Synthesis of 2-cyanoacrylates *via* 2-cyanoacryloyl chloride

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Monomers that are difficult to obtain, such as *tert*-butyl 2-cyanoacrylate, trimethylsilylmethyl 2-cyanoacrylate, 2,2,3,3-tetrafluoropropyl 2-cyanoacrylate, and the previously unknown adamantyl 2-cyanoacrylate were prepared starting from 2-cyanoacryloyl chloride.

Key words: 2-cyanoacrylate; 2-cyanoacryloyl chloride.

Once the synthesis of free 2-cyanoacrylic acid by thermolysis of ethyl 2-cyanoacrylate had been reported,[1] it became possible to prepare some 2-cyanoacrylates both by direct esterification of the acid[2] and *via* the acyl chloride.[3]

We showed that various alkyl 2-cyanoacrylates can be prepared according to Scheme 1.

Scheme 1

$$PCl_5 + CH_2{=}C(CN)COOH \longrightarrow [CH_2{=}C(CN)COCl] \xrightarrow{ROH} CH_2{=}C(CN)COOR$$

1—4

We could not isolate pure 2-cyanoacryloyl chloride, since it polymerizes when its solution is concentrated. However, this compound may be used for further reactions in solution. The corresponding alkyl 2-cyanoacrylates were prepared by the reactions with excess alcohols.[1—3] The physicochemical characteristics of compound **1** (Table 1) are consistent with the literature data.[4]

Monomers that are difficult to obtain, *viz.*, *tert*-butyl 2-cyanoacrylate (**2**) and trimethylsilylmethyl 2-cyanoacrylate (**3**), and the previously unknown adamantyl 2-cyanoacrylate (**4**) can be prepared using the same reaction.

Experimental

2,2,3,3-Tetrafluoropropyl 2-cyanoacrylate (1). A mixture of 2-cyanoacrylic acid (3.65 g), PCl_5 (8.5 g), hydroquinone (0.01 g), *o*-xylene (30 mL), and toluene (30 mL) was stirred under an argon atmosphere until a transparent solution formed. Then $POCl_3$ and a part of the solvent were evaporated (to a volume of 25 mL) *in vacuo* at 20 °C. 2,2,3,3-Tetrafluoropropanol (6 g) in toluene (30 mL) was added to the resulting solution, and the mixture was stirred for 15 min and fractionated *in vacuo* under argon to give 7.9 g of compound **1**.

Compounds **2—4** were prepared in a similar way. Cyanoacrylate **4** was recrystallized from toluene. The physicochemical properties and ^1H NMR spectral data for compounds **1—4** are given in Table 1.

Table 1. Properties of 2-cyanoacrylates

Compound	R	Yield (%)	B.p./°C (*p*/Torr)	^1H NMR ($(CD_3)_2CO$, δ, *J*/Hz)
1	$CH_2CF_2CF_2H$	70	68—69 (1)	4.79 (t.t, $^3J_{F-H}$ = 13.3, $^4J_{F-H}$ = 1.5, 2 H, OCH_2); 6.40 (t.t, $^2J_{F-H}$ = 52.3, $^3J_{F-H}$ = 4.7, 1 H, CF_2H); 6.99 and 7.21 (both s, 2 H, $C{=}CH_2$)
2	CMe_3	45	50—52 (1)	1.54 (s, 9 H, Me_3); 6.76 and 7.00 (both s, 2 H, $C{=}CH_2$)
3	CH_2SiMe_3	55	75—76 (1)	0.16 (s, 9 H, $SiMe_3$); 4.05 (s, 2 H, CH_2Si); 6.90 and 7.12 (both s, 2 H, $C{=}CH_2$)
4*	Adamantyl	50	M.p. 85 °C	1.61, 2.08, 2.16 (m, 3 H, 6 H, 6 H, Ad-fragment); 6.92 and 7.10 (both s, 2 H, $C{=}CH_2$)

* Found (%): C, 72.79; H, 7.24; N, 6.01. $C_{14}H_{17}NO_2$.
Calculated (%): C, 72.72; H, 7.30; N, 6.06.

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