149. Highly Diastereoselective Aldol Reaction of Bicyclo[3.2.1]oct-6-en-3-ones and 8-Oxabicyclo[3.2.1]oct-6-en-3-ones. (*E*)-Selective Conversion into α-Alkylidene Ketones

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(22.I.93)

The bicyclic ketones **1–6** entered into diastereoselective (> 95% d.e.) aldol reactions with a variety of aldehydes (*Scheme 1* and *Table 1*). A representative series of aldols was converted (*E*)-selectively into α,β-unsaturated ketones by *i*) spontaneous base-promoted dehydration (*Scheme 1* and *Table 2*) and also by *ii*) conversion into brosylate and base-mediated elimination with lithium diisopropylamide/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (LDA/TMEDA; *Scheme 2*). The simple α-methylidene ketones **17a** and **18a** were obtained *via* oxidation of the phenylselenides **19** and **20**, respectively (*Scheme 4*). The tertiary aldol **27** was synthesized best by treatment of 1,3-diketone **26** with Me_4Zr (*Table 4*). In this fashion, the facile *retro*-aldol reaction of **27** was suppressed effectively.

In context with a synthesis of patchouli analogs, we observed that the base-mediated reaction of 2,2,4-trimethylbicyclo[3.2.1]oct-6-en-3-one (**1**) with acetaldehyde afforded just one of four possible diastereoisomers. While the *exo*-selectivity of the reaction is not surprising, the defined configuration at the newly introduced C-atom (C(1′)) in the product was unexpected. We, therefore, investigated the reaction in some detail using a series of representative aldehydes and the two types of [3.2.1]bicyclic ketones **1–3** and **4–6** (see *Scheme 1* and *Table 1*).

Table 1. *Aldol Reactions of [3.2.1]Bicyclic Ketones*

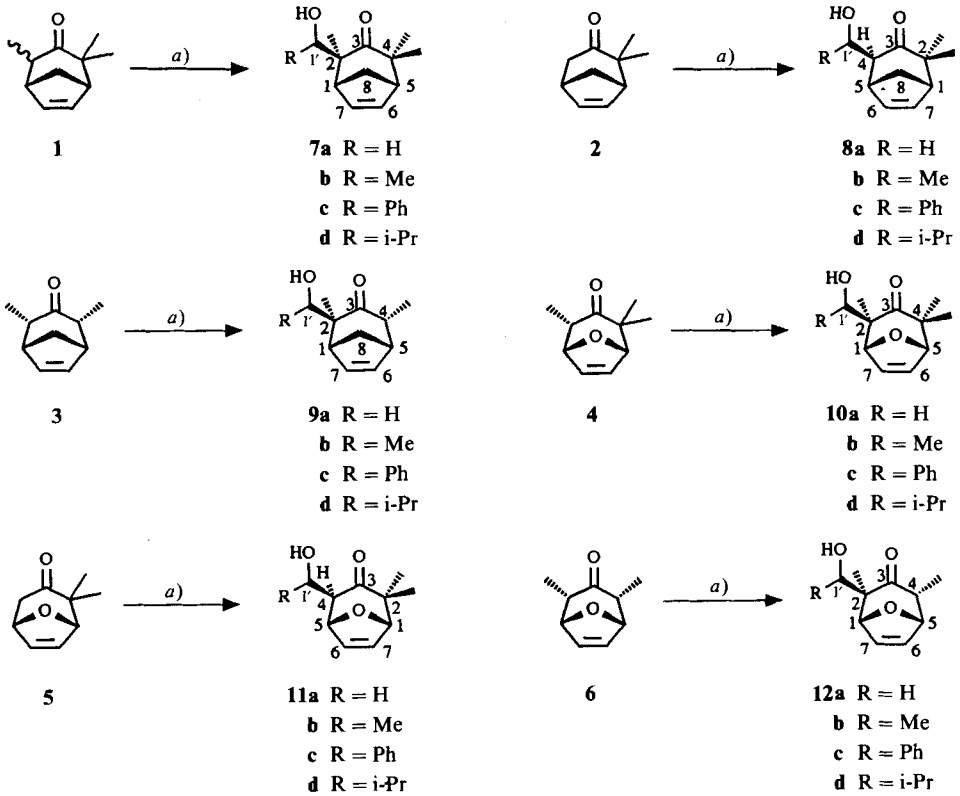
Ketone	R in aldehyde RCHO	Reaction conditions[a])	Product	Yield [%]
1	H	−15°, 15 min	**7a**	43
	Me	−15°, 30 min	**b**	83
	Ph	−10°, 1 h	**c**	54
	i-Pr	r.t., 2 h	**d**	24
2	H	−20°, 30 min	**8a**	0
	Me	−20°, 30 min	**b**	74
	Ph	0°, 30 min	**c**	49
	i-Pr	r.t., 2.5 h	**d**	0[b])
3	H	−20°, 15 min	**9a**	16
	Me	−20°, 20 min	**b**	70
	Ph	−10°, 20 min	**c**	41
	i-Pr	0°, 30 min	**d**	41
4	H	−10°, 15 min	**10a**	61
	Me	−15°, 10 min	**b**	91
	Ph	−10°, 30 min	**c**	59
	i-Pr	0°, 1 h	**d**	24

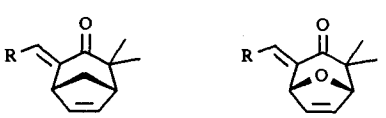
Table 1 (cont.)

Ketone	R in aldehyde RCHO	Reaction conditions[a])	Product	Yield [%]
5	H	−30°, 30 min	**11a**	0
	Me	−40°, 15 min	**b**	84
	Ph	−30°, 30 min	**c**	67
	i-Pr	−30°, 30 min	**d**	46
6	H	−10°, 30 min	**12a**	0
	Me	−40°, 15 min	**b**	76
	Ph	−30°, 30 min	**c**	55
	i-Pr	−30°, 30 min	**d**	27

[a]) Lithium diisopropylamide (LDA; 1.1 equiv.), bicyclic ketone (1 equiv.), and RCHO (5 equiv.) in THF.
[b]) Only dehydration product isolated (see *Table 2*).

Scheme 1. *Aldol Reactions of [3.2.1]Bicyclic Ketones*[a])





a) LDA, RCHO, THF.

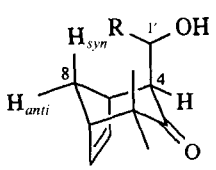
[a]) Only one enantiomer shown.
For yields of **7**–**12**, see *Table 1*;
for yields of **17** and **18**, see *Table 2*.

Results and Discussion. – *Aldol Condensation.* Our experimental data of the aldol condensations of ketones **1**–**6** given in *Table 1* can be summarized as follows. *i*) Oxabicyclic ketones **4**–**6** reacted with aldehydes at lower temperature and more readily than the corresponding carbocyclic analogs **1**–**3**. Apparently, the oxabicycles are less rigid and, in addition, sterically more accessible than the carbocycles. *ii*) For the symmetrically dimethyl-substituted ketones **3** and **6** (steric factor) and the geminally dimethyl-substituted ketones **2** and **5** (more acidic), the reaction temperature was lower than for the trimethyl-substituted **1** and **4**. *iii*) Pivalaldehyde failed to react with **1**–**6**. *iv*) The reaction with isobutyraldehyde required a relatively high temperature. Bicyclic ketone **2** and isobutyraldehyde furnished dehydration product **17d** only (*cf.* below, *Table 2*). *v*) Formaldehyde reacted selectively, provided that the ketone was trimethyl-substituted (**1** → **7a**, **4** → **10a**) or the bicyclic ketone was not too reactive (**3** → **9a** (16%); **6** ↛ **12a**). Bicyclic ketones **2** and **5** containing a CH_2 group in α position to the carbonyl group failed to give 1:1 adducts (**2** ↛ **8a**; **5** ↛ **11a**). *vi*) Along the series of aldehydes MeCHO > PhCHO > Me_2CHCHO, the yield of aldol adduct decreased.

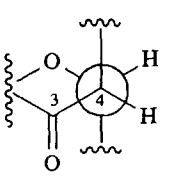
The aldol reactions of *Scheme 1* were highly diastereoselective (d.e. > 95% by ^{1}H-NMR). Only **7d** (from **1**) and **11b** (from **5**) were formed with a d.e. > 90%. In fact, of all bicyclic ketones investigated, ketone **1** was least reactive. Combination with isobutyraldehyde to **7d** required 2 h at r.t. In contrast, bicyclic ketone **5** was the most reactive ketone, reacting readily at −78° with acetaldehyde in low yield, acetaldol (MeCHOH·CH_2CHO) being the major product. However, at −40° the desired crossed aldol **11b** was isolated in 84% yield (d.e. > 90%). The preparation of aldols **7b**, **10b**, and **11b** was also scaled up (80–150 mmol) without a drop in yield. The structures of the products **7**–**12** were established by spectroscopic means.

The *exo*-configuration of the hydroxyalkyl group in hydroxy ketones **7**–**12** was established as follows. Trimethylated aldols **7a**–**d** and **10a**–**d** were identified by the ^{1}H-NMR chemical shift of the Me *s*'s. Only 1 Me signal appeared downfield, corresponding to the *axial* Me group at C(4)[1]. For NOE experiments, aldol **7b** was not suitable, because the *s*'s of the 2 equatorial Me groups were too close together. However, its brosylate **13b** (see below, *Table 3*) allowed a clear assignment of the *exo*-configuration at C(2). Double irradiation of the equatorial Me–C(2) and Me–C(4) of **13b** gave two NOE's with H–C(6) (3.2%) and H–C(7) (3.7%), thus establishing the vicinity of the corresponding protons. Double irradiation of the axial Me–C(4) confirmed the assignment (NOE at H_{syn}–C(8) and H–C(1′)). Double irradiation of H–C(6), H–C(7), H_{syn}–C(8) and H–C(1′) did not increase the intensity of the signals of the 3 Me groups at C(2) and C(4); relaxation effects of the Me protons are probably responsible. Oxacycles **10a**–**d** were assigned analogously (see *Exper. Part* and *Table 3* for brosylate **15b**).

The equatorial position of H–C(4) in carbocycles **8b**, **c** was assigned by ^4J coupling. For example, H–C(4) and H_{anti}–C(8) showed $^4J = 2$ Hz (W coupling). For oxabicycles **11b**–**d**, $^3J(4,5) \approx 0$ Hz, because of the presence of the electronegative ether O-atom, which is oriented antiperiplanar to H–C(4)[2]. Had the hydroxyalkyl group in **11b**–**d**



8b,c



11b–d

[1]) In aldols **9a**–**d** and **12b**–**d**, both Me–C(2) and Me–C(4) appeared highfield. Thus, the equatorial position of Me–C(2) is maintained.

[2]) In aldols **7a**–**d**, **9a**–**d**, **10a**–**d**, and **12b**–**d**, C(2) is attached to C(1′). For aldols **8b**, **c** and **11b**–**d**, the analogous C–C bond must be numbered as C(4)–C(1′) (see *Scheme 1*).

been in an equatorial position, $^3J(4,5)$ should be > 4 Hz, as observed for **12b–d** (see *Exper. Part*). In support of this assignment, oxabicyclic brosylate **16b** (from **11b**) showed NOE's corresponding to **15b** (from **10b**; see below, *Table 3*).

The facile *retro*-aldol reaction of all compounds **7–12** is in accord with the axial position of the hydroxyalkyl group. In this fashion, overlap of the carbonyl π system and the C(2)–C(1′) σ-bond that has to be cleaved, is optimized. Consistently, the MS molecular ions of the aldols were hard to detect. Only FAB measurements showed the $[M + H]^+$ peaks.

α-Alkylidene-Substituted [3.2.1]Bicyclic Ketones and Configuration of the Aldols at C(1′). α,β-Unsaturated enones were formed as by-products of the aldol reaction in poor yield (see **17b–d** and **18b–d** in *Scheme 1, Table 2,* and *Table 1, Footnote b*). Dehydration was facile for 1′-phenyl- and 1′-isopropyl-substituted aldols, suggesting *Saytzeff*-type behavior and release of steric strain in forming the corresponding substituted enones.

Table 2. *Dehydration Products of the Aldol Reaction*

Ketone	R in aldehyde RCHO	Reaction conditions[a])	Product[b])	Yield [%]
2	Me	−20°, 30 min	**17b**	5
	Ph	0°, 30 min	**c**	17
	i-Pr	r.t., 2.5 h	**d**	9
5	Me	−40°, 15 min	**18b**	3
	Ph	−30°, 30 min	**c**	8
	i-Pr	−30°, 30 min	**d**	11

[a]) LDA (1.1 equiv.), bicyclic ketone (1 equiv.), and RCHO (5 equiv.) in THF.

[b]) (*E*)-Configuration assigned by analogy to **18b** (NOE). MMX calculations suggest that (*E*)-configurated enones are more stable than (*Z*)-isomers by *ca.* 3 kcal/mol.

Table 3. *Brosylates from Aldols*

Aldol	**7b**	**8b**	**8c**	**10b**	**11b**	**11c**
Brosylate[a])	**13b**	**14b**	**14c**	**15b**	**16b**	**16c**
Yield [%]	54	72	0[b])	68	76	0[b])

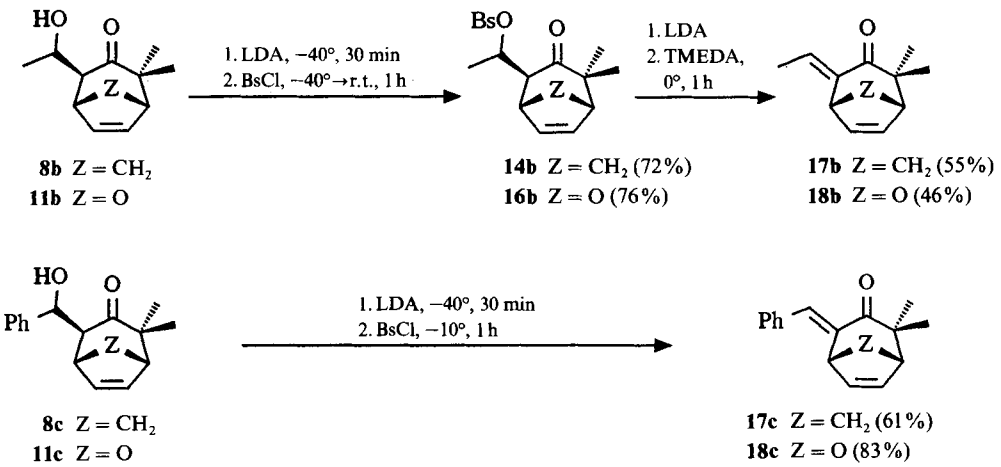
[a]) 4-$BrC_6H_4SO_3$ instead of OH in the *Formulae* **7b**, **8b**, **c**, **10b**, and **11b**, **c**, respectively.

