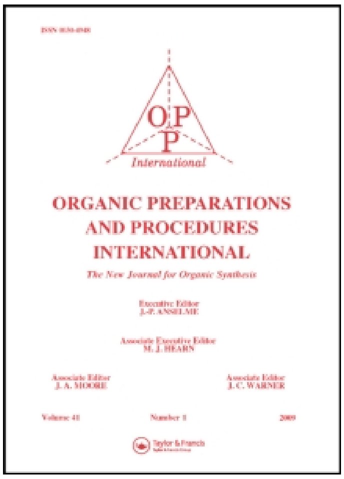

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PREPARATION OF β-BROMOTRIMETHYLSILOXYENOLETHERS FROM α-BROMOCARBONYL COMPOUNDS

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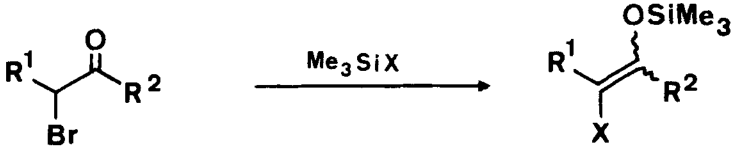
β-Bromotrimethylsiloxyenolethers 2 are versatile synthetic intermediates which can be regarded as synthetic equivalents of α-keto cations[1] or α-keto anions.[2,3] They have been prepared from trimethylsiloxyenolethers by a bromination-deshydrobromination sequence[4,5] and from β-tribromomethyltrialkylsilylethers by reaction with n-butyllithium.[3] Some examples have recently been obtained using α-bromoketones and trimethylsilyltriflate.[6] We report here our results starting from α-bromoaldehydes 1a-d and α-bromoketone 1e.



1

	a	b	c	d	e
R^1 =	CH_3	C_2H_5	nC_5H_{11}	tC_4H_9	H
R^2 =	H	H	H	H	Ph

2 X = Br
3 X = Cl
4 X = I

With standard methods C ($ClSiMe_3$, NEt_3, Et_2O or C_6H_6, Δ), D ($ClSiMe_3$, $ZnCl_2$, NEt_3, Et_2O or C_6H_6, Δ)[7] and E ($ClSiMe_3$, NaI, NEt_3, CH_3CN, RT),[8] we obtained mixtures of β-bromo and β-chloroenolethers 2 and 3 (methods C and D) or of β-bromo and β-iodoenolethers 2 and 4 (method E, Table 1).

TABLE 1. α-Bromotrimethylsiloxyenolethers 2 from 1

Cmpd	Method[a]	Solvent	Time[b] (hrs)	Ratio[c] 2/3	Ratio[c] 2/4	Ratio[d] 2 Z/2 E	bp. (°/mmHg)	Yield (%)
2a	A	Et_2O	5	100/0		67/33	57-60/16	50
	B	CH_3CN	2	100/0		67/33	52-58/15	66
	C	Et_2O	18.5	44/56		67/33		46
	D	Et_2O	3	100/0		63/37	51-59/17	62
2b	A	Et_2O	5.5	100/0		75/25	65-72/15	65
	B	CH_3CN	3	100/0		76/24	65-68/12	70
	C	Et_2O	17	80/20		77/23		52
	D	Et_2O	4	100/0		80/20	68-73/13	71
	E	CH_3CN	2		65/35	76/24	71-76/15	55
2c	A	Et_2O	7	100/0		80/20	60-70/0.35	53
	B	CH_3CN	4	100/0		82/18	64-66/0.25	55
	C	Et_2O	27	100/0		82/18		49
	D	Et_2O	23	100/0		83/17	65-70/0.45	67
2d	A	C_6H_6	22	100/0		92/8	81/13	44
	B	CH_3CN	4	100/0		93/7	82/12	68
	D	C_6H_6	45	100/0		100/0	84/14	48
2e	A	C_6H_6	16	100/0		e	80-85/0.5	55
	B	CH_3CN	6	80/20		e		55
	D	C_6H_6	18	35/65		e		60

[a] A : $BrSiMe_3/NEt_3/Et_2O$ or C_6H_6, Δ.
B : $ClSiMe_3/LiBr/NEt_3/CH_3CN$, RT.
C : $ClSiMe_3/NEt_3/Et_2O$ or C_6H_6, Δ.
D : $ClSiMe_3/ZnCl_2/NEt_3/Et_2O$ or C_6H_6 , Δ.
E : $ClSiMe_3/NaI/NEt_3/CH_3CN$, RT.

