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SHORT COMMUNICATIONS

Reaction of Ethyl 3-(4-Methoxyphenyl)-1,2,4-oxadiazol-5-yl-(nitro)chloroacetate with Diazo Compounds

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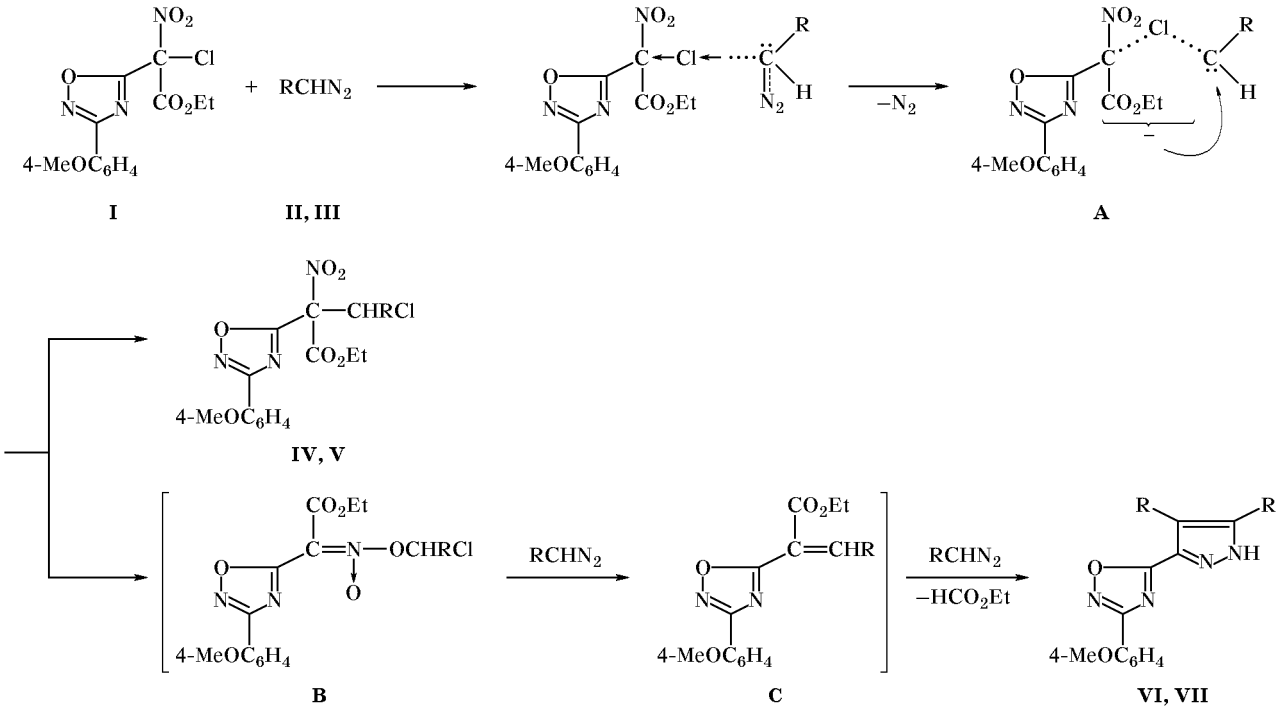
Reactions of substituted halonitromethanes with aliphatic diazo compounds give rise to wide spectrum of products, depending on the nature of functional group in the nitromethane and substituent in the diazo component. Among these, dihydroisoxazole *N*-oxides, halotrinitroalkanes, and dinitroalkenes [1, 2]. With the goal of studying the effect of halonitromethane nature on the direction of its reaction with diazo compounds, we examined reactions of ethyl 3-(4-methoxyphenyl)-1,2,4-oxadiazol-5-yl(nitro)chloroacetate (**I**) with diazomethane (**II**) and diazoethane (**III**). We found that, unlike those studied previously, these reactions lead to formation of separable mixtures of C-alkylation products and secondary O-alkylation products, namely oxadiazolylacetic acid esters **IV** and **V** and oxadiazolylpyrazoles **VI** and **VII**, respectively. The structure of the products suggests the following reaction scheme (Scheme 1). Attack by diazoalkane **II** or **III** at the halogen atom in **I** yields reactive species **A** in which the emerging carbene center withdraws electron density from the halogen and carbon atoms of ambident 3-(4-methoxyphenyl)-1,2,4-oxadiazol-5-yl(nitro)-

Scheme 1.