[b]) Not isolated. Instead, an α-alkylidene derivative is formed spontaneously (**14c** → **17c**, **16c** → **18c**; see *Scheme 2*).

To develop a convenient route to this class of compounds, we also converted the aldols into their brosylates (see *Table 3*) and tried base-induced eliminations. Thus, aldols **8b** and **11b** yielded, *via* **14b** and **16b**, the enones **17b** and **18b**, respectively (*Scheme 2*). As expected, the brosylates of 1-phenylethanol derivatives **8c** and **11c** could not be isolated [1] and produced the enones **17c** and **18c**, respectively, directly (*Scheme 2*). The directed synthesis *via* brosylate and spontaneous dehydration produced identical enones in each case. The configuration of the aldol (and derived brosylate) at C(1′) is either (*R*) or (*S*) (*Scheme 3*)[3]). The proton in α position to C=O which must be abstracted is acidified by

[3]) Attempts to determine the X-ray crystal structure of **10b** failed because of crystal twinning (*D. Schomburg*, unpublished experiments). A recent X-ray diffractometric analysis of the aldol adduct of benzaldehyde and tropinone revealed axial attack and stereoselectivity analogous to the formation of (4*R*,1′*S*)-**16b** [2].

Scheme 2. *Enones from β-(Brosyloxy)ketones*



8b Z = CH_2
11b Z = O

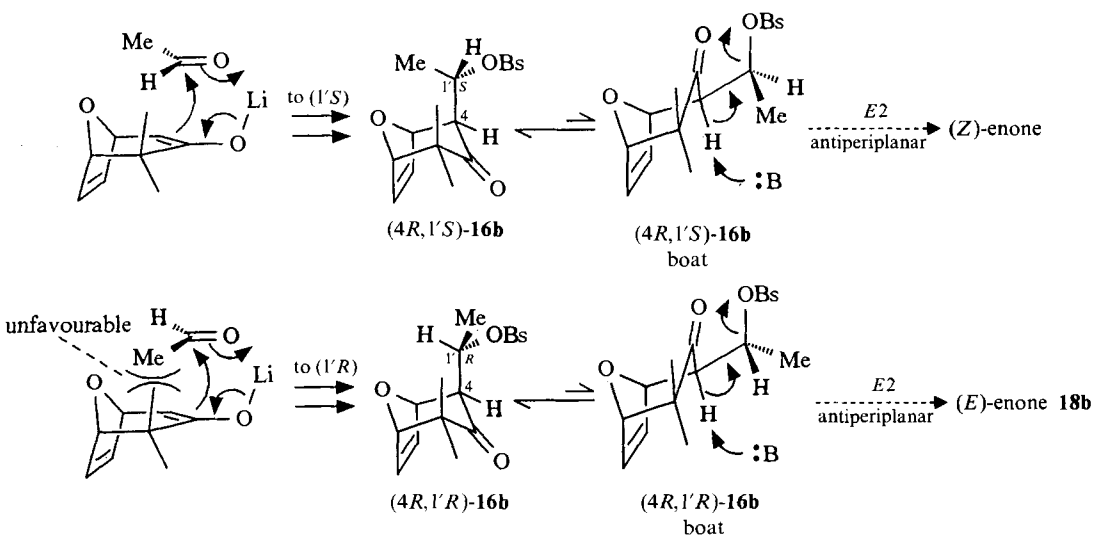
14b Z = CH_2 (72%)
16b Z = O (76%)

17b Z = CH_2 (55%)
18b Z = O (46%)

8c Z = CH_2
11c Z = O

17c Z = CH_2 (61%)
18c Z = O (83%)

Scheme 3. *(1′R) vs. (1′S) Transition States*[2])



(4*R*,1′*S*)-**16b**

(4*R*,1′*S*)-**16b** boat

(4*R*,1′*R*)-**16b**

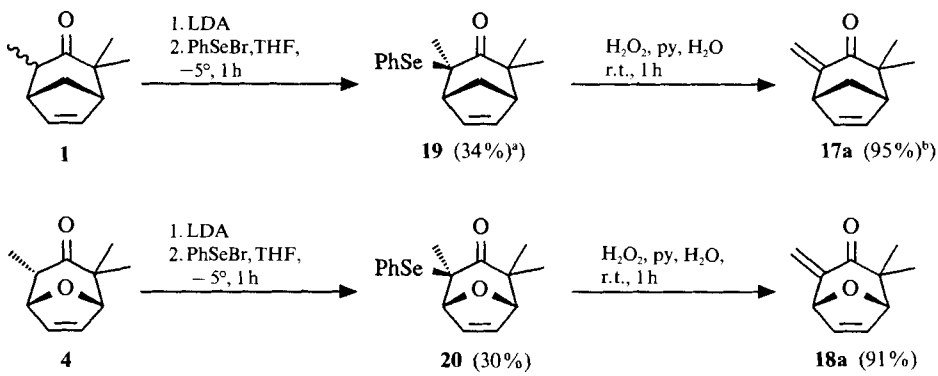
(4*R*,1′*R*)-**16b** boat

leakage of the six-membered ring into the boat conformation (for chair-boat equilibria and boat atropisomers in structurally related systems, see [3]). Assuming an antiperiplanar elimination, one would expect the (*E*)-configurated enone from (4*R*,1′*R*)-**16b** and the (*Z*)-configurated enone from (4*R*,1′*S*)-**16b** (*Scheme 3*). Following the work of *Majewsky* and coworkers [2], the (4*R*,1′*S*)-configuration of **16b** is more likely. Indeed, steric factors favour the (4*R*,1′*S*)-route, because the Me group of acetaldehyde is in the least hindered position with respect to the axial Me–C(2). More generally, *cis*-diaxial repulsion of the substituents at C(2) and C(4) is minimized if the axial Me group (or axial H-atom in series **9** and **12**) faces the smallest substituent of the incoming aldehyde. Since the (*Z*)-configu-

rated enone was not observed (see *Table 2, Footnote b*), a stepwise elimination *via* a preceding *E*1*cb*-like enolization is assumed. In fact, the conversion of brosylates into enones required comparatively drastic conditions (LDA *and N,N,N′,N′*-tetramethylethylenediamine (TMEDA)).

Since the simple hydroxy ketones **8a** and **11a** and hence their brosylates could not be prepared, the corresponding methylidene derivatives **17a** and **18a** were prepared from **1** and **4** *via* **19** and **20**, respectively, by a selenenylalkyl-ketone route (*Scheme 4*).

Scheme 4. *α-Methylidene Ketones* via *Selenenylalkyl Ketones*



a) Purity 70%.

b) Isolated in 80% purity, since starting ketone **1**, selenide **19**, and enone **17a** showed similar polarity on LC in a variety of solvents.

Tertiary Aldols. Since tertiary aldols were not accessible by base-induced reaction of bicyclic ketones and ketonic acceptors such as acetone, a change of mechanism towards an S_N1-like aldol reaction was tried (*Scheme 5*). The *Mukaiyama* procedure gave indeed adduct **22** (*via* **21**), albeit only in 21% yield. The three-step procedure *via* **7b** and **23** produced the desired alcohol **22** in 43% overall yield. When MeMgI was replaced by MeLi for the step **23** → **22**, only the *retro*-aldolization product **1** was observed. Of the two carbonyl groups in 1,3-diketone **23**, the less hindered carbonyl was attacked chemoselectively[4]).

Attempts to bring about a $TiCl_4$-induced aldol reaction of oxacyclic enol ether **24** (obtained from **4**) with acetone failed and gave **25** instead (*Scheme 5*). This reaction was recently generalized to afford a series of previously unknown, modified tropones (6-hydroxycyclohepta-2,4-dien-1-ones) [5].

Finally, a tertiary alcohol **27** was obtained from **10b** by *Jones* oxidation followed by reaction of diketone **26** with an organometallic reagent, although a number of side reactions occurred (*Table 4*). *E.g.*, MeLi and **26** furnished the *retro*-aldolization product **4** in high yield (87%). With MeMgI, the reaction was unspecific although the carbaanalog **23** of **26** produced tertiary alcohol **22** with MeMgI (*Scheme 5*). Other

4) Attack of the more hindered C(3)=O in non-enolizable bicyclo[3.2.1]oct-6-en-3-ones occurs with MeLi activated by *t*-BuOK (see [4]).

Scheme 5. *Two Routes to Tertiary Aldol* **22** *and Preparation of Modified Tropone* **25**

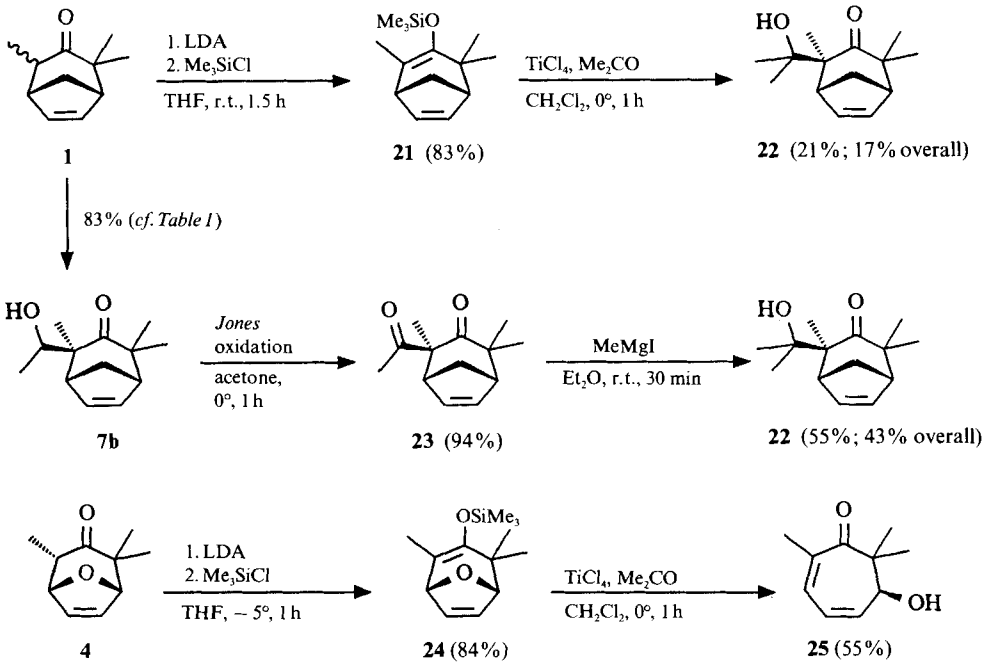
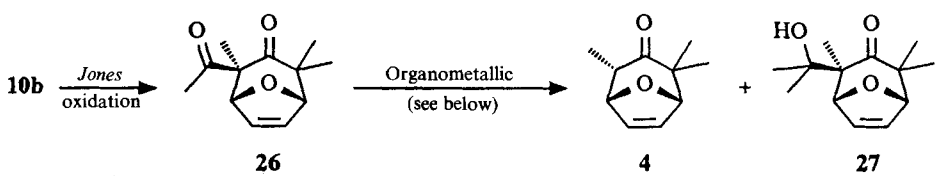


Table 4. *Reactions of Diketone* **26** *with Organometallics*



Entry	Organometallic	Reaction conditions	Yields [%]		Remarks
			4	**27**	
1	MeLi	−78 → −30°, 1 h	87	–	
2	MeMgI	0 → r.t., 30 min	–	–	unknown products
3	$MeMgBr/CeCl_3$	r.t., 24 h	–	–	no reaction
4	$Me_2Ti[O(i\text{-}Pr)]_2$	r.t., 48 h	–	–	no reaction
5	Me_4Ti	0°, 1 h	33	41	
6	Me_4Zr	−30°, 2 h	–	71	

conditions applied to **26** (*Table 4, Entries 3* and *4*) were also unsuccessful. Unlike MeLi and MeMgI, methylating agents derived from transition metals such as Me_4Ti and Me_4Zr are more oxophilic and interact strongly with the carbonyl O-atom. We were pleased to find that Me_4Zr allowed the formation of tertiary alcohol **27** in high yield (71%) under very mild conditions (2 h at −30°). Me_4Ti was less effective (*Table 4*) [6] and gave some *retro*-aldolization product.

Conclusion. – The reactions described underline the potential of the unsaturated [3.2.1]bicyclic ketones in stereocontrolled reactions. Both aldol reaction and subsequent elimination are highly diastereoselective. The bicyclic skeleton in **1–6** was also elaborated to tertiary aldols. The experimental and spectroscopic findings, together with mechanistic considerations, will be useful in the further development of this field [7].

We thank the *Fonds der Chemischen Industrie* for support of our work.

