purification, was dissolved in THF and treated with (carbethoxymethylene)triphenylphosphorane[14] (2 g, 5.7 mmol). The reaction was stirred at room temperature for 10 h and was evaporated. The residue was chromatographed on silica gel, eluting with ether–hexanes (1:1) to give an oily ester that was dissolved in methanol–water (4:1) and treated with sodium hydroxide (500 mg) in water (1 mL). This mixture was stirred at room temperature for 30 min, the solvent was evaporated, and the residue was dissolved in water. This solution was washed with ether and acidified to pH 2 with 1 N HCl, and the product was extracted into ethyl acetate. The organic layer was dried and evaporated to obtain, after recrystallization from MeOH–H_2O, **8**: 520 mg (45% yield); mp 149–151 °C; $[\alpha]^{25}_D$ −100° (*c* 0.64, MeOH); IR (KBr) 3400, 1710, 1695, 1675, 1660 cm^{-1}; ^1H NMR (CD_3OD) δ 1.35 (s, 9 H), 2.6–3.0 (m, 2 H), 3.85–3.95 (m, 1 H), 4.3 (br s, 1 H), 6.0–6.15 (m, 1 H, J = 17 Hz), 6.92–7.05 (m, 1 H, J = 17 Hz), 7.15–7.35 (m, 5 H). Anal. Calcd for $C_{17}H_{23}NO_5$: C, 63.43; H, 7.21; N, 4.36. Found: C, 63.52; H, 7.16; N, 4.32.

(4*R*,5*S*)-*trans*-*N*-[(*tert*-Butyloxy)carbonyl]-5-amino-4-hydroxy-6-phenylhex-2-enoic Acid (9). Allylic alcohol **5** (1 g, 3.6 mmol) was subjected to the same reaction conditions as described for **4** in the above procedure to give **9** (560 mg, 49% yield) after recrystallization from MeOH–H_2O: mp 167–168 °C; $[\alpha]^{25}_D$ +5.3° (*c* 1, MeOH); IR (KBr) 3380, 1690, 1640 cm^{-1}; ^1H NMR (CD_3COCD_3/$CDCl_3$) 1.35 (s, 9 H), 2.5–3.2 (m, 2 H), 3.7–4.2 (m, 1 H), 4.30–4.55 (m, 1 H), 5.65 (d, 1 H), 5.95–6.30 (m, 1 H, J = 17 Hz), 6.9–7.4 (m, 6 H). Anal. Found: C, 63.75; H, 7.32; N, 4.43.

Boc-L-Phe-ψ-[(R)CHOHCH=]Gly-L-Pro-OMe (10). Compound **9** (159 mg, 0.5 mmol) was dissolved in a solution of methylene chloride (3 mL) and *N*-methylpiperidine[15] (NMP) (52 mg, 0.52 mmol) and cooled to −10 °C. Isobutyl chloroformate (63 mg, 0.46 mmol) was added in methylene chloride; the solution was stirred for 3.5 min, and a mixture of L-proline methyl ester hydrochloride (250 mg, 1.5 mmol) and *N*-methylpiperidine (150 mg, 1.5 mmol) in methylene chloride was added. The reaction was stirred at −10 °C for 0.5 h and at 0 °C for 5 h. The solvent was evaporated and the residue partitioned between ethyl acetate and water. The organic phase was washed with citric acid (0.5 M), 5% $NaHCO_3$, water, and brine and then dried and evaporated to give **10** (131 mg, 61% yield), which was recrystallized from EtOAc–hexanes: mp 182.5–184 °C; $[\alpha]^{25}_D$ −62° (*c* 0.96, $CHCl_3$); ^1H NMR δ 1.35 (s, 9 H), 1.9–2.3 (m, 5 H), 2.8 (d, 2 H), 3.75 (s, 3 H), 3.5–4.2 (m, 3 H), 4.3–4.8 (m, 3 H), 6.35–6.65 (m, 1 H, J = 17 Hz), 6.85–7.40 (m, 6 H). Anal. Calcd for $C_{23}H_{32}N_2O_6$: C, 63.87; H, 7.45; N, 6.47. Found: C, 63.90; H, 7.43; N, 6.48.

