

SHORT
COMMUNICATIONSReaction of Ethyl Cyano(dinitro)acetate
with 3-Amino-1,2,5-oxadiazole-4-carbonitrile Oxide

A. G. Tyrkov, A. B. Sheremetev, and O. I. Serebryakov

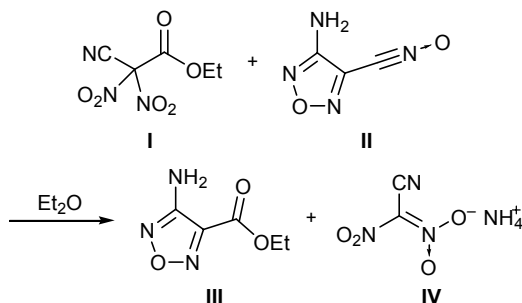
Astrakhan State University, pl. Shaumyana 1, Astrakhan, 414000 Russia

e-mail: tyrkov@rambler.ru

Received May 7, 2011

DOI: 10.1134/S107042801203027X

Ethyl cyano(dinitro)acetate was reported to react with benzonitrile and 3-nitrobenzonitrile oxides under mild conditions according to the 1,3-dipolar cycloaddition pattern with formation of ethyl (3-aryl-1,2,4-oxadiazol-5-yl)dinitroacetates [1]. We found that replacement of the benzene ring in the initial nitrile oxide by 1,2,5-oxadiazole changes the reaction direction. Ethyl cyano(dinitro)acetate (**I**) reacted with 3-amino-1,2,5-oxadiazole-4-carbonitrile oxide (**II**) to give ethyl 4-amino-1,2,5-oxadiazole-3-carboxylate (**III**) and *aci*-dinitroacetonitrile ammonium salt (**IV**) instead of expected 3,5-disubstituted 1,2,4-oxadiazole.



In this reaction, the cyano group in molecule **I** does not act as dipolarophile, presumably due to reduction of the reactivity of compound **II** as 1,3-dipole as a result of change of the substituent at the nitrile oxide fragment. The structure of compound **III** was determined on the basis of its IR, ^1H and ^{13}C NMR, and mass spectra and elemental composition. Initial ester **I** was synthesized as described in [2], and nitrile oxide **II** was prepared according to [3].

A solution of 5 mmol of compound **II** in 100 ml of anhydrous diethyl ether was added at 20°C to a solution of 5 mmol of compound **I** in 10 ml of anhydrous diethyl ether. The mixture was kept for 2 days at 25°C and evaporated, and the residue was subjected to column chromatography on a glass column ($d = 10$ mm,

$l = 500$ mm) charged with activated silica (Silicagel 100–400 μm). Compound **III** was eluted with benzene, and compound **IV**, with acetone.

Ethyl 4-amino-1,2,5-oxadiazole-3-carboxylate (III). Yield 0.324 g (41%), mp $67\text{--}68^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 3436, 3324 (NH_2), 1725 ($\text{C}=\text{O}$). ^1H NMR spectrum, δ , ppm: 1.32 t (3H, CH_3), 4.41 q (2H, CH_2), 6.35 br.s (2H, NH_2). ^{13}C NMR spectrum, δ_{C} , ppm: 13.8 (CH_3), 62.2 (CH_2), 139.4 (C^3), 156.3 (C^4), 158.6 ($\text{C}=\text{O}$). Mass spectrum, m/z (I_{rel} , %): 157 (14) [$\text{M}]^+$, 58 (100), 55 (48), 53 (53), 43 (22). Found, %: C 38.03; H 4.28; N 26.55. $\text{C}_5\text{H}_7\text{N}_3\text{O}_3$. Calculated, %: C 38.22; H 4.46; N 26.75. M 157.13.

***aci*-Dinitroacetonitrile ammonium salt (IV).** Yield 0.164 g (22%), mp 179°C [4].

The IR spectra were recorded in KBr on an Infra-lyum FT-02 spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker Avance II 300 SF instrument at 300 and 75 MHz, respectively, in $\text{DMSO}-d_6$ using HMDS as internal reference. The mass spectrum (electron impact, 70 eV) was obtained on a Finnigan SSQ-7000 instrument with direct sample admission into the ion source (vaporizer temperature $90\text{--}150^\circ\text{C}$). The progress of the reaction and the purity of the isolated compounds were monitored by TLC on Silufol UV-254 plates using acetone–hexane (2:3) as eluent; development with iodine vapor.

REFERENCES

1. Tyrkov, A.G., Pashchenko, K.P., Ladyzhnikova, T.D., and Altukhov, K.V., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.*, 2004, no. 7, p. 148.
2. Parker, C., *Tetrahedron*, 1962, vol. 17, p. 109.
3. Rheiboldt, H., *Justus Liebigs Ann. Chem.*, 1927, vol. 451, p. 161.
4. Parker, C., Emmons, W., Pagano, A., Rolewicz, H., and McCallum, K., *Tetrahedron*, 1962, vol. 17, p. 79.