8)); 25.99 (C(6)); 25.01 (C(5)); 20.07 (Me(9)); 19.35 (Me(10)).

Data of **22a**: M.p. 99–100° (hexane). $[\alpha]_{21}^{D} = -14.7$ (*c* = 4.01, $CHCl_3$). IR (CCl_4): 3626 (OH, free), 3450 (br., OH), 2943, 2863, 1466, 1450, 1383, 1363, 1116, 1083, 1050, 970. ^{1}H-NMR (*DRX-250*)[1]): 3.71 (*dd*, *J* = 10.8,

5.4, H_a–C(1′)); 3.61 (*dd*, *J* = 10.8, 4.6, H_b–C(1′)); 2.38 (br. *s*, OH); 2.11 (br. *s*, OH); 2.05–1.93 (*m*, H_{endo}–C(6)); 1.78–1.67 (*m*, H_{endo}–C(5)); 1.63–1.57 (*m*, H–C(4), H_{syn}–C(7)); 1.48–1.36 (*m*, H_{exo}–C(5)); 1.15–0.94 (*m*, H_{exo}–C(6), H_{anti}–C(7)); 1.09 (*s*, Me(10)); 1.02 (*s*, Me(8)); 0.97 (*s*, Me(9)). CI-MS: 202 (9, $[M+18]^+$), 184 (10, $M^{+\cdot}$), 167 (42, $[M-OH]^+$), 153 (25), 81 (100). Anal. calc. for $C_{11}H_{20}O_2$ (184.28): C 71.70, H 10.94; found: C 71.66, H 10.86.

*(1*R*,2*R*)-2-(2-Hydroxyethyl)-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol* (**23**). Following the *GP*, **7** (1.12 g; 5.76 mmol) in Et_2O (40 ml) was ozonized and then treated with $LiAlH_4$ (0.88 g; 23.16 mmol). Recrystallization (hexane) of the crude product gave 1.02 g (89%) of **23**. Colorless crystals. M.p. 70.6–71.3°. $[\alpha]_{21}^{D} = -23.5$ (*c* = 4.20, $CHCl_3$). IR: 3620 (OH, free), 3440 (br., OH), 2950, 2880, 1465, 1415, 1390, 1370, 1245, 1165, 1115, 1060, 1020, 850. ^{1}H-NMR (*AC-300*)[1]): 3.89–3.84 (*m*, 2 H–C(2′)); 2.58 (br. *s*, OH); 2.39 (br. *s*, OH); 1.93–1.78 (*m*, 2 H–C(1′), H_{endo}–C(6)); 1.74–1.62 (*m*, H–C(4), H_{endo}–C(5)); 1.57–1.52 (*m*, H_{syn}–C(7)); 1.48–1.37 (*m*, H_{exo}–C(5)); 1.11–1.00 (*m*, H_{exo}–C(6), H_{anti}–C(7)); 1.04 (*s*, Me(10)); 1.02 (*s*, Me(8)); 1.00 (*s*, Me(9)). CI-MS: 216 (3, $[M+18]^+$), 198 (38, $M^{+\cdot}$), 181 (100, $[M-OH]^+$). Anal. calc. for $C_{12}H_{22}O_2$ (198.31): C 72.68, H 11.18; found: C 72.71, H 11.14.

*(1*R*,2*R*)-2-[(2*S*)-2-Hydroxypropyl]-1,3,3-trimethylbicyclo[2.2.1]heptan-2-ol* (**24**). Following the *GP*, **8** (7.00 g, 33.61 mmol) in Et_2O (130 ml) was ozonized and then treated with $LiAlH_4$ (5.15 g, 135.53 mmol). The crude product was chromatographed (4.2 × 83 cm column, silica gel (500 g), hexane/Et_2O 2 : 1): 0.18 g of *endo*-fenchol and 5.60 g (79%) of **24** as colorless crystals. M.p. 68.8–69.9° (hexane). $[\alpha]_{21}^{D} = +5.8$ (*c* = 4.00, $CHCl_3$). IR: 3610 (OH, free), 3460 (br., OH), 2960, 2880, 1465, 1415, 1375, 1290, 1165, 1120, 1105, 1085, 1070, 995, 930, 840. ^{1}H-NMR (*DRX-250*)[1]): 4.19 (*m*, H–C(2′)); 2.77 (*s*, 2 OH); 1.93–1.52 (*m*, H–C(4), H_{endo}–C(5), H_{endo}–C(6), H_{syn}–C(7)); 1.82 (*dd*, *J* = 15.1, 9.3, H_a–C(1′)); 1.62 (*dd*, *J* = 15.2, 1.3, H_b–C(1′)); 1.50–1.36 (*m*, H_{exo}–C(5)); 1.20–0.91 (*m*, H_{exo}–C(6), H_{anti}–C(7)); 1.17 (*d*, *J* = 6.2, Me(3′)); 1.07 (*s*, Me(10)); 0.98 (*s*, Me(8)); 0.91 (*s*, Me(9)). CI-MS: 230 (46, $[M+18]^+$), 212 (100, $M^{+\cdot}$), 195 (82, $[M-OH]^+$). Anal. calc. for $C_{13}H_{24}O_2$ (212.33): C 73.54, H 11.39; found: C 73.35, H 11.19.

