

SHORT
COMMUNICATIONS

Reaction of Octyl Ether with Nitric Acid and its Mixtures

N. V. Svetlakov, V. G. Nikitin, and F. F. Ruziev

Kazan State Technological University, Kazan, 420015, Russia

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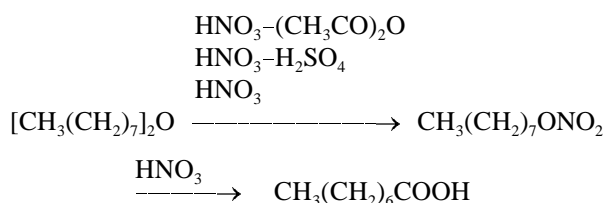
We reported previously that alkanes reacted at 15–20°C with a mixture $\text{HNO}_3-(\text{CH}_3\text{CO})_2\text{O}$ to afford mononitrates of secondary alcohols [1]. To outline the application range of the process we studied a reaction between octyl ether and the mixture of nitric acid with acetic anhydride. It was presumed that the reaction could proceed at the carbon–hydrogen bond in the aliphatic moiety or at the carbon–oxygen bond or in both directions.

The octyl ether was added while stirring at 10–15°C to the mixture $\text{HNO}_3-(\text{CH}_3\text{CO})_2\text{O}$, and the reaction was carried out for 30 min at temperature no higher than 20°C. The reaction is accompanied by heat evolution and nitrogen oxides liberation. The reaction products were purified by vacuum distillation. The ^1H NMR and IR spectra indicated that the reaction product was 1-octyl nitrate with up to 3% of carbonyl-containing impurities.

Alongside the octyl nitrate we isolated a fraction with a wide boiling temperature interval. It is presumably a mixture of oxidized compounds formed from the primary reaction product, octyl nitrate, since the components of the mixture contain both carbonyl and nitroxyl groups.

The reaction of the octyl ether with a mixture of nitric and sulfuric acids was vigorous and accompanied with nitrogen oxides liberation. Vacuum distillation of the reaction products provided two fractions. As show ^1H NMR and IR spectra the first fraction contains 1-octyl nitrate with caprylic acid as impurity, and the second fraction consists of caprylic acid apparently formed by oxidation of the octyl nitrate. The concentrated nitric acid reacts with octyl nitrate in a similar way.

Thus under the applied conditions aliphatic moiety virtually does not undergo nitroxylation, and the reaction takes as the main course the rupture of the carbon–oxygen bond to afford octyl nitrate and its oxidation products.



(1) To 85 g (1.35 mol) of 97.5% nitric acid was added 37.8 g (0.37 mol) of acetic anhydride at temperature not exceeding 25°C. To the acid mixture was added at 5–10°C while stirring 14.5 g (0.06 mol) of octyl ether, and the resulting reaction mixture was maintained at 20°C for 30 min. The reaction mixture was poured into cold water, the organic part was extracted with chloroform (3 × 50 ml), the extract was washed with water, 3% solution of sodium carbonate, again with water, and was dried on sodium sulfate. The solvent was distilled off, and the reaction products were distilled in a vacuum. We obtained 11.6 g (56%) of octyl nitrate, bp 91–92°C (17 mm Hg), d_n^{20} 0.9510, n_D^{20} 1.4246. IR spectrum (ν , cm^{-1}): 875, 1630 (ONO_2). The IR spectrum contains a weak absorption band at 1730 cm^{-1} ($\text{C}=\text{O}$) evidencing the presence of a carbonyl-containing impurity. ^1H NMR spectrum (δ , ppm): 0.98 t (3H, CH_3), 1.4–1.8 m (12H, 6CH_2), 4.0 t, 4.4 t [2H, $\text{H}_A\text{CH}_B-\text{ONO}_2$, $J(\text{H}_A, \text{H}_B)$ 14 Hz], the signal 7.9 s (CHO) indicates the presence of aldehyde traces. Found, %: C 54.79; H 9.90; N 8.64. M_{R_D} 47.81. $\text{C}_8\text{H}_{17}\text{NO}_3$. Calculated, %: C 54.85; H 9.71; N 8.00. M_{R_D} 47.31.

The second fraction (4 g) was separated at 115–130°C (17 mm Hg). In the IR spectrum appear absorption bands at 875, 1630 (ONO_2) and 1730 cm^{-1} ($\text{C}=\text{O}$). This fraction presumably consists of the substances arising at octyl nitrate decomposition.

(2) To a mixture of 41.5 g (0.4 mol) of technical grade concn. sulfuric acid and 85 g (1.35 mol) of 97.5% nitric acid was added at temperature not exceeding 15°C 14.5 g (0.06 mol) of octyl ether, and the resulting reaction mixture was kept for 30 min.

The reaction mixture was worked up as described above. The first fraction was octyl nitrate with caprylic acid impurity. We obtained 11.4 g (55%) of octyl nitrate. IR spectrum (ν , cm^{-1}): 870, 1650 (ONO_2), 1710, 2800–3100 (COOH). ^1H NMR spectrum (δ , ppm): 1.1 t (3H, CH_3), 1.2–1.8 m (12H, 6CH_2), 4.2 t (2H, CH_2ONO_2). The signal 2.1 t (2H, CH_2COOH) and a small singlet at 11.0 s (1H, COOH) show the presence of acid impurity.

The second fraction (3 g) contained caprylic acid, bp 105–106°C (2 mm Hg), n_D^{20} 1.4270 in accordance with the published data [2]. IR spectrum (ν , cm^{-1}): 1700, 2800–3100 (COOH). ^1H NMR spectrum (δ , ppm): 1.1 t (3H, CH_3), 1.2–1.8 m (10H, 5CH_2), 2.1 t (2H, CH_2COO), 11.0 s (1H, COOH).

(3) To 85 g (1.35 mol) of nitric acid at 5–10°C was added 14.5 g (0.06 mol) of octyl ether, and the mixture was kept for 30 min at this temperature. The

workup was as above. Yield of octyl nitrate 12.3 g (59%). The physical constants and spectral characteristics were the same as described before.

The experiments were carried out with octyl ether of “pure” grade, acetic anhydride, concn. nitric and sulfuric acid of “technical grade.” IR spectra were recorded on spectrometer UR-20. ^1H NMR spectra were registered on Tesla BS-497 instrument at operating frequency 100 MHz from solutions in deuterioacetone, internal reference HMDS.

REFERENCES

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