# Academician A. V. TOPCHIEV, V. P. ALANIYA, and Z. A. MAKAROVA

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## Abstract

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Academician A. V. TOPCHIEV, V. P. ALANIYA, and Z. A. MAKAROVA

# SYNTHESIS OF 1-NITROPROPYLENE AND TESTING OF ITS ABILITY TO POLYMERIZE

Nitroolefins are of interest from the standpoint of their possible use for the synthesis of various products.

The principal routes for the processing of nitroolefins are the following:

$$C_{nH_{2n-1}}NO_2$$

Dinitro compounds $C_{nH_{2n-1}}(NO_2)_2$

Nitropolymers

$\alpha$-Chlorocarboxylic acids $C_{nH_{2n}}ClCOOH$

$\gamma$-Aminosulfonic acids $C_{nH_{2n}}(NH_2)COOH$

Amines and diamines $C_{nH_{2n+1}}NH_2$; $C_{nH_{2n}}(NH_2)_2$

Thioamines $C_{nH_{2n+1}}(S)NO_2$

Amino acids $C_{nH_{2n}}(NH_2)COOH$

The aim of the present work was to obtain 1-nitropropylene on the basis of nitromethane and to test its ability to polymerize. The synthesis of 1-nitropropylene was carried out according to the schemes:

$$\mathrm{CH_3NO_2 + CH_3CHO \longrightarrow NO_2CH_2{-}CH(OH){-}CH_3}$$

$$\mathrm{NO_2CH_2{-}CH(OH){-}CH_3} \xrightarrow[\text{dehydration}]{} \mathrm{CH_3CH{=}CHNO_2 + H_2O}$$

$$\mathrm{NO_2CH_2{-}CH(OH){-}CH_3 + C_6H_{11}COCl \longrightarrow C_6H_{11}COCH(CH_3)CH_2NO_2}$$

$$\mathrm{C_6H_{11}COCH(CH_3)CH_2NO_2} \xrightarrow{\text{pyrolysis}} \mathrm{CH_3CH{=}CHNO_2 + C_6H_{11}COOH}$$

The synthesis of 1-nitropropanol was carried out by condensation of nitromethane with acetaldehyde, with a yield of 39–50%. The magnitude of the yield of nitropropanol varied depending on the rate of addition of acetaldehyde to the reaction mixture. 1-Nitropropylene was prepared by two methods ([2,3]): 1) by pyrolysis of 1-nitropropyl benzoate, obtained from 1-nitropropanol and benzoyl chloride, with a yield of 80%; 2) by dehydration of 1-nitropropanol in the presence of phthalic anhydride (Table 1).

The yield of 1-nitropropylene when it was obtained from 1-nitropropyl benzoate was 28%; the yield in the case of dehydration of 1-nitropropanol in the pres-

Table 1

Comparative evaluation of methods for obtaining 1-nitropropylene

| Methods of preparation | Yield of nitropropylene, g | Yield of nitropropylene, % | Experimental mol. wt. | Experimental b.p., °C | Experimental $d_4^{20}$ | Experimental $n_D^{20}$ | Literature mol. wt. | Literature b.p., °C | Literature $d_4^{20}$ | Literature $n_D^{20}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Pyrolysis of 1-nitropropyl benzoate | 18 | 27.7 | 88 | 156 | 1.0655 | 1.4526 | 87 | 156 | 1.0661 | 1.4527 |
| Dehydration of 1-nitropropanol in the presence of phthalic anhydride | 58.5 | 67 | 89 | 156 | 1.0654 | 1.4526 | 87 | 156 | 1.0661 | 1.4527 |

in the presence of phthalic anhydride was 67% of theory. The constants of the products obtained differed little from the literature data.

The possibility of polymerizing 1-nitropropylene in the presence of $BF_3$, saturated aqueous sodium bicarbonate solution, and sodium methoxide was investigated. When $BF_3$ was used as the catalyst for the polymerization of 1-nitropropylene, polymers were practically not obtained. In sodium bicarbonate solution, a light-yellow polymer powder was obtained, which melted with decomposition at +115°.

The investigations carried out on the polymerization of 1-nitropropylene in the presence of sodium methoxide showed the possibility of a deeper polymerization of 1-nitropropylene in the presence of this catalyst. Moreover, as the investigations showed, temperature is the main factor affecting the polymerization reaction of 1-nitropropylene in the presence of sodium methoxide. The degree of polymerization and the yield of polymer increase with decreasing temperature, as is seen from Table 2.

