

Substituted 5-Dinitromethyl-3-phenyl-1,2,4-oxadiazoles in Reactions with Arylethenes

A. G. Tyrkov

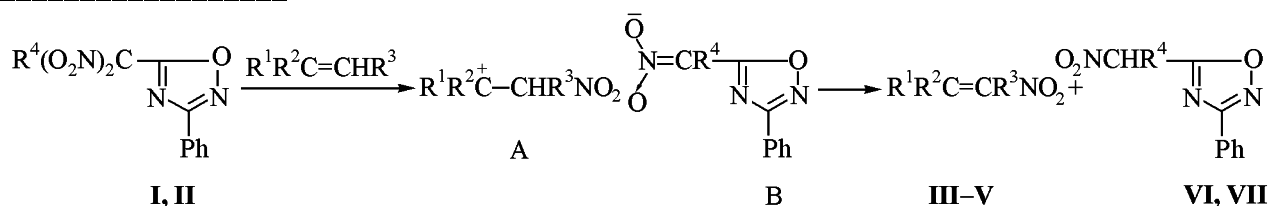
Astrakhan State Pedagogical University, Astrakhan, 414056 Russia

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Abstract—Reactions of substituted 5-dinitromethyl-3-phenyl-1,2,4-oxadiazoles with arylethenes of various nucleophilicity, number and position of substituents attached to the double bond give rise to nitroalkenes and secondary products resulting from α -nitroketones or nitroalcohols O-alkylation. The direction of transformations in the arising ion pair is governed predominantly by steric effects.

A specific character of dual reactivity of tetra-nitromethane [1], halotrinitromethanes [2], or trinitroacetone [3] with arylalkenes originates from intermediate formation of ambidental anions of trinitromethane or dinitrocyanoacetate which depending on the nature of the reacting partner are capable of nucleophilic addition either at carbon (C-alkylation) or oxygen (O-alkylation) atom. At the same time the data on reactions with alkenes of polynitromethanes possessing an oxadiazole moiety are scanty. The only known example of reaction between 5-trinitromethyl-3-phenyl-1,2,4-oxadiazole with phenylethene resulted in denitration of azole and furnished α -nitroketones or 1-methyl-2-nitro-1-phenyl-1-ethanol [4]. Aiming at revealing the main rules governing the reactions of substituted 5-trinitromethyl-3-phenyl-1,2,4-oxadiazoles with arylalkenes we studied under comparable conditions the reactions between 5-trinitromethyl-3-phenyl-

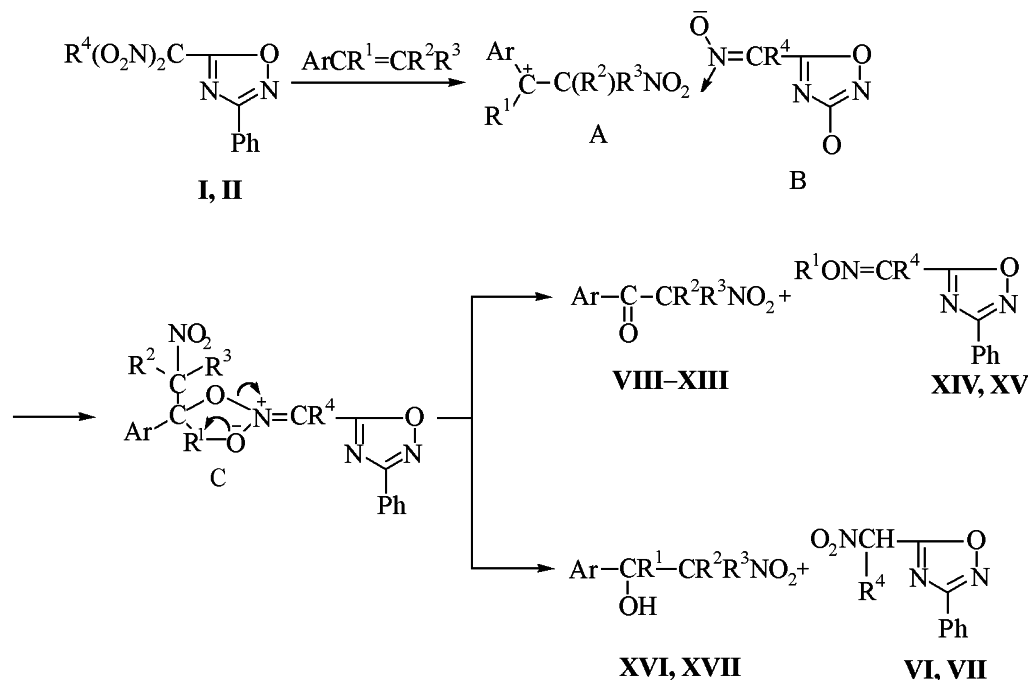
1,2,4-oxadiazole (**I**) and its analog, substituted ester **II** with a series of arylethenes of various nucleophilicity, number and position of substituents attached to the double bond. The structure and some spectral characteristics of compounds **I**, **II** are similar to those of trinitromethane; therefore it is reasonable to expect that their electrophilic addition to arylalkenes would proceed through formation of a π -complex which transforms into a reactive ion pair β -nitrocarbocation-ambidentate anions of 5-dinitromethyl-3-phenyl-1,2,4-oxadiazole or ethyl 3-phenyl-1,2,4-oxadiazol-5-yl-nitroacetate followed by conversion into the final products. In the reaction of nitroalkenes **I**, **II** with substituted 1,1-diphenylethenes the arising nitrocarbocations **A** because of significant shielding effect of two benzene rings are incapable to react with anions **B** and undergo stabilization by ejecting a proton and affording conjugated nitroalkenes **III-V**.