Experimental Part

1. *Aldol Reactions of [3.2.1]Bicyclic Ketones* **1–6**. *General Procedure.* To a soln. of freshly prepared lithium diisopropylamide (LDA, prepared from (i-Pr)$_2$NH (349 mg, 484 µl, 3.45 mmol) and BuLi (1.6M in hexane); 2.1 ml, 3.3 mmol) in THF (10 ml) was added the bicyclic ketone (3 mmol) in THF (5 ml) at −20°. The resulting mixture was stirred for 1 h at −5°, then cooled to the indicated temp., and the aldehyde (15 mmol) added carefully (for reaction time and temp., see *Table 1* or below). Sat. aq. NH_4Cl soln. was added and the mixture allowed to reach r.t. The aq. layer was extracted with Et_2O (3 × 20 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the crude product purified by FC. Generally, scale up (80 mmol) is possible.

(1RS,2SR,5SR)-2-(1'-Hydroxymethyl)-2,4,4-trimethylbicyclo[3.2.1]oct-6-en-3-one (**7a**). From **1** (492 mg) and gaseous formaldehyde (450 mg; 15 min, −15°). Chromatography (LC; *t*-BuOMe/cyclohexane 1:9) gave 250 mg (43%) of colorless crystals. M.p. 29°. IR ($CHCl_3$): 3524, 3067, 2968, 2940, 2876, 1672, 1464, 1400, 1380, 1340, 1084, 1004. ^{1}H-NMR ($CDCl_3$): 6.25, 6.20 (2*dd*, ^3J = 5.5, 2.5, H–C(6), H–C(7)); 3.81–3.66, 3.62–3.48 (2 br. *m*, 2 H–C(1')); 2.49 (*dd*, ^3J = 5.5, 2.5, H–C(1)); 2.40 (*dd*, ^3J = 5.5, 2.5, H–C(5)); 2.32–2.18 (br. *m*, OH); 2.28 (*d*, ^2J = 11.5, H_{syn}–C(8)); 1.90 (*ddd*, ^2J = 11.5, ^3J = 5.5, 5.5, H_{anti}–C(8)); 1.21 (*s*, Me_{ax}–C(4)); 1.08, 1.04 (2*s*, 2 Me_{eq}). ^{13}C-NMR (APT, $CDCl_3$)[5]: 222.16 (↑, C(3)); 137.09, 136.19 (2↓, C(6), C(7)); 69.43 (↑, C(1')); 55.29 (↑, C(2)); 49.85 (↑, C(4)); 49.48, 45.06 (2↓, C(1), C(5)); 35.01 (↑, C(8)); 27.87, 25.25, 20.29 (3↓, 3 Me). MS: 194 (1, M^+), 164 (8), 149 (5), 135 (31), 121 (7), 108 (26), 107 (100), 105 (14), 94 (17), 93 (91), 91 (42), 79 (30), 77 (37), 70 (8), 66 (13). FAB-MS: 195 (100, $[M + H]^+$), 149 (57, [*retro*-aldolisation product – Me]$^+$), 107 (77, $C_8H_{11}^+$).

(1RS,2SR,5SR,1'SR)-2-(1'-Hydroxyethyl)-2,4,4-trimethylbicyclo[3.2.1]oct-6-en-3-one (**7b**). From **1** and acetaldehyde (660 mg, 0.85 ml; 30 min, −15°). LC (*t*-BuOMe/cyclohexane 1:9) afforded **7b** (518 mg, 83%; scale up: 80 mmol → 85%). Colorless crystals. M.p. 67°. IR ($CHCl_3$): 3510, 3070, 2978, 2945, 2880, 1672, 1460, 1395, 1380, 1359, 1060, 1038, 942. ^{1}H-NMR ($CDCl_3$): 6.28, 6.17 (2 *dd*, ^3J = 6, 3, H–C(6), H–C(7)); 4.11 (*q*, ^3J = 6.5, H–C(1')); 2.82–2.44 (br. *s*, OH); 2.56 (*dd*, ^3J = 5, 3, H–C(1)); 2.42 (*dd*, ^3J = 5, 3, H–C(5)); 2.27 (*d*, ^2J = 11.5, H_{syn}–C(8)); 1.82 (*ddd*, ^2J = 11.5, ^3J = 5, 5, H_{anti}–C(8)); 1.25 (*s*, Me_{ax}–C(4)); 1.16 (*d*, ^3J = 6.5, Me–C(1')); 1.05, 0.96 (2*s*, 2 Me_{eq}). ^{13}C-NMR ($CDCl_3$): 224.01 (*s*, C(3)); 138.05, 136.29 (2*d*, C(6), C(7)); 69.87 (*d*, C(1')); 57.40 (*s*, C(2)); 50.55 (*s*, C(4)); 49.78, 45.67 (2*d*, C(1), C(5)); 33.81 (*t*, C(8)); 28.70, 25.57, 16.52, 15.24 (4*q*, 4 Me). MS: 165 (8), 164 (75), 149 (14), 135 (14), 121 (59), 120 (9), 108 (17), 107 (18), 99 (13), 94 (81), 93 (100), 91 (39), 79 (33), 77 (38), 70 (14), 66 (10), 55 (12). FAB-MS: 209 (100, $[M + H]^+$), 191 (47, $[M + H - H_2O]^+$), 164 (22, [*retro*-aldolisation product]$^+$), 163 (24, [*retro*-aldolisation product – H]$^+$).

(1RS,2SR,5SR,1'SR)-2-(1'-Hydroxybenzyl)-2,4,4-trimethylbicyclo[3.2.1]oct-6-en-3-one (**7c**). From **1** and benzaldehyde (1.59 g, 1.5 ml; 1 h, −10°). LC (*t*-BuOMe/cyclohexane 1:15) afforded **7c** (438 mg, 54%). Colorless crystals. M.p. 118°. IR (KBr): 3440, 3030, 2984, 2950, 2918, 2870, 1668, 1493, 1467, 1452, 1419, 1382, 1371, 1352, 1052, 1015, 763, 746, 705. ^{1}H-NMR ($CDCl_3$): 7.50–7.24 (*m*, 5 arom. H); 6.42, 6.31 (2*dd*, ^3J = 6, 2.5, H–C(6), H–C(7)); 5.31 (*d*, ^3J = 1, H–C(1')); 4.85 (br. *s*, OH); 2.41 (*dd*, ^3J = 5.5, 2.5, H–C(1)); 2.30 (*d*, ^2J = 12, H_{syn}–C(8)); 2.02 (*dd*, ^3J = 5.5, 2.5, H–C(5)); 1.78 (*ddd*, ^2J = 12, ^3J = 5.5, 5.5, H_{anti}–C(8)); 1.36, 1.32, 1.11 (3*s*, 3 Me). ^{13}C-NMR ($CDCl_3$): 226.07 (*s*, C(3)); 139.04 (*s*, arom. C); 138.09, 135.91 (2*d*, C(6), C(7)); 128.41, 127.78 (2 × 2*d*, 4 arom. C); 127.74 (*d*, arom. C); 76.47 (*d*, C(1')); 56.98 (*s*, C(2)); 51.14 (*s*, C(4)); 49.89, 46.93 (2*d*, C(1), C(5)); 34.80 (*t*, C(8)); 29.05, 25.47, 17.92 (3*q*, 3 Me). MS (90°): 181 (1), 165 (9), 164 (92), 149 (19), 121 (26), 107 (20), 106 (18), 105 (24), 94 (100), 93 (44), 91 (33), 79 (40), 77 (59), 70 (15), 66 (5). FAB-MS: 271 (27, $[M + H]^+$), 253 (100, $[M + H - H_2O]^+$), 225 (33, $[M + H - H_2O - CO]^+$), 164 (41, [*retro*-aldolisation product **1**]$^+$), 105 (33, [*retro*-aldolization product PhCHO – H]$^+$), 91 (53, $C_7H_7^+$), 77 (17, [Ph – H]$^+$).

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[5]) APT (*a*ttached *p*roton *t*est): Spin-echo-based selection of multiplicities of ^{13}C-NMR signals; quaternary C-atoms and CH_2 groups give positive signals (↑), while CH and Me groups give negative signals (↓) [8].

(1RS,2SR,5SR,1'SR)-2-(1'-Hydroxy-2'-methylpropyl)-2,4,4-trimethylbicyclo[3.2.1]oct-6-en-3-one (**7d**). From **1** and isobutyraldehyde (1.08 g, 1.4 ml; 2 h, r.t.). LC (*t*-BuOMe/cyclohexane 1:20) afforded **7d** (170 mg, 24%). Light yellow crystals. M.p. 48°. IR (KBr): 3468, 3061, 2976, 2938, 2874, 1695, 1472, 1460, 1381, 1360, 1055, 1030, 1017, 744. ^{1}H-NMR ($CDCl_3$): 6.28, 6.17 (*2dd*, ^3J = 5.5, 3, H–C(6), H–C(7)); 3.71 (*dd*, ^3J = 3, 2, H–C(1')); 2.70 (*dd*, ^3J = 5.5, 3, H–C(1)); 2.63 (*dd*, ^3J = 2, ^4J = 1, OH); 2.40 (*dd*, ^3J = 5.5, 3, H–C(5)); 2.26 (*d*, ^2J = 11.5, H_{syn}–C(8)); 2.02 (*ddqq*, ^3J = 7, 7, 3, ^4J = 1, Me_2CH); 1.84 (*ddd*, ^2J = 11.5, ^3J = 5.5, 5.5, H_{anti}–C(8)); 1.27 (*s*, Me_{ax}–C(4)); 1.08, 0.97 (*2d*, ^3J = 7, Me_2CH); 1.03, 1.02 (*2s*, 2 Me_{eq}). MS: 194 (1), 193 (6), 165 (13), 164 (82), 149 (21), 135 (11), 134 (1), 121 (26), 108 (13), 107 (16), 105 (15), 94 (100), 93 (95), 91 (35), 79 (28), 77 (30), 73 (13), 72 (13), 70 (16), 66 (7). FAB-MS: 237 (56, $[M + H]^+$), 164 (42, [*retro*-aldolization product]$^+$), 149 (100, [*retro*-aldolization product – Me]$^+$). HR-MS: 193.1228 ($C_{12}H_{17}O_2$, calc. 193.1229).

(1RS,4RS,5SR,1'SR)-4-(1'-Hydroxyethyl)-2,2-dimethylbicyclo[3.2.1]oct-6-en-3-one (**8b**). From **2** (451 mg) and acetaldehyde (30 min, –20°). LC (*t*-BuOMe/cyclohexane 1:5): 431 mg (74%) of yellow oil. IR (film): 3451, 3060, 2971, 2927, 2875, 1694, 1462, 1407, 1381, 1361, 1343, 1121, 1063, 1013, 934, 900, 733. ^{1}H-NMR ($CDCl_3$): 6.20, 6.10 (*2ddd*, ^3J = 5.5, 3, J = 0.5, H–C(6), H–C(7)); 3.96 (*ddq*, ^3J = 9, 6, 2, H–C(1')); 3.17 (*d*, ^3J = 2, OH); 2.75 (*m*, H–C(5)); 2.45 (*dd*, ^3J = 5.5, 3, H–C(1)); 2.15 (*d*, ^2J = 11, H_{syn}–C(8)); 2.07 (*ddd*, ^3J = 9, 2, ^4J = 2, H–C(4)); 1.84 (*dddd*, ^2J = 11, ^3J = 5.5, 5.5, ^4J = 2, H_{anti}–C(8)); 1.28 (*d*, ^3J = 6, Me–C(1')); 1.23 (*s*, Me_{ax}); 1.06 (*s*, Me_{eq}). ^{13}C-NMR ($CDCl_3$): 220.24 (*s*, C(3)); 137.10, 136.92 (*2d*, C(6), C(7)); 68.90 (*d*, C(1')); 60.73 (*d*, C(4)); 50.81 (*s*, C(2)); 49.43, 40.19 (*2d*, C(1), C(5)); 33.92 (*t*, C(8)); 27.68, 24.76, 21.96 (*3q*, 3 Me). MS: 176 (4), 161 (3), 150 (67), 135 (11), 128 (34), 122 (6), 121 (7), 108 (37), 107 (71), 93 (100), 91 (46), 85 (5), 80 (41), 79 (68), 77 (43), 70 (27), 66 (20), 45 (24), 44 (37), 43 (32), 42 (12). FAB-MS: 193 (100, $[M-H]^+$). HR-MS: 176.1202 ($C_{12}H_{16}O$, calc. 176.1201).

(1RS,4RS,5SR,1'SR)-4-(1'-Hydroxybenzyl)-2,2-dimethylbicyclo[3.2.1]oct-6-en-3-one (**8c**). From **2** and benzaldehyde (30 min, 0°). LC (*t*-BuOMe/cyclohexane 1:20 → 1:7) afforded **8c** (377 mg, 49%). Colorless crystals. M.p. 109°. IR (KBr): 3469, 3058, 2966, 2926, 2875, 1698, 1492, 1465, 1455, 1384, 1363, 1107, 1061, 1042, 1001, 765, 738, 723, 700. ^{1}H-NMR ($CDCl_3$): 7.44–7.27 (*m*, 5 arom. H); 6.16, 5.93 (*2dd*, ^3J = 5.5, 3, H–C(6), H–C(7)); 4.81 (*dd*, ^3J = 9.5, 1.5, H–C(1')); 3.85 (*d*, ^3J = 1.5, OH); 2.44 (*dd*, ^3J = 5.5, 3, H–C(1)); 2.38 (*ddd*, ^3J = 9.5, 2, ^4J = 2, H–C(4)); 2.21 (*d*, ^2J = 12, H_{syn}–C(8)); 2.20 (*m*, H–C(5)); 1.76 (*dddd*, ^2J = 12, ^3J = 5.5, 5.5, ^4J = 2, H_{anti}–C(8)); 1.31 (*s*, Me_{ax}); 1.10 (*s*, Me_{eq}). ^{13}C-NMR (APT, $CDCl_3$)[5]: 219.98 (↑, C(3)); 141.59 (↑, arom. C); 136.91, 136.80 (2↓, C(6), C(7)); 128.43 (2↓, 2 arom. C); 127.98 (↓, arom. C); 126.83 (2↓, 2 arom. C); 75.52 (↓, C(1')); 60.15 (↓, C(4)); 50.79 (↑, C(2)); 49.23, 39.51 (2↓, C(1), C(5)); 33.83 (↑, C(8)); 27.73, 24.76 (2↓, 2 Me). MS (60°): 256 (3, M^+), 190 (5), 151 (14), 150 (100), 135 (10), 122 (8), 107 (28), 106 (38), 105 (44), 93 (35), 91 (22), 80 (44), 79 (40), 78 (15), 77 (60), 70 (27), 66 (10), 43 (10), 41 (15). HR-MS: 256.1463 ($C_{17}H_{20}O_2$, calc. 256.1463).