[b] Reaction time to obtain ⩾ 90% conversion.

[c] Determined by CPG.

[d] Determined by ^1H NMR (C_6D_6).

[e] A single isomer of non-determined configuration.

These results can be explained by an halogen exchange on the starting bromocarbonyl compounds 1, prior to conversion into halo enolether,[9,10] due to the presence of chloride or iodide ions. Satisfactory results were obtained by method A (modification of method C, using bromotrimethylsilane instead of chlorotrimethylsilane) and by method B (modification of method E using lithium bromide instead of sodium iodide, Table 1).

The Z configuration of the predominant isomer of 2a-d was established by NOE experiments[11] and by ^{13}C NMR data (Table 3) :

δ C-1 Z < δ C-1 E, $J_{^{13}C^1H}$ Z = 178 Hz, $J_{^{13}C^1H}$ E = 185 Hz, δ C-2 Z < δ C-2 E.

It should be observed that the amount of Z isomer increases with the bulkiness of R^1 (Table 1).

The advantages of the procedures A and B lie in their simplicity and it is unnecessary to use aqueous work-up. Method B is attractive because of the mild conditions, the short reaction time and the ready availability of the reagents, but is somewhat limited because of the partial halogen exchange observed from the bromoketone 1e; method A appears to be quite general.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Perkin-Elmer 60 MHz R 12 instrument and ^{13}C NMR spectra were determined on a Varian CFT 20 spectrometer. All chemical shifts are reported in δ units (ppm) down field of internal tetramethylsilane in C_6D_6 solutions. IR spectra (film) were obtained with a Perkin-Elmer 237 instrument. Mass spectra were recorded with a Jeol JMSD 100 spectrometer.

α-Bromoaldehydes 1a-d were prepared according to literature procedures.[12,13]

General Procedures.

Method A.- To a solution of α-bromocarbonyl compound 1 (0.175 mol) and triethylamine (20.0 g, 0.198 mol) in 200 mL of ether or benzene was added at 0° and under nitrogen, bromotrimethylsilane (35.2 g, 0.23 mol).

TABLE 2. Infrared and ^{1}H NMR data of compounds 2

Cmpd	IR (cm^{-1})		^{1}H NMR (δ values)
2a	1675 - 1665	Z	6.30 (q, 1 H, J = 1.3 Hz), 1.85 (d, 3 H), 0.20 (s, 9 H)
		E	6.66 (q, 1 H, J = 1.3 Hz), 2.20 (d, 3 H), 0.10 (s, 9 H)
2b	1655	Z	6.35 (t, 1 H, J < 1 Hz), 2.20 (q, 2 H), 1.05 (t, 3 H), 0.20 (s, 9 H)
		E	6.55 (t, 1 H, J < 1 Hz), 2.55 (q, 2 H), 1.10 (t, 3 H), 0.10 (s, 9 H)
2c	1660	Z	6.40 (br.s, 1 H), 2.0 (t, 2 H), 1.85-0.85 (m, 9 H), 0.13 (s, 9 H)
		E	6.52 (br.s, 1 H), 2.0 (t, 2 H), 1.85-0.85 (m, 9 H), 0.13 (s, 9 H)
2d	1645	Z	6.50 (s, 1 H), 1.15 (s, 9 H), 0.15 (s, 9 H)
		E	6.60 (s, 1 H), 1.15 (s, 9 H), 0.15 (s, 9 H)
2e	1610		7.25 (m, 5 H), 5.85 (s, 1 H), 0.18 (s, 9 H)

The mixture was refluxed for the specified amount time (see Table 1). After cooling, the precipitated solid was collected, washed with ether and the combined filtrate was concentrated *in vacuo*. The residual product was purified by distillation under reduced pressure.

