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Abstract

Full Text

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INTERACTION OF CYANOGEN CHLORIDE WITH VINYL ETHYL ETHER IN THE PRESENCE OF INITIATORS OF RADICAL PROCESSES

Recently, the use of cyanogen chloride for the synthesis of nitriles of chloro-substituted carboxylic acids has been acquiring ever greater importance. Thus, several patents have been taken out on the telomerization of ethylene with cyanogen chloride in the presence of free-radical initiators to obtain ω-chloro-substituted alkylnitriles (^{1}). The addition of cyanogen chloride to olefins (^{2}) with the formation of both 3-chloro-substituted nitriles and dehydrochlorinated addition products has been described, as has its addition to butadiene (^{3}) in the presence of Friedel—Crafts reaction catalysts. The addition of cyanogen chloride to unsaturated compounds containing functional groups is unknown.

We have studied the addition of cyanogen chloride to vinyl ethyl ether in the presence of free-radical initiators. The reaction of vinyl ethyl ether with cyanogen chloride was carried out with an excess of the latter in the presence of dicyclohexyl peroxydicarbonate, the dinitrile of azo-bis-isobutyric acid, and also under the action of ultraviolet light. The amount of initiator was 5—10% by weight of the ether. The experiments were carried out in glass. The reaction temperature was 60° for the peroxide and 70° for azo coupling. The reaction under irradiation with ultraviolet light was carried out at −10—20°.

The addition product, β-chloro-α-ethoxypropionitrile, was obtained in a yield of 9—10% of theory (calculated on vinyl ethyl ether) with the peroxide initiator. In the case of the azodinitrile the yield was 6% of theory; upon irradiation for 9 hours with a PRK lamp, only traces of the addition product were isolated. From the reaction mixture, after distillation, acetaldehyde acetal was also isolated; it was identified as the 2,4-dinitrophenylhydrazone. The structure of the addition product was proved by converting the nitrile into the solid amide of β-chloro-α-ethoxypropionic acid by the known method (^{4}). Since the melting point of the amide obtained (124—125°) did not coincide with the melting point of the amide of β-chloro-α-ethoxypropionic acid described in the literature (114°), its synthesis was repeated from α,β-dichloroethyl ether and mercuric cyanide by the known method (^{4}). This amide had m.p. 122—123°. A mixed sample of the two amides showed no depression of the melting point.

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$$CH_2{=}CH{-}OC_2H_5 + ClCN \longrightarrow ClCH_2{-}CH(OC_2H_5)CN$$

$$ClCH_2CHClOC_2H_5 + Hg(CN)_2 \longrightarrow ClCH_2{-}CH(OC_2H_5)C(=O)\,NH_2 \quad (I)$$

In addition, dehydrochlorination of β-chloro-α-ethoxypropionitrile with triethylamine to α-ethoxyacrylonitrile was carried out; its constants agreed with those in the literature. Under the action of sodium alcoholate on the addition product, the amide of α-ethoxyacrylic acid was obtained.

The results obtained for the addition of cyanogen chloride to vinyl ethyl ether show that this reaction is a radical chain reaction with short chains, since the yield of the adduct was 4—5 moles per 1 mole of initiator, and in the absence of initiators the reaction does not proceed.

For cyanogen chloride one may expect reactions with radicals according to routes "a" or "b" of scheme (II)

$$R\cdot + ClCN \begin{cases} \xrightarrow{a} RCN + Cl\cdot \\ \xrightarrow{b} RCl + CN\cdot \end{cases} \quad (II)$$

The formation in our reaction of β-chloro-α-ethoxypropionitrile testifies in favor of the reaction according to scheme "a" (see scheme III)

$$\begin{gathered} \text{initiator} \to 2R\cdot \\ R\cdot + ClCN \overset{a}{\to} RCN + Cl\cdot \\ Cl\cdot + CH_2 = CHOC_2H_5 \to ClCH_2\dot{C}HOC_2H_5 \\ ClCH_2\dot{C}HOC_2H_5 + ClCN \overset{a}{\to} ClCH_2CH(OC_2H_5)CN + Cl\cdot\,. \end{gathered} \quad (III)$$

In the case of reaction according to scheme "b," the formation of β-chloro-β-ethoxypropionitrile would have taken place.

It was recently reported (^{5}) that the radical interaction of cyanogen chloride with saturated and alicyclic hydrocarbons leads to the formation of the corresponding nitriles, rather than chloro derivatives, which was interpreted by the authors as proof that the reaction of radicals with cyanogen chloride proceeds according to scheme "a."

The formation of acetaldehyde ethyl acetal in the reaction studied by us is unexpected. It should be noted that neither in the absence of peroxide nor in the absence of cyanogen chloride is the acetal formed. The mechanism of formation of acetaldehyde ethyl acetal in this reaction has not been investigated.

Experimental Part

1. Reaction of cyanogen chloride with vinyl ethyl ether. Into a glass ampoule equipped with a jacket for heating with water from a thermostat, while cooling with ice water, were placed 3.4 g of dicyclohexyl peroxydicarbonate (10% of the weight of the ether), 34.6 g (0.48 mole) of vinyl ethyl ether, and 49 ml (0.96 mole) of liquid cyanogen chloride. After stirring, bringing the temperature of the reaction solution to room temperature, and releasing the excess pressure, the ampoule was heated with stirring for 6 hr at 60°. The mixture was distilled. There were obtained 26 ml of a mixture of cyanogen chloride with vinyl ethyl ether (b.p. 21-28°), 18.0 g of a fraction with b.p. 77-96°, n_D^{20} 1.3830, 8.3 g of a fraction of the addition product with b.p. 79-96°/32 mm, n_D^{20} 1.4270, and 12.7 g of resin, which was not further investigated.