I, VI, $R^4 = NO_2$; **II, VII**, $R^4 = CO_2C_2H_5$; **III**, $R^1 = R^2 = Ph$, $R^3 = H$; **IV**, $R^1 = R^2 = 4-CH_3OC_6H_4$, $R^3 = H$; **V**, $R^1 = R^2 = 4-Me_2NC_6H_4$, $R^3 = Me$.

From the reaction mixture were additionally isolated the products of decomposition of the initial reagents: 5-dinitromethyl-3-phenyl-1,2,4-oxadiazole (**VI**) from compound **I** or ethyl nitro(oxadiazolyl)-acetate (**VII**) from compound **II**. The structure of nitroalkenes **III-V** was established by means of IR spectra and confirmed by comparison of their physical constants with the published data.

Reactions of oxadiazoles with arylalkenes where the number of bulky phenyl substituents did not exceed one at each carbon atom of the multiple bond had more complicated pattern and depending on the number and position of alkyl groups attached to the double bond afforded α -nitroketones or nitroalcohols. This is due to reduction of steric hindrances at the reaction site of the intermediate β -nitrocarbocations **A**



I, VI, XIV, R⁴ = NO₂; II, VII, XV, R⁴ = CO₂Et; VIII-XI, XVI, R² = R³ = H; VIII, Ar = Ph; IX, Ar = 4-MeC₆H₄; X, Ar = 4-BrC₆H₄; XI, Ar = 4-CH₃OC₆H₄; XII, Ar = 4-CH₃OC₆H₄, R² = R³ = Me; XIII, Ar = Ph, R² = H, R³ = Ph; XIV, XV, R¹ = H; XVI, Ar = Ph, R¹ = Me; XVII, Ar = Ph, R¹ = R² = Me, R³ = H.

making possible their interaction with anions B. For instance, the reaction of nitroalkanes **I** and **II** with arylethenes disregarding the extent of their nucleophilicity in the presence of a hydrogen in the α -position to the double bond gives rise to O-alkylated products, α -nitroketones **VIII-XIII** and oximes **XIV, XV**.

The structure of nitroketones was established from their IR spectra, by comparison of the physical constants with the published data, and also by preparation of the corresponding 2,4-dinitrophenylhydrazones. The reaction between nitroalkanes and arylethenes having a methyl group instead of a hydrogen in the α -position to the multiple bond provides nitroalcohols **XVI, XVII** and products of compounds **I, II** decomposition (oxadiazoles **VI, VII**). The structure of nitroalcohols was established using IR and ¹H NMR spectra, and also by comparison of their physical constants with the published data. In none of the reactions under study products of C-alkylation were obtained. The single pathway taken by reaction of oxadiazolenitroalkanes **I, II** with arylalkenes evidences that the intermediate anions are prone to O-alkylation with the arising nitrocarbocations. Intermediately forming nitron esters C in all cases studied evidently are not able to undergo 1,3-dipolar cyclo-

addition to the initial alkene due to steric hindrances created by the presence of a bulky heterocycle. Therefore they suffer decomposition along the mechanism of intramolecular oxidation-reduction [5] into α -nitroketones **VIII-XIII**. We proved the lack of formation of the product originating from 1,3-dipolar addition (the respective isoxalidine) by the method of "chemical trap": carrying out reaction of compound **I** with 1-(4-methoxyphenyl)ethene in solution of active dipolarophile, acrylonitrile. The formation of nitroalcohols **XVI, XVII** within the framework of the assumed scheme may be rationalized as resulting from hydration of intermediates A with water present in the reaction mixture [6]. It should be noted that nitroalkane **II** unlike compound **I** is inert in reaction with 1,1- and 1,2-diphenylethenes apparently due to its lower dipolarophile activity than that of compound **I**.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer IKS-29 from solutions in chloroform. ¹H NMR spectra were registered on spectrometer Tesla BS-487C980 MHz) in acetone-*d*₆, internal reference HMDS. Compounds **I** and **II** were synthesized as in [7], arylalkenes were prepared from appropriate carbonyl compounds and alkylmagnesium halides

with isolation of alcohols followed by their dehydration [8]. Physical constants of arylenes were in agreement with the published values.

