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Synthesis of bis(2-cyanoacrylates) from 2-cyanoacryloyl chloride and 2-butene- and 2-butyne-1,4-diols

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The interaction of 2-cyanoacryloyl chloride with unsaturated 1,4-diols leads to bis(2-cyanoacrylates) with a double or triple C—C bond.

Key words: bis(2-cyanoacrylates), 2-cyanoacryloyl chloride, unsaturated diols.

Bis(2-cyanoacrylates) (BCAs) used as cross-linking agents for cold-setting glues[1] are now synthesized by two main methods, *viz.*, by a laborious five-step synthesis[1] or by the direct esterification of 2-cyanoacrylic acid with alkane-1,6- or alkane-1,8-diols in the presence of hydroquinone and *p*-toluenesulfonic acid with continious azeotropic distillation with benzene of the water thus formed.[2] The latter of these methods was later found to be inefficient for the synthesis of BCAs of unsaturated 1,4-diols. A far more useful route for the preparative synthesis of BCAs appeared to be the method that we developed earlier for the preparation of thiolic and oxygen esters of 2-cyanoacrylic acid. This method was based on the interaction of 2-cyanoacryloyl chloride[3] with lead thiolates[4] or alcohols,[5] respectively. Using this approach with somewhat modified reaction conditions, we obtained the BCAs of 2-butene- and 2-butyne-1,4-diols in moderate yields (Scheme 1).

Under the experimental conditions described earlier,[2] the BCAs obtained from unsaturated diols undergo considerable polymerization. The structures of the BCAs in question follow from their NMR spectra as well as from the identity of their melting points with those present in the literature[1] for the respective compounds.

Experimental

2-Butene-1,4-diol bis(2-cyanoacrylate) (1a). 2-Butene-1,4-diol (1.5 g, 0.017 mol) and toluene (50 mL) were added to a solution of 2-cyanoacryloyl chloride obtained from 2-cyanoacrylic acid (4.2 g, 0.04 mol) by the known method.[3] The mixture was stirred for 3—4 h at 20 °C, two thirds of the solvent was removed *in vacuo*, and the residue was poured into hot heptane (300 mL) saturated with SO_2. The solution was allowed to stay in a freezer overnight, then the precipitate was filtered off and recrystallized from octane to afford **1a** in 42 % yield. M.p. 105—107 °C (*cf.* Ref. 1: m.p. 106—108 °C).

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Scheme 1

$$H_2C{=}C(CN)COOH \xrightarrow[-(POCl_3,\ HCl)]{PCl_5} H_2C{=}C(CN)C(O)Cl \xrightarrow[-HCl]{HO{-}R{-}OH} H_2C{=}C(CN)COO{-}R{-}OOC(CN)C{=}CH_2$$

1a,b

R = $CH_2CH{=}CHCH_2$ (**a**), $CH_2C{\equiv}CCH_2$ (**b**)

^{1}H NMR (C_6D_6), δ: 4.2—4.3 (s, 4 H, OCH_2); 5.51 (s, 2 H, —CH=); 6.40 (s, 2 H, —CH=).

2-Butyne-1,4-diol bis(2-cyanoacrylate) (1b) was prepared under the same conditions in 45 % yield. M.p. 92—93 °C (*cf.* Ref. 1: 92—93 °C). ^{1}H NMR (C_6D_6), δ: 4.47 (s, 4 H, OCH_2); 5.52 (s, 2 H, —CH=); 6.44 (s, 2 H, —CH=).

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Synthesis of η^6-tricarbonylchromium derivatives of diphenylmethanofullerene using an organometallic derivative of diazomethane

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Isomeric chromotricarbonyl derivatives of diphenylmethanofullerene and -fulleroid have been obtained by the reaction of C_{60} with benchrotrenyl(phenyl)diazomethane.

Key words: fullerenes, methanofullerene, fulleroids, arenechromiumtricarbonyls.

Combining fragments of fullerene and a metal π-complex in the same molecule may disclose some new interesting aspects of reactivity. Though the highly unsaturated structure of fullerenes allows different types of coordination with a metal,[1] only complexes with η^2-coordination of fullerene, although twofold, are known so far.[2,3] Our attempt at direct π-metallocarbonylation by refluxing C_{60} with $(NH_3)_3Cr(CO)_3$ in decalin also failed to afford the η^6-complex. But the common benzene rings of diphenylmethanofullerene are capable of complexation under these conditions. This follows from the appearance of the absorption bands of the valent oscillations of C=O bond at 1910 and 1980 cm^{-1} in the IR spectra of the reaction product, although the yield of the complex is very low. A modification of the Wudl reaction,[4] *i.e.*, the interaction of C_{60} with hitherto unknown (benchrotrenyl)phenyldiazomethane obtained by Scheme 1, appeared to be a far more convenient route for the introduction of the benchrotrenyl fragment into the fullerene molecule.

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