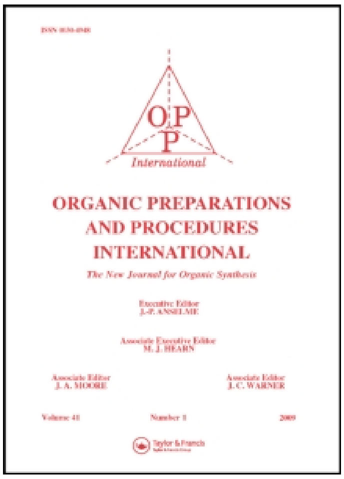

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β-IODOTRIMETHYLSILYLENOL ETHERS AND α-IODOALDEHYDES AND KETONES FROM α-CHLORO AND α-BROMOCARBONYL COMPOUNDS

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β-IODOTRIMETHYLSILYLENOL ETHERS AND α-IODOALDEHYDES AND KETONES FROM α-CHLORO AND α-BROMOCARBONYL COMPOUNDS

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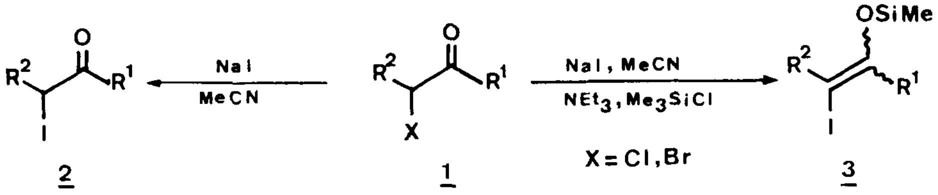
In the course of our investigations to prepare β-bromotrimethylsilylenolethers from α-bromoaldehydes by the $Me_3SiCl/NaI/MeCN/NEt_3$ method, attention was paid to the partial formation of β-iodotrimethylsilylenolethers.[1] This observation leads us to verify the intermediate formation of α-iodoaldehydes by an halogen exchange. We now describe a convenient synthesis of α-iodocarbonyl compounds 2 and report the preparation of hitherto unknown β-iodotrimethylsilylenol ethers 3 from α-chloro or α-bromocarbonyl compounds 1.



α-Iodoaldehydes are usually prepared by halogen-interchange of chloro or bromo compounds with sodium iodide in acetone [2,3] or by halogenation of enamines,[4] enol ethers,[5], enol acetates[6] or potassium enolates.[7] α-Iodoketones have been obtained by the same techniques[5,6,8] and by direct halogenation of ketones;[9] alternative methods starting from epoxides and alkenes and involving oxidation processes have also been recently described.[10]

In acetonitrile, sodium iodide reacts rapidly with α-chloro or α-bromocarbonyl compounds 1 (Table 1). After filtration and subsequent extraction with pentane, the iodo compounds 2 were isolated easily. Further purification of the crude iodo compounds 2 generally proved unnecessary.

While β-chloro [12] and β-bromotrimethylsilylenol ethers [13] have been obtained by a number of methods, the corresponding β-iodo compounds 3 were not as yet available. We report their preparation by reaction of α-iodoaldenydes (generated in situ from α-chloro- or α-bromoaldehydes and sodium iodide in acetonitrile) with iodotrimethylsilane (generated in situ from chlorotrimethylsilane and sodium iodide) in the presence of triethylamine at room temperature (Table 2). The yields of β-iodoenol ethers 3 are modest because in all cases; we observed appreciable amounts (∿ 40 %) of the parent non-halogenated enol ethers (easily separated by distillation) corresponding to a dehalogenation of the haloaldehyde. A facile dehalogenation of α-haloketones was recently described by Olah [14] under similar experimental conditions except for the presence of tertiary amine. The reaction gives iodotrimethylsilylenol ethers 3 as a mixture of Z- and E-isomers. The configurational assignments were established as for the corresponding bromo derivatives, [1] by NOE experiments and by ^{13}C NMR data (Table 3). The structures of compounds 3 were confirmed by microanalytical, IR and NMR data (Tables 2 and 3).

The present reaction proceeds under conveniently mild conditions from readily available and inexpensive materials and avoids the preparation of the sensitive intermediate iodoaldehydes 2.

Table 1. α-IODOCARBONYL COMPOUNDS (2) [a]

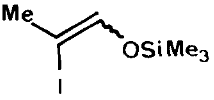
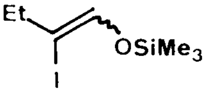
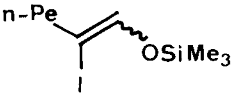
Product 2		Starting halogen (X)	Time (hrs)	Yield (%)
R^1	R^2			
H	CH_3	Br	2	50 [b]
H	C_2H_5	Cl	6	71 [c]
		Br	3	80 [c]
H	n-C_5H_{11}	Cl	3	90 [c]
H	t-C_4H_9	Br	48	80 [c]
				71 [b]
t-C_4H_9	H	Br	4	79 [c]
				68 [b]
C_6H_5	H	Br	20 [d]	90 [c]
4-CH_3O-C_6H_4	H	Br	15	66 [c]
$(CH_2)_4$		Br	4	80 [c]

a. IR, ^1H NMR and ^{13}C NMR spectra are identical with those of authentic samples[3] (see ref. 3 and 11); b. Yield of distilled product; c. Yield of pure crude product; d. 3 Eq. of NaI were used.