*(1*R*,2*S*)-2-(2,2-Dimethoxyethyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol* (**31**). According to a modified *GP*, **2** (1.00 g, 5.15 mmol) in MeOH/CH_2Cl_2 1:1 (30 ml) was ozonized and then treated with Me_2S (0.64 g, 10.30 mmol). Then the mixture was washed with H_2O and evaporated and the crude product chromatographed (2.3 × 36 cm column, silica gel (55 g), hexane/Et_2O 10 : 1): 0.81 g (65%) of **31**. Colorless oil. $[\alpha]_{21}^{D} = +0.7$ (*c* = 4.10, $CHCl_3$). IR: 3480 (br., OH), 2990, 2940, 2870, 2830, 1485, 1455, 1385, 1370, 1290, 1240, 1190, 1115, 1100, 1075, 1040, 990. ^{1}H-NMR (*AC-300*)[1]): 4.69 (*t*, *J* = 5.7, H–C(2′)); 3.61 (*s*, OH); 3.35 (*s*, 2 MeO); 2.03 (*dt*, *J* = 13.0, 3.7, H_{exo}–C(3)); 1.87 (*dd*, *J* = 14.3, 5.9, H_a–C(1′)); 1.80 (*dd*, *J* = 14.3, 5.5, H_b–C(1′)); 1.73–1.63 (*m*, H–C(4), H_{exo}–C(5)); 1.45–1.25 (*m*, 2 H–C(6)); 1.36 (*d*, *J* = 13.0, H_{endo}–C(3)); 1.06 (*s*, Me(8)); 1.01–0.90 (*m*, H_{endo}–C(5)); 0.83 (*s*, Me(10)); 0.82 (*s*, Me(9)). EI-MS: 242 (6, $M^{+\cdot}$), 225 (0.7, $[M-OH]^+$), 211 (26), 210 (100), 195 (98), 179 (29), 167 (25), 153 (16), 151 (21), 123 (9), 95 (21), 81 (18), 75 (58), 69 (24), 67 (20), 59 (14), 58 (34), 55 (41). CI-MS: 225 (3, $[M-OH]^+$), 210 (22), 196 (80), 193 (100), 170 (91). ESI-MS: 507 ($[2M+Na]^+$), 265 ($[M+Na]^+$). Anal. calc. for $C_{14}H_{26}O_3$ (242.36): C 69.38, H 10.81; found: C 69.15, H 10.71.

