REDUCTION OF AMMONIUM HALONITROACETATE DERIVATIVES BY THIONYL CHLORIDE

A. I. Yurtanov, A. N. Chekhlov, and I. V. Martynov

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Anhydrous ammonium bromonitroacetate and ammonium chloronitroacetate derivatives (I) readily react with thionyl chloride to form derivatives of halooximinoacetic acids (II) and halonitroacetic acids (III).

$$NH_4^+[O_2NCXCOR]^- \xrightarrow[1)-NH_4Cl;\ 2)-H_2SO_4]{1)\ SOCl_2;\ 2)\ H_2O} \underset{(IIa-d)}{HON=CXCOR} + \underset{(IIIa-d)}{O_2NCHXCOR}$$

where X = Cl, R = NH_2 (a), X = Cl, R = OMe (b), X = Cl, R = OEt (c), and X = Br, R = OEt (d).

A solution of 2.5 ml (35 mmoles) thionyl chloride in 10 ml ether was added dropwise with stirring to 10 g (64 mmoles) (Ia) in 20 ml abs. ether excluding contact with atmospheric moisture. Refluxing of the reaction mass was noted. The mass turned blue and then yellow. After 15 min heating at reflux, ammonium chloride was separated. The filtrate was evaporated, washed with three 5-ml portions of water, dried over anhydrous sodium sulfate, and evaporated to dryness. The crystals formed were washed with ether and dried to give 2 g (26%) (IIa), mp 167°C (from ethyl acetate) [1]. PMR spectrum in acetone-d_6 (δ, ppm, TMS): 7.04, 7.3 d (NH_2), 11.96 s (OH). IR spectrum in vaseline mull (ν, cm^{-1}): 1560 (C=N), 1640 (C=O), 3179, 3280 (NH), 3400 (OH). The filtrate was evaporated and chloroform was added to the residue to give 2.6 (29%) (IIIa), mp 67°C [2]. Products (IIb)-(IId) crystallized in the refrigerator after distilling off (IIIb)-(IIId). The yield of (IIb) was 10%, mp 62-63°C [3]. The yield of (IIIb) was 25.6%, bp 86-88°C (18 mm), n_D^{20} 1.4450 [4]. The yield of (IIc) was 10%, mp 78-79°C [1]. The elemental analysis data corresponded to the calculated values. PMR spectrum in $CDCl_3$ (TMS): 1.39 t (CH_3), 4.42 q (CH_2), 10.59 s (OH). IR spectrum: 1740 (COEt), 3300 cm^{-1} (OH) (vaseline mull). The yield of (IIIc) was 36%, bp 85-86°C (12 mm), n_D^{20} 1.4373 [4]. The yield of (IId) was 37%, mp 84-85°C [5]. The yield of (IIId) was 38%. The IR spectra of (IIIa)-(IIId) were identical to those of authentic samples. H_2SO_4 was detected as $BaSO_4$. The low yields of (IIb)-(IId) are related to the subsequent conversion of these compounds to heterocyclic compounds. For example, (IIc) is converted to 3,4-dicarboethoxy-1-oxa-2,5-diazole-2-oxide, mass spectrum (m/z) 262.

The structure of (IIa) was determined and studied by x-ray diffraction analysis. The unit cell parameters for the colorless monocrystals of the monohydrate of (IIa) (crystallized from 96% ethanol), $C_2H_3ClN_2O_2 \cdot H_2O$ are as follows: a = 17.598(4), b = 7.400(2), c = 9.053(3) Å, β = 98.26(2)°, z = 8, space group $P2_1/n$.

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