Table 2. β-IODOTRIMETHYLSILYLENOL ETHERS (3)

Product	R^1	R^2	X Starting material 1	Yield (%)	3Z/3E	bp. (°C) /torr	Analysis (Found) C	H
3a	H	CH_3	Br	25	40/60	72-77/22	28.13 (28.27)	5.12 (5.20)
3b	H	C_2H_5	Cl Br	28 28	45/55 45/55	68-72/15	31.12 (31.01)	5.60 (5.90)
3c	H	nC_5H_{11}	Cl Br	34 36	67/33 80/20	72-78/0.4	38.46 (38.80)	6.78 (6.89)

Table 3. NMR and IR DATA OF β-IODOTRIMETHYLSILYLENOL ETHER (3)

Product		^{1}H NMR (δ)	^{13}C NMR (δ)	IR (cm^{-1})
	Z	6.15 (q, 1H, J = 1.5 Hz) 2.2 (d, 3H); 0.08 (s,9H)	141.15(d,J=177 Hz, J_3 = 6.7 Hz, c-1) 79.13 (c-2); 26.26 (c-3); 0.62 (SiMe$_3$)	1650
3a	E	6.75 (q, 1H, J = 1.3 Hz); 2.35 (d, 3H); 0.15 (s,9H)	143,93 (d, J=185 Hz, J_3 = 4.9 Hz, c-1); 78.16 (c-2); 22.98 (c-3); 0.30 (SiMe$_3$)	1635
	Z	6.15 (s, 1H); 2.25 (q,2H) 1.0 (t, 3H); 0.03 (s,9H)	140.12 (d, J=177 Hz, J_3 = 6.7 Hz); 90.08 (c-2); 32.13 (c-3); 16.49 (c-4); 0.38 (SiMe$_3$)	1645
3b	E	6.65 (s, 1H); 2.45 (q,2H) 1.0 (t, 3H); 0.12 (s,9H)	142.91 (d, J=186 Hz, J_3 = 4.5 Hz, c-1); 89.84 (c-2); 28.17 (c-3); 14.89 (c-4); 0.72 (SiMe$_3$)	1630
 3c	Z	6.14 (s, 1H); 2.22 (t,2H) 1.65-0.85 (m, 9 H); 0.12 (s, 9H) *a*	140.37 (d, J=178 Hz, J_3 = 6.7 Hz, c-1); 88.27 (c-2); 38.02 (c-3); 31.14 (c-4); 30.07 (c-5); 23.14 (c-6); 14.73 (c-7); 0.32 (SiMe$_3$)	1650
	E	6.68 (s, 1H); 2.22 (t,2H) 1.65-0.85 (m,9H); 0.12 (s, 9H) *a*	143.29 (d, J=187 Hz, J_3 = 4.2 Hz, c-1); 87.73 (c-2); 34.07 (c-3); 30.07 (c-4); 29.08 (c-5); 23.14 (c-6); 14.73 (c-7); 0.62 (SiMe$_3$)	1635

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a : NOE experiments were recorded on Brücker WH 90 D. Irradiation of the methylen signal of 3c at 2.22 ppm causes an increase of 20 % in the integrated intensity of the vinyl signal at 6.14 ppm, while no increase occurs on the corresponding vinylic signal at 6.68 ppm.

EXPERIMENTAL SECTION

^1H 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) downfield from internal tetramethylsilane in C_6D_6 solutions. IR spectra (film) were obtained with a Perkin Elmer 237 instrument.

α-Iodocarbonyl Compounds 2. General Procedure.- To α-halo (α-chloro or α-bromo) carbonyl compound 1 (10 mml) was added the solution of dry sodium iodide (2.25 g, 15 mmol) in acetonitrile (16 ml). The mixture was stirred at room temperature further until the completion of the reaction was indicated by tlc (silica gel; petroleum ether/ether : 1/1) or GC, and extracted with pentane (5 x 100 ml) (continuous extraction with 250 ml of pentane was used for the aryl iodoketones). The solvent was then removed under reduced pressure to give the crude iodocarbonyl compounds 2, which,in some cases, were distilled (Table 1).

β-Iodotrimethylsilylenol Ethers 3. General Procedure.- To the α-halo (α-chloro or α-bromo) aldehyde 1 (30 mmol) in acetonitrile (5 ml) was added a solution of dry sodium iodide (9.5 g, 63 mmol) in acetonitrile (65 ml). The mixture was stirred at room temperature until the GC or tlc analysis (silica gel; petroleum ether/ether : 1/1) indicated completion of the halogen exchange. To the vigorously stirred mixture was been added a mixture of chlorotrimethylsilane (4.3 g, 40 mmol) and triethylamine (4.1 g, 40 mmol); the temperature was kept below 20°. Stirring was continued for 2-4 hrs and the resultant suspension was extracted with pentane (5 x 30 ml). The organic extract was concentrated and the residue distilled.

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