Boc-L-Phe-ψ-[COCH=]Gly-L-Pro-OMe (11). To Dess-Martin periodinane[16] (152 mg, 0.36 mmol) in methylene chloride (2 mL) at room temperature was added a solution of **10** (78 mg, 0.18 mmol) in methylene chloride (1 mL). The resulting cloudy suspension, which became clear over a 20-min period, was stirred at room temperature for 1.5 h and was added to a stirred aqueous mixture of sodium thiosulfate (1 g) and $NaHCO_3$ (2 g). After the mixture was stirred for 20 min, the organic layer was separated from the aqueous layer, washed with 5% $NaHCO_3$, dried, and evaporated to give crude **11** as a yellow foam, 66 mg. A more polar impurity was removed by silica gel chromatography, eluting with ether, to give pure **11** (45 mg, 58% yield) as an off-white foam: mp 60 °C (with previous softening); $[\alpha]^{25}_D$ −43° (*c* 0.43, $CHCl_3$); HPLC one peak, retention time 2.20 min (70% MeOH in H_2O, 2 mL/min); IR 1742, 1700, 1645 cm^{-1}; UV λ_{max} (MeOH) 229 nm (12 300); ^1H NMR δ 1.42 (s, 9 H), 1.9–2.2 (m, 4 H), 2.9–3.3 (m, 2 H), 3.66 (s, 3 H), 3.6–3.9 (m, 2 H), 4.5–4.7 (m, 1 H), 4.70–4.83 (m, 1 H), 5.15 (d, 1 H), 6.95–7.40 (m, 7 H). Anal. Calcd for $C_{23}H_{30}N_2O_6$: C, 64.17; H, 7.02; N, 6.50. Found: C, 64.11; H, 7.19; N, 6.40.

(2*R*,3*S*)-*N*-[(*tert*-Butyloxy)carbonyl]-3-amino-2-hydroxy-4-phenylbutanol (12). The allylic alcohol **4** (1 g, 3.6 mmol) was acetylated as described above in the preparation of **8**, and crystalline acetate of **4** was dissolved in methanol (20 mL) and cooled to −78 °C. Ozone was bubbled into the solution until a blue color persisted, and the excess ozone was purged with oxygen. A solution of sodium borohydride (240 mg) in methanol (1 mL) was added, and the mixture was allowed to warm to room temperature and stir for 0.5 h. A solution of sodium hydroxide (300 mg) in water (5 mL) was added, and the mixture was stirred for an additional 1 h at room temperature. Citric acid (0.5 M) was added until pH 7 was obtained, and the solution was evaporated; the product was extracted with ethyl acetate, and this solution was washed with citric acid (0.5 M), sodium bicarbonate (5%), and brine and evaporated to obtain **12** as an oil. Compound **12** was purified by crystallization from ethyl acetate–hexanes to give pure **12** as colorless crystals: 820 mg (80% yield); mp 88.5–90.5 °C; $[\alpha]^{25}_D$ −36.8° (*c* 1, $CHCl_3$); ^1H NMR δ 1.40 (s, 9 H), 2.90 (d, 2 H), 3.40–3.70 (m, 5 H), 3.80–4.00 (m, 1 H), 5.10 (d, 1 H), 7.20–7.41 (m, 5 H). Anal. Calcd for $C_{15}H_{23}NO_4$: C, 64.03; H, 8.23; N, 4.97. Found: C, 64.02; H, 8.31; N, 4.86.

(2*R*,3*S*)-*N*-[(*tert*-Butyloxy)carbonyl]-3-amino-2-acetoxy-4-phenylbutyl Acetate (13). Diol **12** was acetylated with acetic anhydride–pyridine at room temperature to give, after recrystallization from CH_2Cl_2–hexanes, pure **13**: 90% yield; mp 94–96 °C; ^1H NMR δ 1.38 (s, 9 H), 2.01 (s, 3 H), 2.10 (s, 3 H), 2.71 (d, 2 H), 3.91–4.30 (m, 3 H), 4.52–4.81 (m, 1 H), 4.95–5.20 (m, 1 H), 6.90–7.41 (m, 5 H). Anal. Calcd for $C_{19}H_{27}NO_6$: C, 62.45; H, 7.44; N, 3.83. Found: C, 62.22; H, 7.29; N, 3.74.

