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Abstract

Full Text

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TELOMERIZATION OF VINYL ACETATE WITH CYANOGEN CHLORIDE

Cyanogen chloride, in its properties and structure, belongs to the "pseudohalides" ; it may be expected that, like the halides, it will prove effective in a broad range of radical reactions. Cyanogen chloride is a product of large-scale manufacture, and therefore the study of its chemical transformations is of considerable interest.

Of what is presently known about radical reactions of cyanogen chloride, the telomerization of ethylene with cyanogen chloride, with the formation of ω-chloroalkylnitriles (^{1}), and the cyanation reaction of acyclic and alicyclic hydrocarbons with cyanogen chloride (^{2}), are of greatest interest.

We have shown that cyanogen chloride is capable of adding to vinyl alkyl ethers by a radical chain mechanism with formation of β-chloro-α-alkoxypropionitriles (^{3}). This mode of addition shows that radicals (at least nucleophilic ones) replace the chlorine atom in cyanogen chloride, and not the nitrile group, reacting according to *a*, and not according to *b*, of scheme 1.

$$\mathrm{ClCN} + \mathrm{R}\cdot \begin{cases} \xrightarrow{a} \mathrm{RCN} + \mathrm{Cl} \\ \xrightarrow{b} \mathrm{RCl} + \mathrm{CN}\cdot \end{cases} \qquad (1)$$

Vinyl acetate is readily telomerized by various telogens, and these reactions are being intensively developed; telomerization of vinyl acetate with cyanogen chloride is unknown.

In the present work we have carried out the telomerization of vinyl acetate with cyanogen chloride. The reaction was conducted in the presence of dicyclohexyl peroxydicarbonate at 60° in glass and may be expressed by scheme 2.

$$\mathrm{ClCN} + \mathrm{nCH_2{=}CHOCOCH_3} \xrightarrow[(\mathrm{C_6H_{11}OCO})_2\mathrm{O_2}]{} \mathrm{Cl[CH_2CH(OCOCH_3)]_{nCN}}. \qquad (2)$$

Although the reaction was carried out with a 3–5-fold excess of cyanogen chloride, there was preferential formation of telomers with $n > 1$; telomers with $n =$

$1, 2, 3$ were obtained in individual form. The structure of the addition product was proved by counter synthesis of β-chloro-α-acetoxypropionitrile according to scheme 3.

$$\mathrm{ClCH_2CHClOCH_2CH_3} \xrightarrow[\mathrm{H_2O}]{\mathrm{KCN}} \mathrm{ClCH_2CH(OH)CN} \xrightarrow{\mathrm{(CH_3CO)_2O}} \mathrm{ClCH_2CH(OCOCH_3)CN}. \tag{3}$$

The identity of the β-chloro-α-acetoxypropionitriles obtained by both routes was proved by gas–liquid chromatography. In addition, from both nitrile samples the same crystalline hydrochloride of the iminoethyl ester of β-chloro-α-acetoxypropionic acid was obtained, which did not show a depression of the melting point of the mixed sample.

Neither the addition product nor the telomers give 2,4-dinitrophenylhydrazones, which also confirms the structure indicated for them in scheme 2. The radical and chain character of the reaction under study is confirmed by the fact that, in the absence of peroxide, the reaction does not proceed; the yield of telomers amounted to 128 moles per 1 mole of dicyclohexyl peroxydicarbonate.

The mechanism of telomerization of vinyl acetate with cyanogen chloride can be described by scheme 4.

$$\mathrm{R}\cdot + \mathrm{ClCN} \xrightarrow{a} \mathrm{RCN} + \mathrm{Cl}$$

$$\mathrm{Cl} + \mathrm{CH_2{=}CHOCOCH_3} \xrightarrow{\sigma} \mathrm{ClCH_2\dot{C}HOCOCH_3}\ (\mathrm{A})$$

$$\mathrm{A} \begin{cases} \xrightarrow[\mathrm{ClCN}]{} \mathrm{ClCH_2CH(OCOCH_3)CN} + \mathrm{Cl} \\ \xrightarrow[n\mathrm{CH_2{=}CHOCOCH_3}]{} \mathrm{Cl(CH_2CHOCOCH_3)}_n\mathrm{CH_2\dot{C}H(OCOCH_3)}\ (\mathrm{B}) \end{cases}$$

$$\mathrm{B} + \mathrm{ClCN} \to \mathrm{Cl(CH_2CHOCOCH_3)}_{n+1}\mathrm{CN} + \mathrm{Cl}\ldots \tag{4}$$

Thus, in the present case as well, the radicals reacted with cyanogen chloride according to reaction type *a* of scheme 1.

The telomers obtained are reactive polyfunctional compounds that can serve as starting substances for various syntheses.