II, IV, **VI**, R = H; **III**, **V**, **VII**, R = Me.

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acetate anion. New C–C bonds thus appear, and products **IV** and **V** are formed. The formation of pyrazoles **VI** and **VII** may be explained by decomposition of *aci*-nitro esters **B** (according to the scheme proposed in [1]) to substituted ethenes **C** which then react with excess diazoalkane. Intermediate dihydropyrazoles are stabilized via elimination of ethyl formate rather than nitrogen, yielding final products **VI** and **VII** (Scheme 1).

The product ratio is likely to be determined by the greater ability of the ambident anion to react with diazoalkanes at the carbon atom.

A solution of 18 mmol of diazoalkane **II** [3] or **III** [4] in 150 ml od dry diethyl ether was added dropwise with stirring at 0°C to a solution of 6 mmol of compound **I** [5] in 10 ml of the same solvent. The mixture was kept for 2 h at 25°C and evaporated, and the residue was subjected to chromatographic separation in a 250 × 10-mm column charged with activated silica gel (100–400 μm). Compounds **IV** and **V** were eluted with CCl_4. The fraction containing diethyl ether was subjected to repeated chromatography. Compounds **VI** and **VII** were eluted with chloroform.

Ethyl 3-(4-methoxyphenyl)-1,2,4-oxadiazol-5-yl-(nitro)(chloromethyl)acetate (IV). Yield 55%, mp 43–44°C [6].

Ethyl 3-(4-methoxyphenyl)-1,2,4-oxadiazol-5-yl-(nitro)(1-chloroethyl)acetate (V). Yield 52%, mp 67–68°C [6].

3-(4-Methoxyphenyl)-5-(3-pyrazolyl)-1,2,4-oxadiazole (VI). Yield 15%, mp 163–165°C. IR spectrum, ν, cm^{-1}: 3220–3180 (NH). ^1H NMR spectrum, δ, ppm: 8.50 br.s (NH), 7.83–6.90 m (C_6H_4), 7.60 t (CH), 6.30 d (CH), 3.82 s (CH_3O). UV spectrum, λ_{max}, nm (log ε): 252 (3.90), 275 (3.64). Found, %: C 59.43; H 3.98; N 23.06. $C_{12}H_{10}N_4O_2$. Calculated, %: C 59.50; H 4.13; N 23.14.

5-(4,5-Dimethyl-3-pyrazolyl)-3-(4-methoxyphenyl)-1,2,4-oxadiazole (VII). Yield 10%, mp 236–238°C. IR spectrum, ν, cm^{-1}: 3220–3180 (NH). ^1H NMR spectrum, δ, ppm: 8.46 br.s (NH), 7.81–6.90 m (C_6H_4), 3.80 s (CH_3O), 2.18 s (CH_3), 2.05 s (CH_3). UV spectrum, λ_{max}, nm (log ε): 252 (3.88), 275 (3.62). Found, %: C 62.09; H 5.11; N 20.63. $C_{14}H_{14}N_4O_2$. Calculated, %: C 62.22; H 5.19; N 20.74.

The IR spectra were recorded on an IKS-29 instrument from solutions in chloroform. The ^1H NMR spectra were obtained on a Tesla BS-487C spectrometer (80 MHz) in acetone-d_6 using HMDS as internal reference. The electron spectra were measured on an SF-8 spectrophotometer from solutions in carbon tetrachloride.

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