Crystals of **13** were orthorhombic, space group $P2_12_12_1$. The cell parameters were a = 9.828 (3) Å, b = 11.732 (3) Å, c = 17.457 (8) Å, V = 2013 Å^3, and d_{calcd} = 1.21 g cm^{-3} for Z = 4. The intensity data were measured on a Nicolet R3m-E diffractometer with Mo Kα radiation (λ = 0.710 73 Å) in the θ–2θ mode. The crystal size was 0.41 × 0.42 × 0.50 mm. The structure was solved by using the direct-methods routine SOLV of G. M. Sheldrick available from Nicolet. Of the 2027 total reflections, 1873 were considered to be observed [$I \geq 1.25\ \sigma(I)$]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and given thermal parameters equal to 1.2× the thermal parameters for carbon atoms to which they were bonded. The largest residual e density peak corresponded to an H atom bonded to an N atom. Refinement (for 238 adjustable parameters) converged at R = 0.043, R_w = 0.046, and GOF = 1.23.

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Registry No. **3**, 72155-45-4; **4**, 99113-28-7; **4** acetate, 99113-29-8; **5**, 99113-30-1; **7**, 99113-31-2; **8**, 99113-32-3; **8** ethyl ester, 99113-33-4; **9**, 99113-34-5; **10**, 99128-00-4; **11**, 99128-01-5; **12**, 99113-35-6; **13**, 99113-36-7; $Ph_3P{=}CHCO_2Et$, 1099-45-2; L-Pro-OMe·HCl, 2133-40-6; vinyl bromide, 593-60-2.

Supplementary Material Available: Lists of atomic coordinates, thermal parameters, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates (5 pages). (Observed and calculated structure factors available from the authors.) Ordering information is given on any current masthead page.

Rearrangements of Oxahomoadamantane Derivatives in Acidic Media. 2[1]

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Rearrangement reactions of 4-oxahomoadamantan-5-one[2] and its 2-*anti*-hydroxy derivative[1] have been reported previously. In continuation of our work we were interested in a systematic study of the rearrangements of all possible isomers of 2-substituted oxahomoadamantanones in acidic

(1) Part 1: Duddeck, H.; Wiskamp, V.; Rosenbaum, D. *J. Org. Chem.* **1981**, *46*, 5332. Cf. also: Duddeck, H.; Brosch, D. *J. Org. Chem.* **1983**, *48*, 3569.

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0022-3263/85/1950-5401$01.50/0

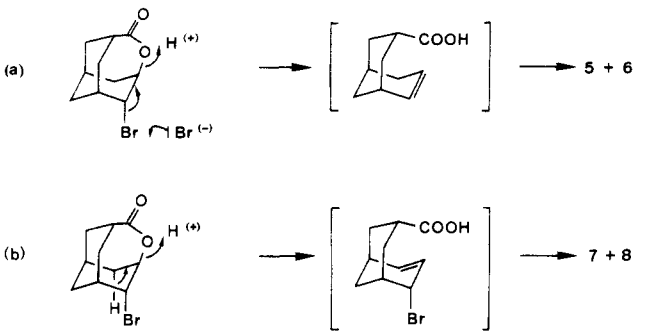
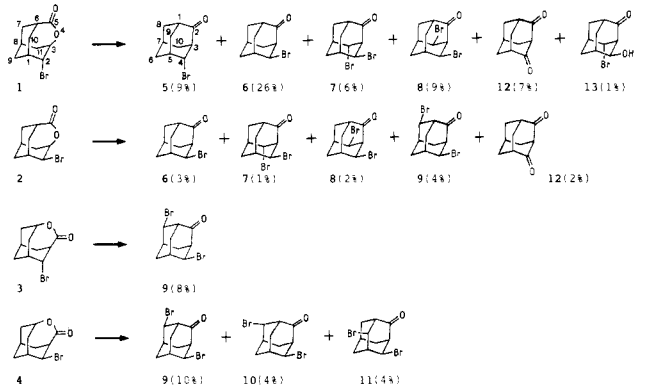


Figure 1. Reductive (a) and nonreductive fragmentation (b) of the bromo lactone **1**.

Scheme I. HBr-Catalyzed Rearrangements of the Bromooxahomoadamantanones 1-4



media. As an example we chose the bromo derivatives **1–4** reacting in 48% hydrobromic acid.

