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REACTION OF ACETYLENIC AND VINYLIC ORGANOLITHIUM REAGENTS WITH TRIETHOXYCARBENIUM TETRAFLUOROBORATE: PREPARATION OF α-ACETYLENIC AND α-ETHYLENIC TRIETHYL ORTHOCARBOXYLATES

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Summary

Acetylenic and vinylic lithium derivatives react with triethoxycarbenium tetrafluoroborate to give α-unsaturated triethyl orthocarboxylates.

Introduction

The initial product of reaction of a Grignard reagent with tetraethyl orthocarbonate is a triethyl orthocarboxylate [1–7]:

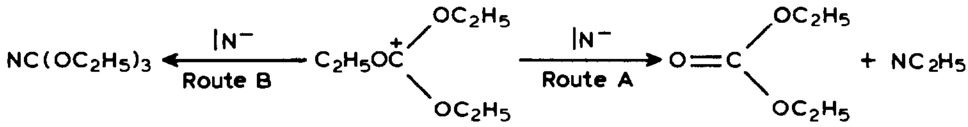
$$C(OC_2H_5)_4 + RMgX \rightarrow RC(OC_2H_5)_3 + C_2H_5OMgX \qquad (1)$$

The synthesis of triethyl orthocarboxylates by this reaction is complicated by subsequent reactions of the initially formed orthoesters with the Grignard reagent to form ketals and ethers. Only very few successful attempts have been reported (eq. 1, $R = HC{\equiv}CCH_2$ [8,9], $R = CH_3C{\equiv}C$ [10]).

Use of triethoxyacetonitrile instead of tetraethyl orthocarbonate, proved satisfactory in reactions with Grignard reagents RMgX, R = Ar or $C_6H_5C{\equiv}C$ [4,11,12]:

$$NCC(OC_2H_5)_3 + RMgX \rightarrow RC(OC_2H_5)_3 + NCMgX \qquad (2)$$

Both the processes in equations (1) and (2) can be looked on as reactions of the Grignard reagent with the intermediate triethoxycarbenium cation $C(OC_2H_5)_3{}^+$. Theoretically, a nucleophilic reagent N^- can react in two ways with triethoxycarbenium cation, one involving dealkylation (route A) and the other addition of N^- to the carbonium centre (route B) [13]:



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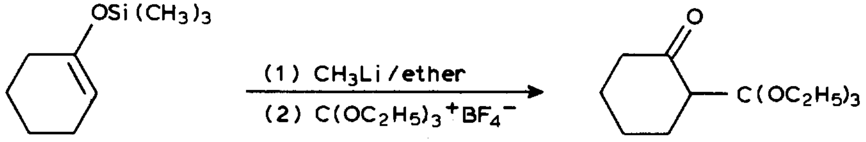
It is known that when the lithium reagent $(CH_3)_3SiC{\equiv}CLi$ is used, the reaction with triethoxycarbenium tetrafluoroborate proceeds via route B [14,15]:

$$(CH_3)_3SiC{\equiv}CLi + C(OC_2H_5)_3{}^+BF_4{}^- \rightarrow (CH_3)_3SiC{\equiv}CC(OC_2H_5)_3$$

We now report that this is the case for a large number of other acetylenic and vinylic lithium reagents (Table 1). This provides a most valuable route to α-acetylenic and α-ethylenic triethyl orthocarboxylates, since the salt $C(OC_2H_5)_3{}^+BF_4{}^-$ can be readily obtained [16–21]. It is relevant to note here that the preparations of the very few known acetylenic or ethylenic orthocarboxylates involve a multistep sequence [22–24].