(1RS,2SR,4RS,5SR)-2-(1'-Hydroxymethyl)-2,4-dimethylbicyclo[3.2.1]oct-6-en-3-one (**9a**). From **3** (451 mg) and gaseous formaldehyde (15 min, –20°). LC (*t*-BuOMe/cyclohexane 1:2) gave colorless crystals (87 mg, 16%). M.p. 53°. IR (KBr): 3474, 3069, 2981, 2966, 2930, 2877, 1686, 1458, 1445, 1384, 1370, 1046, 1003, 999, 739. ^{1}H-NMR ($CDCl_3$): 6.20 (*m*, H–C(6), H–C(7)); 3.84–3.72, 3.70–3.57 (2 br. *m*, 2 H–C(1')); 2.75–2.66, 2.64–2.47 (*2m* (1:2), H–C(1), H–C(4), H–C(5)); 2.23 (*d*, ^2J = 11.5, H_{syn}–C(8)); 1.94 (*ddd*, ^2J = 11.5, ^3J = 5, 5, H_{anti}–C(8)); 1.75 (br. *m*, OH); 1.08 (*s*, Me–C(2)); 1.04 (*d*, ^3J = 6.5, Me–C(4)). ^{13}C-NMR (APT, $CDCl_3$)[5]: 216.43 (↑, C(3)); 137.04, 135.88 (2↓, C(6), C(7)); 68.71 (↑, C(1')); 55.77 (↑, C(2)); 48.80, 46.74, 45.39 (3↓, C(1), C(4), C(5)); 38.51 (↑, C(8)); 19.45, 14.75 (2↓, 2 Me). MS: 181 (1), 180 (7, M^+), 165 (2), 162 (2), 150 (8), 135 (7), 121 (12), 114 (3), 107 (100), 106 (31), 94 (15), 93 (58), 91 (35), 79 (48), 77 (28), 66 (14), 55 (6). HR-MS: 180.1151 ($C_{11}H_{16}O_2$, calc. 180.1150).

(1RS,2SR,4RS,5SR,1'SR)-2-(1'-Hydroxyethyl)-2,4-dimethylbicyclo[3.2.1]oct-6-en-3-one (**9b**). From **3** and acetaldehyde (20 min, –20°). LC (*t*-BuOMe/cyclohexane 1:7) afforded **9b** (408 mg, 70%). Colorless crystals. M.p. 92°. IR (KBr): 3489, 3064, 2972, 2936, 2883, 1699, 1459, 1448, 1374, 1360, 1347, 1107, 1075, 1026, 749. ^{1}H-NMR ($CDCl_3$): 6.23, 6.16 (*dd*, *ddd*, ^3J = 5.5, ^3J = 2.5, J = 0.5, H–C(6), H–C(7)); 4.19 (*dq*, ^3J = 6.5, 3, H–C(1')); 2.75–2.63 (*m*, H–C(4), H–C(5)); 2.60 (*dd*, ^3J = 5, 2.5, H–C(1)); 2.19 (*d*, ^2J = 11, H_{syn}–C(8)); 1.94 (*d*, ^3J = 3, OH); 1.87 (*ddd*, ^2J = 11, ^3J = 5, 5, H_{anti}–C(8)); 1.20, 1.05 (*2d*, ^3J = 6.5, Me–C(4), Me–C(1')); 0.97 (*s*, Me–C(2)). ^{13}C-NMR (APT, $CDCl_3$)[5]: 216.56 (↑, C(3)); 136.89, 136.29 (2↓, C(6), C(7)); 69.33 (↓, C(1')); 57.64 (↑, C(2)); 47.57, 47.47, 45.55 (3↓, C(1), C(4), C(5)); 37.36 (↑, C(8)); 16.22, 14.39, 14.01 (3↓, 3 Me). MS: 179 (1), 161 (1), 151 (13), 150 (100), 149 (2), 135 (26), 128 (1), 121 (49), 120 (13), 107 (13), 94 (60), 93 (51), 91 (31), 79 (53), 77 (26), 66 (7), 55 (9), 44 (5), 43 (14). FAB-MS: 195 (100, $[M + H]^+$), 177 (53, $[M + H - H_2O]^+$), 150 (37, [*retro*-aldolisation product]$^+$).

(1RS,2SR,4RS,5SR,1'SR)-2-(1'-Hydroxybenzyl)-2,4-dimethylbicyclo[3.2.1]oct-6-en-3-one (**9c**). From **3** and benzaldehyde (20 min, –10°). LC (*t*-BuOMe/cyclohexane 1:5) gave colorless crystals (316 mg, 41%). M.p. 82°. IR (KBr): 3438, 3058, 2983, 2969, 2935, 1703, 1492, 1455, 1373, 1350, 1048, 1031, 999, 991, 769, 735, 725, 703. ^{1}H-NMR ($CDCl_3$): 7.44–7.28 (*m*, 5 arom. H); 6.21, 6.11 (*2dd*, ^3J = 6, 3, H–C(6), H–C(7)); 5.17 (*s*, H–C(1')); 2.81–2.67 (*m*, H–C(4), H–C(5), OH); 2.53 (*d*, ^2J = 11.5, H_{syn}–C(8)); 2.26 (*dd*, ^3J = 5, 3, H–C(1)); 1.97 (*ddd*,

^2J = 11.5, ^3J = 5, 5, H_{anti}–C(8)); 1.10 (*d*, ^3J = 6.5, Me–C(4)); 0.94 (*s*, Me–C(2)). ^{13}C-NMR (APT, $CDCl_3$)[5]): 217.45 (↑, C(3)); 139.20 (↑, arom. C); 136.82, 136.29 (2↓, C(6), C(7)); 127.78 (2↓, 2 arom. C); 127.72 (↓, arom. C); 127.41 (2↓, 2 arom. C); 75.32 (↓, C(1′)); 57.94 (↑, C(2)); 48.67, 46.99, 45.43 (3↓, C(1), C(4), C(5)); 38.43 (↑, C(8)); 15.40, 14.69 (2↓, 2 Me). MS (50°): 151 (12), 150 (100), 149 (2), 135 (17), 121 (13), 107 (11), 106 (16), 105 (18), 94 (35), 93 (19), 91 (14), 79 (28), 77 (32), 66 (3), 55 (3). FAB-MS: 257 (22, $[M + H]^+$), 239 (100, $[M + H - H_2O]^+$), 150 (62, [*retro*-aldolization product]$^+$), 105 (23, [*retro*-aldolization product PhCHO – H]$^+$), 77 (18, $C_6H_5^+$).

(1RS,2SR,4RS,5SR,1′SR)-2-(1′-Hydroxy-2′-methylpropyl)-2,4-dimethylbicyclo[3.2.1]oct-6-en-3-one (**9d**). From **3** and isobutyraldehyde (30 min, 0°). LC (*t*-BuOMe/cyclohexane 1:7) gave colorless crystals (273 mg, 41%). M.p. 37°. IR ($CHCl_3$): 3535, 3065, 2985, 2968, 2877, 1687, 1460, 1376, 1348, 1040, 1001, 986. ^{1}H-NMR ($CDCl_3$): 6.22, 6.17 (2*dd*, ^3J = 5.5, 2.5, H–C(6), H–C(7)); 3.80 (*dd*, ^3J = 4, 3, H–C(1′)); 2.79–2.66 (*m*, H–C(4), H–C(5)); 2.75 (*dd*, ^3J = 5.5, 2.5, H–C(1)); 2.20 (*d*, ^2J = 11, H_{syn}–C(8)); 2.07 (br. *dqq*, ^3J = 6.5, 6.5, 3, Me_2CH); 1.89 (*ddd*, ^2J = 11, ^3J = 5.5, 5.5, H_{anti}–C(8)); 1.79 (*dd*, ^3J = 4, ^4J = 0.5, OH); 1.08, 1.04, 0.97 (3*d*, ^3J = 6.5, Me_2CH, Me–C(4)); 1.03 (*s*, Me–C(2)). ^{13}C-NMR (APT, $CDCl_3$)[5]): 216.41 (↑, C(3)); 136.91, 136.42 (2↓, C(6), C(7)); 76.26 (↓, C(1′)); 58.14 (↑, C(2)); 47.55, 47.39, 45.52 (3↓, C(1), C(4), C(5)); 37.77 (↑, C(8)); 28.75 (↓, Me_2CH); 22.86, 16.60, 15.94, 14.47 (4↓, 4 Me). MS: 179 (7), 161 (2), 151 (12), 150 (100), 149 (6), 135 (19), 122 (5), 121 (14), 107 (10), 94 (45), 93 (39), 91 (17), 79 (37), 77 (16), 72 (11), 66 (5), 55 (8), 43 (25). FAB-MS: 223 (100, $[M + H]^+$), 205 (97, $[M + H - H_2O]^+$), 150 (76, [*retro*-aldolization product]$^+$). HR-MS: 179.1072 ($C_{11}H_{15}O_2$, calc. 179.1072).

(1RS,2RS,5SR)-2-(1′-Hydroxymethyl)-2,4,4-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**10a**). From **4** (500 mg) and gaseous formaldehyde (15 min, –10°). LC (*t*-BuOMe/cyclohexane 1:7→1:1) afforded **10a** (360 mg, 61%). Colorless, amorphous crystals. M.p. 90°. IR (KBr): 3506, 3082, 2975, 2936, 2872, 1697, 1472, 1465, 1405, 1384, 1362, 1061, 1047, 923, 735. ^{1}H-NMR ($CDCl_3$): 6.44, 6.38 (2*dd*, ^3J = 6, 1.5, H–C(6), H–C(7)); 4.70 (*d*, ^3J = 1.5, H–C(1)); 4.48 (*d*, ^3J = 1.5, H–C(5)); 3.85, 3.78 (2*d*, ^2J = 10, 2 H–C(9)); 2.19 (br. *s*, OH); 1.33 (*s*, Me_{ax}–C(4)); 0.98, 0.96 (2*s*, Me_{eq}). ^{13}C-NMR (APT, $CDCl_3$)[5]): 216.13 (↑, C(3)); 134.34, 133.31 (2↓, C(6), C(7)); 86.53, 82.38 (2↓, C(1), C(5)); 68.38 (↑, C(1′)); 57.23 (↑, C(2)); 51.18 (↑, C(4)); 26.19, 21.22, 16.27 (3↓, 3 Me). MS: 197 (2), 196 (14, M^+), 178 (2), 165 (49), 137 (10), 128 (2), 123 (4), 122 (4), 110 (19), 109 (100), 108 (33), 95 (75), 86 (6), 70 (31), 68 (6), 67 (12), 42 (18), 41 (41). HR-MS: 196.1099 ($C_{11}H_{16}O_3$, calc. 196.1100).

(1RS,2RS,5SR,1′SR)-2-(1′-Hydroxyethyl)-2,4,4-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**10b**). From **4** and acetaldehyde (10 min, –15°). LC ($CHCl_3$/AcOEt/cyclohexane 4:1:5→1:1:1) afforded **10b** (575 mg, 91%; scale up: 150 mmol→93%). Colorless crystals. M.p. 98°. IR (KBr): 3478, 3085, 2981, 2942, 2872, 1689, 1461, 1407, 1388, 1365, 1284, 1061, 931, 911, 741, 729. ^{1}H-NMR ($CDCl_3$): 6.46, 6.36 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 4.70 (*d*, ^3J = 2, H–C(1)); 4.48 (*d*, ^3J = 2, H–C(5)); 4.28 (*dq*, ^3J = 6.5, 2.5, H–C(1′)); 2.72 (*d*, ^3J = 2.5, OH); 1.37 (*s*, Me_{ax}–C(4)); 1.21 (*d*, ^3J = 6.5, Me–C(1′)); 0.98, 0.88 (2*s*, 2 Me_{eq}). ^{13}C-NMR (APT, $CDCl_3$)[5]): 216.90 (↑, C(3)); 134.92, 133.24 (2↓, C(6), C(7)); 86.70, 83.71 (2↓, C(1), C(5)); 71.09 (↓, C(1′)); 59.08 (↑, C(2)); 51.51 (↑, C(4)); 26.12, 21.57, 17.30, 13.68 (4↓, 4 Me). MS: 210 (1, M^+), 192 (1), 177 (1), 167 (13), 166 (19), 165 (14), 151 (15), 149 (11), 148 (68), 137 (46), 123 (32), 122 (25), 109 (50), 96 (26), 95 (100), 70 (26), 68 (6), 67 (17), 55 (19), 45 (15), 43 (43), 42 (16). HR-MS: 192.1160 ($C_{12}H_{16}O_2$, calc. 192.1150).

