Reactions of Terminal Alkynes with Bis(trimethylsilyl) Peroxide and Zinc(II) Iodide: A Convenient Method for the Preparation of 1-Iodo-1-alkynes

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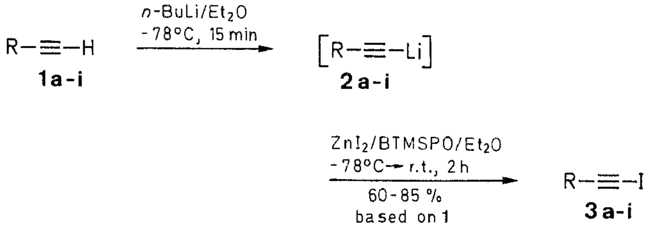
A convenient, mild, and general one-pot synthesis of 1-iodo-1-alkynes from terminal acetylenes, bis(trimethylsilyl) peroxide, and zinc(II) iodide in the presence of *n*-butyllithium is reported.

During the course of our recent work[1] dealing with the synthetic applications of bis(trimethylsilyl) peroxide (BTMSPO), we observed that alkynyl anions unexpectedly reacted with BTMSPO in the presence of zinc(II) iodide giving rise to the terminal iodoalkynes.

In the view of the high synthetic interest of this class of compounds,[2] we thought it worthwhile to develop the above reaction into a mild general method for the synthesis of 1-iodo-1-alkynes.



The acetylides **2** were usually generated by treatment of the corresponding alkynes **1** with *n*-butyllithium. The use of sodium trimethylsilanolate (Me_3SiONa) was also found suitable in one case (see **3i** in Table 1), but generally resulted in somewhat lower yields.

The very easily available[3] BTMSPO turned out to be the reagent of choice, since the reactions performed with di(*tert*-butyl) peroxide were unsuccessful. Also the choice of the iodine source was crucial: with zinc(II) iodide and copper(I) iodide, the iodination reaction occurred smoothly and with very high yields, but failed when potassium or sodium iodide were used.

Due to the mild reaction conditions, this procedure (A) could be usefully applied to a wide range of terminal acetylenes, leading in very good yields, to the corresponding iodo derivatives (Table 1).

This reaction cannot be simply accounted for by an oxidative process, iodine generation not having been noticed even after prolonged reaction times in the reaction of BTMSPO with zinc(II) iodide (or copper(I) iodide). Furthermore, the iodination of the terminal alkynes to 1-iodo-1-alkynes, without previous formation of the acetylide, also occurs (see procedure B), even though at a slower rate and with somewhat lower yields (see **3a, 3b, 3e** in Table 1). This is possibly due to a competing rearrangement of BTMSPO during the slow iodination process in the absence of a lithiating agent, thus suggesting a more complex reaction mechanism, which is now being investigated.

The described procedure offers major advantages in terms of yields and simplicity in comparison to the older methods based on the use of liquid ammonia[2,9] as solvent and for the complete

Table 1. 1-Iodo-1-alkynes **3** Prepared

Product	R	Yield[a] (%)	mp (°C)[b] or bp (°C)/mbar	Molecular Formula[c] or Lit. mp (°C) or bp (°C)/mbar
3a	Ph	85, 45[d], 60[e]	128/12	82/1.7[4]
3b	n-C_6H_{13}	80, 50[e]	105/20	84/0.7[5]
3c	t-Bu	77	120/760	51/22[4]
3d	$HOCH_2$	78, 30[d]	41–42	43–44[6]
3e	$(Me_3Si)_2NCH_2$	67	83–85/7	$C_9H_{20}NSi_2I$ (325.3)
3f	$HO(CH_3)_2C$	73, 50[e]	98–102/18	C_5H_7IO (210.0)
3g	$(CH_3)_2CHCH_2C(CH_3)OH$	80	75/2.2	$C_8H_{13}IO$ (252.1)
3h	Me_3Si	75	96/760	55/20[7]
3i	4-$O_2NC_6H_4$	60[d]	180	181–182[8]

[a] Yields of isolated products, not optimized, based on starting alkynes.

[b] Uncorrected.

[c] Satisfactory microanalyses obtained: C ±0.3, H ±0.2.

[d] Reactions carried out with Me_3SiONa as base.

[e] Reactions performed without n-BuLi, according to procedure B.