The reaction works equally well with n-C_4H_9Li, to give the orthocarboxylate n-$C_4H_9C(OC_2H_5)_3$ (yield 70%), but we were unable to obtain any orthocarboxylate from the following reagents: $CH_2{=}CHCH_2MgBr$/ether, $CH_2{=}CHCH_2ZnBr$/THF, n-C_4H_9MgBr/ether, $CH_3CH{=}CHMgBr$/THF, $C_6H_5C{\equiv}CMgBr$/ether, $CH_2{=}CHCH_2Si(CH_3)_3$/ether [26], 1-trimethylsilyloxycyclohexene/CH_2Cl_2/CH_3NO_2 [27]. The cyclohexanone lithium enolate, prepared [28,29] from 1-trimethylsilyloxycyclohexene and methyllithium, gave the corresponding keto-orthocarboxylate but only 90% pure (yield 40%):



It is evident that triethoxycarbenium tetrafluoroborate shows a rather low reactivity towards organometallic compounds, only the organolithium reagents being reactive enough to allow the preparation of triethyl orthocarboxylates. This

TABLE 1

$RLi + C(OC_2H_5)_3{}^+BF_4{}^- \rightarrow RC(OC_2H_5)_3$

	R	Yield (%)	B.p. (°C/torr)	n_D^{20}
1	n-$C_4H_9C{\equiv}C$	65	77–78/0.1	1.4329
2	i-$C_3H_7CH_2C{\equiv}C$	48	73–74/0.25	1.4313
3	n-$C_6H_{13}C{\equiv}C$	54	97/0.1	1.4362
4	$C_6H_5C{\equiv}C$ [a]	57	109–111/0.1	1.5013
5	1-cyclohexenyl-$C{\equiv}C$	50	96/0.07	1.4779
6	$CH_3OCH_2C{\equiv}C$	42	72–73/0.1	1.4321
7	THPO-$CH_2C{\equiv}C$ [b]	51	114/0.08	1.4540
8	THPO-$CH_2CH{=}CHC{\equiv}C$ [b]	50	150/0.08	1.4748
9	$ClCH_2C{\equiv}C$	59	79–80/0.3	1.4508
10	$(CH_3)_2NCH_2C{\equiv}C$	50	65–67/0.05	1.4390
11	$CH_3CH{=}CH$	50	65/8	1.4190
12	$CH_2{=}C(CH_3)$	80	64/12	1.4172
13	$(CH_3)_2C{=}CH$	66	81–82/13	1.4238
14	$CH_3CH{=}C(CH_3)$	81	80/12	1.4253
15	1-cyclopentenyl	46	61–63/0.4	1.4435
16	1-cyclohexenyl	55	74–76/0.25	1.4487

[a] Ref. 25: yield 14%. [b] THP = tetrahydropyranyl.

low reactivity is best explained in terms of delocalization of the positive charge over the three oxygen atoms, to give a fairly stable species.

Experimental

1,2-Dibromo-2-methylpropane

A stream of 2-methylpropene is bubbled into bromine (320 g, 2 mol) at $-10\,^\circ$C until the colour disappears. The mixture is washed with aqueous 5% $NaHCO_3$ (3 × 125 ml), dried ($CaCl_2$), and distilled to give a liquid of b.p. 43–45 °C/13 torr. Yield: 38% (164 g). The residue from the distillation is mainly 1,2,3-tribromo-2-methylpropane: b.p. 97–98 °C/760 torr [30].

1-Bromo-2-methyl-1-propene

A solution of potassium hydroxide (23 g, 0.41 mol) in ethylene glycol (84 ml) is stirred in a three-necked flask fitted with a short fractionating column and heated at 140 °C. 1,2-Dibromo-2-methylpropane (40 g, 0.185 mol) is slowly added; the mixture which distills out (b.p. 80–98 °C/760 torr) is cooled to $-15\,^\circ$C and the liquid decanted from the ice formed. After being dried ($CaCl_2$), the product is distilled. B.p. 90–93 °C/760 torr. Yield: 48% (12 g) [31–33].

