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Abstract

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ON THE QUESTION OF OBTAINING α-NITROACRYLIC ESTER

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Nitroacetic ester can be used as a starting material for the synthesis of a wide range of α-amino acids ([1–2]).

Of special interest in this direction is the reaction of nitroacetic ester with formaldehyde, ultimately leading to the ester of α-nitroacrylic acid according to the scheme:

$$O_2N{-}CH_2{-}COOC_2H_5 + CH_2O \rightarrow \underset{\displaystyle NO_2}{\underset{|}{HO{-}CH_2{-}CH{-}COOC_2H_5}} \xrightarrow[-H_2O]{} \underset{\displaystyle NO_2}{\underset{|}{CH_2{=}C{-}COOC_2H_5}}$$

Early attempts to carry out this reaction ended in failure ([4]). In all cases unstable resins were obtained, which is explained by the strong tendency of the methylol derivatives of aliphatic nitro compounds toward dehydration and formation of bisadducts.

We succeeded in carrying out the condensation of ethyl nitroacetate with formaldehyde in such a way that side products of the reaction were almost completely absent, and in isolating ethyl α-nitro-β-hydroxypropionate in pure form.

The maximum yield of this ester (48.5%) was obtained when a twofold excess of 33% aqueous formaldehyde was used and at a temperature of $-10(-15)^\circ$.

Increasing the temperature and changing the ratio of the reactants always led to the formation of large amounts of resins, which on standing decompose with evolution of gas bubbles and do not distill even in a high vacuum.

Ethyl α-nitro-β-hydroxypropionate is very close in its properties to 1,1-dinitroethyl alcohol. Like 1,1-dinitroethyl alcohol, it is unstable and is comparatively readily dehydrated at elevated temperatures ([5]); the hydroxyl group of this compound is readily acylated under the action of acetyl chloride. However, all attempts to obtain the free ester of α-nitroacrylic acid were

unsuccessful. The possibility of intermediate formation of α-nitroacrylate was shown by heating a mixture of ethyl α-nitro-β-hydroxypropionate with cyclopentadiene in an ampoule.

In this case, 2-nitro-2-carbethoxybicyclo-2,2,1-heptene-5 was obtained, i.e., the product expected from the Diels–Alder reaction of α-nitroacrylate with cyclopentadiene:

$$\mathrm{HO{-}CH_2{-}\underset{\displaystyle|}{\underset{\mathrm{NO_2}}{CH}}{-}COOC_2H_5 \rightarrow CH_2{=}\underset{\displaystyle|}{\underset{\mathrm{NO_2}}{C}}{-}COOC_2H_5 + H_2O}$$

$$\mathrm{CH_2{=}\underset{\displaystyle|}{\underset{\mathrm{NO_2}}{C}}{-}COOC_2H_5 + \text{cyclopentadiene} \rightarrow \underset{\displaystyle|}{\underset{\mathrm{NO_2}}{\text{2-nitro-2-carbethoxybicyclo[2.2.1]hept-5-ene}}}}$$

The interaction of ethyl α-nitro-β-hydroxypropionate with anthracene and butadiene proceeds analogously.

Experimental Part

1. Condensation of formaldehyde with ethyl nitroacetate. To 8.5 g (0.064 mol) of ethyl nitroacetate (6) and 10 ml (0.12 mol) of 33% aqueous formalin, cooled to −15°, a solution of 0.16 g of sodium acetate in 1 ml of water was added with vigorous stirring.

After the addition of the catalyst was complete, the mixture was stirred at −15° for another 3 hours and poured onto 50 g of crushed ice containing 1 ml of conc. hydrochloric acid. The oil that separated was extracted with ether, and the ethereal solution was dried over Na_2SO_4 and evaporated in vacuo without heating. Distillation gave 3 fractions: 1) b.p. 68–70°/3 mm; n_D^{20} 1.4255; 4.2 g –nitroacetate ester; 2) b.p. 80–92°/3 mm; n_D^{20} 1.4356; 0.78 g –intermediate fraction; 3) b.p. 98–103°/3 mm; n_D^{20} 1.4473; 2.65 g –ethyl α-nitro-β-hydroxypropionate (yield 48.5%, based on nitroacetate ester introduced into the reaction). The redistilled product was a colorless liquid with b.p. 102–103°/2 mm, n_D^{20} 1.4482, d_D^{20} 1.2662; MR_D 34.02 (calculated 33.91).

