

SHORT
COMMUNICATIONS

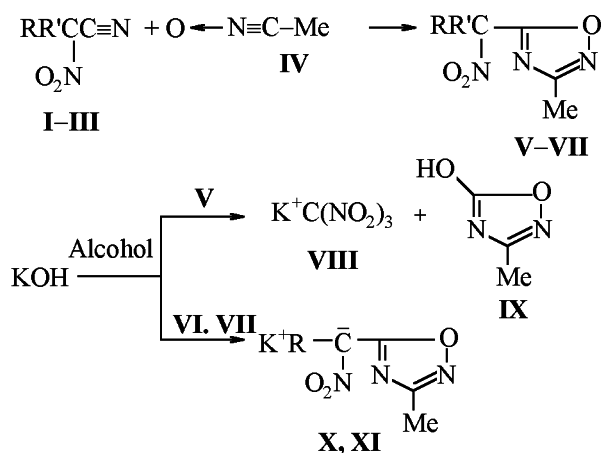
Reaction of Substituted Cyanonitromethanes with Acetonitrile N-Oxide

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Trinitroacetonitrile [1] and dinitrochloroacetonitrile [2] react with 3-nitrobenzonitrile N-oxide giving rise to products of 1,3-dipolar cycloaddition, 3-(3-nitrophenyl)-5-polynitromethyl-1,2,4-oxadiazoles. In order to elucidate whether this reaction may be general we attempted to extend it to aliphatic nitriles N-oxides. We established that cyanonitromethanes **I-III** with electron-withdrawing substituents cleanly reacted with acetonitrile N-oxide (**IV**) furnishing in low yield previously unknown 3-methyl-5-nitromethyl-1,2,4-oxadiazoles (**V-VII**).



R = R' = NO₂ (**I, V**), R = NO₂, R' = Cl (**II, VI, X**),
R = CO₂C₂H₅, R' = Cl (**III, VII, XI**).

The structure of oxadiazoles **V-VII** was unambiguously proved by IR, ¹H and ¹³C NMR spectra, and by chemical reactions. The reaction of compound **V** with alcoholic solution of potassium hydroxide involves nucleophilic substitution of the trinitromethyl group and results in 5-hydroxy-3-methyl-1,2,4-oxadiazole (**IX**). Under similar conditions compounds **VI, VII** lose halogen and transform into potassium salts **X, XI** whose structure was confirmed

by UV spectra. Compounds **I-III** were prepared by procedures [3-5]. Acetonitrile N-oxide (**IV**) was generated by treating the sodium salt of nitroethane *aci*-form with acetyl chloride by procedure [6]. It was introduced into reaction with compounds **I-III** *in situ*.

Reaction of cyanonitromethanes I-III with acetonitrile N-oxide (IV). To a solution of the sodium salt of nitroethane *aci*-form in 30 ml of anhydrous *N,N*-dimethylacetamide was added at 20°C while stirring 5 mmol of acetyl chloride. In 15 min 5 mmol of compounds **I-III** in 10 ml of the same solvent was added, and the solution was mixed for 12 h. Then 50 ml of a mixture water-benzene, 3:1, was added, and the reaction mixture was stirred for 30 min. The water layer was extracted with benzene (2 × 15 ml), the benzene solution was dried on Na₂SO₄, the solvent was evaporated in a vacuum, the residue was subjected to column chromatography on Silicagel 100/400μ, eluent CCl₄.

3-Methyl-5-trinitromethyl-1,2,4-oxadiazole (V). Yield 39%, *n*_D²⁰ 1.4915. IR spectrum, *v*, cm⁻¹: 1600, 1300 (NO₂). ¹H NMR spectrum, *δ*, ppm: 2.52 s (CH₃). ¹³C NMR spectrum, *δ*, ppm: 172.16 (C⁵), 164.47 (C³), 127.42 (C-NO₂), 48.82 (CH₃). Found, %: C 20.52; H 1.21; N 29.93. C₄H₃N₅O₇. Calculated, %: C 20.60; H 1.29; N 30.04.

5-Dinitrochloromethyl-3-methyl-1,2,4-oxadiazole (VI). Yield 34%, *n*_D²⁰ 1.4873. IR spectrum, *v*, cm⁻¹: 1600, 1340 (NO₂). ¹H NMR spectrum, *δ*, ppm: 2.51 s (CH₃). ¹³C NMR spectrum, *δ*, ppm: 172.10 (C⁵), 164.42 (C³), 123.62 (C-NO₂), 48.77 (CH₃). Found, %: C 21.48; H 1.26; N 25.08. C₄H₃ClN₄O₅. Calculated, %: C 21.57; H 1.35; N 25.17.

Ethyl 3-methyl-1,2,4-oxadiazol-5-ylnitrochloroacetate (VII). Yield 37%, *n*_D²⁰ 1.4856. IR spectrum, *v*, cm⁻¹: 1775 (C=O), 1590, 1350 (NO₂). ¹H NMR spectrum, *δ*, ppm: 4.55 q (CH₂O), 2.50 s (CH₃),

1.34 t (CH₃). ¹³C NMR spectrum, δ, ppm: 184.23 (COO), 172.15 (C⁵), 164.58 (C³), 105.63 (C-NO₂), 65.43 (CH₂), 48.25 (CH₃), 16.31 (CH₃). Found, %: C 33.58; H 3.12; N 16.74. C₇H₈ClN₃O₅. Calculated, %: C 33.67; H 3.21; N 16.83.

Reaction of 3-methyl-5-nitromethyl-1,2,4-oxadiazoles V-VII with alcoholic KOH solution. To a solution of 3 mmol of compounds V-VII in 10 ml of ethanol was added excess of alcoholic KOH solution. The mixture was kept for 1 h at 0±5°C, the precipitate was filtered off, and salts VIII, X, XI were recrystallized from ethanol. After reaction of compound V with alcoholic KOH solution the precipitate was subjected to chromatography, and from elute with ethyl ether oxadiazole IX was isolated.

Trinitromethane potassium salt (VIII). Yield 66%, mp 97°C [7].

5-Hydroxy-3-methyl-1,2,4-oxadiazole (IX). Yield 51%, mp 62°C [8].

5-Dinitromethyl-3-methyl-1,2,4-oxadiazole potassium salt (X). Yield 62%, mp 273–275°C. UV spectrum, λ_{max}, nm: 232 (log ε 3.72), 365 (log ε 3.88). Found, %: N 24.72. C₄H₃KN₄O₅. Calculated, %: N 24.78.

Ethyl 3-methyl-1,2,4-oxadiazol-5-ylnitroacetate potassium salt (XI). Yield 67%, mp 257°C. UV spectrum, λ_{max}, nm: 315 (log ε 3.92). Found, %: N 16.51. C₇H₈KN₃O₅. Calculated, %: N 16.60.

IR spectra were recorded on spectrophotometer IKS-29 from solutions in chloroform. ¹H NMR spectra were registered on spectrometer Tesla BS-487C (80 MHz) in acetone-*d*₆ internal reference HMDS. ¹³C NMR spectra were measured on spectrometer Tesla BS-567A at operating frequency 25,142 MHz in acetone-*d*₆, internal reference HMDS. Electronic spectra of water solutions of compounds were taken on spectrophotometer SF-8.

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