Upon redistillation of 18.0 g of the product, 5.8 g of a mixture of ethyl alcohol and acetaldehyde ethyl acetal (according to gas-liquid chromatography data) was obtained, with b.p. 76-78°, and 6.2 g of acetaldehyde acetal, b.p. 101-103°, n_D^{20} 1.3820, d_4^{20} 0.8278, identified in the form of acetaldehyde 2,4-dinitrophenylhydrazone.

Literature data (6): b.p. 102.5°/755 mm, n_D^{20} 1.3805, d_4^{20} 0.8264.

After redistillation of the fraction of the addition product, there were obtained 6.0 g (9% of theory) of β-chloro-α-ethoxypropionitrile, b.p. 71°/12 mm, n_D^{20} 1.4328, d_4^{20} 1.0928. Found *MR* 31.75, calculated 31.62.

C_5H_8ClNO.	Found %:	C 45.32; 45.32;	H 5.96; 5.95;	Cl 26.93; 27.08;	N 11.17; 11.10
	Calculated %:	C 44.95;	H 6.04;	Cl 26.54;	N 10.49

Literature data (4): b.p. 75°/13 mm.

The addition product does not give a 2,4-dinitrophenylhydrazone upon prolonged boiling of the solution with 2,4-dinitrophenylhydrazine. From the fraction of the addition product, bis-2,4-dinitrophenylhydrazone of glyoxal was obtained in insignificant yield (2%), m.p. 304°.

Literature data (7): m.p. 309-312°.

$C_{14}H_{10}N_8O_8$.	Found %:	C 40.60;	H 2.57
	Calculated %:	C 40.20;	H 2.41

2. Preparation of the amide from β-chloro-α-ethoxypropionitrile: To an ethereal solution containing 3.8 g of β-chloro-α-ethoxypropionitrile and 1.3 g of absolute ethyl alcohol (equimolecular quantities) at

with cooling, a stream of dry HCl was passed through to saturation, and the reaction mixture was left overnight at room temperature. The precipitated crystals were filtered off, washed with abs. ether, and dried. This gave 4.6 g (74.6%

of theory) of the hydrochloride of the imino ether of β-chloro-α-ethoxypropionic acid (m.p. 83–84°), which was heated at 120° for one hour. The solid, dark melt (3.1 g) was recrystallized from water. This gave 2.2 g (77.5% of theory) of the amide of β-chloro-α-ethoxypropionic acid, m.p. 124–125°.

Found, %: C 39.63; 39.51; H 6.69; 6.65; Cl 22.91; 22.83; N 9.36; 9.13
$C_5H_{10}ClNO_2$. Calculated, %: C 39.58; H 6.64; Cl 23.39; N 9.23

Literature data (^{4}): m.p. 114°.

3. **Synthesis of the nitrile and amide of β-chloro-α-ethoxypropionic acid according to the literature procedure** (^{4}): the nitrile of β-chloro-α-ethoxypropionic acid was obtained from α,β-dichloroethyl ether and mercuric cyanide with the constants: b.p. 76°/16 mm, n_D^{20} 1.4340, d_4^{20} 1.0985. From this nitrile the amide was obtained as described in experiment 2 and in the procedure (^{4}), with m.p. 122–123°. A mixed melting-point test with the amide obtained in experiment 2 melts without depression.

4. **Dehydrochlorination of β-chloro-α-ethoxypropionitrile.** To a solution of 4 g of the nitrile in 10 ml of abs. ether, with stirring at room temperature, was added a solution of 3.8 g of triethylamine in 10 ml of ether; the reaction mixture was stirred for 9 h and left overnight. The precipitated triethylamine hydrochloride was filtered off, the ether was distilled from the mother liquor, dry heptane was added to the residue, the crystals were filtered off, the heptane was distilled off, and the residue was distilled. This gave 1.2 g (41.4% of theory) of α-ethoxyacrylonitrile, which after redistillation had the constants: b.p. 74°/96 mm, n_D^{20} 1.4165, d_4^{20} 0.8944. Found MR 27.69, calculated 27.38.

Literature data for α-ethoxyacrylonitrile (^{8}): b.p. 63°/60 mm, n_D^{20} 1.4170, d_4^{20} 0.9090.

Literature data for β-ethoxyacrylonitrile (^{9}): b.p. 71–72°/8 mm, n_D^{25} 1.4520, d_4^{25} 0.945.

5. **Action of sodium ethoxide on β-chloro-α-ethoxypropionitrile.** To sodium ethoxide prepared from 0.4 g (0.017 g-atom) of sodium and 6 ml of abs. alcohol, 2.1 g (0.016 mole) of the nitrile of β-chloro-α-ethoxypropionic acid was added dropwise with cooling. The reaction mixture was heated on a water bath for 2.5 h. The precipitated NaCl (0.6 g) was filtered off, the alcohol was distilled off, and the residue was distilled in vacuo. This gave 0.7 g (38.9% of theory) of the amide of α-ethoxyacrylic acid, b.p. 130–135°/15 mm. Upon addition of hot heptane the oil crystallized, m.p. 63–64°. After recrystallization from a benzene–heptane mixture, m.p. 68°.

Found, %: C 52.56; 52.45 H 7.74; 7.92; N 12.44; 12.60
$C_5H_9NO_2$. Calculated, %: C 52.16; H 7.88; N 12.17

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