Ozonolysis of **2** *and Reduction with* $NaBH_4$*: Mixture of 2,2′-Oxybis[(1*R*,2*S*)-1,7,7-trimethylspiro[bicyclo[2.2.1]heptane-2,4′-[1,3,2]dioxaborinane]* (**32**) *and (1*R*,2*S*)-2′-Hydroxy-1,7,7-trimethylspiro[bicyclo[2.2.1]-heptane-2,4′-[1,3,2]dioxaborinane]* (**33**). According to a modified *GP*, **2** (1.00 g, 5.15 mmol) in Et_2O (40 ml) was ozonized and then treated with $NaBH_4$ (0.68 g, 17.98 mmol). The mixture was allowed to warm to r.t., stirred for 1.5 h at r.t., then hydrolyzed (2N aq. HCl), washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated: 1.15 g of **32**/**33** 1:2 (by ^{1}H-NMR). Colorless crystalline solid. ^{1}H-NMR (*DRX-250*, C_6D_6; only some important signals are given)[1]) 3.86, 3.78 (2*m*, CH_2O); 2.13, 2.03 (2*dt*, H_{exo}–C(3) 1.42, 1.34 (2*s*, Me(8)); 1.03, 0.95 (2*s*, Me(10)); 0.95, 0.92 (2*s*, Me(9)). ^{13}C-NMR (*AM-400*, C_6D_6)[1]): 82.63, 82.38 (C(2)); 60.32, 60.28 (CH_2CH_2O); 52.34 (C(1)); 49.62 (C(7)); 46.34, 46.23 (C(3)); 45.45, 45.43 (C(4)); 33.75, 33.66 (CH_2CH_2O); 30.16 (C(6)); 27.06, 27.02 (C(5)); 21.61 (Me(9)); 21.22, 21.18 (Me(8)); 10.49 (Me(10)). EI-MS: 430 (36, $M^{+\cdot}$ of **32**), 223 (57, $[M-1]^+$ of **33**). CI-MS: 448 (60, $[M+18]^+$ of **32**), 242 (100, $[M+18]^+$ of **33**). ESI-MS: 499 ($[M+3\,Na]^+$ of **32**), 247 ($[M+Na]^+$ of **33**).

Hydrolysis of Products **32**/**33**. To a stirred soln. of **32**/**33** (0.70 g) in Et_2O (30 ml), conc. aq. HCl soln. (10 ml) was introduced. The mixture was vigorously stirred for 1.5 h and diluted with H_2O (30 ml). After separation, the aq. layer was extracted with Et_2O (2 × 20 ml), the combined Et_2O phase washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated, and the crude product (0.57 g) chromatographed (2 × 40 cm column, silica gel (36 g), hexane/Et_2O 10 : 1): 0.33 g of **35** and 0.12 g of **36** as colorless oils.

Data of 2-(1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene)ethanol (**35**). ^{1}H-NMR (*AC-300*)[1]): 5.25 (*tt*, *J* = 7.9, 2.4, H–C(1′)); 4.03 (*dd*, *J* = 10.9, 8.1, H_a–C(2′)); 3.97 (*dd*, *J* = 10.9, 7.8, H_b–C(2′)); 2.37 (*dq*, *J* = 16.5, 3.0,

H_{exo}–C(3)); 1.85 (*dd*, *J* = 16.5, 2.1, H_{endo}–C(3)); 1.76–1.62 (*m*, H–C(4), H_{exo}–C(5)); 1.60–1.53 (*m*, H_{endo}–C(5)); 1.22-1.06 (*m*, 2 H–C(6)); 0.86 (*s*, Me(10)); 0.83 (*s*, Me(9)); 0.66 (*s*, Me(8)). ^{13}C-NMR (*XL-200*; tentative assignments are marked with asterisks)[1]): 157.30 (C(2)); 112.45 (C(1′)); 51.47 (C(1)); 47.69 (C(7)); 44.40 (C(4)); 42.29 (C(2′)); 34.50* (C(3)); 33.91* (C(6)); 27.76 (C(5)); 19.51* (Me(8)); 18.79* (Me(9)); 12.53 (Me(10)). CI-MS: 180 (8, $M^{+\cdot}$), 163 (100, $[M-OH]^+$). Anal. calc. for $C_{12}H_{20}O$ (180.29): C 79.94, H 11.18; found: C 79.99, H 11.24.

*Hexahydro-7,7,7a-trimethyl-3a,6-methano-3*H*-[1]benzofuran* (**36**). ^{1}H-NMR (*AC-300*): 4.00–3.86 (*m*, 2 H–C(2)); 1.97–1.76 (*m*, 2 H–C(3), H_{syn}–C(8)); 1.69–1.25 (*m*, H–C(6), 2 H–C(4), 2 H–C(5)); 1.01 (*s*, Me–C(7a)); 0.97 overlapped (*d*, H_{anti}–C(8)); 0.95 (*s*, Me_{β}–C(7)); 0.94 (*s*, 3 Me_{α}–C(7)). ^{13}C-NMR (*XL-200*): 90.68 (C(7a)); 66.37 (C(2)); 58.96 (C(3a)); 49.70 (C(6)); 44.87 (C(7)); 39.23 (C(8)); 28.68 (C(4)); 25.82 (C(3)); 24.81 (Me_{β}–C(7)); 23.92 (C(5)); 23.19 (Me_{α}–C(7)); 17.03 (*Me*–C(7a)). CI-MS: 180 (21, $M^{+\cdot}$), 163 (100, $[M-OH]^+$). Anal. calc. for $C_{12}H_{20}O$ (180.29): C 79.94, H 11.18; found: C 80.01, H 11.23.

