

SHORT
COMMUNICATIONS

Reaction of 2,2-Dinitro-2-(3-phenyl-1,2,4-oxadiazol-5-yl)acetonitrile with Substituted Phenyl Azides

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Received November 9, 2007

DOI: 10.1134/S1070428009020250

The reaction of diazomethane with 2,2-dinitro-2-(3-phenyl-1,2,4-oxadiazol-5-yl)acetonitrile (**I**) proceeded under mild conditions and led to the formation of products of 1,3-dipolar cycloaddition, N-methylated isomeric 1,2,3-triazol-4-yl-(3-phenyl-1,2,4-oxadiazol-5-yl)dinitromethanes [1].

In contrast the reaction of the substituted dinitroacetonitrile **I** with phenyl azide (**II**) proceeded at heating and resulted in *N*-(dinitromethylene)aniline (**V**) and 3-phenyl-5-cyano-1,2,4-oxadiazole (**VIII**) (see the scheme). The cyano group at this conversion of compound **I** lost the quality of a dipolarophile.

Likewise behaved 4-tolyl azide (**III**) and 4-nitrophenyl azide (**IV**) in the reaction with compound **I**.

It is presumable that in the elimination of nitrogen from aryl azides **II–IV** at the thermolysis the corresponding nitrenes were generated [2] which reacting at the electron-deficient carbon atom of the dinitroacetonitrile fragment of compound **I** followed by the elimination of nitrogen-containing fragments undergo stabilization into sterically less loaded compounds **V–VII** and the decomposition product **VIII**. The structure of compounds **VI–VIII** were established from the IR and ¹H NMR spectra, and that of compound **V**, by comparison the physical

characteristics with the published data. In the IR spectra of compounds **VI** and **VII** absorption bands are observed of *gem*-dinitromethyl group at 1555 (ν_{as}) and 1280 (ν_s) and of C=N bond at 1635 cm^{-1} . The CN group in 1,2,4-oxadiazol **VIII** gave rise to a band at 2250 cm^{-1} . ¹H NMR spectra of compounds **VI–VIII** are characterized by the presence of multiplet proton signals in the region of aryl ring at 6.95–8.15 ppm

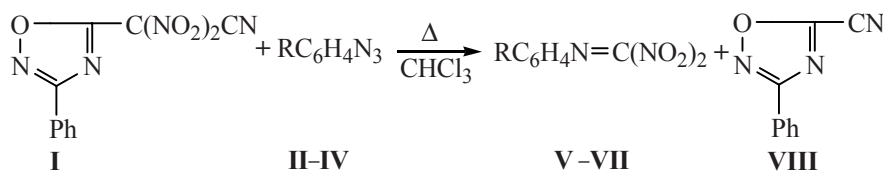
Synthesis of compound **I** was performed by procedure [1], of aryl azides **II–IV**, by procedure [3].

Reaction of 2,2-dinitro-2-(3-phenyl-1,2,4-oxadiazol-5-yl)acetonitrile (I) with aryl azides II–IV. To a solution of 10 mmol of compound **I** in 20 ml of chloroform was added at 25°C 10 mmol of aryl azide **II–IV** in 30 ml of the same solvent. The reaction mixture was heated at reflux for 5 h, the solution was evaporated in a vacuum, and the residue was subjected to chromatography on a column (500 × 10 mm) packed with Silicagel 100/400 μ using Trappe set of eluents. Eluent for compounds **V–VII** was benzene, for compound **VIII**, ethyl ether.

***N*-(Dinitromethylene)aniline (V).** Yield 28%, mp 97°C [4].

***N*-(Dinitromethylene)-4-methylaniline (VI).** Yield 32%, mp 112–113°C. IR spectrum, ν , cm^{-1} : 1555, 1280

Scheme.



R = H (**II, V**), 4-Me (**III, VI**), 4-NO₂ (**IV, VII**).

(NO₂). ¹H NMR spectrum, δ, ppm: 7.24–6.95 m (C₆H₄), 2.10 s (CH₃). Found, %: C 45.75; H 3.16; N 19.92. C₈H₇N₃O₄. Calculated, %: C 45.93; H 3.35; N 20.10.

N-(Dinitromethylene)-4-nitroaniline (VII). Yield 18%, mp 158–160°C. IR spectrum, ν, cm⁻¹: 1555, 1280 (NO₂), 1540, 1365 (NO₂). ¹H NMR spectrum, δ, ppm: 8.15–7.21 m (C₆H₄). Found, %: C 34.82; H 1.51; N 23.16. C₇H₄N₄O₆. Calculated, %: C 35.00; H 1.67; N 23.33.

3-Phenyl-5-cyano-1,2,4-oxadiazol (VIII). Yield 15%, mp 77–78°C. IR spectrum, ν, cm⁻¹: 2250 (CN). ¹H NMR spectrum, δ, ppm: 7.72 m (C₆H₅). Found, %: C 62.96; H 2.76; N 24.42. C₉H₅N₃O. Calculated, %: C 63.16; H 2.92; N 24.56.

IR spectra were recorded on a spectrophotometer IKS-29 from solutions in chloroform of concentration 40 mg/ml. ¹H NMR spectra were registered on a spec-

trometer Tesla BS-487C (80 MHz) in acetone-*d*₆, internal reference HMDS. The homogeneity of compounds obtained was checked and the reaction progress was monitored by ascending TLC on Silufol UV-254 plates in the system acetone–hexane, 2:3, development in iodine vapor.

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