1-Alkynes $RC{\equiv}CH$ ($R = n\text{-}C_4H_9$ [34a], $i\text{-}C_3H_7CH_2$ [35,36], $n\text{-}C_6H_{13}$ [34b], 1-cyclohexenyl [34c], CH_3OCH_2 [37,41a], THPO-CH_2 [38], THPO-$CH_2CH{=}CH$ [39] $(CH_3)_2NCH_2$ [40,41b]), 1-chloro-1-cyclopentene [42,43], 1-chloro-1-cyclohexene [43–45] and 1-trimethylsilyloxycyclohexene [46] were prepared by published procedures. All the other starting compounds were commercial products and were distilled before use.

Organolithium reagents

$RC{\equiv}CLi$: a commercial 1.6 *M* solution of n-butyllithium in n-hexane (13.8 ml, 0.022 mol) is added dropwise to a solution of the 1-alkyne (0.025 mol) in ether (15 ml) the temperature being kept below $-10\,^\circ$C [41c] or, in the formation of $LiC{\equiv}CCH_2Cl$, below $-70\,^\circ$C [41d,47]. The vinyllithium derivatives are prepared in ether from $CH_3CH{=}CHBr$ (3 g, 0.025 mol) [48,49], $CH_2{=}C(CH_3)Br$ (3.5 g, 0.029 mol) [50], $(CH_3)_2{=}CHBr$ (4.7 g, 0.035 mol) [32,51,52], $CH_3CH{=}C(CH_3)Br$ (4.7 g, 0.035 mol) [53–57], 1-chloro-1-cyclopentene (3.6 g, 0.035 mol) [42], 1-chloro-1-cyclohexene (4.1 g, 0.035 mol) [44] by published procedures.

Triethoxycarbenium tetrafluoroborate [18,19]

Boron trifluoride diethyl etherate (3.8 g, 0.027 mol) is added from a syringe to a deoxygenated diethyl ether (distilled from sodium benzophenone) (5 ml) and the mixture is rapidly transferred to a pressure equalized dropping funnel then added dropwise during 10–15 min under nitrogen to a stirred solution of tetraethyl orthocarbonate (3.8 g, 0.02 mol) in deoxygenated ether (10 ml) kept at 5 °C. Salt separates from the beginning of the addition. Stirring is continued for only 5 min (longer stirring is harmful) then dry diethyl ether is added (50 ml) and the mixture is poured onto a fritted glass funnel protected from the atmosphere by an inverted funnel carrying a nitrogen stream. The solid is washed with ether (5 × 50 ml) under a slight suction until the washing ether is colorless and the salt completely white. The fritted glass funnel is next fitted with a rubber stopper and the salt is kept for 1 h under the suction of a water pump. The funnel is then transferred, still under vacuum, to a dry-box where the hygroscopic salt is collected. Yield 89% (4.1 g, 0.0175 mol).

General procedure for the preparation of α-unsaturated triethyl orthocarboxylates

The lithium reagent is added dropwise under nitrogen during 30 min to a stirred suspension of triethyoxycarbenium tetrafluoroborate (4.1 g, 0.0175 mol) in ether (30 ml). The mixture is allowed to warm slowly to room temperature (about 3 h), except for the reaction involving $LiC{\equiv}CCH_2Cl$, in which the temperature is kept below $-25\,°C$. The mixture is cooled to $-50\,°C$ and a saturated K_2CO_3 solution (50 ml) is added. After extraction with ether (3 × 50 ml), the combined organic phases are dried (K_2CO_3) and the orthocarboxylate isolated by distillation (see Table 1). Since a trialkyl orthocarboxylate is very rapidly converted into an ester in the presence of a trace of an acid, all the glassware used in the preparation should be immersed for one night in a 5 *M* sodium hydroxide solution before being thoroughly rinsed with water and dried.