*(1*R,2S*)-1,7,7-Trimethyl-2-[(1,2,4-trioxolan-3-yl)methyl]bicyclo[2.2.1]heptan-2-ol* (**37a**/**b**; diastereoisomer mixture). Following the *GP*, **2** (2.50 g, 12.87 mmol) in Et_2O (40 ml) was ozonized. The mixture was warmed to r.t., washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated. The crude product (diastereoisomer mixture **37a**/**37b** 71:29 by NMR; it may contain up to 4% of aldehyde **10**) was chromatographed (3.2 × 76 cm column, silica gel (250 g), hexane/Et_2O 5:1): 1.66 g of **37a**, 0.41 g of mixed fractions, and 0.26 g of **37b** as colorless oils. Total yield of **37**: 2.33 g (75%). IR (Film): 3540 (br., OH), 2960, 2880, 1490, 1455, 1430, 1390, 1370, 1080. CI-MS: 260 (15, $[M+18]^+$), 242 (10, $M^{+\cdot}$), 225 (74, $[M-OH]^+$), 179 (100). ESI-MS: 281 ($[M+K]^+$), 265 ($[M+Na]^+$).

Data of **37a**: $[\alpha]_{21}^{D} = +19.0$ (*c* = 4.63, $CHCl_3$). ^{1}H-NMR (*AC-300*; tentative assignments are marked with asterisks)[1]): 5.43 (*t*, *J* = 5.2, H–C(3′)); 5.18 (*s*, H_a–C(5′)); 5.08 (*s*, H_b–C(5′)); 2.08 (*s*, OH); 2.07 (*dt*, *J* = 13.4, 3.7, H_{exo}–C(3)); 2.02 (*dd*, *J* = 14.4, 4.8, H_a–C(6′)); 1.92 (*dd*, *J* = 14.4, 5.6, H_b–C(6′)); 1.77–1.68 (*m*, H–C(4), H_{exo}–C(5)); 1.52 (*d*, *J* = 13.4, H_{endo}–C(3)); 1.47–1.40* (*m*, H_{endo}–C(6)); 1.35–1.25* (*m*, H_{exo}–C(6)); 1.09 (*s*, Me(8)); 1.09–0.98 (*m*, H_{endo}–C(5)); 0.88 (*s*, Me(10)); 0.86 (*s*, Me(9)).

Data of **37b**: ^{1}H-NMR (*AC-300*)[1]): 5.40 (*t*, *J* = 4.9, H–C(3′)); 5.22 (*s*, H_a–C(5′)); 5.06 (*s*, H_b–C(5′)); 2.06 (*dt*, *J* = 13.2, 3.7, H_{exo}–C(3)); 1.99 (*s*, OH); 2.00–1.87 (*m*, 2 H–C(6′)); 1.78–1.66 (*m*, H–C(4), H_{exo}–C(5)); 1.49 (*d*, *J* = 13.2, H_{endo}–C(3)); 1.51–1.25 (*m*, 2 H–C(6)); 1.10 (*s*, Me(8)); 1.06–0.96 (*m*, H_{endo}–C(5)); 0.88 (*s*, Me(10)); 0.86 (*s*, Me(9)).