(1RS,2SR,5SR,1′SR)-2-(1′-Hydroxybenzyl)-2,4,4-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**10c**). From **4** and benzaldehyde (30 min, –10°). LC (*t*-BuOMe/cyclohexane 1:8) gave 482 mg (59%) of colorless crystals. M.p. 137°. IR (KBr): 3538, 3480, 3033, 2980, 2947, 1699, 1455, 1399, 1385, 1201, 1044, 1028, 933, 704. ^{1}H-NMR ($CDCl_3$): 7.48–7.26 (*m*, 5 arom. H); 6.44, 6.18 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 5.36 (*d*, ^3J = 2, H–C(1′)); 4.55 (*d*, ^3J = 2, H–C(1)); 4.42 (*d*, ^3J = 2, H–C(5)); 2.72 (*d*, ^3J = 2, OH); 1.51 (*s*, Me_{ax}–C(4)); 1.01, 0.81 (2*s*, 2 Me_{eq}). ^{13}H-NMR (APT, $CDCl_3$)[5]): 217.33 (↑, C(3)); 139.61 (↑, arom. C); 135.00, 132.98 (2↓, C(6), C(7)); 128.01 (↓↓, 2 arom. C); 127.95 (↓, arom. C); 127.88 (↓↓, 2 arom. C); 86.72, 82.68 (2↓, C(1), C(5)); 75.44 (↓, C(1′)); 59.19 (↑, C(2)); 51.91 (↑, C(4)); 26.74, 21.49, 12.49 (3↓, 3 Me). MS (110°): 272 (1, M^+), 166 (51), 151 (16), 138 (14), 137 (100), 123 (17), 122 (10), 109 (7), 106 (22), 105 (26), 95 (27), 77 (38), 70 (7), 68 (2), 67 (9), 42 (6), 41 (19). HR-MS: 272.1409 ($C_{17}H_{20}O_3$, calc. 272.1413).

(1RS,2SR,5SR,1′SR)-2-(1′-Hydroxy-2′-methylpropyl)-2,4,4-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**10d**). From **4** and isobutyraldehyde (1 h, 0°). LC (Et_2O/cyclohexane 1:12) afforded **10d** (172 mg, 24%). Colorless crystals. M.p. 101°. IR (KBr): 3472, 3084, 2986, 2964, 2875, 1695, 1470, 1415, 1383, 1365, 1090, 1047, 934, 728. ^{1}H-NMR ($CDCl_3$): 6.39, 6.32 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 4.97 (*d*, ^3J = 2, H–C(1)); 4.45 (*d*, ^3J = 2, H–C(5)); 4.21 (br. *dd*, ^3J = 7.5, 2, H–C(1′)); 2.24 (br. *d*, ^3J = 7.5, OH); 1.69 (*dsept.*, ^3J = 7, 2, Me_2CH); 1.30 (*s*, Me_{ax}–C(4)); 0.98 (*d*, ^3J = 7, Me_2CH); 0.96, 0.95 (2*s*, 2 Me_{eq}). ^{13}C-NMR ($CDCl_3$): 215.34 (*s*, C(3)); 134.25, 133.27 (2*d*, C(6), C(7)); 86.72, 83.14 (2*d*, C(1), C(5)); 76.61 (*d*, C(1′)); 61.69 (*s*, C(2)); 51.91 (*s*, C(4)); 30.28 (*d*, Me_2CH); 25.60, 22.81, 21.44, 16.29, 13.91 (5*q*, 5 Me). MS: 195 (12), 166 (5), 165 (1), 151 (5), 138 (3), 137 (12), 123 (5), 111 (31), 109 (7), 95 (19), 85 (100), 70 (3), 67 (5), 43 (11), 42 (3), 41 (15). FAB-MS: 239 (47, $[M + H]^+$), 221 (100, $[M + H - H_2O]^+$). HR-MS: 195.1021 ($C_{11}H_{15}O_3$, calc. 195.1021).

(1RS,4SR,5SR,1'RS)-4-(1'-Hydroxyethyl)-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**11b**). From **5** (457 mg) and acetaldehyde (15 min, −40°). LC (*t*-BuOMe/cyclohexane 1:2→1:1) gave **11b** (495 mg, 84%; scale up: 150 mmol→80%). Light yellow oil. IR (film): 3452, 3086, 2972, 2933, 2872, 1703, 1472, 1460, 1383, 1112, 1073, 1049, 918, 901, 725. ^{1}H-NMR ($CDCl_3$): 6.38, 6.30 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 4.88 (*d*, ^3J = 2, H–C(5)); 4.48 (*d*, ^3J = 2, H–C(1)); 4.24 (*ddq*, ^3J = 8, 6, 3.5, H–C(1')); 2.64 (*d*, ^3J = 3.5, OH); 2.11 (*d*, ^3J = 8, H–C(4)); 1.35 (*s*, Me_{ax}); 1.33 (*d*, ^3J = 6, Me–C(1')); 0.99 (*s*, Me_{eq}); on H/D-exchange, *d* at 2.64 disappeared. ^{13}C-NMR (APT, $CDCl_3$)[5]: 213.21 (↑, C(3)); 133.88, 133.42 (2↓, C(6), C(7)); 85.82, 79.38 (2↓, C(1), C(5)); 68.14 (↓, C(1')); 61.60 (↓, C(4)); 52.10 (↑, C(2)); 25.16, 21.67, 20.50 (3↓, 3 Me). MS: 196 (1, M^+), 152 (98), 151 (41), 137 (13), 135 (13), 134 (100), 123 (22), 109 (45), 95 (95), 82 (36), 81 (40), 70 (49), 68 (15), 67 (16), 55 (13), 45 (26). FAB-MS: 197 (33, $[M + H]^+$), 179 (100, $[M + H - H_2O]^+$).

(1RS,4RS,5SR,1'RS)-4-(1'-Hydroxybenzyl)-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**11c**). From **5** and benzaldehyde (30 min, −30°). LC (*t*-BuOMe/cyclohexane 1:12) gave colorless crystals (519 mg, 67%). M.p. 89°. IR (KBr): 3525, 3079, 3033, 2962, 2875, 1695, 1496, 1458, 1383, 1362, 1203, 1100, 1056, 918, 902, 891, 706. ^{1}H-NMR ($CDCl_3$): 7.50–7.28 (*m*, 5 arom. H); 6.35, 6.13 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 5.07 (*dd*, ^3J = 10, 2.5, H–C(1')); 4.50 (*d*, ^3J = 2, H–C(5)); 4.41 (*d*, ^3J = 2, H–C(1)); 3.06 (*d*, ^3J = 2.5, OH); 2.38 (*d*, ^3J = 10, H–C(4)); 1.44 (*s*, Me_{ax}); 1.02 (*s*, Me_{eq}); on H/D-exchange, *d* at 3.06 disappeared. ^{13}C-NMR (APT, $CDCl_3$)[5]: 213.27 (↑, C(3)); 141.50 (↑, arom. C); 133.66, 133.63 (2↓, C(6), C(7)); 128.61 (2↓, 2 arom. C); 128.25 (↓, arom. C); 127.05 (2↓, 2 arom. C); 86.02, 78.09 (2↓, C(1), C(5)); 74.62 (↓, C(1')); 61.77 (↓, C(4)); 52.47 (↑, C(2)); 25.68, 20.55 (2↓, 2 Me). MS (60°): 259 (2), 258 (9, M^+), 229 (1), 190 (2), 170 (12), 152 (100), 151 (26), 137 (13), 123 (90), 106 (38), 105 (48), 95 (44), 77 (63), 70 (26), 68 (7), 67 (7), 43 (9), 41 (23). HR-MS: 258.1255 ($C_{16}H_{18}O_3$, calc. 258.1256).

(1RS,4RS,5SR,1'RS)-4-(1'-Hydroxy-2'-methylpropyl)-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**11d**). From **5** and isobutyraldehyde (30 min, −30°). LC (*t*-BuOMe/cyclohexane 1:5) gave colorless crystals (310 mg, 46%). M.p. 43°. IR (KBr): 3447, 3082, 2965, 2931, 2874, 1704, 1469, 1382, 1364, 1211, 1090, 1055, 905, 739, 716. ^{1}H-NMR ($CDCl_3$): 6.38, 6.29 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 4.83 (*d*, ^3J = 2, H–C(5)); 4.48 (*d*, ^3J = 2, H–C(1)); 3.88 (*ddd*, ^3J = 8.5, 4.5, 4, H–C(1')); 2.46 (*d*, ^3J = 4.5, OH); 2.27 (*d*, ^3J = 8.5, H–C(4)); 1.92 (*dqq*, ^3J = 6.5, 6.5, 4, Me_2CH); 1.34 (*s*, Me_{ax}); 1.07, 0.89 (2*d*, ^3J = 6.5, Me_2CH); 0.98 (*s*, Me_{eq}); on H/D-exchange, *d* at 2.46 disappeared. ^{13}C-NMR (APT, $CDCl_3$)[5]: 213.83 (↑, C(3)); 133.76, 133.66 (2↓, C(6), C(7)); 86.00, 79.82 (2↓, C(1), C(5)); 75.91 (↓, C(1')); 57.62 (↓, C(4)); 52.29 (↑, C(2)); 30.57 (↓, Me_2CH); 25.35, 20.56, 19.95, 14.88 (4↓, 4 Me). MS: 181 (5), 152 (100), 151 (16), 137 (13), 134 (58), 123 (22), 111 (27), 95 (63), 82 (29), 81 (24), 72 (8), 71 (18), 70 (29), 68 (12), 67 (11), 55 (17). FAB-MS: 225 (27, $[M + H]^+$), 207 (100, $[M + H - H_2O]^+$). HR-MS: 181.0813 ($C_{10}H_{13}O_3$, calc. 181.0865).

(1RS,2RS,4RS,5SR,1'RS)-2-(1'-Hydroxyethyl)-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**12b**). From **6** (457 mg) and acetaldehyde (15 min, −40°). LC (*t*-BuOMe/cyclohexane 1:3) afforded **12b** (447 mg, 76%). Colorless crystals. M.p. 68°. IR (KBr): 3446, 3084, 2976, 2938, 2873, 1694, 1459, 1420, 1377, 1342, 1182, 1041, 940, 923, 749, 735. ^{1}H-NMR ($CDCl_3$): 6.46, 6.39 (2*dd*, ^3J = 6, 1.5, H–C(6), H–C(7)); 4.87 (*dd*, ^3J = 5, 1.5, H–C(5)); 4.77 (*d*, ^3J = 1.5, H–C(1)); 4.19 (*dq*, ^3J = 6, 2, H–C(1')); 3.79 (br. *d*, ^3J = 2, OH); 2.96 (*dq*, ^3J = 7, 5, H–C(4)); 1.16 (*d*, ^3J = 6, Me–C(1')); 0.98 (*d*, ^3J = 7, Me–C(4)); 0.87 (*s*, Me–C(2)). ^{13}C-NMR (APT, $CDCl_3$)[5]: 210.08 (↑, C(3)); 134.32, 134.00 (2↓, C(6), C(7)); 85.71, 82.69 (2↓, C(1), C(5)); 72.61 (↓, C(1')); 59.11 (↑, C(2)); 49.55 (↓, C(4)); 17.82, 13.75, 10.45 (3↓, 3 Me). MS: 196 (2, M^+), 178 (18), 163 (2), 152 (25), 151 (9), 137 (12), 134 (15), 128 (2), 124 (7), 123 (35), 111 (2), 109 (13), 96 (25), 95 (39), 83 (100), 81 (45), 68 (4), 67 (5), 53 (22). HR-MS: 178.0991 ($C_{11}H_{14}O_2$, calc. 178.0994).

(1RS,2RS,4RS,5SR,1'RS)-2-(1'-Hydroxybenzyl)-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**12c**). From **6** and benzaldehyde (30 min, −30°). LC (*t*-BuOMe/cyclohexane 1:5) gave colorless crystals (426 mg, 55%). M.p. 123°. IR (KBr): 3425, 3081, 3062, 3031, 2971, 2949, 2933, 2876, 1700, 1492, 1455, 1375, 1342, 1182, 1045, 949, 912, 738, 709. ^{1}H-NMR ($CDCl_3$): 7.41–7.22 (*m*, 5 arom. H); 6.46, 6.24 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 4.98–4.88 (*m*, H–C(1), H–C(5), H–C(1')); 4.23 (br. *d*, ^3J = 8, OH); 3.11 (*dq*, ^3J = 7, 4.5, H–C(4)); 1.01 (*d*, ^3J = 7, Me–C(4)); 0.76 (*s*, Me–C(2)). ^{13}C-NMR (APT, $CDCl_3$)[5]: 210.99 (↑, C(3)); 140.28 (↑, arom. C); 134.66, 133.84 (2↓, C(6), C(7)); 127.98 (2↓, 2 arom. C); 127.80 (↓, arom. C); 127.23 (2↓, 2 arom. C); 82.72, 82.35, 79.05 (3↓, C(1), C(5), C(1')); 58.71 (↑, C(2)); 50.64 (↓, C(4)); 15.57, 10.79 (2↓, 2 Me). MS (90°): 258 (1, M^+), 240 (2), 190 (9), 152 (73), 145 (48), 137 (11), 124 (14), 123 (100), 106 (33), 105 (42), 96 (25), 95 (32), 81 (35), 77 (58), 68 (6), 66 (13).

(1RS,2SR,4RS,5SR,1'RS)-2-(1'-Hydroxy-2'-methylpropyl)-2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**12d**). From **6** and isobutyraldehyde (30 min, −30°). LC (*t*-BuOMe/cyclohexane 1:3) afforded **12d** (182 mg, 27%). Colorless, fine needles. M.p. 71°. IR (KBr): 3480, 3100, 2966, 2931, 2871, 1713, 1462, 1375, 1338, 1200, 1049, 1018, 944, 920, 734. ^{1}H-NMR ($CDCl_3$): 6.43, 6.33 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 4.85 (*dd*, ^3J = 4.5, 2, H–C(5)); 4.80 (*d*, ^3J = 2, H–C(1)); 3.87 (*m*, H–C(1')); 3.07 (*dq*, ^3J = 7, 4.5, H–C(4)); 2.03 (*dqq*, ^3J = 6.5, 6.5, 2, Me_2CH); 1.05, 0.78 (2*d*, ^3J = 6.5, Me_2CH); 0.97 (*d*, ^3J = 7, Me–C(4)); 0.92 (*s*, Me–C(2)). ^{13}C-NMR (APT, $CDCl_3$)[5]: 210.18

(↑, C(3)); 134.47, 133.51 (2↓, C(6), C(7)); 87.00, 82.84, 81.29 (3↓, C(1), C(5), C(1')); 59.02 (↑, C(2)); 50.35 (↓, C(4)); 29.00 (↓, Me_2CH); 22.74, 15.33, 14.86, 10.35 (4↓, 4 Me). MS: 206 (1), 183 (2), 182 (13), 181 (99), 152 (25), 151 (3), 137 (9), 123 (51), 109 (27), 97 (89), 95 (27), 85 (100), 81 (26), 72 (6), 68 (5), 67 (11), 55 (10). FAB-MS: 225 (100, $[M + H]^+$).