^1H NMR spectra: Perkin–Elmer 24A (60 MHz) (CCl_4, TMS) (δ (ppm)). $C(OCH_2CH_3)_3$: **1–10** (1.15, t, 9H, *J* 7Hz); **12, 13, 15, 16** (1.1, t, 9H, *J* 7 Hz); **11, 14** (*Z/E*) (0.9–1.3, 2t, 9H, *J* 7 Hz). $C(OCH_2)_3$: **1–3, 5–10** (3.55, t, 6H, *J* 7 Hz); **4** (3.65, t, 6H, *J* 7 Hz); **12, 13, 15, 16** (3.3, t, 6H, *J* 7 Hz); **11** (*Z/E*) (3.1–3.7, 2q, 6H, *J* 7 Hz); **14** (*Z/E*) (2.9–3.5, 2q, 6H, *J* 7 Hz). **1, 3**: 2–2.4 (m, 2H, $CH_2\text{-}C{\equiv}$); **2**: 1.5–2.2 (m, 3H, $CH\text{-}CH_2\text{-}C{\equiv}$); **4**: 7–7.6 (m, 5H, C_6H_5); **5**: 1.4–1.8 (m, 4H, $(CH_2)_2$), 1.9–2.3 (m, 4H, $CH_2\text{-}C{=}C\text{-}CH_2$), 5.9–6.2 (m, 1H, $CH{=}$); **6**: 3.3 (s, 3H, CH_3O), 4.05 (s, 2H, $CH_2\text{-}C{\equiv}$); **7**: 1.3–1.8 (m, 6H, $(CH_2)_3$), 4.2 (s, 2H, ${\equiv}C\text{-}CH_2$), 4.7–4.9 (m, 1H, $CH(O\text{-})_2$); **8** (*E*): 1.3–1.8 (m, 6H, $(CH_2)_3$), 3.9–4.3 (m, 2H, $=C\text{-}CH_2$), 4.5–4.7 (m, 1H, $CH(O\text{-})_2$), 5.7 (d, 1H, ${\equiv}C\text{-}CH{=}$, *J* 15 Hz), 6.1 and 6.35 (2t, 1H, $=CH\text{-}CH_2O$); **9**: 4.1 (s, 2H, ClCH); **10**: 2.2 (s, 6H, $N(CH_3)_2$), 3.25 (s, 2H, NCH_2); **11** (*Z/E*): 1.5–1.9 (m, 3H, $CH_3\text{-}C{=}$), 5–6.1 (m, 2H, $CH{=}CH$); **12**: 1.55–1.65 (m, 3H, $=C\text{-}CH_3$), 4.9–5.1 and 5.1–5.3 (2m, 2H, $CH_2{=}$); **13** 1.6–1.9 (m, 6H, $(CH_3)_2C{=}$), 4.9–5.1 (m, 1H, $=CH$); **14** (*Z/E*): 1.3–1.9 (m, 6H, $CH_3\text{-}C{=}C\text{-}CH_3$), 5.2–6.0 (m, 1H, $=CH$); **15** 1.5–2.5 (m, 6H, $(CH_2)_3$), 5.7–5.9 (m, 1H, $=CH$); **16**: 1.4–2.3 (m, 8H, $(CH_2)_4$), 5.8–6.1 (m, 1H, $=CH$).

Triethyl 2-cyclohexanoneorthocarboxylate

Methyllithium is prepared from lithium (0.95 g, 0.137 mol), methyl iodide (9.5 g, 0.067 mol) and ether (40 ml). The solution is decanted from the excess lithium and added dropwise at room temperature to a solution of 1-trimethylsilyloxycyclohexene (11.4 g, 0.067 mol) in ether (10 ml). After 2 h stirring at room temperature, the lithium enolate solution is added to a stirred suspension of triethoxycarbenium tetrafluoroborate (7.7 g, 0.033 mol) in ether (50 ml) kept at $-80\,°C$. After the usual work-up (see above), the product is distilled. b.p. 63 °C/0.06 torr. Yield 40% of liquid 90% pure (by GLC). A pure sample isolated by preparative gas chromatography had $n_D^{20} = 1.4402$; ^1H NMR: 1.1 (t, 9H, $C(OCH_2CH_3)_3$, *J* 7 Hz); 1.3–2.4 (2m, 9H, $CH(CH_2)_4$); 3.55 (q, 6H, $C(OCH_2\text{-})_3$, *J*7 Hz).

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