Found %:	C 37.15, 37.40;	H 5.58, 5.60;	N 8.72, 8.95
$C_5H_9O_5N$. Calculated %:	C 36.80;	H 5.56;	N 8.70

IR spectrum (thin film, UR-10): 1375 and 1572 cm^{-1} –nitro group; 1756 cm^{-1} –keto group in esters; 3535 cm^{-1} –hydroxy group.

2. Acylation of ethyl α-nitro-β-hydroxypropionate. To 4.9 g (0.03 mol) of ethyl α-nitro-β-hydroxypropionate placed in a flask with a reflux condenser, 5 ml of acetyl chloride was added. After the vigorous reaction had ceased, the mixture was heated at 60° for 2 hours, cooled, and evaporated under reduced pressure. The residue was distilled in a quartz flask, collecting the fraction boiling at 102–104°/3 mm, n_D^{20} 1.4368. The yield of the acyl derivative was 6.0 g (98% of theory).

Found %:	C 41.12, 40.96; H 5.38, 5.24; N 6.79, 6.90
$C_7H_{11}O_6N$. Calculated %:	C 40.98; H 5.40; N 6.83

Ethyl α-nitro-β-hydroxypropionate and its acetyl derivative, on storage, are converted into viscous oils that decompose on heating.

IR spectrum (thin film, UR-10): 1375 and 1576 cm^{-1} –nitro group; 1760 cm^{-1} –keto group in esters.

3. Diene synthesis reaction of ethyl α-nitro-β-hydroxypropionate with cyclopentadiene. A mixture of 2.4 g (0.036 mol) of distilled cyclopentadiene and 3.0 g (0.018 mol) of ethyl α-nitro-β-hydroxypropionate was heated in an ampoule at 120–125° for 2.5 hours. During this time the reaction mixture darkened and drops of water appeared on the walls of the ampoule. The contents of the ampoule were diluted with ether, dried over Na_2SO_4, and evaporated. The product of the diene synthesis –2-nitro-2-carbethoxybicyclo-(2,2,1)-heptene-5 –was distilled at 84–85°/2 mm. Yield 2.40 g (58% of theory); n_D^{20} 1.4815.

Found %:	C 56.97, 56.95; H 6.27, 6.23; N 6.86, 6.88
$C_{10}H_{13}ON$. Calculated %:	C 56.86; H 6.20; N 6.63

IR spectrum (thin film, UR-10): 1360 and 1565 cm^{-1} –nitro group; 1750 cm^{-1} –keto group in esters.

4. **Diene synthesis reaction of ethyl α-nitro-β-hydroxypropionate with butadiene.** From 4.9 g (0.03 mole) of ethyl α-nitro-β-hydroxypropionate and 3.2 g (0.06 mole) of butadiene, under the conditions of the preceding experiment, there was obtained 0.96 g (16% of theory) of 1-nitro-1-carbethoxycyclohexene-3, b.p. 80-82°/2 mm; n_D^{20} 1.4695.

Found, %:	C 53.80, 53.90; H 6.66, 6.47
$C_9H_{13}O_4N$. Calculated, %:	C 54.26; H 6.58

IR spectrum (thin film, UR-10): 1374 and 1562 cm^{-1}–nitro group; 1760 cm^{-1} –ketone group in esters.

5. **Diene synthesis reaction of ethyl α-nitro-β-hydroxypropionate with anthracene.** Into a round-bottom flask equipped with a reflux condenser, stirrer, and thermometer were placed 4.0 g (0.022 mole) of anthracene, 50 ml of chlorobenzene, and 4.3 g (0.022 mole) of ethyl α-nitro-β-hydroxypropionate. The mixture was heated for 8 h at 135°, cooled, and the crystals of anthracene were filtered off. From the filtrate, on standing, the diene-synthesis product crystallized. Yield 3.24 g (93% based on anthracene that entered into the reaction); m.p. 102.5-103° (from alcohol).

Found, %:	C 70.50, 70.48; H 5.36, 5.16; N 4.43, 4.68
$C_{19}H_{17}O_4N$. Calculated, %:	C 70.58; H 5.26; N 4.33

IR spectrum (pressed in KBr, UR-10): 1355 and 1562 cm^{-1}—nitro group, 1760 cm^{-1}—ketone group in esters.

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