Highly Efficient Hydroxylation of Carbonyl Compounds with Dimethyldioxirane

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The enolates and/or enols of ketones, esters, β-diketones, β-oxo esters, and β-oxo lactones were transformed by dimethyldioxirane (isolated in acetone solution or generated in situ) into their α-hydroxy compounds in good to excellent yields. The direct hydroxylation of the enols was significantly enhanced by the use of fluoride ion. For the enolate of camphor the *exo*/*endo* diastereoselectivity depended significantly on the metal ligand; the highest *exo*/*endo* ratio (93:7) was observed for the enol trimethylsilyl ether of camphor.

Since our review[1] on the synthetic utility of dimethyldioxirane in oxidation chemistry, we have demonstrated[2] that it is unquestionably the most convenient and versatile epoxidant to date. Especially advantageous is the isolated dimethyldioxirane (in acetone)[3], which allows preparing hydrolytically and thermally labile epoxides, most of which were prior to our efforts not accessible. The related oxaziridines[4], which are considerably less reactive than dioxiranes in transferring an oxygen atom, have recently been extensively used in the α-hydroxylation of electron-rich enolates. Similary, dioxiranes should serve this purpose and, indeed, it was recently reported[5] that isolated dimethyldioxirane is a useful oxidant to convert enolates into α-hydroxy carbonyl products. The latter preliminary communication urges us to disclose our own results in this area. Herein we show, that also enols derived from 1,3-dicarbonyl compounds can directly be α-hydroxylated by dimethyldioxirane, provided elevated temperatures, longer reaction times, and a larger excess of oxidant are employed.

Results and Discussion

The carbonyl compounds **1a–i** were transformed into their α-hydroxy derivatives **2a–i** by dimethyldioxirane, the latter either isolated (as acetone solution) or generated in situ. The results are summarized in Table 1, in which the three different Methods A, B, and C, reaction conditions and yields are stated. In Method A the carbonyl compounds **1a–e** were transformed by sodium disilazane into their enolates (Scheme 1) and subsequently the enolate solution was added rapidly to the dioxirane (in acetone). After aqueous workup, the α-hydroxy derivatives **2a–e** were isolated in good yields. This inverse addition proved to be the best method and resulted in the highest yields.

In comparison to the corresponding lithium enolates, generated from **1** by lithium diisopropylamide, the sodium enolates employed here offer several advantages. For the sodium enolates, prepared by using sodium disilazane as base (Method A), the yields of the acyloins were usually (except for **2d**) up to 30% higher. This trend was also observed in the hydroxylation of enolates by oxaziridines[4b,c]. Presumably, the more dissociated sodium enolates react more efficiently with dioxirane than the more aggregated lithium enolates, so that for the latter deprotonation of the acetone (the solvent for the dioxirane) competes more effectively to regenerate **1**.

Table 1. Hydroxylation of the carbonyl derivatives **1a–i** with dimethyldioxirane

	Substrate 1				Method[a]	Reaction Conditions	Equiv. 	Conversion [%][b]	Yield of **2** [%]
	R^1	R^2	R^3	X					
a	Me	Ph	H	Na	A	-78°C/2 min[c]	1.2	95	74
b	Ph	Ph	H	Na	A	-78°C/2 min[c]	1.2	97	92
c			H	Na	A	-78°C/2 min[c]	1.2	93	80
d			H	Na	A	-78°C/2 min[c]	1.2	75	57
e	OMe	Ph	H	Na	A	-78°C/2 min[c]	1.2	90	60[d]
f	Ph	COPh	H	H	B	20°C/4 d[c]	4.0	>98	98[e]
g	Me	CO_2Et	Bzl	H	B	20°C/3 d	4.0	>98	ca. 100
				"	C	20°C/1 h	3.0[f]	95	76
h	Me			H	B	20°C/3 d	3.0	>98	98
				"	C	20°C/1 h	1.1[f]	>98	85
i	OEt			H	B	20°C/3 d	3.0	>98	ca. 100
				"	C	20C/1 h	3.0[f]	95	85

[a] Cf. Experimental section. — [b] Determined by integration of the ^{1}H-NMR spectrum of the crude reaction mixture. — [c] Reaction was run under dry N_2 atmosphere. — [d] Column chromatography yielded also 20% of methyl 3-hydroxy-2-*methyl*-2-phenylbutanoate (**3e**). — [e] Mixture of the 1,3-diphenylpropanetrione **2f** (15%) and the corresponding hydrate **4f** (85%). — [f] Equivalents of caroate.