Method B.- To a solution of chlorotrimethylsilane (2.035 g, 18.75 mmol) and triethylamine (1.89 g, 18.75 mmol) in 5 mL of acetonitrile, was added a solution of dry lithium bromide (1.65 g, 19 mmol) in 35 mL of acetonitrile, then after 30 min, a solution of carbonyl compound 1 (15.0 mmol) in 5 mL of acetonitrile. The mixture was stirred 2-6 hrs at room temperature

TABLE 3. Elemental analysis, ^{13}C NMR and mass spectrography of compounds 2

Cmpd	Analysis (Found)			^{13}C NMR	Mass Spectrum
	C	H			
2a	34.44 (34.70)	6.29 (6.32)	Z	136.66 (d, J_{C-H} = 178 Hz; q, ^3J = 6.0 Hz, C-1), 103.90 (C-2), 22.86 (C-3), 0.27 ($SiMe_3$)	210 (13), 208 (13), 195 (20), 193 (20), 139 (67), 137 (67), 73 (100)
			E	139.35 (d, J_{C-H} = 185 Hz, q, ^3J = 4.2 Hz, C-1), 106.68 (C-2), 19.98 (C-3), 0.73 ($SiMe_3$)	
2b	37.65 (37.58)	6.77 (6.71)	Z	135.93 (d, J_{C-H} = 178 Hz, t, ^3J = 5.8 Hz, C-1), 122.06 (C-2), 29.86 (C-3), 14.95 (C-4), 0.29 ($SiMe_3$)	224 (12), 222 (12), 209 (21), 207 (21), 139 (33), 137 (33), 73 (100)
			E	138.42 (d, J_{C-H} = 185 Hz; t, ^3J = 3.8 Hz, C-1), 115.11 (C-2), 26.04 (C-3), 13.58 (C-4), 0.73 ($SiMe_3$)	
2c	45.26 (45.29)	7.98 (8.10)	Z	136.51 (d, J_{C-H} = 178 Hz; t, ^3J = 6 Hz, C-1), 110.49 (C-2), 35.95 (C-3), 31.34 (C-4), 28.82 (C-5), 23.16 (C-6), 14.67 (C-7), 0.24 ($SiMe_3$)	266 (7), 264 (7), 209 (13), 207 (13), 144 (16), 140 (8), 138 (8), 85 (34), 75 (8), 74 (10), 73 (100)
			E	139.11 (d, J_{C-H} = 185 Hz, t, ^3J = 3 Hz, C-1), 113.36 (C-2), 36.89 (C-3), 32.11 (C-4), 27.97 (C-5), 23.16 (C-6), 14.67 (C-7), 0.69 ($SiMe_3$)	
2d	43.03 (43.28)	7.63 (7.70)	Z	134.71 (d, J_{C-H} = 178 Hz, C-1), 123.56 (C-2), 37.04 (C-3), 30.50 (C-4), 0.31 ($SiMe_3$)	252 (4), 250 (4), 237 (31), 235 (31), 149 (6), 147 (6), 75 (8), 74 (8), 73 (100)
2e	48.69 (48.53)	5.57 (5.59)		153.62 (C-1), 137.14, 128.73, 128.42, 125.81 (C_6H_5), 88.56 (d, J_{C-H} = 194.6 Hz, C-2), 0.72 ($SiMe_3$)	272 (20), 270 (20), 257 (5), 255 (5), 229 (15), 227 (15), 201 (25), 199 (25), 191 (25), 190 (15), 177 (10), 150 (20), 149 (100), 139 (60), 102 (20), 73 (95)

(see Table 1) and 50 mL of pentane were added then the solid was collected. The filtrate was extracted with pentane (5 X 30 mL) and the solvent was removed in vacuo and the residu was distilled.

Method C.- The reaction was carried out according to method A, but chlorotrimethylsilane (21.0 g, 0.198 mol) was added instead of bromotrimethylsilane.

Method D.- The reaction was carried out according to method A, but chloromethylsilane (21.0 g, 0.198 mol) and zinc chloride (0.5 g, 3.6 mmol) was added instead of bromotrimethylsilane.

Method E.- The reaction was carried out according to method B with the modification that dry sodium iodide (2.92 g, 19.5 mmol) in 25 mL of acetonitrile was added instead of lithium bromide.

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