Table 2

| Starting material | Amount of catalyst, g | Amount of catalyst, % | Reaction temperature, °C | Reaction duration, h | Polymer yield, % |
|---|---|---|---|---|---|
| 1-Nitropropylene | 0.62 | 6 | −18 | 3 | 86 |
| 1-Nitropropylene | 0.62 | 6 | +20 | 3 | 33 |

The polymer obtained was a solid, readily inflammable substance, insoluble in mineral and organic acids, alkalis, nitro compounds, amines, hydrocarbons, chloro derivatives, and alcohols, and partially soluble in dimethylformamide.

## Experimental Part

**1-Nitropropanol.** To a mixture of 122 g (2 mol) of nitromethane, 100 ml of 95% ethyl alcohol, and 4 ml of 10 N sodium hydroxide solution, with constant stirring, 88 g (2 mol) of acetaldehyde was added at such a rate that the temperature was maintained at 30–35°. After addition of 2/3 of the aldehyde to the reaction mixture, a further 4 ml of 10 N alkali solution and 15 ml of water were added, and then the remaining aldehyde was added. The solution was left at room temperature for 4 days. The mixture was then neutralized with hydrochloric acid and the ethyl alcohol was distilled off. The remaining product was subjected to vacuum distillation. 1-Nitropropanol was obtained as a weakly yellow oily liquid in 39–44% yield; b.p. 84–86° at 5–6 mm, mol. wt. 107, $d_4^{20}$ 1.1301; $n_D^{20}$ 1.4384. Literature data: b.p. 84° at 5 mm, mol. wt. 105, $d_4^{20}$ 1.1296; $n_D^{20}$ 1.4379.

**1-Nitropropylene (from 1-nitropropyl benzoate).** A mixture of 189 g (1.8 mole) of 1-nitropropanol, 222.6 g (1.8 mole) of benzoyl chloride, and 450 ml of benzene was heated to boiling for 12–14 hr with constant stirring.

After removal of the benzene by distillation under a vacuum of 100 mm, 100 ml of 95% ethyl alcohol was added to the reaction mass, after which the ethyl benzoate formed was distilled off under a vacuum of 20 mm at 100°.

The remaining reddish-brown residue was dissolved in 50 ml of ether, washed, dried, and the ether was then removed; the resulting 1-nitropropyl benzoate was heated in a Claisen flask on an oil bath to a temperature of 150–160°. Under these conditions the nitropropylene formed distilled off; it was purified by distillation under vacuum: b.p. 62–64° at 45 mm, mol. wt. 89, $d_4^{20}$ 1.0655; $n_D^{20}$ 1.4526. Literature data: b.p. 64° at 45 mm, mol. wt. 87, $d_4^{20}$ 1.0661; $n_D^{20}$ 1.4527.

**1-Nitropropylene (dehydration of 1-nitropropanol in the presence of phthalic anhydride).** A mixture of 105 g (1 mole) of nitropropanol and 150 g (1 mole) of phthalic anhydride, placed in a Claisen flask connected to a Liebig condenser, was heated at 140–150° under vacuum until it became homogeneous. The temperature was then raised to 175–180°. Heating was continued as long as distillation was observed. The distillate obtained was separated from water and dried. Yield 66.5%; b.p. 54° at 28 mm, mol. wt. 90, $d_4^{20}$ 1.0654; $n_D^{20}$ 1.4520.

**Polymerization of 1-nitropropylene in the presence of $BF_3$.** Into a flask were charged 22 g (0.2 mole) of 1-nitropropylene, and $BF_3$ was passed in ($BF_3$ was obtained by the reaction $CaF_2 + 3H_2SO_4 + B_2O_3$ ($^4$)). The reaction was carried out in the temperature range from 0 to +50°. The duration of the reaction was varied from 30 min to 3 hr. Under these conditions the polymerization reaction practically did not proceed.

**Polymerization of 1-nitropropylene in the presence of a saturated solution of sodium bicarbonate.** A mixture of 11 g (0.1 mole) of nitropropylene and 30 ml of a saturated aqueous solution of sodium bicarbonate was heated to 50° with vigorous stirring for 60 min. The end of the reaction was recorded when the mass formed reached ambient temperature. After this, the solid polymer was filtered off and washed. The polymer obtained was dried in air. Polymer yield 80% of theory.

**Polymerization of nitropropylene in the presence of sodium methylate.** The reaction was carried out in a round-bottomed flask equipped with a mechanical stirrer, thermometer, and reflux condenser. After completion of the polymerization, the contents of the flask were treated with acetone (at ordinary temperature). As a result of treating the polymer with acetone, a pasty mass was formed. To coagulate the polymer, this mass was treated with water. As a result, a solid polymer, completely neutral to water, separated. The water was removed by decantation, and the polymer was dried in air. Yield 86% of theory (at −18°).

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