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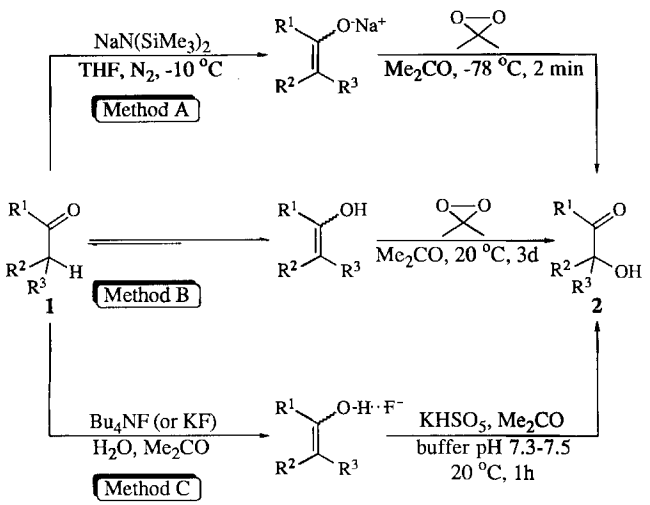
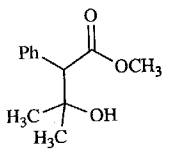
Scheme 1

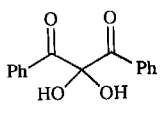


The other advantage concerns the amount of the aldol product between the enolate with acetone. For the sodium enolates of the carbonyl compounds **1a–d** no aldol condensation with acetone was detected, but for the more nucleophilic ester enolate of **1e** as much as 20% of the aldol product **3e** with acetone was isolated. For the lithium enolate of **1e** the major product (62%) was the aldol **3e**, with only small amounts (14%) of the desired oxidation product **2e**.

In Method B the enols of the 1,3-dicarbonyl starting materials **1f–i** were oxidized directly without the use of base to preform the enolate ion (Scheme 1). Long reaction times, much higher temperatures, and large excess of dimethyldioxirane were necessary to run the reaction to completion; nevertheless, in this manner the hydroxy derivatives **2f–i** were isolated in approximately quantitative yield. Presumably direct epoxidation of the enols takes place, followed by tautomeric isomerization into the α-hydroxylated products.



3e



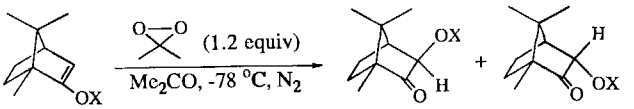
4f

This α-hydroxylation route could be significantly accelerated by using fluoride ion as a catalyst (Method C, Scheme 1). The reaction time was shortened from 72 h to 1 h for essentially complete conversion. Whether the role of the fluoride ion is to act as a base[6] and thus forms the intermediary enolate ion or the electron density of the enol is increased by hydrogen bonding[7] of the fluoride ion with the enolic proton is presently cause for debate in such fluoride ion catalyzed reactions.

Further oxidation of the α-hydroxylated product by dioxirane was of no major concern, except for dibenzoylmethane (**1f**). The oxygen transfer could not be controlled at the stage of the monohydroxy product, so that subsequent oxidation afforded the 1,3-diphenylpropantrione (**2f**) and its hydrate **4f** after complete consumption of the carbonyl compound **1f**.

