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Reaction of 2,2-Dinitromalononitrile with Arylalkenes

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Abstract—2,2-Dinitromalononitrile reacted with phenylethene and 1-phenylpropene through intermediate *aci*-nitromalononitrile ester and subsequent 1,3-dipolar cycloaddition of the second alkene molecule with formation of substituted 5-phenyltetrahydroisoxazole-3,3-dicarbonitriles. Reactions of 2,2-dinitromalononitrile with 2-phenylpropene or *p*-methoxyphenylethene resulted in the formation of 2-(1-aryl-2-nitroethyl)-2-nitromalononitriles. 1,1-Diarylethenes reacted with 2,2-dinitromalononitrile to give conjugated 1,1-diaryl-2-nitroethenes due to steric hindrances.

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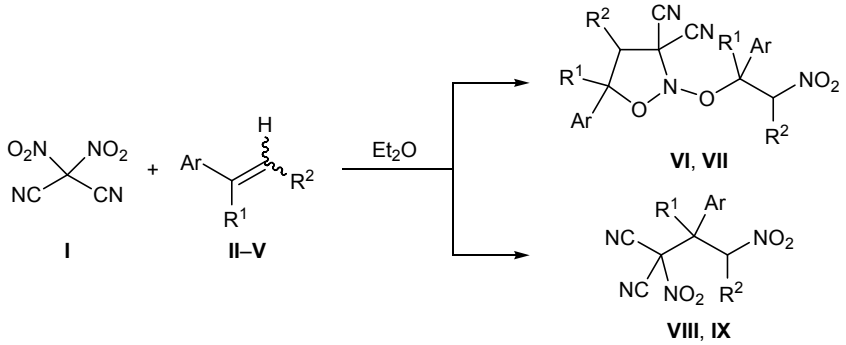
The reaction of 2,2-dinitrobutanenitrile with phenylethenes gives a mixture of O- (2-nitro-1-phenylethanone) and C-alkylation products (ethyl 2-cyano-2,4-dinitro-3-phenylbutanoate) which can be separated [1]. However, there are no published data on reactions of 2,2-dinitromalononitrile (which is an analog of 2,2-dinitrobutanenitrile) with arylethenes. We examined reactions of 2,2-dinitromalononitrile (**I**) with such arylethenes as styrene (**II**), 1-phenylpropene (**III**), 2-phenylpropene (**IV**), and *p*-methoxystyrene (**V**) and found that this process is accompanied by elimination of one nitro group from compound **I**, leading to the formation of 5-phenyltetrahydroisoxazole-3,3-dicarbonitriles **VI** and **VII** from alkenes **II** and **III** or 2-nitromalononitriles **VIII** and **IX** from alkenes **IV** and **V** (Scheme 1).

The product structure led us to presume that the reaction of dinitromalononitrile (**I**) with arylalkenes **II**–**V** follows the known scheme [2, 3] involving formation of a charge-transfer complex which is then converted into ion pair β-nitrocarbocation–*aci*-nitromalononitrile anion. Depending on the degree of charge delocalization in the cation, the anion adds thereto either at the oxygen atom with formation of nitrone ester and subsequent 1,3-dipolar cycloaddition to the second alkene molecule (compounds **VI** and **VII**) or at the carbon atom (compounds **VIII** and **IX**).

The reaction of 2,2-dinitromalononitrile (**I**) with 1,1-diarylethenes **X** and **XI** is likely to involve intermediate formation of nitrocarbocation **A** which is incapable of reacting with *aci*-nitromalononitrile anion because of considerable steric shielding by two benzene rings; therefore, intermediate **A** is stabilized via elimination of proton with formation of conjugated 1,1-diaryl-2-nitroethenes **XII** and **XIII**; the other reaction product is nitromalononitrile (**XIV**) (Scheme 2).

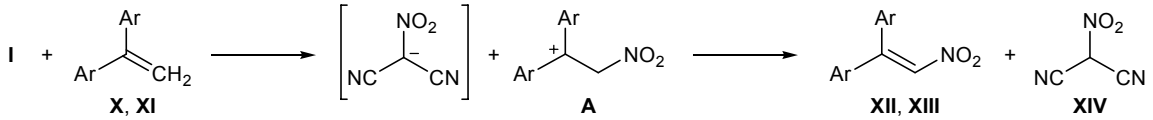
Scheme 1.



I **II–V** **VI**, **VII** **VIII**, **IX**

II, **VI**, Ar = Ph, $R^1 = R^2 = H$; **III**, **VII**, Ar = Ph, $R^1 = H$, $R^2 = Me$; **IV**, **VIII**, Ar = Ph, $R^1 = Me$, $R^2 = H$; **V**, **IX**, Ar = 4-$MeOC_6H_4$, $R^1 = R^2 = H$.

Scheme 2.



X, **XII**, Ar = Ph; **XI**, **XIII**, R = 4-$MeOC_6H_4$.

The structure of compounds **VI**–**IX** was confirmed by their IR and ^{1}H NMR spectra and elemental analyses. Compounds **XII**–**XIV** were identified by comparing their melting points with those of authentic samples. The IR spectra of **VI** and **VII** contained absorption bands at 1550 and 1380 cm^{-1}, which are typical of stretching vibrations of nitro group, and a band at 1070–1030 cm^{-1} due to vibrations of the O–N–O fragment in the heteroring [4]. Compounds **VIII** and **IX** displayed in the IR spectra two couples of absorption bands at 1550/1380 and 1580/1310 cm^{-1} due to the presence of two nonequivalent nitro groups. The ^{1}H NMR spectra of **VI**–**IX** were consistent with the assumed structures and were similar to those of structurally related model compounds of the isoxazole [5] and nitroalkane series [6]. In the ^{1}H NMR spectra of **VI** and **VII**, apart from multiplets belonging to aromatic protons and signals from protons in the nitroalkyl fragment, we observed signals in the region δ 2.81–5.46 ppm from protons in the tetrahydroisoxazole ring.