2. *Brosylates of* **7b**, **8b**, **10b**, *and* **11b**. *General Procedure*. To a soln. of LDA (3.3 mmol) in THF (10 ml) was added the aldol (3 mmol) in THF (10 ml) at −40°. After stirring for 30 min at the same temp., brosyl chloride (= 4-bromobenzenesulfonyl chloride; 3 mmol) in THF (10 ml) was added. The mixture was allowed to react for 1 h at r.t. Then, H_2O was added, the aq. layer extracted with Et_2O (3 × 20 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue purified by LC.

(1RS,2SR,5SR,1'SR)-2-[1'-(4-Bromophenylsulfonyloxy)ethyl]-2,4,4-trimethylbicyclo[3.2.1]oct-6-en-3-one (**13b**). From aldol **7b** (625 mg, 3 mmol) and brosyl chloride (767 mg, 3 mmol). LC (Et_2O/cyclohexane 1:12) afforded **13b** (692 mg, 54%). Colorless crystals. M.p. 84°. IR (KBr): 3052, 2982, 2968, 2913, 1698, 1575, 1471, 1460, 1392, 1376, 1355, 1343, 1191, 1177, 1069, 1011, 905, 899, 801, 751, 740, 608. ^{1}H-NMR ($CDCl_3$): 7.78, 7.68 (2*ddd*, ^3J = 9, ^4J = 2, ^5J = 2, 4 arom. H); 6.27 (*dd*, ^3J = 5.5, 3, H–C(6)); 6.08 (*dd*, ^3J = 5.5, 3, H–C(7)); 5.18 (*q*, ^3J = 6.5, H–C(1')); 2.62 (*dd*, ^3J = 5, 3, H–C(1)); 2.41 (*dd*, ^3J = 5, 3, H–C(5)); 2.25 (*d*, ^2J = 12, H_{syn}–C(8)); 1.86 (*ddd*, ^2J = 12, ^3J = 5, 5, H_{anti}–C(8)); 1.39 (*d*, ^3J = 6.5, Me–C(1')); 1.19 (*s*, Me_{ax}–C(4)); 0.99 (*s*, Me_{eq}–C(4)); 0.93 (*s*, Me–C(2)). NOE: H–C(6)→H–C(5) (3.5); H–C(7)→H–C(1) (4.8); H_{syn}–C(8)→H–C(1') (12.1), H_{anti}–C(8) (27.7); H–C(1')→H–C(1) (1.8), H_{syn}–C(8) (5.9); Me–C(1')→H–C(1) (3.4), H_{syn}–C(8) (2.0), H–C(1') (3.4); Me–C(2)→H–C(1) (2.0), H–C(1') (1.4), H–C(7) (3.7); Me_{ax}–C(4)→H–C(5) (2.9), H_{syn}–C(8) (1.8), H–C(1') (1.8); Me_{eq}–C(4)→H–C(5) (2.3), H–C(6) (3.2). ^{13}C-NMR ($CDCl_3$): 216.46 (*s*, C(3)); 138.37, 135.33 (2*d*, C(6), C(7)); 136.62, 128.63 (2*s*, 2 arom. C); 132.31, 129.31 (2 × 2*d*, 4 arom. C); 82.83 (*d*, C(1')); 56.20 (*s*, C(2)); 50.30 (*s*, C(4)); 49.80, 45.00 (2*d*, C(1), C(5)); 34.96 (*t*, C(8)); 27.74, 25.95, 19.03, 17.38 (4*q*, 4 Me). MS (110°): 426 (2, M^+), 238 (2), 236 (2), 208 (13), 190 (7), 163 (5), 162 (19), 147 (17), 135 (11), 121 (100), 120 (29), 108 (8), 107 (11), 94 (5), 93 (33), 91 (17), 79 (8), 77 (13), 70 (4), 66 (3), 55 (11). HR-MS: 426.0485 ($C_{19}H_{23}BrO_4S$, calc. 426.0500).

(1RS,4RS,5SR,1'RS)-4-[1'-(4-Bromophenylsulfonyloxy)ethyl]-2,2-dimethylbicyclo[3.2.1]oct-6-en-3-one (**14b**). From aldol **8b** (389 mg, 2 mmol) and brosyl chloride (511 mg, 2 mmol). LC (Et_2O/cyclohexane 1:12) afforded **14b** (557 mg, 72%). Colorless crystals. M.p. 87°. IR (KBr): 3082, 3046, 2970, 2933, 1693, 1577, 1473, 1393, 1372, 1360, 1190, 1174, 1068, 1012, 923, 909, 896, 824, 734, 609. ^{1}H-NMR ($CDCl_3$): 7.79, 7.70 (2*ddd*, ^3J = 9, ^4J = 2, ^5J = 2, 4 arom. H); 6.17, 6.07 (2*dd*, ^3J = 5.5, 3, H–C(6), H–C(7)); 5.10 (*dq*, ^3J = 6.5, 4.5, H–C(1')); 2.84 (*m*, H–C(5)); 2.40 (*m*, H–C(1), H–C(4)); 2.05 (*d*, ^2J = 11.5, H_{syn}–C(8)); 1.89 (*dddd*, ^2J = 11.5, ^3J = 5, 5, ^4J = 2, H_{anti}–C(8)); 1.29 (*d*, ^3J = 6.5, Me–C(1')); 1.13 (*s*, Me_{ax}); 1.00 (*s*, Me_{eq}). ^{13}C-NMR ($CDCl_3$): 214.78 (*s*, C(3)); 137.33, 136.96 (2*d*, C(6), C(7)); 136.41, 128.90 (2*s*, 2 arom. C); 132.57, 129.24 (2 × 2*d*, 4 arom. C); 80.85 (*d*, C(1')); 56.57 (*d*, C(4)); 50.69 (*s*, C(2)); 49.01, 39.15 (2*d*, C(1), C(5)); 35.41 (*t*, C(8)); 26.99, 25.08, 18.91 (3*q*, 3 Me). MS (130°): 238 (1), 236 (1), 221 (7), 219 (6), 193 (21), 176 (16), 157 (16), 155 (16), 148 (35), 133 (28), 119 (7), 108 (37), 107 (100), 106 (57), 93 (46), 91 (32), 79 (30), 77 (19), 70 (11), 69 (16), 66 (6). FAB-MS: 416 (21, $[M + 2 + 2H]^+$), 415 (100, $[M + 2 + H]^+$), 414 (25, $[M + 2]^+ = [M + 2H]^+$), 413 (97, $[M + H]^+$), 412 (6, M^+).

(1RS,2RS,5SR,1'SR)-2-[1'-(4-Bromophenylsulfonyloxy)ethyl]-2,4,4-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**15b**). From aldol **10b** (631 mg, 3 mmol) and brosyl chloride (767 mg, 3 mmol). LC (*t*-BuOMe/cyclohexane 1:12) afforded **15b** (876 mg, 68%). Colorless crystals. M.p. 121°. IR (KBr): 3100, 2983, 2945, 2875, 1716, 1577, 1473, 1391, 1359, 1185, 1071, 1061, 931, 901. ^{1}H-NMR ($CDCl_3$): 7.77, 7.68 (2*ddd*, ^3J = 9, ^4J = 1.5, ^5J = 1.5, 4 arom. H); 6.44 (*dd*, ^3J = 6, 2, H–C(6)); 6.28 (*dd*, ^3J = 6, 2, H–C(7)); 5.31 (*q*, ^3J = 6.5, H–C(1')); 4.72 (*d*, ^3J = 2, H–C(1)); 4.46 (*d*, ^3J = 2, H–C(5)); 1.44 (*d*, ^3J = 6.5, Me–C(1')); 1.32 (*s*, Me_{ax}–C(4)); 0.92 (*s*, Me_{eq}–C(4)); 0.88 (*s*, Me–C(2)). NOE: H–C(1')→H–C(1) (2.3), Me–C(1') (4.2), Me–C(2) (4.2), Me_{ax}–C(4) (4.4); Me–C(1')→H–C(1) (3.8); Me–C(2)→H–C(1) (2.3), H–C(7) (3.6), H–C(1') (2.5); Me_{ax}–C(4)→H–C(5) (4.2), H–C(1') (4.0); Me_{eq}–C(4)→H–C(5) (2.4), H–C(6) (3.2), Me_{ax}–C(4) (1.6). ^{13}H-NMR (APT, $CDCl_3$)[5]: 212.98 (↑, C(3)); 136.73, 128.73 (2↑, 2 arom. C); 135.23, 132.51 (2↓, C(6), C(7)); 132.41, 129.19 (2 × 2↓, 4 arom. C); 86.74, 82.30, 81.69 (3↓, C(1), C(5), C(1')); 58.11 (↑, C(2)); 51.65 (↑, C(4)); 26.62, 22.01, 17.20, 15.54 (4↓, 4 Me). MS (100°): 428 (1, M^+), 238 (2), 236 (1), 221 (6), 219 (6), 193 (4), 192 (16), 165 (13), 123 (59), 122 (100), 109 (64), 95 (57), 83 (87), 70 (17), 68 (4), 67 (9), 55 (28), 42 (19). FAB-MS: 431 (100, $[M + 2 + H]^+$), 429 (92, $[M + H]^+$). HR-MS: 192.1149 ($C_{12}H_{16}O_2$, calc. 192.1150).

(1RS,4SR,5SR,1'RS)-4-[1'-(4-Bromophenylsulfonyloxy)ethyl]-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**16b**). From aldol **11b** (590 mg, 3 mmol) and brosyl chloride (767 mg, 3 mmol). LC (*t*-BuOMe/cyclohexane 1:9) afforded **16b** (947 mg, 76%). Colorless crystals. M.p. 104°. IR (KBr): 3074, 2968, 2942, 2875, 1697, 1576, 1474, 1391, 1368, 1188, 1095, 1087, 1070, 942, 921, 900, 820. ^{1}H-NMR ($CDCl_3$): 7.81, 7.70 (*ddd*, ^3J = 9, ^4J = 2, ^5J = 2, 4 arom. H); 6.37 (*dd*, ^3J = 6, 2, H–C(7)); 6.26 (*dd*, ^3J = 6, 2, H–C(6)); 5.10 (*dq*, ^3J = 6, 6, H–C(1')); 4.98 (*d*, ^3J = 2, H–C(5)); 4.45 (*d*, ^3J = 2, H–C(1)); 2.44 (*d*, ^3J = 6, H–C(4)); 1.40 (*d*, ^3J = 6, Me–C(1')); 1.24 (*s*, Me_{ax}–C(2)); 0.94

(*s*, Me_{eq}–C(2)). NOE: H–C(4)→H–C(5) (5.3), H–C(6) (4.3), H–C(1′) (8.5); H–C(6)→H–C(4) (4.4), H–C(5) (5.2); H–C(7)→H–C(1) (4.7); Me_{ax}–C(2)→H–C(1) (4.3), H–C(1′) (2.6), Me_{eq}–C(2) (2.1); Me_{eq}–C(2)→H–C(1) (2.3), H–C(7) (2.8). ^{13}H-NMR (APT, $CDCl_3$)[5]: 210.42 (↑, C(3)); 136.02, 128.95 (2↑, 2 arom. C); 134.08, 133.83 (2↓, C(6), C(7)); 132.54, 129.27 (2 × 2↓, 4 arom. C); 85.70, 79.64, 77.76 (3↓, C(1), C(5), C(1′)); 57.78 (↓, C(4)); 52.12 (↑, C(2)); 26.05, 21.07, 18.91 (3↓, 3 Me). MS (160°): 221 (5), 219 (5), 179 (5), 178 (32), 135 (23), 134 (86), 109 (52), 108 (100), 95 (40), 81 (18), 69 (32), 68 (6), 67 (8), 55 (7), 43 (17), 42 (15), 41 (30). FAB-MS: 418 (22, $[M + 2 + 2H]^+$), 417 (100, $[M + 2 + H]^+$), 416 (42, $[M + 2H]^+ = [M + 2]^+$), 415 (99, $[M + H]^+$), 414 (24, M^+). HR-MS: 178.0994 ($C_{11}H_{14}O_2$, calc. 178.0994).

3. *Enones* **17a–d** *and* **18a–d**. *(1*RS,*5*SR,*4*E*)-4-Ethylidene-2,2-dimethylbicyclo[3.2.1]oct-6-en-3-one* (**17b**). To a soln. of LDA (3.3 mmol) in THF (10 ml) was added **14b** (1.24 g, 3 mmol) in THF (5 ml) at −5°. After 1 h, the mixture was cooled to −20°, and TMEDA (0.38 g, 0.5 ml, 3.3 mmol) added, and the mixture stirred for 1 h at 0°. Then sat. aq. NH_4Cl soln. (10 ml) was added. The aq. phase was extracted with Et_2O (3 × 20 ml), the combined org. layer dried ($MgSO_4$) and evaporated and the crude product purified by LC (Et_2O/petroleum ether 1:12): **17b** (274 mg, 55%). Enone **17b** was also formed as minor product in the reaction of **2** (3 mmol) with acetaldehyde (**2**→**8b**): 25 mg (5%). Colorless oil. IR ($CHCl_3$): 3064, 2968, 2944, 2924, 2868, 1684, 1620, 1456, 1380, 1360, 1104, 1016. ^{1}H-NMR ($CDCl_3$): 6.51 (*dq*, ^3J = 7.5, ^4J = 0.5, H–C(1′)); 6.16, 6.02 (*2dd*, ^3J = 6, 3, H–C(6), H–C(7)); 3.58 (*m*, H–C(5)); 2.48 (*m*, H–C(1)); 2.06 (*m*, 2H–C(8)); 1.78 (*d*, ^3J = 7.5, Me–C(1′)); 1.19 (*s*, Me_{ax}); 1.07 (*s*, Me_{eq}). MS: 177 (11), 176 (96, M^+), 162 (7), 161 (47), 147 (9), 133 (21), 119 (10), 108 (42), 106 (21), 105 (87), 94 (9), 93 (100), 91 (58), 79 (32), 77 (42), 70 (4), 67 (11), 66 (17), 42 (8). HR-MS: 176.1202 ($C_{12}H_{16}O$, calc. 176.1201).