A point of interest is the appreciable variation of the diastereoselectivity in the reaction of the enolate derivatives **5d** of camphor with dimethyldioxirane (Scheme 2), determined directly by ^{1}H NMR on the crude reaction mixture after workup. Steric effects of the enolate moiety appear to dictate the observed diastereoselectivity. Thus, the relatively unassociated sodium enolate [**5d**, (X = Na)] exhibited the lowest diastereoselectivity (64:36), the bulky silyloxy substituent [**5d**, (X = $SiMe_3$)] the largest (93:7), and the aggregated lithium [**5d**, (X = Li)] enolate is in the middle (75:25). The preferred *exo* attack is not surprising, because most electrophilic additions to the enolate ion or the silyl enol ether of camphor (**1d**) proceed in that manner[8]. Exceptions are the cycloaddition of $^1O_2$[9] and the oxidation with the pydridine complex of MoO_5[10], but in none of these cases was a high *exo* selectivity such as 93:7 observed.

Scheme 2



5d **2d**

	Yield [%]		*exo*	*endo*
5d (X = Na)	57	**2d** (X = H)	64	35
5d (X = Li)	70	**2d** (X = H)	75	25
5d (X = $SiMe_3$)	99	**2d** (X = $SiMe_3$)	93	7

In summary, we have established herein, that dimethyldioxirane is a general and convenient oxidant for the α-hydroxylation of metal enolates, particularly sodium enolates. The direct α-hydroxylation of enols derived from 1,3-dicarbonyl compounds is also feasible, for which fluoride ion catalysis is advantageous. Once again the utility and convenience of dimethyldioxirane in modern oxidation chemistry has been demonstrated.

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Experimental

Melting points: Büchi 535. – IR: Perkin-Elmer 1420. – ^{1}H and ^{13}C NMR: Bruker WM 200 (200 MHz) or WM 250 (250 MHz); chemical shifts refer to TMS. – All solvents were purified by standard literature methods; acetone and water used in the preparation of dimethyldioxirane (isolated or *in situ*) were doubly distilled from EDTA. Caroate (potassium monopersulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was used as received. The substrates **1c**[11], **1g**[12], and **4d**[8] were prepared according to literature syntheses, the others were commercially available. BuLi (1.6 M as hexane solution) was purchased from Aldrich and $Bu_4NF \cdot 3H_2O$ from Janssen Chimica. Sodium hexamethyldisilazane was prepared according to the literature procedure[13] and used as a 0.5 M stock solution in THF.

Dimethyldioxirane (in acetone solution) was prepared following the published procedure[3] and dried two days over molecular sieves (4 Å) at −20°C before use. All glassware employed in the preparation of enolates was oven-dried (110°C) for 1 h.

General Procedures. — Method A: Hydroxylation of the Sodium Enolates of the Carbonyl Compounds **1a–e** *by Dimethyldioxirane (as Acetone Solution):* A solution of 1.0 equiv. of the carbonyl compound **1a–e** in 2 ml of dry THF was slowly added (15 min) to a cooled (−10°C) solution of sodium hexamethyldisilazane (1.2 equiv., 0.5 M) under N_2 atmosphere. The stirring at this temperature was continued for additional 60 min. The resulting solution was cooled to −78°C and rapidly added to a solution of dimethyldioxirane cooled at −78°C (1.2 equiv., 0.06–0.09 M in acetone), which was stored prior to use for 15 min over 2 g Na_2CO_3 to remove final traces of water. After 2 min, the reaction mixture was quenched by adding 0.5 ml aqueous NH_4Cl solution and allowed to reach room temperature. Na_2CO_3 was removed by filtration, and the solvent was evaporated under vacuum (20°C; 20 Torr). The residue was diluted with 10 ml of ether, washed with 3 ml of 2 N HCl and 3 ml of satd. aqueous NaCl solution, and dried with $MgSO_4$. After removal of the drying agent, the solvent was evaporated (20°C; 20 Torr) and the residue purified by column chromatography.

1-Hydroxy-1-phenyl-2-propanone (**2a**): According to Method A, 111 mg (74%) of **2a** was obtained after column chromatography (silica gel, CH_2Cl_2 as eluent) as a pale yellow oil, by starting from 134 mg (1.00 mmol) **1a** and 19 ml of a 0.063 M (1.20 mmol) dimethyldioxirane solution. The spectral data match those reported[4b].

