S-ALKYL ESTERS OF α-CYANOTHIOACRYLIC ACID

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In contrast to α-cyanoacrylates [1], their sulfur analogs, $CH_2{=}C(CN)COSR$ (I), have not yet been obtained in pure monomeric form despite numerous attempts [2]. In the present communication, we describe a synthesis for the first representatives of this class, R = C_2H_5 (Ia) and R = t-C_4H_9 (Ib), according to the scheme:

$$CH_2{=}C(CN)COOH \xrightarrow[2)\ Pb(SR)_2]{1)\ PCl_5} \underset{(I)}{CH_2{=}C(CN)COSR}$$

An equimolar amount of PCl_5 was added with stirring to a suspension of α-cyanoacrylic acid [3] in xylene. Then, $POCl_3$ was distilled off and lead salt of the thiol was added. The mixture was stirred and $PbCl_2$ was filtered off. Distillation of the solvent and vacuum distillation of the residue gave thiol esters (Ia) and (Ib) in 40-50% yield. Ester (Ia) is a mobile, colorless liquid, bp 65°C (1.5 mm), which readily polymerizes at room temperature even in the presence of radical and ionic polymerization inhibitors. PMR spectrum (δ, ppm): 0.85 t (3H, CH_3), 2.52 q (2H, CH_2), 5.23 s (1H), 6.08 s (1H) (olefinic protons). Ester (Ib) does not polymerize as readily as (Ia) and may be stored for a prolonged period at 0°C in the absence of inhibitors, bp 70°C (1 mm). PMR spectrum: 1.24 s (9H, t-Bu), 5.20 s (1H), and 6.08 s (1H) (olefinic protons). The elemental analysis data for these compounds were satisfactory.

LITERATURE CITED

1. H. Lee (ed.), Cyanoacrylate Resins – The Instant Adhesives, Pasadena Technology Press, Pasadena (1981).
2. S. Harris, J. Polym. Sci., Polym. Chem. Ed., 19, No. 10, 2655 (1981).
3. West German Patent No. 3,415,181 (1985).

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