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# TRIMETHYLSILYL ETHYL ORTHOPROPIOLATE - PREPARATION AND USE AS A PROPIOLATE ANION EQUIVALENT

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Abstract: Lithio ethyl orthopropiolate (4b), prepared from trimethylsilyl ethyl orthopropiolate (4a), is introduced as an easy to handle propiolate anion (1a) equivalent.

Lithio propiolate 1a[1] or the dilithio propiolate 1b[2,3] allow for the introduction of an electrophile E into the ß-position of an alkoxycarbonyl (carboxylate) group to give 2 (reaction (1)).

$$(1)\qquad \underset{\text{1a}}{\text{Li-C}\equiv\text{C-CO}_2\text{R}} \quad \text{or} \quad \underset{\text{1b}}{\text{Li-C}\equiv\text{C-CO}_2\text{Li}} \xrightarrow{E} \underset{\text{2}}{\text{E-C}\equiv\text{C-CO}_2\text{R(Li)}}$$

Although compounds of the type 2 are useful intermediates for all kinds of syntheses[1,2], reaction (1) has found only little application: a few additions of 1a to aldehydes and ketones, mainly at low (∿ -70 to -120°C) temperatures[1], and the reaction of 1b with four different epoxides[2] have been described.

Since the normally observed sluggish reactivity of alkali metal acetylides with many electrophiles[4] has been overcome by using hexamethylphosphoricacidtriamide (HMPT) as a (co)solvent[5], the main obstacle for a more general use of, e.g., 1a according to equation (1) seems to be the inclination of the alkyl carboxylate and the lithium acetylide groups in 1a to react with each other[4].

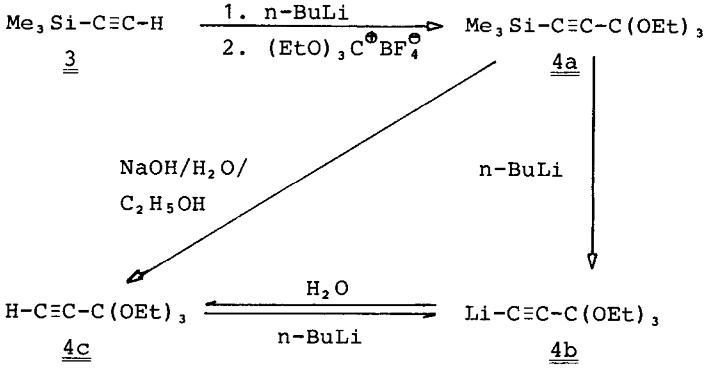
We have solved this problem by using lithium ethyl orthopropiolate (4b) which bears a protected carboxylate group[6], and reacting it with electrophiles to give 5 (equation (2)).

$$(2)\qquad \underset{\text{4b}}{\text{Li-C}\equiv\text{C-C(OEt)}_3} \xrightarrow{E} \underset{\text{5}}{\text{E-C}\equiv\text{C-C(OEt)}_3}$$

The lithiated orthoester 4b is easily prepared by reacting ethyl orthopropiolate (4c) with n-butyllithium (n-BuLi) in tetrahydrofuran (THF) (equation

(3)). However, since there is no facile access to ortho propiolates like 4c in high yields in the literature[7,8], and since an alternative route to lithium species like 4b starts from the corresponding trimethylsilyl compounds like 4a

(3)



with alkyllithium species (e.g. n-BuLi)[9a] (equation (3)), we first synthesized 4a. This was achieved in a convergent synthesis in high yields (83%) by reacting trimethylsilylacetylene (3)[10] first with n-BuLi and then with triethoxycarbenium tetrafluoroborate[11] in diethyl ether at -78°C and allowing the reaction mixture to warm to room temperature[12]. The desired lithium species 4b was formed from 4a with n-BuLi in diethylether or THF after < 1 h at 0°C quantitatively. Protonation of 4b with water led to ethyl orthopropiolate (4c), which was formed directly from 4a with sodium hydroxide in an alcohol/water mixture[9b].

We have not been able to transform either the mono-Grignard or the monolithium acetylide with triethoxycarbenium tetrafluoroborate into ethyl orthopropiolate (4c) in decent yields[13]. Both acetylides are known to disproportionate into acetylene and the dimetalled acetylides in a facile manner[14]. When the more stable complex of lithium acetylide with ethylene diamine[15] was used, the amino groups reacted with triethoxycarbenium tetrafluoroborate.

The reactions of 4b with different electrophiles E are listed in Tab. 1. Entries 1-6 demonstrate the conveniently performed addition of 4b to aldehydes and ketones. The preparation of a ketone with an anhydride is shown in entry 7. The reaction with methyl iodide (8) required the addition of tetramethylethylendiamin (TMEDA). Butylbromide reacted only in the presence of HMPT as a cosolvent (9). In the case of allylbromide (10) the $CuBr \cdot S(CH_3)_2$-complex[16] had to be added to 4b. Propylene oxide (11) reacted only slowly and in poor yield (53%) with 4b.