β-Hydroxy-β-phenylacetophenone (**2b**): According to Method A, 262 mg (92%) of **2b** was obtained after column chromatography (silica gel, CH_2Cl_2 as eluent) as a colorless powder, m.p. 132–134°C ref.[14] 132–135°C), by starting from 264 mg (1.34 mmol) **1b** and 18 ml of a 0.090 M (1.62 mmol) dimethyldioxirane solution. The spectral data match those of the commercially available sample (Aldrich).

2,3-Dihydro-2-hydroxy-3,3-dimethyl-1-indenone (**2c**): According to Method A, 141 mg (80%) of **2c** was obtained after column chromatography (silica gel, CH_2Cl_2 as eluent) as a colorless oil, by starting from 160 mg (1.00 mmol) of **1c** and 19 ml of a 0.063 M (1.20 mmol) dimethyldioxirane solution. — IR (neat): $\tilde{\nu}$ = 3700–3200 cm^{-1}, 3090, 2990, 2940, 2880, 1735, 1620, 1480, 1335, 1290, 1150, 1130, 1090, 1000, 960, 775, 750, 700. — ^1H NMR (200 MHz, $CDCl_3$): δ = 1.17 (s, 3H, 8-H), 1.59 (s, 3H, 8-H), 3.58 (s, 1H, OH), 4.28 (s, 1H, 2-H), 7.41 (dt, *J* = 7.4 Hz, *J* = 1.1 Hz, 1H, 5-H), 7.53 (td, *J* = 7.7 Hz, *J* = 0.9 Hz, 1H, 4-H), 7.68 (dt, *J* = 7.4 HZ, *J* = 1.3 Hz, 1H, 6-H), 7.75 (td, *J* = 7.6 Hz, *J* = 0.9 Hz, 1H, 7-H). — ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.1 (q), 26.3 (q), 43.2 (s), 83.8 (d), 123.6 (d), 123.9 (d), 127.8 (d), 131.8 (s), 135.7 (d), 160.2 (s), 205.5 (s). — MS (70 eV): *m/z*(%) = 176 (75) [M^+], 161 (100) [$M^+ - CH_3$], 158 (28) [$M^+ - H_2O$], 143 (18) [$M^+ - CH_3, - H_2O$], 131 (14), 130 (24), 129 (25), 115 (31), 91 (25), 77 (18) [$M^+ - C_5H_7O_2$], 51 (13).

$C_{11}H_{12}O_2$ (176.2) Calcd. C 74.98 H 6.86
Found C 74.96 H 6.99

3-Hydroxy-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one [**2d** (X = H)]: According to Method A, 96.0 mg (57%) of **2d** (X = H) was obtained after column chromatography [silica gel, petroleum ether (30–50°C)/ether as eluent] as a colorless solid, m.p. 192–196°C (ref.[15] *exo* 210–211°C) by starting from 152 mg (1.00 mmol) of **1d** and 19 ml of a 0.063 M (1.20 mmol) dimethyldioxirane solution. The *exo*:*endo* ratio was 66:34, as determined by integration of the α-hydroxy proton *exo*-H [δ = 3.72 (s)] and *endo*-H [δ = 4.18 (d, *J* = 5.0 Hz)]. The spectral data match those reported[15].

Methyl 2-Hydroxy-2-phenylacetate (**2e**) *and Methyl 3-Hydroxy-3-methyl-2-phenylbutyrate* (**3e**): According to Method A, 99.6 mg (60%) of **2e** was obtained as a colorless solid after column chromatography [silica gel, petroleum ether (30–50°C)/ether as eluent], m.p. 54–55°C (ref.[16] 57°C) and 40.5 mg (20%) of **3e** as a colorless oil by starting from 150 mg (1.00 mmol) of **1e** and 17 ml of a 0.071 M (1.21 mmol) dimethyldioxirane solution. The spectral data of **2e** match those of the commercially available sample (Aldrich).

3e: IR (CCl_4): $\tilde{\nu}$ = 3500–3300 cm^{-1}, 3070, 3040, 2980, 2960, 2840, 1720, 1600, 1490, 1450, 1430, 1380, 1360, 1210, 1180, 1150, 700. — ^1H NMR (250 MHz, $CDCl_3$): δ = 1.07 (s, 3H, 4-H), 1.35 (s, 3H, 4′-H), 3.60 (s, 1H, 2-H), 3.65 (s, 1H, OH), 3.69 (s, 3H, 5-H), 7.30–7.40 (m, 5H, arom. H). — ^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.7 (q), 29.6 (q), 52.0 (q), 60.5 (d), 71.8 (d), 127.6 (d), 128.3 (d), 129.5 (d), 135.3 (s), 174.6 (s).

