SYNTHESIS AND SOME PROPERTIES OF 2,2,2-TRICHLORO-1-ALKOXY-1-NITROXYETHANES

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Previously [1] the theory was expressed that the reaction of cellulose nitrate with chloral proceeds via the step of forming 2,2,2-trichloro-1-nitroxyethylcellulose. As model compounds, in the present paper we synthesized the 2,2,2-trichloro-1-alkoxy-1-nitroxyethanes (I) from the corresponding chloral hemiacetals and an acetic anhydride–HNO_3 mixture.

The presence in the IR spectra of the synthesized products of absorption bands that are characteristic for the ester group (1780-1790 and 1750-1760 cm^{-1}), and also a shift of the frequencies of the antisymmetric vibrations of the nitro group in the 1660-1690 cm^{-1} region, testify to the fact that, together with the reaction for the preparation of (I), acetylation probably occurs with the formation of compounds (II) and (III)

$$\underset{(I)}{CCl_3CH(ONO_2)OR}\quad \underset{(II)}{CCl_3CH(OAc)OR}\quad \underset{(III)}{CCl_3CH(ONO_2)OAc}$$

$$R = CH_3(a);\ C_2H_5(b);\ C_3H_7\ (c);\ i\text{-}C_3H_7\ (d)$$

A shift of the absorption frequencies of the carbonyl and nitro groups probably occurs as the result of a decrease in the contribution made by the resonance structures $C^+{-}O^-$ and $\equiv N^+{-}O^-$, which is caused by the $-I$ effects of the trichloromethyl group and the oxygen atom of the ester linkage [2].

The (I) compounds react easily with diethylamine to give N-nitrosodiethylamine, during thermal decomposition they give the corresponding trichloroacetates, and when treated with glacial AcOH or AcONa in alcohol they give the (II) compounds.

EXPERIMENTAL METHOD

The chloral hemiacetals were obtained as described in [3].

2,2,2-Trichloro-1-ethoxy-1-nitroxyethane (Ib). To a mixture of 8.5 ml of acetic anhydride and 7 ml of HNO_3 (d 1.5), cooled to 0°C, was added in drops a solution of 10 g of chloral monoethyl acetal in 10 ml of acetic anhydride. The mixture was kept at 20° for 0.5 h and then poured into water. The lower layer was separated, while the aqueous layer was extracted with CH_2Cl_2. The extract was combined with the separated layer, neutralized with 5% $NaHCO_3$ solution, washed with water, dried over $MgSO_4$, and vacuum-distilled. The yield of (Ib) was 50%, bp 71-73° (3 mm). Infrared spectrum: (ν, cm^{-1}): 1695, 1290, 845 (ONO_2), 799 (CCl_3). Found: C 20.13; H 2.37; N 5.66; Cl 45.09%. $C_4H_6NCl_3O_4$. Calculated: C 20.12, H 2.51; N 5.86; Cl 44.65%.

Compounds (Ia, c, d) were obtained in a similar manner. The yield of (Ia) was 60%, bp 54-64° (2 mm). Found: N 6.44; Cl 46.19%. $C_3H_4NCl_3O_4$. Calculated: N 6.23; Cl 47.43%. The yield of (Ic) was 60%, bp 72-73° (3 mm). Found: C 22.15; H 2.69; N 5.08; Cl 41.60%. $C_5H_8NCl_3O_4$. Calculated: C 23.76; H 3.16; N 5.54; Cl 42.17%. The yield of (Id) was 66%, bp 60.5-61° (3 mm). Found: C 23.11; H 2.61; N 5.05; Cl 42.12%. $C_5H_8NCl_3O_4$. Calculated: C 23.76; H 3.16; N 5.54; Cl 42.17%.

Reaction of 2,2,2-Trichloro-1-ethoxy-1-nitroxyethane with Diethylamine. To 29 ml of (Ib) in 50 ml of absolute ether at 0° was added 94.5 ml of diethylamine in drops. When the precipitate had disappeared the mixture was kept at ~20° for 1 h, concentrated on the water bath, and the residue was vacuum-distilled.

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We obtained 1.5 g of N-nitrosodiethylamine, bp 54-55° (6 mm); n_D^{21} 1.4390; cf. [4]. Bands at 1450 and 1070 cm^{-1} (N=O and N-N) [5] are present in the IR spectrum, and a weak band at 1723 cm^{-1}, which can be assigned to diethylformamide [6]. The higher boiling products are devoid of chlorine and give a positive test for nitroamine [7]. Infrared spectrum (ν, cm^{-1}): 1623, 1289 ($N-NO_2$), 1723 (NCHO).

Decomposition of 2,2,2-Trichloro-1-ethoxy-1-nitroxyethane. A mixture of 9.3 g of (Ib) in 30 ml of benzene and 0.5 g of BF_3 · etherate was heated on the water bath for 7 h and then vacuum-distilled. Based on the data of the IR spectra, the fractions with 64-65° (11 mm) (1 g) and 88-90° (11 mm) (2 g) were composed of nitrobenzene and ethyl trichloroacetate.

2,2,2-Trichloro-1-ethoxy-1-acetoxyethane (II). a) A mixture of 8.25 g of (Ib) and 5.4 g of CH_3COONa in 25 ml of alcohol was heated for 10 h. After cooling, the mixture was decomposed with water and the lower layer was separated. The aqueous alcohol solution was extracted twice with chloroform, and the extracts were combined with the lower layer and dried over $MgSO_4$. We obtained 0.8 g of (II), bp 74-75° (5 mm); n_D^{21} 1.4544. Infrared spectrum (ν, cm^{-1}): 1765 (C=O); cf. [8]. Found: Cl 45.70%. $C_6H_9O_3Cl_3$. Calculated: Cl 45.20%. A small amount of the chloral monoethyl acetal, with mp 49-50°, was also isolated.

b) A mixture of 8.25 g of (Ib) and 20 ml of CH_3COOH in 10 ml of alcohol was heated at 97° for 1.5 h. We obtained 1.3 g of (II), bp 75° (5 mm); n_D^{20} 1.4541.

CONCLUSIONS

A number of 2,2,2-trichloro-1-alkoxy-1-nitroxyethanes were synthesized and some of their properties were studied.

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