Experimental Part

1. Telomerization of vinyl acetate with cyanogen chloride.

Into a glass ampoule equipped with a jacket for heating with water from a thermostat, while cooling with ice water, were placed 0.1 g of dicyclohexyl peroxydicarbonate (0.5% of the weight of vinyl acetate), 27.6 g (0.32 mole) of vinyl acetate, and 49 ml (0.96 mole) of liquid cyanogen chloride. After mixing, bringing the temperature of the reaction mixture to room temperature, and releasing the excess pressure, the ampoule was heated with stirring for 6 h at 60°. The reaction mixture was distilled, and 45 ml of cyanogen chloride, 11.5 g of vinyl acetate (b.p. 70-72°), 0.7 g (5.5% of the total products) of an addition-product fraction with b.p. 95-105°/4 mm, n_D^{20} 1.4440, d_4^{20} 1.2290, 3.6 g (28.6% of the total products) of a telomer fraction with $n = 2$, b.p. 153-158°/4 mm; n_D^{20} 1.4540, 6.3 g (50.1% of the total products) of a fraction of telomers with $n > 2$, b.p. 182-240°/2 mm, n_D^{35} 1.4538, and 2.0 g of residue were obtained.

After redistillation of the addition-product fractions from several experiments, β-chloro-α-acetoxypropionitrile was obtained, b.p. 57°/1 mm, n_D^{20} 1.4422; d_4^{20} 1.2306. Found MR 31.75, calculated 31.63.

Found %: C 40.75, 40.96; H 3.93, 4.13; Cl 23.28, 23.66; N 9.75, 9.67
$C_5H_6ClNO_2$, Calculated %: C 40.69; H 4.07; Cl 24.02; N 9.49.

Literature data (4): b.p. 65°/1 mm; n_D^{35} 1.4355.

On redistillation of the telomer fraction with $n = 2$, δ-chloro-α,γ-diacetoxyvaleronitrile was isolated, b.p. 121-122°/1 mm, n_D^{20} 1.4545; d_4^{20} 1.2243. Found MR 51.77, calculated 51.45.

Found %: C 46.16, 46.24; H 5.16, 5.12; Cl 15.02, 14.98.
$C_9H_{12}ClNO_4$. Calculated %: C 46.36; H 5.17; Cl 15.17.

On redistillation of telomer fractions with $n > 2$, collected from several experiments, a telomer with $n = 3$—ω-chloro-α,γ,ϵ-triacetoxyenanthic nitrile—was isolated, b.p. 193-194°/2 mm; n_D^{35} 1.4548, d_4^{35} 1.2060. Found MR 71.92, calculated 71.83.

Found %: C 49.21, 49.15; H 5.67, 5.82; Cl 10.81, 10.56.
$C_{13}H_{18}ClNO_6$. Calculated %: C 48.83; H 5.67; Cl 11.09.

and a mixture of telomers with $n = 3$ and $n = 4$, b.p. 199-203°/3 mm, n_D^{35} 1.4552, d_4^{35} 1.1986.

Found %: Cl 9.76, 9.92.

Conversion of vinyl acetate: 37%.

All the telomers do not give 2,4-dinitrophenylhydrazones upon prolonged boiling of the corresponding telomers with a solution of 2,4-dinitrophenylhydrazine in sulfuric acid.

2. Preparation of the hydrochloride of the iminoethyl ester of β-chloro-α-acetoxypropionic acid.
A stream of dry hydrogen chloride was passed, with cooling to saturation, through an ethereal solution containing 0.3 g of β-chloro-α-acetoxypropionitrile and 0.1 g of absolute ethyl alcohol (equimolecular amounts); the reaction mixture was left for 2 hours at room temperature. The precipitated crystals were filtered off, washed with absolute ether, and dried. This gave 0.4 g (76.2% of theory) of the hydrochloride of the iminoethyl ester of β-chloro-α-acetoxypropionic acid, m.p. 93.5–94°.

For $C_7H_{13}Cl_2NO_3$. Found, %: C 36.68, 36.65; H 6.03, 5.82; N 6.44, 6.60, 6.47. Calculated, %: C 36.54; H 5.69; N 6.08.

Literature data (^{5}): b.p. 120°.

3. Preparation of β-chloro-α-acetoxypropionitrile according to (^{5}).
β-Chloro-α-acetoxypropionitrile was synthesized by the known method and has the following constants: b.p. 79°/2 mm, n_D^{20} 1.4420; d_4^{20} 1.2277. Found MR 31.81, calculated 31.63.

For $C_5H_6ClNO_2$. Found, %: C 40.71, 40.57; H 4.17, 4.13; Cl 24.16, 23.81; N 9.50, 9.63.
Calculated, %: C 40.69; H 4.07; Cl 24.02; N 9.49.

Literature data (^{5}): b.p. 96–97°/10 mm.

From this sample of β-chloro-α-acetoxypropionitrile, the hydrochloride of the iminoethyl ester was obtained in 90% yield of theory, with m.p. 93°. A mixed melting-point sample with the hydrochloride of the iminoethyl ester of β-chloro-α-acetoxypropionic acid obtained in experiment 2 melts without depression.

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Note: Figure translations are in progress. See original paper for figures.

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