$C_{12}H_{16}O_3$ (208.3) Calcd. C 69.21 H 7.74
Found C 69.48 H 7.57

Method B: Hydroxylation of Dicarbonyl Compounds **1f–i** *by Dimethyldioxirane:* One equivalent of dimethyldioxirane (as acetone solution) was added rapidly at room temperature to the dicarbonyl compounds **1f–i**, and the solution was stirred for 24h at ca. 20°C. After this period, a new equivalent of dimethyldioxirane was added and the stirring was continued for 24 h. This procedure was continued until total conversion (monitored by TLC) was reached. The solvent was removed under vacuum (20°C; 20 Torr), and the hydroxy compounds **2f–i** were obtained in high purity and excellent yields.

1,3-Diphenylpropanetrione (**2f**) *and Its Monohydrate* (**4f**): According to Method B (total reaction time of 4d), 8.9 mg (15%) of **2f** was obtained as a yellow solid, m.p. 68–69°C (ref.[17] 68–70°C), and 53.1 mg (83%) of **4f** was obtained after sublimation (40°C; 20 Torr) by employing 56.0 mg (0.25 mmol) of **1f** and a total of 12.5 ml of a 0.08 M (1.00 mmol) dimethyldioxirane solution. The spectral data of **2f**[17] and **4f**[18] match those reported.

Ethyl 2-Hydroxy-3-oxo-2-phenylmethylbutanoate (**2g**): According to Method B (total reaction time of 4d), 235 mg (ca. 100%) of **2g** was obtained as a colorless oil by employing 220 mg (1.00 mmol) of **1g** and a total of 55 ml of a 0.073 M (4.00 mmol) dimethyldioxirane solution. — IR (CCl_4): $\tilde{\nu}$ = 3530 cm^{-1}, 3100, 3080, 3060, 3000, 2950, 1740, 1560, 1505, 1460, 1370, 1280, 1240, 1200, 1140. — ^1H NMR (250 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.1 Hz, 3H, 7-H), 2.27 (s, 3H, 4–H), AB system (δ_A = 3.18, δ_B = 3.42, J_{AB} = 14.1 Hz, 2H, 5-H), 4.14 (s, 1H, OH), 4.22 (q, *J* = 7.1 Hz, 2H, 6-H), 7.24 (m, 5H, arom. H.). — ^{13}C NMR (63 MHz, $CDCl_3$): δ = 13.9 (q), 25.0 (q), 40.6 (t), 62.7 (t), 84.1 (s), 127.0 (d), 128.1 (d), 130.1 (d), 134.5 (s), 170.4 (s), 193.9 (s). — MS (70 eV): *m/z* (%) = 236 (4, M^+), 194 (57) [$M^+ - C_2H_2O$], 119 (23), 116 (17), 92 (17) [$M^+ - C_6H_8O_4$], 91 (100) [$M^+ - C_6H_9O_4$], 78 (33), 65 (11), 43 (75) [$M^+ - C_{11}H_{14}O_3$].