Thus, unlike 2,2-dinitrobutanenitrile, reactions of 2,2-dinitromalononitrile with arylalkenes are characterized by higher selectivity, and they lead to the formation of previously unknown 5-phenyltetrahydroisoxazole-3,3-dicarbonitriles or 2-(1-aryl-2-nitroethyl)-2-nitromalononitriles which attract interest from both theoretical and practical viewpoints.

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrometer from solutions in chloroform with a concentration of 40 mg/ml (cell path length 0.1 mm). The ^{1}H NMR spectra were obtained on a Bruker DRX 500 SF instrument at 500 MHz using DMSO-d_6 as solvent and hexamethyldisiloxane as internal reference. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates using acetone–hexane (2:3) as eluent; development with iodine vapor.

2,2-Dinitromalononitrile (**I**) was synthesized according to the procedure described in [7]. Arylalkenes were prepared from the corresponding carbonyl compounds and alkylmagnesium halides with isolation of intermediate alcohols and their subsequent dehydration according to [8]; the physical constants of arylalkenes were consistent with published data.

Reaction of 2,2-dinitromalononitrile (I) with arylalkenes (*general procedure*). A solution of 10 mmol of alkene **II** or **III** or 5 mmol of alkene **IV**, **V**, **X**, or **XI** in diethyl ether was added to a solution of 5 mmol of 2,2-dinitromalononitrile (**I**) in 10 ml of anhydrous diethyl ether on cooling to 0±5°C. The mixture was kept for 10 days at 25°C, the solvent was evaporated, and the residue was purified by chromatography on a 10 × 500-mm column charged with activated silica gel (Silicagel 100–400 μm) using chloroform (compounds **VI**, **VII**), benzene (**VIII**, **IX**, **XII**, **XIII**), or diethyl ether (**XIV**) as eluent.

2-(2-Nitro-1-phenylethoxy)-5-phenyltetrahydro-1,2-oxazole-3,3-dicarbonitrile (VI). Yield 0.464 g (25%), mp 115°C. IR spectrum, ν, cm^{-1}: 2245 (CN); 1550, 1380 (NO_2); 1070–1030 (ONO). ^{1}H NMR spectrum, δ, ppm: 3.14 d (2H, CH_2), 4.28 d (2H, CH_2), 5.46 t (1H, CH), 5.82 t (1H, CH), 7.53–7.62 m (10H, C_6H_5). Found, %: C 62.46; H 4.22; N 15.18. $C_{19}H_{16}N_4O_4$. Calculated, %: C 62.64; H 4.40; N 15.38.

2-(2-Nitro-1-phenylpropoxy)-4-methyl-5-phenyltetrahydro-1,2-oxazole-3,3-dicarbonitrile (VII). Yield 0.519 g (27%), mp 127°C. IR spectrum, ν, cm^{-1}: 2245 (CN); 1550, 1380 (NO_2); 1070–1030 (ONO). ^{1}H NMR spectrum, δ, ppm: 1.29 d (3H, CH_3), 1.34 d (3H, CH_3), 2.81 m (1H, CH), 4.25 m (1H, CH), 5.44 d (1H, CH), 5.80 d (1H, CH), 7.56–7.65 m (10H, C_6H_5). Found, %: C 64.11; H 4.96; N 14.07. $C_{21}H_{20}N_4O_4$. Calculated, %: C 64.29; H 5.10; N 14.29.

2-Nitro-2-(1-nitro-2-phenylpropan-2-yl)malononitrile (VIII). Yield 0.698 g (51%), mp 49°C. IR spectrum, ν, cm^{-1}: 2250 (CN); 1580, 1310 (NO_2); 1550, 1380 (NO_2). ^{1}H NMR spectrum, δ, ppm: 1.70 s (3H, CH_3), 4.23 s (2H, CH_2), 7.59 m (5H, C_6H_5). Found, %: C 52.38; H 3.47; N 20.24. $C_{12}H_{10}N_4O_4$. Calculated, %: C 52.55; H 3.65; N 20.44.

2-[1-(4-Methoxyphenyl)-2-nitroethyl]-2-nitromalononitrile (IX). Yield 0.914 g (63%), mp 54°C. IR spectrum, ν, cm^{-1}: 2250 (CN); 1580, 1310 (NO_2);

1550, 1380 (NO_2). ^{1}H NMR spectrum, δ, ppm: 3.80 s (3H, CH_3O), 4.25 d (2H, CH_2), 5.12 t (1H, CH), 6.90–7.84 m (4H, C_6H_4). Found, %: C 49.47; H 3.28; N 19.16. $C_{12}H_{10}N_4O_5$. Calculated, %: C 49.66; H 3.45; N 19.31.

1,1-Diphenyl-2-nitroethene (XII). Yield 0.508 g (45%), mp 88°C [9].

1,1-Bis(4-methoxyphenyl)-2-nitroethene (XIII). Yield 0.686 g (48%), mp 114°C [10].

Nitromalononitrile (XIV). Yield 0.044 g (8%), mp 112°C [11].

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