Results and Discussion

Rearrangement Reactions. It can be seen from Scheme I that generally the yields of adamantanone derivatives are low, probably due to the drastic reaction conditions in our experiments (reflux in 48% hydrobromic acid for 24 h). The temperature appeared to be necessary to start the reaction at all. In order to ensure thermodynamical control we chose a long reaction time (24 h) so that reproducible results were obtained. Shorter times (1–5 h) resulted in more complex product mixtures. This is in agreement with earlier reports.[3] Beside the adamantanones listed in Scheme I we found olefinic and bromine-containing carboxylic acid mixtures (as detected by ^{13}C NMR and mass spectra), the amount of which could not be reduced by shorter reaction times. Nevertheless, our approach offers one of the rare opportunities to obtain tritopic secondarily substituted adamantanes.[3,4]

The lactones **1** and **2** gave the reduction products **5** and **6** (Figure 1a), which are able to undergo mutual interconversion under these conditions.[5] This is reminiscent of our earlier findings with the 2-*anti*-hydroxy lactone (cf. Scheme VI in ref 1). In contrast to **2** the reduction is clearly dominating in the reaction of **1** because the stereoelectronic prerequisites are optimal in that case. A corresponding reduction associated with a fragmentation (Figure 1a) is impossible with **3** and **4**. Consequently, we did not find any monobromoadamantanones when refluxing these lactones in HBr.

Table I. 400-MHz ^1H NMR Data of the Dibromoadamantanones 7–11[a-c]

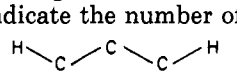
H	7	8	9	10	11
1	2.61 (m)	2.52 (m)	2.88 (m)	2.79 (m)	2.82 (m)
3	3.14 (m)	3.14 (m)	2.88 (m)	2.93 (m)	2.96 (m)
4e	5.19 (qa)	4.66 (qa)	4.72 (qa)	4.64 (m)	4.76 (t)
5	2.25 (m)	2.27 (m)	2.32 (m)	2.24 (m)	2.54 (m)
6	2.62 (d/m)	2.10 (d/qi)	2.27 (d/m)	1.87 (d/m)	1.88 (d/m)
6′	2.02 (d/qa)	2.38 (d/t)	2.27 (d/m)	2.70 (d/qa)	2.70 (d/qa)
7	2.30 (m)	2.27 (m)	2.32 (m)	2.29 (m)	2.01 (m)
8a	1.89 (d/qi)	2.55 (d/m)		4.42 (m)	1.84 (d/m)
8e	2.23 (d/t)	1.99 (d/qa)	4.72 (qa)		2.60 (d/qa)
9a	2.62 (d/m)	2.55 (d/m)	2.74 (d/m)	2.49 (d/m)	5.07 (m)
9e	1.96 (d/qa)	1.99 (d/qa)	2.12 (d/qa)	2.57 (d/qa)	
10a	4.43 (qa)		2.74 (d/m)	2.01 (d/qa)	2.12 (d/qa)
10e		4.66 (qa)	2.12 (d/qa)	2.32 (d/t)	2.16 (d/qa)

[a] In ppm, relative to internal tetramethylsilane, solvent $CDCl_3$. [b] For the numbering compare ref 9; H^6 and $H^{6'}$ have been assigned arbitrarily to the hydrogen atoms that are in axial or equatorial position, respectively, in the six-membered ring C^3–C^7 and C^{10}. [c] Letters in parentheses indicate the shape of the signals: d = doublet; t = triplet; qa = quartet; qi = quintet; m = complex multiplet.

Various dibromoadamantanones result from the reactions shown in Scheme I. This can be explained simply by a nonreductive fragmentation (Figure 1b) followed by a recyclization so that 4,10-dibromoadamantanones (**7** and **8**) are obtained from **1** and **2** whereas 4,8- and/or 4,9-dibromoadamantanones (**9–11**) were formed from **3** and **4**. The formation of **9** from **2**, however, is an exception that is not explained by simple mechanisms.[6] The fact that the diketone **12** is found in the product mixtures of **1** and **2** but not in those of **3** and **4** is a further argument that **12** is formed via an epoxonium–ketone rearrangment as proposed by us previously.[1]

The existence of the brominated hydroxyadamantanone **13** can be rationalized by an attack of a water molecule in the recylization step. It has been reported[7] that this can occur even in concentrated HBr to a small extent.