*(1*RS,*5*SR,*4*E*)-4-Benzylidene-2,2-dimethylbicyclo[3.2.1]oct-6-en-3-one* (**17c**). To a soln. of LDA (3.3 mmol) in THF (10 ml) was added **8c** (770 mg, 3 mmol) in THF (10 ml) at −40°. The mixture was stirred for 30 min at −40°, then brosyl chloride (767 mg, 3 mmol) in THF (15 ml) was added. Stirring was continued for 1 h at −10°. Then H_2O was added, the aq. phase extracted with Et_2O (3 × 20 ml), the combined org. phase dried and evaporated, and the residue purified by LC (*t*-BuOMe/cyclohexane 1:25→1:9): **17c** (436 mg, 61%). Enone **17c** was also formed as minor product in the reaction of **2** (3 mmol) with benzaldehyde (**2**→**8c**): 122 mg (17%). Colorless platelets. M.p. 99°. IR (KBr): 3060, 2980, 2913, 2868, 1682, 1610, 1574, 1493, 1472, 1456, 1446, 1379, 1359, 1106, 1032, 1020, 931, 767, 740, 701. ^{1}H-NMR ($CDCl_3$): 7.46–7.27 (*m*, 5 arom. H, H–C(1′)); 6.27, 6.17 (*2dd*, ^3J = 5.5, 3, H–C(6), H–C(7)); 3.88 (*m*, H–C(5)); 2.53 (*m*, H–C(1)); 2.09 (*m*, 2H–C(8)); 1.26 (*s*, Me_{ax}); 1.14 (*s*, Me_{eq}). MS (60°): 238 (100, M^+), 223 (25), 211 (17), 196 (17), 168 (20), 167 (60), 166 (32), 153 (9), 152 (18), 145 (5), 144 (21), 129 (10), 128 (13), 116 (18), 108 (37), 93 (73), 91 (35), 77 (26), 66 (7), 42 (16). HR-MS: 238.1358 ($C_{17}H_{18}O$, calc. 238.1358).

*(1*RS,*5*SR,*4*E*)-4-Isobutylidene-2,2-dimethylbicyclo[3.2.1]oct-6-en-3-one* (**17d**). From **2** (451 mg, 3 mmol) and isobutyraldehyde (1.08 g, 1.4 ml, 3 mmol) according to the *General Procedure* of *Chapt. 1* (2.5 h, r.t.). LC (*t*-BuOMe/cyclohexane 1:12) afforded **17d** (55 mg, 9%; isolation of the aldol was not possible). Yellow oil. IR ($CHCl_3$): 3064, 2966, 2928, 2871, 1684, 1620, 1461, 1382, 1362, 1108, 940, 905. ^{1}H-NMR ($CDCl_3$): 6.27 (*d*, ^3J = 10, H–C(1′)); 6.16, 6.00 (*2dd*, ^3J = 5.5, 3, H–C(6), H–C(7)); 3.54 (*m*, H–C(5)); 2.65 (*dqq*, ^3J = 10, 6.5, 6.5, Me_2CH); 2.47 (*m*, H–C(1)); 2.04 (*m*, 2H–C(8)); 1.20 (*s*, Me_{ax}); 1.07 (*s*, Me_{eq}); 1.03, 1.01 (*2d*, ^3J = 6.5, Me_2CH). ^{13}C-NMR (APT, $CDCl_3$)[5]: 206.71 (↑, C(3)); 141.09 (↓, C(1′)); 136.16 (↑, C(4)); 135.96, 135.76 (2↓, C(6), C(7)); 49.64 (↓, C(5)); 48.15 (↑, C(2)); 40.63 (↓, C(1)); 38.12 (↑, C(8)); 27.62, 26.91, 24.61, 22.65, 22.54 (5↓, 5 Me). MS: 205 (16), 204 (84, M^+), 190 (13), 189 (58), 162 (7), 161 (40), 147 (11), 134 (23), 133 (34), 119 (20), 108 (42), 107 (14), 105 (39), 95 (7), 93 (100), 91 (90), 79 (29), 77 (39), 70 (6), 69 (18), 67 (20), 66 (12). HR-MS: 204.1515 ($C_{14}H_{20}O$, calc. 204.1514).

*(1*RS,*5*SR,*4*E*)-4-Ethylidene-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one* (**18b**). As described for **17b**, from **16b** (1.25 g, 3 mmol) and TMEDA (0.38 g, 0.5 ml, 3.3 mmol). LC (*t*-BuOMe/cyclohexane 1:9) afforded **18b** (246 mg, 46%). Enone **18b** was also formed as minor product in the reaction of **5** (3 mmol) with acetaldehyde (**5**→**11b**): 16 mg (3%). Colorless crystals. M.p. 34°. IR (KBr): 3079, 2971, 2931, 2867, 1696, 1636, 1467, 1445, 1381, 1360, 1219, 1046, 948, 923, 733. ^{1}H-NMR ($CDCl_3$): 6.56 (*dq*, ^3J = 7.5, ^4J = 1, H–C(1′)); 6.35, 6.29 (*dd*, *ddd*, ^3J = 6, 1.5, J = 0.5, H–C(6), H–C(7)); 5.51 (*dd*, ^3J = 1.5, ^4J = 1, H–C(5)); 4.50 (*d*, ^3J = 1.5, H–C(1)); 1.80 (*d*, ^3J = 7.5, Me–C(1′)); 1.30 (*s*, Me_{ax}); 1.00 (*s*, Me_{eq}). NOE: H–C(5)→Me–C(1′) (6.2); Me–C(1′)→H–C(5) (3.1), H–C(1′) (2.3). ^{13}C-NMR (APT, $CDCl_3$)[5]: 202.37 (↑, C(3)); 135.89 (↑, C(4)); 133.79, 132.20, 129.76 (3↓, C(6), C(7), C(1′)); 86.40, 77.06 (2↓, C(1), C(5)); 49.18 (↑, C(2)); 26.15, 20.09, 12.97 (3↓, 3 Me). MS: 179 (11), 178 (89, M^+), 163 (23), 150 (11), 149 (35), 135 (36), 110 (13), 108 (21), 107 (67), 95 (100), 93 (18), 91 (41), 79 (56), 77 (47), 70 (35), 68 (16), 67 (19), 42 (33), 41 (73). HR-MS: 178.0994 ($C_{11}H_{14}O_2$, calc. 178.0994).

*(1*RS,*5*SR,*4*E*)-4-Benzylidene-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one* (**18c**). As described for **17c**, from **11c** (775 mg, 3 mmol) and brosyl chloride (767 mg, 3 mmol). LC (*t*-BuOMe/cyclohexane 1:9) gave **18c** (598 mg, 83%). Enone **18c** was also formed as minor product in the reaction of **5** (3 mmol) with benzaldehyde (**5**→**11c**): 58 mg (8%). Colorless crystals. M.p. 121°. IR (KBr): 3085, 3058, 2976, 2931, 2875, 1688, 1616, 1573, 1493, 1471,

1445, 1381, 1359, 1147, 1048, 930, 898, 703. ^{1}H-NMR ($CDCl_3$): 7.50–7.26 (*m*, 5 arom. H, H–C(1′)); 6.51, 6.44 (*ddd*, *dd*, ^3J = 6, 2, J = 0.5, H–C(6), H–C(7)); 5.69 (*dd*, ^3J = 2, ^4J = 1, H–C(5)); 4.55 (*d*, ^3J = 2, H–C(1)); 1.37 (*s*, Me_{ax}); 1.08 (*s*, Me_{eq}). ^{13}C-NMR (APT, $CDCl_3$)[5]): 203.11 (↑, C(3)); 134.91, 134.53 (2↑, arom. C, C(4)); 133.55, 132.75, 132.05 (3↓, C(6), C(7), C(1′)); 129.45 (2↓, 2 arom. C); 128.88 (↓, arom. C); 128.54 (2↓, 2 arom. C); 86.57, 78.06 (2↓, C(1), C(5)); 49.87 (↑, C(2)); 26.35, 20.24 (2↓, 2 Me). MS (90°): 241 (8), 240 (42, M^+), 225 (64), 211 (40), 197 (27), 170 (10), 169 (18), 149 (19), 142 (15), 141 (60), 115 (62), 102 (29), 95 (100), 91 (32), 77 (23), 70 (9), 68 (4), 67 (10), 42 (15), 41 (36). HR-MS: 240.1151 ($C_{16}H_{16}O_2$, calc. 240.1150).

*(1*RS,5SR,*4*E*)-4-Isobutylidene-2,2-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one* (**18d**). From **5** (3 mmol) and isobutyraldehyde according to the *General Procedure* of *Chapt. 1* (30 min, −30°): 68 mg (11%). Light yellow crystals. M.p. 71°. IR (KBr): 3081, 2968, 2928, 2869, 1691, 1626, 1463, 1379, 1356, 1119, 1045, 946, 929, 740. ^{1}H-NMR ($CDCl_3$): 6.35, 6.26 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 6.32 (*dd*, ^3J = 11, ^4J = 1, H–C(1′)); 5.48 (br. *m*, H–C(5)); 4.49 (*d*, ^3J = 2, H–C(1)); 2.62 (*dqq*, ^3J = 6.5, 6.5, 11, Me_2CH); 1.30 (*s*, Me_{ax}); 1.08, 1.02 (2*d*, ^3J = 6.5, Me_2CH); 1.00 (*s*, Me_{eq}). ^{13}C-NMR (APT, $CDCl_3$)[5]): 202.95 (↑, C(3)); 141.51, 134.11, 132.15 (3↓, C(6), C(7), C(1′)); 132.62 (↑, C(4)); 86.41, 77.51 (2↓, C(1), C(5)); 49.37 (↑, C(2)); 26.84, 26.24, 22.73, 22.45, 20.15 (5↓, 5 Me). MS: 207 (13), 206 (96, M^+), 191 (43), 173 (22), 163 (32), 135 (49), 121 (34), 105 (21), 95 (100), 91 (36), 70 (16), 68 (5), 67 (16), 55 (26). HR-MS: 206.1306 ($C_{13}H_{18}O_2$, calc. 206.1307).

*(1*RS,*4*SR,*5*SR*)-2,2,4-Trimethyl-4-(phenylselenenyl)bicyclo[3.2.1]oct-6-en-3-one* (**19**). To a soln. of LDA (5.3 mmol) in THF (15 ml) was added **1** (790 mg, 4.8 mmol) in THF (10 ml) at −20°. After 1 h at −5°, benzeneselenenyl bromide (945 mg, 4 mmol) in THF (10 ml) was added and stirring continued for 1 h at −5°. Then half-conc. aq. NaCl soln. (15 ml) was added, the aq. layer extracted with Et_2O (3 × 15 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue submitted to LC (*t*-BuOMe/cyclohexane 1:50): **19**/**1** 7:3 (693 mg, 34%). Yellow oil. ^{1}H-NMR ($CDCl_3$): 7.57–7.47, 7.44–7.25 (2*m*, 2 and 3 arom. H); 6.29, 6.14 (2*dd*, ^3J = 5.5, 3, H–C(6), H–C(7)); 2.86 (*dd*, ^3J = 5, 3, H–C(5)); 2.73 (*d*, ^3J = 12, H_{syn}–C(8)); 2.47 (*dd*, ^3J = 5, 3, H–C(1)); 1.95 (*ddd*, ^2J = 12, ^3J = 5, 5, H_{anti}–C(8)); 1.65 (*s*, Me_{ax}–C(2)); 1.28 (*s*, Me–C(4)); 1.02 (*s*, Me_{eq}–C(2)).

*(1*RS,*5*SR*)-2,2-Dimethyl-4-methylidenebicyclo[3.2.1]oct-6-en-3-one* (**17a**). To a soln. of **19** (300 mg, 0.77 mmol) in CH_2Cl_2 (5 ml) were added pyridine (670 mg, 685 µl, 8.47 mmol), H_2O_2 (875 µl, 7.7 mmol, 30%), and H_2O (1 ml) at 0°. After 1 h at r.t., the mixture was extracted with CH_2Cl_2 (3 × 30 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the residue chromatographed: **17a**/**1** 8:2 (132 mg, 95%). Yellow oil. IR (film): 3062, 2969, 2944, 2871, 1695, 1615, 1474, 1460, 1381, 1360, 1047, 943, 752. ^{1}H-NMR (CD_2Cl_2): 6.20, 6.04 (2*ddd*, ^3J = 6, 3, J = 0.5, H–C(6), H–C(7)); 5.69 (*d*, ^2J = 2, H–C(1′) *cis* to C(3)); 5.04 (*d*, ^2J = 2, H–C(1′) *trans* to C(3)); 3.33 (*m*, H–C(5)); 2.50 (*m*, H–C(1)); 2.08 (*m*, 2 H–C(8)); 1.16 (*s*, Me_{ax}); 1.05 (*s*, Me_{eq}).

