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SYNTHESIS OF CHLORO- AND DICHLORONITROMETHANES

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In the present work, chloronitromethane and dichloronitromethane were synthesized from accessible derivatives of chloronitroacetic and dichloronitroacetic acids. The action of concentrated hydrochloric acid on chloronitroacetyl chloride leads to the formation of dichloroformoxime [1]. We have found that the hydrolysis of chloronitroacetyl and dichloronitroacetyl chlorides by a large excess of water gives chloronitromethane and dichloronitromethane, respectively, in satisfactory yields:

UDC 542.91:547.414.8

$$\begin{array}{l} \text{XCCINO}_2\text{COCI} \xrightarrow[-\text{CO}_2]{H_2\text{O}} \text{XCHCINO}_2 \\ \hline \text{X} = \text{H}, \text{ Cl.} \end{array}$$

These products were also isolated upon heating ethyl chloronitroacetate and ethyl dichloronitroacetate at reflux in 16% hydrochloric acid:

 $XCCINO_2COOEt \xrightarrow{16\%HCl} XCHCINO_2$

X = H, CI.

We should note the high stability of ethyl dichloronitroacetate toward acid hydrolysis relative to ethyl chloronitroacetate.

Chloronitromethane, which has two labile hydrogen atoms, readily reacts with formaldehyde in the presence of K_2CO_3 to form 2-chloro-2-nitro-1,3-propanediol [2]:

 $\mathrm{ClCH_2NO_2} \xrightarrow[\mathrm{K_2CO_3}]{} \mathrm{(HOCH_2)_2CClNO_2}$

EXPERIMENTAL

The IR spectra were taken neat on a Specord IR-75 spectrometer. The PMR spectra were taken on a Bruker CXP-200 spectrometer. The purity of the starting reagents and products was checked on an LKhM-8MD-5 chromatograph on a 3 m \times 3 mm column packed with Inerton AV-DMCS with helium as the carrier gas.

The acid chlorides and ethyl esters of chloro- and dichloronitroacetic acids were obtained according to our previous procedures [3-5].

<u>Chloronitromethane.</u> A mixture of 16.6 g (0.1 mole) ethyl chloronitroacetate and 60 ml 16% hydrochloric acid was heated at reflux for 4.5 h until CO_2 was no longer released. The mixture was extracted thrice with ether. The extract was dried over MgSO₄ and evaporated.

Institute of Physiologically Active Compounds, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 941-942, April, 1986. Original article submitted July 3, 1985.

The residue was distilled to give 2.0 g (21%) product, bp 58-62°C (60 mm), $n_{\rm D}^{20}$ 1.4492, d_4^{20} 1.4631. Found: C 12.69; H 2.03; C1 41.02%. Calculated for CH_2CINO_2 : C 12.58; H 2.12; C1 37.15%. IR spectrum (δ , ppm): 5.92 s (CH₂).

A sample of chloronitroacetyl chloride was added dropwise with stirring to a mixture of 600 ml water and 160 ml ether at 20-25°C. After the termination of CO_2 liberation, the mixture was stirred for 15 min and the organic layer was separated. The aqueous layer was saturated with NaCl and thrice extracted with ether. The extract was dried over MgSO₄ and evaporated. The residue was distilled to give 13.6 g product, bp 60-62°C (65 mm), which contained monochloronitromethane and 10% pentachloroethane as indicated by gas-liquid chromatography; pentachloroethane could not be separated by distillation.

<u>Dichloronitromethane.</u> A mixture of 20.1 g (0.1 mole) ethyl dichloronitroacetate and 50 ml 16% hydrochloric acid was heated at reflux for 19 h until no further CO₂ was released. The mixture was extracted thrice with ether. The extract was dried over MgSO₄ and evaporated. The residue was distilled to give 1.8 g (15%) product, bp 110-112°C, n_D^{20} 1.4509, d_4^{20} 2.122. Found: C 10.53; H 0.80; Cl 54.72%. Calculated for CHCl₂No₂: C 9.26; H 0.77; Cl 54.60%. IR Spectrum (v, cm⁻¹): 1580 (No₂), 2994 (CH). PMR spectrum (δ , ppm): 7.40 s (CH).

Hydrolysis of dichloronitroacetyl chloride according to the procedures for the hydrolysis of chloronitroacetyl chloride give dichloronitromethane in 37% yield, bp 108-110°C.

<u>2-Chloro-2-nitro-1,3-propanediol.</u> A saturated aqueous solution of K_2CO_3 was added dropwise with stirring to a mixture of 40 ml 37% formaldehyde, 70 ml water, and 19 g (0.2 mole) chloronitromethane at 20°C until the mixture was basic. Stirring was continued for 20 min at 25°C and the mixture was poured into acidified ice water, saturated with NaCl, and extracted five times with ethyl acetate. The organic layer was dried over MgSO₄ and evaporated to give 19.37 g (61%) white crystals, which were recrystallized from 1:1 chloroform-ethyl acetate to give 16.15 g product, mp 116°C [6]. Found: C 23.33; H 3.84; Cl 22.80%. Calculated for $C_3H_6CINO_4$: C 23.33; H 3.84; Cl 22.71%. IR spectrum (ν , cm⁻¹): 1550 (NO₂), 3660-2900 br. sh (OH).

CONCLUSIONS

The hydrolysis of the acid chlorides and ethyl esters of chloro- and dichloronitroacetic acids gave chloronitromethane and dichloronitromethane, respectively.

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