NMR Spectra. The structural assignment of the dibromoadamantanones **7–11** is based on high-field two-dimensional NMR methods.[8] Due to the high magnetic field 9.4 T; 400 MHz for ^1H) each proton signal could be identified separately, and in many cases valuable information was available from the signal splittings that are noted in Table I. Typical proton–proton coupling constants are 10–12 Hz for $^2J(^1H,^1H)$ (geminal) and 1.5–2.5 Hz for $^3J(^1H,^1H)$ (vicinal) and $^4J(^1H,^1H)$ in *W* orientation. Especially, the long-range couplings proved to be useful for stereochemical assignments of nonbridgehead hydrogens since they indicate the number of coplanar



moieties. Moreover, ^1H–^1H connectivities were derived

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(6) We have experimental hint that **3** is formed intermediately when **2** is treated with 48% HBr. This isomerization is not explainable at the moment but makes the formation of **9** understandable.
(7) Třiska, J.; Vodička, L.; Hlavatý, J. *Collect. Czech. Chem. Commun.* **1979**, *44*, 1448.
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Table II. ^{13}C Chemical Shifts of the Tritopic Adamantanes 7–11 and 13[a]

C	7	8	9	10	11	13
1	44.6	45.4	54.1	53.4	54.3	45.1
2	208.1	207.9	207.7	207.7	208.5	210.9
3	62.2	62.0	54.1	54.1	54.3	61.8
4	55.9	56.7	59.2	59.1	56.0	74.4
5	34.8	34.1	34.1	34.8	42.3	34.2[b]
6	31.8	36.7	37.7	31.5	34.6	30.3
7	34.1	34.1	34.1	33.8	25.8	33.6[b]
8	36.2	34.2	59.2	55.5	32.2	35.7
9	34.1	34.2	35.6	28.7	52.3	33.1
10	56.3	56.7	35.6	37.4	41.5	55.2

[a] In ppm, relative to internal tetramethylsilane, solvent $CDCl_3$. [b] May be interchanged.

from COSY45-2D NMR (homonuclear) experiments[8] so that unequivocal ^1H signal assignments were possible. Heteronuclear two-dimensional ^{13}C–^1H correlated spectra[8] afforded unambiguous ^{13}C signal assignments as well.

The structure determination of **13** was made by a comparison of its ^{13}C chemical shifts with those of the related dibromoadamantanones **7** and **8**. The CH_2 (C^6) signal at δ 30.3 is consistent only with formula **13**, which is structurally related to **7**; the diaxial[9] isomer can be excluded since no CH_2 signal below $\delta \sim 34$ is expected for that structure. The 4[e]-hydroxy 10[a]-bromo isomer can be excluded also because its C^8 chemical shift must be in the range of $\delta \sim 39$–40.[10]

For a number of tritopic adamantanes[4,10] we were able to show that interaction effects of pairs of substituents on the ^{13}C chemical shifts are additive to a large extent so that their ^{13}C chemical shifts can easily be calculated if those of the corresponding mono- and ditopic adamantanes are known. This rule can be applied to the dibromoadamantanones as well as is demonstrated for C^4 of **7**:

$\delta(C^4)$ in adamantanone	39.2
α subst effect of Br^4	25.9
γ-gauche subst effect of Br^{10}	−6.1
interactn effect (C=O, Br^4)	−5.0
interactn effect (Br^4, Br^{10})	0.4
calcd ^{13}C chem shift	54.4
exptl ^{13}C chem shift	55.9

Substantial deviations (>|2| ppm) between calculated and experimental chemical shifts are occasionally found only for carbonyl and brominated carbon atoms. Thus, the structural assignment may be carried out unequivocally also by such increment rules.

Experimental Section

Melting points were determined on a Büchi-Tottoli melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer; ^1H NMR spectra were obtained on Varian T-60 and Bruker WP-80 and AM-400 and ^{13}C NMR spectra on Bruker WH-90, WM-250, and AM-400 spectrometers. For the measurement of the two-dimensional NMR spectra[8] Bruker software was employed. ^1H and ^{13}C chemical shifts are referenced to internal tetramethylsilane. Mass spectra and high-resolution mass spectra (HRMS) were recorded on Varian MAT CH-5, CH-7, and 731 spectrometers.

All compounds were purified by column chromatography using Lobar columns (Merck) under medium pressure with various ligroin–acetone mixtures as eluants and were >98% pure. Compounds already known (**1**-4[11], **5**[10], **6**,[10] and **12**[1]) were identified by comparing their spectra. In most cases authentic samples were available for comparison by thin-layer chromatography. All yields refer to isolated material after purification and are uncorrected.

General Synthetic Procedure. The bromo lactones **1**–**4**, respectively (1.0 g, 4.08 mmol), were refluxed in 40–50 mL of 48% hydrobromic acid for 24 h. After cooling, the mixture was extracted with methylene chloride, washed with sodium bicarbonate and water, and dried over anhydrous magnesium sulfate. After evaporation of the solvent the crude brown oil was subjected to column chromatography.

