A Convenient Route to Various 1-Chloro-1-alkynes

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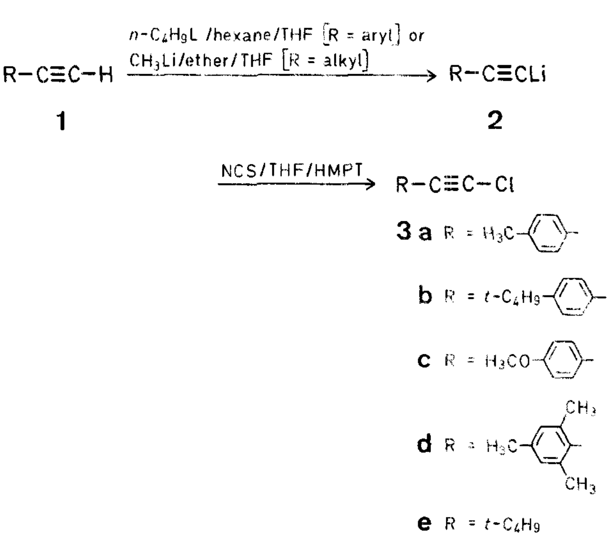
The synthetically useful[1-7] 1-chloro-1-alkynes **3** have been previously prepared by various methods[8-17]. For our research on the thermal and photochemical behaviour of ynamines toward *o*-quinones (c.f.[18,19]), we needed some aryl ynamines with an electron-donating group in the aryl moiety. Such ynamines are, in principle, accessible from the corresponding arylchloroacetylenes[20]. Pangon et al.[12] prepared such chloroacetylenes and alkylchloroacetylenes in low yield (7–15%) by heating the acetylene with *N*-chlorosuccinimide in hexamethylphosphoric triamide at 55–60°. Using some of the other methods we obtained disappointing results. For instance, reaction of lithium mesitylacetylenide in tetrahydrofuran with benzenesulfonyl chloride does not afford the desired chloroacetylene **3**. Ott et al.[14] prepared substituted arylchloroacetylenes from dichloroacetylene and the aryl Grignard reagent. This route is unattractive, however, as dichloroacetylene is unstable and on several occasions violent explosions have been reported[5,21].

We now present a general method for the preparation of various substituted arylchloroacetylenes and alkylchloroacetylenes. Treatment of the lithium acetylenide **2** with *N*-chlorosuccinimide in a mixture of tetrahydrofuran und hexamethylphosphoric triamide, affords the chloroacetylenes **3** after distillation in about 65% yield (10–15% of the starting acetylene **1** was recovered in all cases).



By this method we have also been able to isolate the otherwise difficultly accessible *t*-butylchloroacetylene[22] in good yield (65%). It is essential to use, in this case, an ethereal solution of the alkyllithium reagent and not the commercially available solution of alkyllithium in hexane for the preparation of the acetylenide **2e**, as the product **3e** is difficult to separate from hexane.

1-Chloro-1-alkynes 3; General Procedure:

To a solution of the acetylene **1** (0.10 mol) in tetrahydrofuran (150 ml) is added, in an atmosphere of dry nitrogen, a solution of *n*-butyllithium (0.11 mol) in hexane (74 ml) in the case **1a–d** or a solution of salt-free methyllithium (0.11 mol) in ether (77 ml) in the case of compound **1e**, at −50°. Subsequently, hexamethyl-

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Table. Physical Constants and Spectral Data of the 1-Chloro-1-alkynes **3**

Product	Yield [%] (Lit. yield [%])	b.p./torr or m.p. (Lit. b.p./torr)	n_D^{20} (Lit. n_D [temp])	I.R. (neat)[a] $\nu_{C\equiv C}$ [cm^{-1}]	^{1}H-N.M.R. (CCl_4)[b] δ [ppm]
3a	69 (52)[14]	88°/14 (80°/15)[14]	1.5729 (1.5676 [26.6°])[8]	2224	2.29 (s, 3H); 7.01 (d, 2H, $J = 9$ Hz); 7.27 (d, 2H, $J = 9$ Hz)
3b[d]	60	77°/0.8 m.p. 46–47°[c]	—	2224	1.31 (s, 9H); 7.31 (s, 4H)
3c	65 (52)[14]	63–64°/0.1 (80°/0.15)[14]	1.5862	2220	3.75 (s, 3H); 6.74 (d, 2H, $J = 9$ Hz); 7.30 (d, 2H, $J = 9$ Hz)
3d[e]	65	69°/0.9 m.p. 38–39°[c]	—	2218	2.17 (s, 3H); 2.31 (s, 6H); 6.70 (s, 2H)
3e	64 (10)[22]	86–88°/760 (35–39°/150)[22]	1.4228 (1.4233)[22]	2207, 2242 (sh)	2.23 (s, 9H)

[a] Spectra recorded on a Perkin-Elmer 457 spectrometer; those of products **3a, 3c,** and **3e** are identical to those reported[8, 23]. Compounds **3b** and **3d** measured as CCl_4 solutions.

[b] Spectra recorded on a Varian EM-390 spectrometer; TMS as internal standard.

[c] Recrystallized from pentane.

[d] $C_{12}H_{13}Cl$	calc.	C 74.80	H 6.80
(192.7)	found	74.73	6.92
[e] $C_{11}H_{11}Cl$	calc.	C 73.95	H 6.21
(178.7)	found	73.90	6.31

phosphoric triamide (50 ml) is added, keeping the temperature of the reaction mixture below −50°. Stirring of the reaction mixture is continued during 15 min at −50°, whereupon *N*-chlorosuccinimide (20 g, 0.15 mol) is added in small portions to this well-stirred solution. During the addition the temperature of the reaction mixture was allowed to rise to −15°. After being stirred at room temperature for 1.5 h, the dark reaction mixture is poured into water (350 ml) and the product extracted with pentane (3 × 100 ml). After eight to ten washings with a saturated aqueous solution of ammonium chloride in order to remove most of the tetrahydrofuran, the combined extracts are dried with magnesium sulfate, and subsequently concentrated under a water pump vacuum in the case **1a–d** or at normal pressure in the case **1e** using a 30 cm Widmer column. Careful distillation of the residue through a 20 cm Vigreux column afforded the pure chloroacetylenes **3**. The compounds **3b** and **3d** were recrystallized from pentane (see Table for physical constants).

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