$C_{13}H_{16}O_4$ (236.3) Calcd. C 66.08 H 6.83
Found C 65.97 H 6.98

2-Acetyl-2-hydroxy-γ-butyrolactone (**2h**): According to Method B (total reaction time of 3d), 142 mg (98%) of **2h** was obtained as a colorless oil by employing 128 mg (1.00 mmol) of **1h** and a total of 41 ml of a 0.070 M (3.00 mmol) dimethyldioxirane solution. — IR (CCl_4): $\tilde{\nu}$ = 3600–3300 cm^{-1}, 3000, 2930, 1800, 1740, 1550, 1385, 1365, 1210, 1170, 1150, 1100, 1030, 730. — ^1H NMR (250 MHz, $CDCl_3$): δ = 2.30 (s, 3H, 6-H), 2.29–2.41 (m, 1H, 3-H), 2.64 (ddd, *J* = 13.6 Hz, *J* = 7.2 Hz, *J* = 4.5 Hz, 1H, 3′-H), 4.30–4.60 (m, 3H, 4-H and OH). — ^{13}C NMR (63 MHz, $CDCl_3$): δ = 24.6 (q), 33.9 (t), 66.1 (t), 81.2 (s), 174.6 (s), 205.0 (s). — MS (70 eV): *m/z* (%) = 128 (0.4), 127 (0.4), [$M^+ - OH$], 102 (32) [$M^+ - C_2H_2O$],

72 (2), 58 (2), 57 (16), 56 (32), 44 (14), 43 (100) [$M^+ - C_4H_5O_3$], 42 (10) [$M^+ - C_4H_6O_3$].

$C_6H_8O_4$ (144.1) Calcd. C 50.00 H 5.59
Found C 49.71 H 5.82

Ethyl 1-Hydroxy-2-oxo-1-cyclopentanecarboxylate (**2i**): According to Method B (total reaction time 3 d), 172 mg (ca. 100%) of **2i** was obtained as a colourless liquid by employing 156 mg (1.00 mmol) of **1i** and a total of 41 ml of a 0.070 M (3.00 mmol) dimethyldioxirane solution. The spectral data match those reported[17].

Method C: Fluoride Ion Catalyzed Hydroxylation of the Dicarbonyl Compounds **1g–i** *by Dimethyldioxirane Generated in situ from Caroate and Acetone:* To a vigorously mechanically stirred mixture of 10 mmol of dicarbonyl compound **1g–i**, 8 ml of acetone, 50 ml of phosphate buffer (prepared from 59.0 mg of KH_2PO_4 and 216 mg of Na_2HPO_4 in 50 ml of H_2O), and 10 mmol of KF was added slowly within 1 h a 15% aqueous solution of the required amount of caroate. In the case of the water-insoluble substrate **1g**, 20 ml CH_2Cl_2 was added and 10 mmol of $Bu_4NF \times 3\ H_2O$ used as fluoride ion source and phase-transfer catalyst. The pH of the mixture was kept throughout the reaction constant at 7.3 to 7.5 with the help of a 10% aqueous KOH solution. After all of the caroate was consumed, the stirring was continued for additional 15 min. Solid NaCl was added until saturation and the cloudy reaction mixture extracted with *tert*-butyl methyl ether (3 × 100 ml). The combined organic layers were dried with $MgSO_4$, the drying agent was removed by filtration, the solvent evaporated (20°C; 20 Torr), and the hydroxy compounds **1g–i** were purified by column chromatography on silica gel.

2g: According to Method C, 1.80 g (76%) of **2g** was obtained after column chromatography (silica gel, CH_2Cl_2 as eluent) by employing 2.20 g (10 mmol) of **1g**, a total of 10.2 g (30 mmol) caroate, and 3.16 g (10 mmol) of $Bu_4NF \times H_2O$ (for spectral data cf. above).

2h: According to Method C, 1.22 g (85%) of **2h** was obtained in high purity after evaporation of the solvent (20°C; 20 Torr) by employing 1.28 g (10 mmol) of **1h**, a total of 4.05 g (12 mmol) caroate, and 0.58 g (10 mmol) of KF (for spectral data cf. above).

2i: According to Method C, 1.46 mg of (85%) **2i** was obtained after column chromatography (silica gel, CH_2Cl_2 as eluent) by employing 1.56 g (10 mmol) **1i** a total 10.2 g (30 mmol) caroate, and 580 mg of KF (for spectral data cf. above).

