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BEHAVIOR OF 3,5-BIS(4-METHOXYPHENYL)-1,2-OXATHIOLAN-2-OXIDE UNDER NITROSATION CONDITIONS

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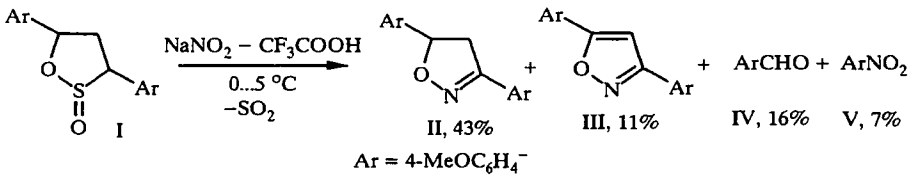
1,2-Oxathiolan-2-oxides (γ-sultins) undergo sultin ring opening under action of nucleophilic reagents [1-4].

We have shown that the electrophilic attack of γ-sultin I in trifluoroacetic acid by the nitrosonium cation leads to its recyclization with formation of the corresponding isoxazoline II and isoxazole III. For example, 3,5-bis(4-methoxyphenyl)-1,2-oxathiolan-2-oxide (I) reacts readily with sodium nitrite in trifluoroacetic acid, producing mixture of 3,5-bis(4-methoxyphenyl)-4,5-dihydroisoxazole (II), 3,5-bis(4-methoxyphenyl)isoxazole (III), anisaldehyde (IV), nitroanisole (V), and a certain amount of unidentified products from the destruction of the heterocyclic compounds.



The reaction was performed by addition of solution of 0.5 g (1.57 mmol) of sultin I in 30 ml of chloroform to mixture of 0.33 g (4.8 mmol) of sodium nitrite in 8 ml of trifluoroacetic acid at 0°C, the mixture being stirred until the release of sulfur dioxide ceased. The mixture was poured into water and extracted with chloroform, washed with 10% solution of sodium bicarbonate, and then with water and dried with calcium chloride. The NMR spectra were recorded on a Varian VXR-400 in $CDCl_3$. The composition of the reaction mixture was determined from the NMR spectra. The compounds were isolated in the pure state by column chromatography (Silpearl, eluent petroleum ether—ether, 4:1).

3,5-Bis(4-methoxyphenyl)-4,5-dihydroisoxazole (II); mp 138°C (from alcohol); according to [5], mp 138°C, but according to [6], mp 141-142°C. ^{1}H NMR spectrum: 3,28 (1H, dd, 4-H, ^2J = 16,6, ^3J = 8,6 Hz); 3,68 (1H, dd, 4'-H ^2J = 16,6, ^3J = 10,7 Hz); 3,79 (3H, s, CH_3O); 5,64 (1H, dd, 5-H, ^2J = 16,6, ^3J = 8,6 Hz); 6,90, 6,92, 7,32, 7,633 ppm (8H, 4 d, H_{arom}). The ^{1}H NMR spectrum is analogous to that reported in [6]. ^{13}C NMR spectrum ($CDCl_3$): 43,04 ($C_{(4)}$); 55,18, 55,23 (CH_3O); 82,11 ($C_{(5)}$); 114,05, 127,27, 128,13 (HC_{arom}); 122,06, 132,83 (C_{arom}); 155,71 ($C_{(3)}$); 159,47, 160,96 ppm (C_{arom}).

3,5-Bis(4-methoxyphenyl)isoxazole (III); mp 163°C (from alcohol), according to [6], mp 176-177°C, or according to [7], 163-164°C. ^{1}H NMR spectrum: 3,85 (3H, s, CH_3O); 3,86 (3H, s, CH_3O); 6,65 (1H, s, 4-H); 6,99 (4H, d, H_{arom}); 7,76 (2H, d, H_{arom}); 7,79 ppm (2H, d, H_{arom}). The spectrum is analogous to that reported in [6].

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