*(1*R,2S*)-1,7,7-Trimethyl-2-[(3-methyl-1,2,4-trioxolan-3-yl)methyl]bicyclo[2.2.1]heptan-2-ol* (**38a**/**b**; diastereoisomer mixture). Following the *GP*, **3** (0.53 g, 2.54 mmol) in Et_2O (20 ml) was ozonized. The mixture was warmed to r.t., washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated. The crude product (diastereoisomer mixture **38a**/**38b** 3:1 by ^{1}H-NMR) was chromatographed (2 × 45 cm column, silica gel (52 g), hexane/Et_2O 10:1): 0.45 g (69%) of pure **38** (diastereoisomer mixture). IR (Film): 3580 (br., OH), 2960, 2880, 1485, 1450, 1390, 1380, 1335, 1220, 1195, 1105, 1085, 1060, 970. ^{1}H-NMR (*ARX-300*)[1]): 5.13 (*s*, H_a–C(5′), **38a**); 5.09 (*s*, H_a–C(5′), **38b**); 5.08 (*s*, H_b–C(5′), **38a**); 5.03 (*s*, H_b–C(5′), **38b**); 2.75 (*s*, OH, **38a**); 2.39 (*s*, OH, **38b**); 2.10–1.94 (*m*, H_{exo}–C(3)); 2.03 (*d*, *J* = 14.3, H_a–C(6′)); 1.88 (*d*, *J* = 14.3, H_b–C(6′)); 1.69–1.55 (*m*, H_{endo}–C(3), H–C(4), H_{exo}–C(5)); 1.53 (*s*, Me(7′)); 1.34–1.24 (*m*, 2 H–C(6)); 1.05 (*s*, Me(8)); 0.99–0.88 (*m*, H_{endo}–C(5)); 0.80 (*s*, Me(10)); 0.79 (*s*, Me(9)). ^{17}O-NMR (81 MHz): 305.5, 271.8 (O(1), O(2)); 103.4 (O(4)); 45.8 (OH). ESI-MS: 535 ($[2M+Na]^+$), 279 ($[M+Na]^+$). Anal. calc. for $C_{14}H_{24}O_4$ (256.34): C 65.60, H 9.44; found: C 65.90, H 9.47.

*(1*R,2R*)-1,3,3-Trimethyl-2-[(1,2,4-trioxolan-3-yl)methyl]bicyclo[2.2.1]heptan-2-ol* (**39a/b** diastereoisomer mixture). Following the *GP*, **7** (2.00 g, 10.29 mmol) in Et_2O (40 ml) was ozonized. The mixture was warmed to r.t., washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated. The crude product (diastereoisomer mixture **39a**/**39b** 47:53; it may contain up to 10% of aldehyde **15**) was chromatographed (3.2 × 76 cm column, silica gel (235 g), hexane/Et_2O 5:1): 0.32 g of **39a**, 0.97 g of mixed fractions, and 0.43 g of **39b** as colorless oils. Total yield of **39**: 1.72 g (69%). IR (Film): 3520 (br., OH), 2950, 2880, 1465, 1425, 1390, 1375, 1115, 1090, 1065, 1015, 965. ESI-MS: 281 ($[M+K]^+$).

Data of **39a**: $[\alpha]_{21}^{D} = +3.0$ (*c* = 4.37, $CHCl_3$). IR: 3590 (br., OH), 2960, 2880, 1465, 1430, 1390, 1380, 1240, 1165, 1135, 1115, 1095, 1065, 1015, 960. ^{1}H-NMR (*AC-300*)[1]): 5.40 (*dd*, *J* = 5.0, 3.6, H–C(3′)); 5.17 (*s*, H_a–C(5′)); 5.06 (*s*, H_b–C(5′)); 2.16 (*dd*, *J* = 15.4, 3.6, H_a–C(6′)); 1.95 (*dd*, *J* = 15.4, 5.0, H_b–C(6′)); 2.01–1.91 (*m*, H_{endo}–C(6)); 1.76–1.65 (*m*, H–C(4), H_{endo}–C(5)); 1.71 (*s*, OH); 1.58–1.54 (*m*, H_{syn}–C(7)); 1.49–1.37 (*m*, H_{exo}–C(5)); 1.15–0.98 (*m*, H_{exo}–C(6), H_{anti}–C(7)); 1.05 (*s*, Me(10)); 1.03 (*s*, Me(8)); 0.98 (*s*, Me(9)).

Data of **39b**: $[\alpha]_{21}^{D} = -4.0$ (*c* = 4.47, $CHCl_3$). ^{1}H-NMR (*AC-300*)[1]): 5.44 (*dd*, *J* = 6.0, 3.1, H–C(3′)); 5.22 (*s*, H_a–C(5′)); 5.06 (*s*, H_b–C(5′)); 2.21 (*s*, OH); 2.09 (*dd*, *J* = 15.0, 3.1, H_a–C(6′)); 2.06–1.93 (*m*, H_{endo}–C(6));

1.92 (*dd*, *J* = 15.0, 6.0, H_b–C(6′)); 1.76–1.65 (*m*, H–C(4), H_{endo}–C(5)); 1.58–1.54 (*m*, H_{syn}–C(7)); 1.48–1.37 (*m*, H_{exo}–C(5)); 1.15–0.98 (*m*, H_{exo}–C(6), H_{anti}–C(7)); 1.04 (*s*, Me(10)); 1.03 (*s*, Me(8)); 0.98 (*s*, Me(9)).