Reaction of 5-R-dinitromethyl-3-phenyl-1,2,4-oxadiazoles I, II with arylenes. To a solution of 5 mmol of compound I or II in 10 ml of anhydrous ethyl ether at $0\pm 5^\circ\text{C}$ was added 5 mmol of arylenes ethereal solution. The reaction mixture was maintained for 10 days at 25°C , the solvent was evaporated, and the residue was subjected to chromatography on a column (10×250 mm) packed with activated silica gel of Silicagel 100/400 μ brand. Eluent for compounds VIII–X, XII, XIII, XVI, XVII C_6H_6 , for compounds III–V, XI CHCl_3 , for compounds VI, VII, XIV, XV ethyl ether.

1,1-Diphenyl-2-nitroethene (III). Yield 48%, mp 88°C [9].

1,1-Bis(4-methoxyphenyl)-2-nitroethene (IV). Yield 55%, mp 114°C [10].

1,1-Bis(4-dimethylaminophenyl)-2-methyl-2-nitroethene (V). Yield 57%, mp $142\text{--}143^\circ\text{C}$ [11].

5-Dinitromethyl-3-phenyl-1,2,4-oxadiazole (VI). Yield 10%, mp $83\text{--}84^\circ\text{C}$ [4].

Ethyl 3-phenyl-1,2,4-oxadiazol-5-yl-nitro-acetate (VII). Yield 10%, mp 115°C . IR spectrum, ν , cm^{-1} : 1775 (C=O); 1590, 1380 (NO_2). ^1H NMR spectrum, δ , ppm: 7.62 m (C_6H_5); 6.84 s (CH); 4.52 q (CH_2); 1.32 t (CH_3). Found, %: C 51.83; H 3.85; N 15.04. $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_5$. Calculated, %: C 51.99; H 3.97; N 15.16.

2-Nitro-1-phenyl-1-ethanone (VIII). Yield 55%, mp 105°C [12].

2-Nitro-1-(4-t $^\circ$ lyl)-1-ethanone (IX). Yield 57%, mp $144\text{--}145^\circ\text{C}$ [13].

1-(4-Bromophenyl)-2-nitro-1-ethanone (X). Yield 52%, mp $177\text{--}178^\circ\text{C}$ [13].

1-(4-Methoxyphenyl)-2-nitro-1-ethanone (XI). Yield 56%, mp $153\text{--}154^\circ\text{C}$ [14].

2-Methyl-1-(4-methoxyphenyl)-2-nitro-1-ethanone (XII). Yield 61%, n_D^{20} 1.5545 [15].

1,2-Diphenyl-2-nitro-1-ethanone (XIII). Yield 48%, mp 64°C [13].

Nitro(3-phenyl-1,2,4-oxadiazol-5-yl)methanal oxime (XIV). Yield 10%, mp $97\text{--}98^\circ\text{C}$ [4].

Ethyl (3-phenyl-1,2,4-oxadiazol-5-yl)acetate oxime (XV). Yield 12%, mp 154°C . IR spectrum, ν ,

cm^{-1} : 1720 (C=O). ^1H NMR spectrum, δ , ppm: 7.75 m (C_6H_5); 4.50 q (CH_2); 1.30 t (CH_3). Found, %: C 55.06; H 4.14; N 16.02. $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_4$. Calculated, %: C 55.17; H 4.22; N 16.09.

1-Methyl-2-nitro-1-phenyl-1-ethanol (XVI). Yield 52%, n_D^{20} 1.5190 [16].

1,2-Dimethyl-2-nitro-1-phenyl-1-ethanol (XVII). Yield 54%, n_D^{20} 1.5216. IR spectrum, ν , cm^{-1} : 3550 (OH); 1560, 1350 (NO_2). ^1H NMR spectrum, δ , ppm: 7.24 m (C_6H_5); 5.47 s (OH); 4.54 q (CH); 1.70 d (CH_3); 1.63 s (CH_3). Found, %: C 61.46; H 6.58; N 7.06. $\text{C}_{10}\text{H}_{13}\text{NO}_3$. Calculated, %: C 61.54; H 6.67; N 7.18.

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