2d (X = H) *from Its Lithium Enolate:* Under N_2 1.00 ml of a 1.5 M (1.50 mmol) BuLi in hexane was cooled to −78°C. To this solution was added 0.215 ml (1.51 mmol) of diisopropylamine, dissolved in 1 ml of dry THF, and the reaction mixture was allowed to reach 0°C. After 5 min, the mixture was cooled again to −78 C, and 200 mg (1.31 mmol) of **1d** in 2 ml of dry THF was added dropwise within 15 min. The reaction mixture was stirred at this temperature for 30 min and then added to 21 ml of a 0.076 M (1.60 mmol) solution of dimethyldioxirane (in acetone), which was stored for 15 min with 2 g of Na_2CO_3 at −78°C. The reaction was terminated after 2 min with 1 ml of an aqueous NH_4Cl solution and allowed to reach room temperature. After filtration, the solvents were evaporated (20°C; 20 Torr), and the residue was diluted with 15 ml of ether. The organic layer was washed with 2 N HCl (2 × 5 ml) and satd. aqueous NaCl solution (5 ml), and dried with $MgSO_4$. After removal of the drying agent, the solvent was evaporated (20°C; 20 Torr) and the residue (188 mg) purified by column chromatography [silica gel, petroleum ether (30–50°C)/ether as eluent] to yield 154 mg (70%) **2d** (X = H) as a colorless solid, m.p. 202–204°C (ref.[16] 210–211°C). The *exo/endo* ratio was 75:25 as determined by integration of the α-hydroxy proton *exo*-H [δ = 3.72 (s)] and *endo*-H [δ = 4.18 (d, *J* = 5.0 Hz)]. The spectral data of **2d** (X = H) matched those reported[15].

1,7,7-Trimethyl-3-(trimethylsilyloxy)bicyclo[2.2.1]heptan-2-one [**2d** (X = $SiMe_3$)]: To a solution of 116 mg (0.52 mmol) of **5d** (X = $SiMe_3$) in 5 ml of dry CH_2Cl_2 cooled to −78°C under a N_2 atmosphere was rapidly added 8 ml of a 0.078 M (0.62 mmol) dimethyldioxirane solution, previously cooled also to −78°C. The reaction mixture was stirred for 30 min at this temperature and then allowed to reach ca. 20°C. The solvent was evaporated (20°C; 20 Torr) and **2d** (X = $SiMe_3$) was isolated in high purity (124 mg, 99%). The *exo/endo* ratio was 93:7 as determined by ^1H NMR integration of the α-silyloxy proton *exo*-H δ = 3.56 (s) and *endo*-H δ = 4.10 (d, *J* = 5.1 Hz). – *exo*-**2d** (X = $SiMe_3$): ^1H NMR (250 MHz, C_6D_6): δ = 0.06 (s, 9H, $SiMe_3$-H), 0.50 [s, 3H, 1(7)-H], 0.73 [s, 3H, 7(1)-H], 0.89 [s, 7(1)-H], 0.60 – 2.20 (complex m, 5H, 4,5,6-H), 3.56 (s, 1H, 3-H). – ^{13}C NMR (63 MHz, C_6D_6): δ = 0.3 (q), 9.5 (q), 20.0 (q), 21.3 (q), 25.1 (t), 29.1 (t), 43.2 (s), 51.0 (d), 56.7 (s), 78.3 (d), 216.6 (s). The spectral data of *endo*-**2d** (X = $SiMe_3$) matched those reported in ref.[8].

CAS Registry Numbers

1a: 103-79-7 / **1b**: 451-40-1 / **1c**: 26465-81-6 / **1d**: 76-22-2 / **1e**: 101-41-7 / **1f**: 120-46-7 / **1g**: 620-79-1 / **1h**: 517-23-7 / **1i**: 611-10-9 / **2a**: 90-63-1 / **2b**: 119-53-9 / **2c**: 135366-62-0 / **2d**, *endo* (X = H): 21488-68-6 / **2d**, *exo* (X = H): 22759-33-7 / **2d**, *exo* (X = TMS): 68546-50-9 / **2d**, *endo* (X = TMS): 68546-51-0 / **2e**: 771-90-4 / **2f**: 643-75-4 / **2g**: 135366-63-1 / **2h**: 135366-64-2 / **2i**: 82415-38-1 / **3e**: 135366-65-3 / **4f**: 29574-75-2 / **5d** (X = TMS): 56613-17-3 / KF: 7789-23-3 / Bu_4NF: 429-41-4 / acetone: 67-64-1 / caroate: 103288-43-3 / dimethyldioxirane: 74087-85-7

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