*(1*R,*2*R*)- and (1*R,*2*S*)-1,3,3-Trimethyl-2-[(3-methyl-1,2,4-trioxolan-3-yl)methyl]bicyclo[2.2.1]heptan-2-ol* (**40a/b** and **40c/d** diastereoisomer mixtures). Following the *GP*, **8** (0.62 g, 2.98 mmol) in Et_2O (20 ml) was ozonized. The mixture was warmed to r.t., washed with 5% aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated. The crude product was chromatographed (2.0 × 45 cm column, silica gel (52 g), hexane/Et_2O 15 : 1): 0.06 g (8%) of **40b/40c** 66 : 34 (by NMR), 0.06 g (8%) of **40b/40c/40d** 29 : 11 : 60 (by NMR), 0.12 g (16%) of **40a** (single diastereoisomer), 0.03 g (5%) of **16b**, and 0.18 g (29%) of **16a**.

Data of **40a**: ^{1}H-NMR (*ARX-300*)[1]): 5.17 (*s*, H_a–C(5′)); 5.15 (*s*, H_b–C(5′)); 2.60 (*s*, OH); 2.32 (*d*, *J* = 15.2, H_a–C(6′)); 2.18–2.08 (*m*, H_{endo}–C(6)); 2.11 (*d*, *J* = 15.2, H_b–C(6′)); 1.75–1.63 (*m*, H–C(4), H_{endo}–C(5)); 1.55 (*s*, Me(7′)); 1.48–1.34 (*m*, H_{exo}–C(5), H_{syn}–C(7)); 1.11–0.94 (*m*, H_{exo}–C(6), H_{anti}–C(7)); 1.07 (*s*, Me(10)); 1.02 (*s*, Me(8)); 0.99 (*s*, Me(9)). EI-MS: 210 (5, $[M - CH_2OO]^{+\cdot}$), 192 (10), 128 (35), 81 (100), 69 (48), ESI-MS: 279 ($[M + Na]^+$).

Data of **40b/40c**. ^{1}H-NMR (*ARX-300*, selected signals)[1]): 5.27 (*s*, H_a–C(5′), **40b**); 5.24 (*s*, H_a–C(5′), **40c**); 5.17 (*s*, H_b–C(5′), **40b**); 5.16 (*s*, H_b–C(5′), **40c**); 1.55 (*s*, Me(7′), **40c**); 1.52 (*s*, Me(7′), **40b**); 1.11, 1.06, 1.04, 1.02, 0.99 (overlapped *s*, Me(8), Me(9), Me(10), **40b/40c**). ESI-MS: 279 ($[M + Na]^+$).

Data of **40b/40c/40d**: ^{1}H-NMR (*ARX-300*; selected signals)[1]): 5.27 (*s*, H_a–C(5′), **40b**); 5.24 (*s*, H_a–C(5′), **40c**); 5.18 (*s*, H_a–C(5′), **40d**); 5.17 (*s*, H_b–C(5′), **40b**); 5.16 (*s*, H_b–C(5′), **40c**); 5.11 (*s*, H_b–C(5′), **40d**); 1.58 (*s*, Me(7′), **40d**); 1.54 (*s*, Me(7′), **40c**); 1.52 (*s*, Me(7′), **40b**); 1.10, 1.05, 1.03, 1.01, 0.99, 0.98 (overlapped *s*, Me(8), Me(9), Me(10), **40b/40c/40d**). ESI-MS: 535 ($[2M + Na]^+$), 279 ($[M + Na]^+$).

REFERENCES

[1] D. G. Lee, T. Chen, in 'Comprehensive Organic Chemistry', Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, Vol. 7, p. 541.

[2] J. F. Callahan, K. A. Newlander, H. G. Bryan, W. F. Huffman, M. L. Moore, N. C. F. Yim, *J. Org. Chem.* **1988**, *53*, 1527.