4[a],10[e]-Dibromoadamantan-2-one (7):[9] Yield 6% as a white solid; mp 132–134 °C; IR ($CHCl_3$) 2940, 1740, 1725 cm^{-1}; mass spectrum *m/e* (relative intensity) 310/308/306 (3/7/3, M^+), 229/227 (78/78), 201/199 (33/33), 119 (100), 93 (20), 91 (70), 79 (88); molecular weight by HRMS for $C_{10}H_{12}Br_2$ (calcd) 309.9211/307.9231/305.9251, (found) 309.9185/307.9202/305.9229.

4[a],10[a]-Dibromoadamantan-2-one (8):[9] yield 9%; IR ($CHCl_3$) 2920, 1730, 1715 cm^{-1}; mass spectrum, *m/e* (relative intensity) 310/308/306 (5/10/5), 229/227 (74/74), 201/199 (35/39), 119 (100), 93 (17), 91 (98), 79 (64); molecular weight by HRMS for $C_{10}H_{12}Br_2$, (calcd) 309.9211/307.9231/305.9251, (found) 309.9193/307.9192/305.9218.

4[a],8[a]-Dibromoadamantan-2-one (9):[9] yield 4% (from **2**), 8% from **3** and **10**% from **4** as a white solid; mp 233–235 °C; IR ($CHCl_3$) 2935, 1735, 1730 cm^{-1}; mass spectrum, *m/e* (relative intensity) 310/308/306 (7/13/6), 229/227 (96/100), 201/199 (18/18), 119 (90), 91 (61), 79 (47); molecular weight by HRMS for $C_{10}H_{12}Br_2$, (calcd) 309.9211/307.9231/305.9251, (found) 309.9178/307.9222/305.9279.

4[a],8[e]-Dibromoadamantan-2-one (10):[9] yield 4% as a white solid; mp 104 °C; IR ($CHCl_3$) 2910, 1720 cm^{-1}; mass spectrum, *m/e* (relative intensity) 310/308/306 (4/8/4), 229/227 (100/99), 201/199 (17/17), 119 (85), 91 (58), 79 (45); molecular weight by HRMS for $C_{10}H_{12}Br_2$, (calcd) 309.9211/307.9231/305.9251, (found) 309.9198/307.9208/305.9225.

4[a],9[e]-Dibromoadamantan-2-one (11):[9] yield 4% as a white solid; mp 99–101 °C; IR ($CHCl_3$) 2910, 1715 cm^{-1}; mass spectrum, *m/e* (relative intensity) 310/308/306 (4/7/4), 229/227 (94/98), 201/199 (18/21), 119 (89), 91 (62), 85 (73), 83 (100), 79 (65); molecular weight by HRMS for $C_{10}H_{12}Br_2$, (calcd) 309.9211/307.9231/305.9251, (found) 309.9215/307.9231/305.9244.

4[a]-Hydroxy-10[e]-bromoadamantan-2-one (13):[9] yield 1%; IR ($CHCl_3$) 3600–3100 (br), 2925, 1740, 1720 cm^{-1}; ^1H NMR (80 MHz) δ ($CDCl_3$) 4.77 (1 H, m), 4.46 (1 H, m), 2.94 (1 H, m), 2.87–1.42 (9 H, complex); mass spectrum, *m/e* (relative intensity) 246/244 (4/4; M^+), 165 (76), 147 (16), 135 (27), 121 (27), 119 (65), 91 (49), 85 (65), 83 (100), 79 (60).

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Registry No. **1**, 85114-85-8; **2**, 85114-87-0; **3**, 85069-88-1; **4**, 85114-86-9; **5**, 32456-49-8; **6**, 32456-48-7; **7**, 99232-54-9; **8**, 99295-19-9; **9**, 94239-95-9; **10**, 94293-63-7; **11**, 99232-55-0; **12**, 19214-00-7; **13**, 99232-56-1.

(9) The designations "a" (axial) and "e" (equatorial) refer to the stereochemical positions of the substituents with respect to the substituent-bearing cyclohexanone subunit in the adamantane molecule.
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Improved Procedure for Introducing the α-Fluoroacetyl Group via the Directed Aldol Reaction

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Recently we have reported several examples of the directed aldol reaction with the lithium enolate of ethyl fluoroacetate[1] and 1-fluoro-3,3-dimethyl-2-butanone.[2]