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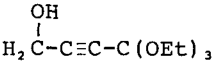
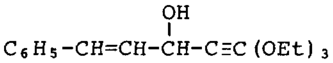
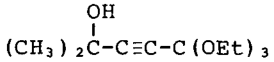
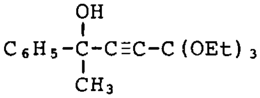
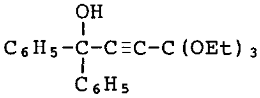
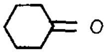
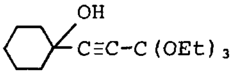
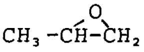
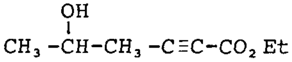
Tab. 1. Reactions of 4b[a] with electrophiles E[b] to give the products 5 (on hydrolysis with water)[c].

| | electrophile E | product 5 | conditions[b] | yield [%] |
|---|---|---|---|---|
| 1 | paraformaldehyde |  $H_2\overset{OH}{C}-C\equiv C-C(OEt)_3$ | b | 85 |
| 2 | $C_6H_5-CH=CH-CHO$ |  $C_6H_5-CH=CH-\overset{OH}{CH}-C\equiv C(OEt)_3$ | b | 92 |
| 3 | $CH_3COCH_3$ |  $(CH_3)_2\overset{OH}{C}-C\equiv C-C(OEt)_3$ | b | 94 |
| 4 | $C_6H_5COCH_3$ |  $C_6H_5-\underset{CH_3}{\overset{OH}{C}}-C\equiv C-C(OEt)_3$ | b | 71 |
| 5 | $C_6H_5COC_6H_5$ |  $C_6H_5-\underset{C_6H_5}{\overset{OH}{C}}-C\equiv C-C(OEt)_3$ | b | 91 |
| 6 |  |  | b | 89 |
| 7 | $(C_6H_5CO)_2O$ | $C_6H_5CO-C\equiv C-C(OEt)_3$ | b; 2 mol. equiv. E | 78 |
| 8 | $CH_3I$ | $CH_3-C\equiv C-C(OEt)_3$ | 4b: TMEDA = 1:1 | 89 |
| 9 | n-ButylBr | n-Butyl-$C\equiv C-C(OEt)_3$ | THF:HMPT = 1:1; 2 h | 82 |
| 10 | $CH_2=CH-CH_2Br$ | $CH_2=CH-CH_2-C\equiv C-C(OEt)_3$ | 4b: $CuBr\cdot Me_2S$ = 1:1 | 83 |
| 11 |  |  $CH_3-\overset{OH}{CH}-CH_3-C\equiv C-CO_2Et$ | d | 52 |

a: 4b was prepared from 4a with 1.05 mol. equiv. n-BuLi in THF at 0°C within 1 h; b: if not otherwise stated the electrophiles E (1.1 mol. equiv.) were reacted with 4b for 1 h at 0°C; after warming to room temperature the reaction mixture was hydrolysed with water and the products 5 extracted with ether, distilled in a Kugelrohr apparatus and analysed by nmr, IR, ms and elementary analysis; in some cases traces of the ethyl propiolates formed; c: acid hydrolysis (oxalic acid in $H_2O$) of 5 led to the corresponding ethyl propiolates; d: 4b, propylene oxide and 0.1 mol. equiv. tetra-n-butylammonium bromide were stirred for 48 h at 20°C The crude material was purified by chromatography on $SiO_2$.

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10. 3 is prepared from $HC{\equiv}CMgBr$ and trimethylsilylchloride in 95% yield, H. Westmijze, P. Vermeer, Synthesis 1979, 390; 3 is also commercially available from, e.g., Fluka.
11. Triethoxycarbenium tetrafluoroborate is prepared by alkylation of diethyl carbonate with triethyloxonium tetrafluoroborate, s. H. Meerwein,P.Borner, O. Fuchs, H.J. Sasse, H. Schrodt, J. Spille, Chem. Ber. 89, 2060 (1956).
12. 4a: bp: 96°C/12 Torr; $^1$H-NMR ($CDCl_3$): $\delta$ = 0.18 (s, 9H, $SiMe_3$), 1.22 (t, 7Hz, 9H, $OCH_2CH_3$), 3.67 (q, 7Hz, 6H, $OCH_2CH_3$); MS: m/c: ($M^+$ absent), 199 (100%, $M^+{-}OC_2H_5$), 171 (18, $^+C{\equiv}C(OEt)_3$), 147 (3, $^+C(OEt)_3$), 97 (5, $Me_3Si{-}C{\equiv}C^+$); 4a gives a correct elementary analysis.
13. From $HC{\equiv}CMgBr$ a yield of 16% has been obtained.
14. See, e.g., a: ref. 4; b: L. Brantsma, Preparative Acetylenic Chemistry, Elsevier, Amsterdam 1971.
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