[3] R. A. Bartsch, B. R. Cho, M. J. Pugia, *J. Org. Chem.* **1987**, *52*, 5492.

[4] G. N. Walker, *J. Am. Chem. Soc.* **1957**, *79*, 3508.

[5] C. R. Bertozzi, M. D. Bednarski, *Tetrahedron Lett.* **1992**, *33*, 3109; M. Isobe, H. Iio, T. Kawai, T. Goto, *ibid.* **1977**, *8*, 703.

[6] a) Y.-S. Hon, L. Lu, S.-Y. Li, *J. Chem. Soc., Chem. Commun.* **1990**, 1627; b) Y.-S. Hon, K.-P. Chu, P.-C. Hong, L. Lu, *Synth. Commun.* **1992**, *22*, 429; c) Y.-S. Hon, S.-W. Lin, Y.-J. Cen, *ibid.* **1993**, *23*, 1543; d) Y.-S. Hon, L. Lu, *Tetrahedron Lett.* **1993**, *34*, 5309; e) Y.-S. Hon, Y.-L. Yan, *ibid.* **1993**, *34*, 6591; f) Y.-S. Hon, J.-L. Yan, *ibid.* **1994**, *35*, 1743; g) Y.-S. Hon, F.-J. Chang, L. Lu, *J. Chem. Soc., Chem. Commun.* **1994**, 2041; h) Y.-S. Hon, L. Lu, *Tetrahedron* **1995**, *51*, 7937.

[7] R. Criegee, *Angew. Chem.* **1975**, *87*, 765.

[8] a) H. Mimoun, *Angew. Chem.* **1982**, *94*, 750; b) R. L. Kuczkowski, *Acc. Chem. Res.* **1983**, *16*, 42.

[9] B. J. Wojciechowski, C.-Y. Chiang, R. L. Kuczkowski, *J. Org. Chem.* **1990**, *55*, 1120.

[10] A. Rieche, R. Meister, H. Sauthoff, *Liebigs Ann. Chem.* **1942**, *553*, 246.

[11] a) J. Lauterwein, K. Griesbaum, P. Krieger-Beck, V. Ball, K. Schlindwein, *J. Chem. Soc., Chem. Commun.* **1991**, 816; b) K. Griesbaum, K. Schlindwein, M. Hilss, *Chem. Ber.* **1993**, *126*, 1843; c) F. Hock, V. Ball, Y. Dong, S.-H. Gutsche, M. Hilss, K. Schlindwein, K. Griesbaum, *J. Magn. Res. Ser. A* **1994**, *111*, 150.

[12] V. Dimitrov, S. Bratovanov, S. Simova, K. Kostova, *Tetrahedron Lett.* **1994**, *35*, 6713; V. Dimitrov, S. Simova, K. Kostova, *Tetrahedron* **1996**, *52*, 1699.

[13] V. Dimitrov, K. Kostova, M. Hesse, *Tetrahedron: Asymmetry* **1994**, *5*, 1891.

[14] a) V. Dimitrov, M. Genov, S. Simova, A. Linden, *J. Organomet. Chem.* **1996**, *525*, 213; b) V. Dimitrov, K. Kostova, M. Genov, *Tetrahedron Lett.* **1996**, *37*, 6887; c) V. Dimitrov, I. Philipova, S. Simova, *Tetrahedron: Asymmetry* **1996**, *7*, 1493; d) M. Genov, K. Kostova, V. Dimitrov, *ibid.* **1997**, *8*, 1869.

[15] D. Gupta, R. Soman, S. Dev, *Tetrahedron* **1982**, *38*, 3013.

[16] M. Pirrot, M. El Idrissi, M. Santelli, *Tetrahedron Lett.* **1989**, *30*, 461.

[17] Y. Ushigoe, S. Tanaka, M. Nojima, K. J. McCullough, *Tetrahedron Lett.* **1994**, *35*, 9741. K. Teshima, S. Kawamura, Y. Ushigoe, M. Nojima, K. J. McCullough, *J. Org. Chem.* **1995**, *60*, 4755.

[18] S. Berger, S. Braun, H.-O. Kalinowski, 'NMR-Spektroskopie von Nichtmetallen, Bd. 1, Grundlagen, ^{17}O-, ^{33}S- und ^{129}Xe-NMR-Spektroskopie', Georg Thieme Verlag, New York, 1992.

Received June 3, 1999