Table 2. Spectral Data of 1-Iodo-1-alkynes **3**

Product	IR (neat)[a] ν (cm^{-1})	^1H-NMR[b] ($CDCl_3$/TMS) δ, J(Hz)	MS (70 eV)[c] m/z (%)
3a	2170	6.8–7.5 (m, H_{arom})	227 (100, M^+); 146 (25); 128 (12); 115 (14); 101 (50); 59 (13); 51 (30)
3b	2190	2.1–2.5 (m, 2H, CH_2); 1.7–1.1 (m, 6H, $3CH_2$); 1.0–0.7 (m, 3H, CH_3)	235 (5, M^+); 206 (3); 164 (22); 109 (25); 81 (22); 79 (25); 67 (100); 55 (45); 51 (19)
3c	2190	1.3–1.0 (m, 9H, $3CH_3$)	207 (28, M^+); 194 (100); 127 (24); 96 (21); 81 (34); 67 (41); 58 (58); 51 (28)
3d	2190	4.4 (d, 2H, $J = 2$); 1.7 (br s, 1H, OH)	254 (2, M^+); 237 (5); 208 (10); 181 (63); 165 (19); 127 (73); 111 (11); 97 (20); 83 (26); 69 (40); 67 (18); 56 (100); 51 (8)
3e	2185	3.7 (s, 2H); 0.17 (s, 18H, $SiMe_3$)	324 (2, M^+); 309 (8); 255 (4); 208 (12); 155 (4); 130 (5); 110 (21); 100 (9); 86 (63); 73 (100); 59 (22)
3f	2190	1.9 (br s, 1H, OH); 1.5 (s, 6H)	209 (14, M^+); 195 (6); 194 (87); 178 (7); 152 (5); 146 (14); 133 (100); 126 (18); 97 (7); 83 (13); 66 (13); 59 (23); 56 (31)
3g	2190	2.1 (br s, 1H); 2.0–1.7 (m, 1H, CH); 1.7–1.4 (m, 5H, CH_3, CH_2); 1.0 (d, 6H, $J = 8$, $2CH_3$)	237 (0.3, $M^+ - 15$); 195 (100); 180 (2); 152 (3); 127 (6); 95 (3); 91 (4); 69 (14); 58 (4); 51 (5)
3h	2100	0.07 (s, 9H, $SiMe_3$)	223 (17, M^+); 208 (100); 178 (9); 157 (1); 127 (6); 97 (29); 73 (2); 67 (21); 53 (15)
3i	2170[d]	8.3–8.1 (d, 2H, $J = 9$, H_{arom}); 7.8–7.6 (m, 2H, H_{arom})	273 (72, M^+); 257 (20); 243 (35); 227 (20); 215 (23); 147 (40); 117 (25); 101 (50); 89 (23); 75 (51); 61 (22); 50 (42)

[a] Recorded on a Perkin-Elmer 252 IR spectrophotometer.

[b] Recorded on a Varian EM-390 spectrometer.

[c] Recorded on a Varian Mat 112S spectrometer.

[d] Recorded in CCl_4.

lack of by-products, which are sometimes present in the reactions of molecular iodine with lithium acetylides[10] from n-butyllithium and 1-alkynes. Furthermore, it compares well with the very recent methods reported by Barluenga[11] and Jeffery,[12] especially for the possibility of applying this new reaction, as in the case of the preparation of the previously unreported 3-[bis(trimethylsilyl)amino]-1-iodo-1-propyne (see **3e** in Table 1), to systems containing Si–N bonds, which would tend not to tolerate molecular iodine or protic solvents.

Caution: Care must be exercized in the preparation and handling of BTMSPO due to the danger of explosion.

1-Iodo-1-alkynes; General Procedure:

Method A: A solution of n-BuLi (2.5 M, 0.02 mol) in hexane (8 mL) is added to a stirred solution of alkyne (0.02 mol) in dry Et_2O (25 mL) at −78 °C. After 15 min ZnI_2 (6.38 g, 0.02 mol) and a solution of BTMSPO[3] (3.56 g, 0.02 mol) in Et_2O (30 mL) is added, and stirring is continued at r.t. for 2 h. The resultant mixture is poured into sat. NH_4Cl solution (30 mL) and extracted with Et_2O (3 × 20 mL). The organic phases are dried (Na_2SO_4), and the solvent is removed. For analytical purposes, purification can be achieved by column chromatography on silica gel with n-hexane/Et_2O (85:15) as eluent and/or distillation.

Method B: The reaction is carried out without using n-BuLi. To a mixture of ZnI_2 (0.02 mol) and BTMSPO (0.02 mol) in Et_2O (20 mL) is added the solution of alkyne in Et_2O (5 mL) at 0 °C. Stirring is continued for several hours (24–48 h) and work-up as described above gives the desired product in lower yields in respect to Method A.

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