*(1*RS,*4*SR,*5*SR*)-2,2,4-Trimethyl-4-(phenylselenenyl)-8-oxabicyclo[3.2.1]oct-6-en-3-one* (**20**). As described for **19**, with **4** (665 mg, 4 mmol) and benzeneselenenyl bromide (944 mg, 4 mmol). LC (AcOEt/$CHCl_3$/cyclohexane 1:2:12) gave **20** (387 mg, 30%). Fine yellow needles. M.p. 71°. ^{1}H-NMR ($CDCl_3$): 7.55–7.46, 7.44–7.25 (2*m*, 2 and 3 arom. H); 6.49, 6.36 (2*dd*, ^3J = 6, 2, H–C(6), H–C(7)); 4.90 (*d*, ^3J = 2, H–C(5)); 4.52 (*d*, ^3J = 2, H–C(1)); 1.81 (*s*, Me_{ax}–C(2)); 1.11, 0.97 (2*s*, 2 Me).

*(1*RS,*5*SR*)-2,2-Dimethyl-4-methylidene-8-oxabicyclo[3.2.1]oct-6-en-3-one* (**18a**). As described for **17a**, with **20** (289 mg, 0.9 mmol), pyridine (783 mg, 801 µl, 9.9 mmol), H_2O_2 (1 ml, 9 mmol, 30%) and H_2O (1 ml). LC (AcOEt/$CHCl_3$/cyclohexane 1:2:12) afforded **18a** (86 mg, 91%). Colorless oil. IR (film): 3090, 2966, 2932, 2871, 1726, 1702, 1628, 1471, 1382, 1360, 1068, 935, 740, 700. ^{1}H-NMR ($CDCl_3$): 6.39, 6.31 (2*dd*, ^3J = 5.5, 2, H–C(6), H–C(7)); 5.87 (br. *s*, H–C(1′) *cis* to C(3)); 5.20 (*d*, ^3J = 2, H–C(5)); 5.16 (br. *s*, H–C(1′) *trans* to C(3)); 4.51 (*d*, ^3J = 2, H–C(1)); 1.31 (*s*, Me_{ax}); 1.03 (*s*, Me_{eq}).

4. *Tertiary-Alcohol Derivatives* **22**, **25**, *and* **27**. *(1*RS,*5*SR*)-2,4,4-Trimethyl-3-(trimethylsiloxy)bicyclo[3.2.1]octa-2,6-diene* (**21**). To a soln. of LDA (9.9 mmol) in THF (20 ml) was added **1** (1.48 g, 9 mmol) in THF (10 ml) at −40°. The mixture was stirred for 1 h at −5°, then Me_3SiCl (0.98 g, 1.14 ml, 9 mmol) was added. After 1.5 h at r.t., the solvent was evaporated and the residue distilled ('Kugelrohr' apparatus, 80°/0.05 Torr): H_2O-sensitive **21** (1.77 g, 83%). Light yellow oil. ^{1}H-NMR (CD_2Cl_2): 6.38, 5.81 (2*dd*, ^3J = 5.5, 3, H–C(6), H–C(7)); 2.48, 2.41 (2*ddd*, ^3J = 4.5, 3, 1, H–C(1), H–C(5)); 1.85 (*ddd*, ^2J = 9, ^3J = 1, 1, H_{syn}–C(8)); 1.71 (*ddd*, ^2J = 9, ^3J = 4.5, 4.5, H_{anti}–C(8)); 1.61 (*s*, Me–C(2)); 1.15 (*s*, Me_{ax}–C(4)); 0.86 (*s*, Me_{eq}–C(4)); 0.18 (*s*, Me_3SiO).

*(1*RS,*2*SR,*5*SR*)-2-(1′-Hydroxy-1′-methylethyl)-2,4,4-trimethylbicyclo[3.2.1]oct-6-en-3-one* (**22**). *Method A.* To a soln. of $TiCl_4$ (400 mg, 0.23 ml, 2.1 mmol) in CH_2Cl_2 (3 ml) was added acetone (134 mg, 0.17 ml, 2.32 mmol) at 0°, and the mixture was stirred for 5 min. A soln. of **21** (500 mg, 2.1 mmol) in CH_2Cl_2 (2 ml) was added dropwise within 15 min and stirring continued for 1 h at 0°. The dark mixture was transferred to a separating funnel with ice-water (50 ml) and extracted with CH_2Cl_2 (2 × 30 ml). The combined org. phase was dried and evaporated and the residue purified by LC (*t*-BuOMe/cyclohexane 1:40): **22** (98 mg, 21%).

Method B. To Mg (113 mg, 4.7 mmol) in Et_2O (10 ml) was added MeI (664 mg, 290 µl, 4.7 mmol). After complete addition, the mixture was refluxed for further 30 min, then cooled to 0°, and **23** (770 mg, 3.75 mmol) in Et_2O (2 ml) added. After 30 min at 0°, ice-water (20 ml) was added (and 2N HCl to dissolve the precipitate). The aq. phase was extracted with Et_2O (3 × 50 ml), the combined org. phase washed with sat. aq. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated; and the crude product purified by LC: **22** (486 mg, 55%). Colorless crystals. M.p. 61°. IR ($CHCl_3$): 3441, 3064, 2982, 2943, 2874, 1670, 1470, 1461, 1392, 1373, 1359, 1015, 948. ^{1}H-NMR ($CDCl_3$): 6.23, 6.16 (*2dd*, ^3J = 6, 3, H–C(6), H–C(7)); 4.26 (br. *m*, OH); 2.69 (*dd*, ^3J = 5.5, 3, H–C(1)); 2.34 (*dd*, ^3J = 5.5, 3, H–C(5)); 2.25 (*d*, ^2J = 11.5, H_{syn}–C(8)); 1.93 (*ddd*, ^2J = 11.5, ^3J = 5.5, 5.5, H_{anti}–C(8)); 1.30 (*s*, Me_{ax}–C(4)); 1.22 (br. *s*, 2Me–C(1′)); 1.09, 1.04 (2*s*, 2Me). ^{13}C-NMR (APT, $CDCl_3$)[5]: 227.63 (↑, C(3)); 137.18, 136.69 (2↓, C(6), C(7)); 75.53 (↑, C(1′)); 58.71 (↑, C(2)); 49.92 (↑, C(4)); 48.77, 43.79 (2↓, C(1), C(5)); 37.34 (↑, C(8)); 29.48, 27.72, 26.54, 25.43, 20.88 (5↓, 5Me). MS: 207 (4), 164 (82), 149 (15), 135 (36), 121 (21), 108 (14), 107 (11), 105 (7), 94 (100), 93 (71), 91 (22), 79 (17), 70 (17), 66 (5), 59 (72), 43 (14), 41 (27). FAB-MS: 223 (32, $[M + H]^+$), 221 (100, $[M - H]^+$). HR-MS: 207.1386 ($C_{13}H_{19}O_2$, calc. 207.1385).

(1RS,2SR,5SR)-2-Acetyl-2,4,4-trimethylbicyclo[3.2.1]oct-6-en-3-one (**23**). Alcohol **7b** (417 mg, 2 mmol) was dissolved in acetone (10 ml) and treated with *Jones* reagent (0.5 ml, 2 mmol) at −78° [9]. The mixture was stirred for 1 h at 0° and then decanted. The solid Cr^{III} salts were washed with acetone and the combined org. layers evaporated. The residue was dissolved in Et_2O, dried ($MgSO_4$), and purified by LC (*t*-BuOMe/cyclohexane 1:12): **23** (388 mg, 94%). Colorless oil. IR (film): 3062, 2975, 2936, 2872, 1717, 1692, 1475, 1461, 1383, 1359, 1210, 744. ^{1}H-NMR ($CDCl_3$): 6.29, 6.19 (br. *ddd*, *dd*, ^3J = 6, 3, *J* = 0.5, H–C(6), H–C(7)); 3.03 (*dd*, ^3J = 5.5, 3, H–C(1)); 2.39 (*dd*, ^3J = 5.5, 3, H–C(5)); 2.21 (*d*, ^2J = 11.5, H_{syn}–C(8)); 2.13 (*s*, Me–C(1′)); 1.92 (*ddd*, ^2J = 11.5, ^3J = 5.5, 5.5, H_{anti}–C(8)); 1.25 (*s*, Me_{ax}–C(4)); 1.13, 1.08 (2*s*, 2 Me). ^{13}C-NMR ($CDCl_3$): 214.62, 207.24 (2*s*, C(3), C(1′)); 139.48, 134.13 (2*d*, C(6), C(7)); 68.59 (*s*, C(2)); 51.70 (*s*, C(4)); 50.25, 45.97 (2*d*, C(1), C(5)); 36.31 (*t*, C(8)); 26.81, 25.45, 24.97, 21.72 (4*q*, 4Me). MS: 207 (5), 206 (24, M^+), 190 (10), 178 (27), 164 (34), 163 (59), 147 (20), 136 (29), 135 (41), 121 (28), 119 (35), 107 (28), 105 (37), 94 (53), 93 (100), 91 (65), 79 (27), 77 (53), 70 (13), 66 (11), 55 (23). HR-MS: 206.1306 ($C_{13}H_{18}O_2$, calc. 206.1307).

(1RS,2SR,5SR)-2-Acetyl-2,4,4-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**26**). As described for **23**, with **10b** (2.1 g, 10 mmol) and *Jones* reagent (2.5 ml, 10 mmol) [9]. LC (*t*-BuOMe/cyclohexane 1:4→1:3) gave **26** (1.92 g, 91%). Colorless crystals. M.p. 42°. IR (film): 3089, 2975, 2934, 2871, 1722, 1698, 1470, 1460, 1447, 1384, 1359, 1057, 935, 740. ^{1}H-NMR ($CDCl_3$): 6.47, 6.31 (*2dd*, ^3J = 6, 2, H–C(6), H–C(7)); 5.26 (*d*, ^3J = 2, H–C(1)); 4.43 (*d*, ^3J = 2, H–C(5)); 2.20 (*s*, Me–C(1′)); 1.22, 1.14 (2*s*, Me_{ax}–C(4), Me_{eq}–C(2)); 0.99 (*s*, Me_{eq}–C(4)). ^{13}C-NMR ($CDCl_3$): 210.24, 204.25 (2*s*, C(3), C(1′)); 136.11, 131.95 (2*d*, C(6), C(7)); 86.51, 82.12 (2*d*, C(1), C(5)); 68.76 (*s*, C(2)), 53.02 (*s*, C(4)); 25.53, 25.37, 20.49, 17.46 (4*q*, 4 Me). MS: 209 (1), 208 (9, M^+), 193 (2), 165 (98), 148 (45), 138 (75), 137 (25), 110 (18), 109 (46), 99 (72), 95 (100), 70 (26), 68 (7), 67 (13), 43 (9), 41 (39). HR-MS: 208.1100 ($C_{12}H_{16}O_3$, calc. 208.1100).

(1RS,2SR,5SR)-2-(1′-Hydroxy-1′-methylethyl)-2,4,4-trimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**27**). *Reagent Me_4Zr:* $ZrCl_4$ (700 mg, 3 mmol) in Et_2O (7.5 ml) and toluene (7.5 ml) were heated under reflux. The resulting soln. was cooled to −78° and the precipitated $ZrCl_4 \cdot OEt_2$ dissolved by addition of MeLi (8.9 ml, 12 mmol, 1.35M in Et_2O). *Reagent Me_4Ti:* To a soln. of MeLi (8.9 ml, 12 mmol, 1.35M in Et_2O) in Et_2O (15 ml) was added carefully $TiCl_4$ (0.57 g, 0.32 ml, 3 mmol) at −78°. The resulting mixture was stirred for 15 min. *Alkylation of* **26**: To the soln. of the reagent was added **26** (625 mg, 3 mmol) in Et_2O (5 ml) at −78°. The mixture was stirred (Me_4Ti: 0°, 1 h; Me_4Zr: −30°, 2 h) and then quenched with sat. aq. NH_4F soln. (25 ml) at −20°. The aq. phase was extracted with Et_2O (3 × 20 ml), the combined org. phase dried ($MgSO_4$) and evaporated, and the crude product purified by LC (AcOEt/$CHCl_3$/cyclohexane 1:8:4): **27** (477 mg, 71%) with Me_4Zr and 276 mg (41%) with Me_4Ti). Colorless crystals. M.p. 94°. IR (KBr): 3462, 3073, 2984, 2940, 1697, 1475, 1384, 1358, 1189, 1047, 935, 925, 751. ^{1}H-NMR (C_6D_6): 5.87, 5.76 (*2dd*, ^3J = 6, 2, H–C(6), H–C(7)); 4.72 (*d*, ^3J = 2, H–C(1)); 4.49 (br. *m*, OH); 4.06 (*d*, ^3J = 2, H–C(5)); 1.28, 1.27, 1.24 (3*s*, 2Me–C(1′), Me_{ax}–C(4)); 0.76, 0.70 (2*s*, 2Me_{eq}); on H/D-exchange, the *m* at 4.49 disappeared; ^{1}H-NMR ($CDCl_3$): 6.47, 6.36 (*2dd*, ^3J = 6, 2, H–C(6), H–C(7)); 5.02 (*d*, ^3J = 2, H–C(1)); 4.49 (*d*, ^3J = 2, H–C(5)); 4.47 (br. *m*, OH); 1.34, 1.33, 1.18 (3*s*, 2Me–C(1′), Me_{ax}–C(4)); 0.97, 0.92 (2*s*, 2Me_{eq}). ^{13}C-NMR (APT, $CDCl_3$)[5]: 218.49 (↑, C(3)); 134.75, 133.35 (2↓, C(6), C(7)); 86.50, 82.29 (2↓, C(1), C(5)); 75.36 (↑, C(1′)); 60.36 (↑, C(2)); 51.39 (↑, C(4)); 27.87, 25.91, 25.66, 22.75, 18.18 (5↓, 5Me). MS: 224 (2, M^+), 209 (4), 191 (2), 166 (48), 165 (2), 151 (22), 138 (15), 137 (100), 123 (37), 111 (23), 110 (18), 109 (15), 97 (66), 96 (36), 95 (70), 70 (14), 68 (4), 67 (12), 59 (41), 43 (43), 42 (8), 41 (28). HR-MS: 224.1412 ($C_{13}H_{20}O_3$, calc. 224.1413).

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