

Synthesis of 2-cyanoacrylates via 2-cyanoacryloyl chloride

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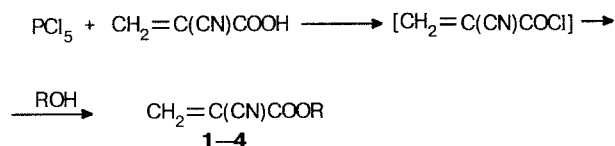
Monomers that are difficult to obtain, such as *tert*-butyl 2-cyanoacrylate, trimethylsilylmethyl 2-cyanoacrylate, 2,2,3,3-tetrafluoropropyl 2-cyanoacrylate, and the previously unknown adamantyl 2-cyanoacrylate were prepared starting from 2-cyanoacryloyl chloride.

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 acid² and *via* the acyl chloride.³

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

Scheme 1



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), PCl₅ (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 POCl₃ 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)	¹ H NMR ((CD ₃) ₂ CO, δ, J/Hz)
1	CH ₂ CF ₂ CF ₂ H	70	68–69 (1)	4.79 (t.t., ³ J _{F–H} = 13.3, ⁴ J _{F–H} = 1.5, 2 H, OCH ₂); 6.40 (t.t., ² J _{F–H} = 52.3, ³ J _{F–H} = 4.7, 1 H, CF ₂ H); 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 ₂ SiMe ₃	55	75–76 (1)	0.16 (s, 9 H, SiMe ₃); 4.05 (s, 2 H, CH ₂ Si); 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. C₁₄H₁₇NO₂.

Calculated (%): C, 72.72; H, 7.30; N, 6.06.

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