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REACTION OF POTASSIUM SALTS OF 2-AMINO-4-METHOXY-6-DINITRO-METHYL-1,3,5-TRIAZINES WITH N_2O_4

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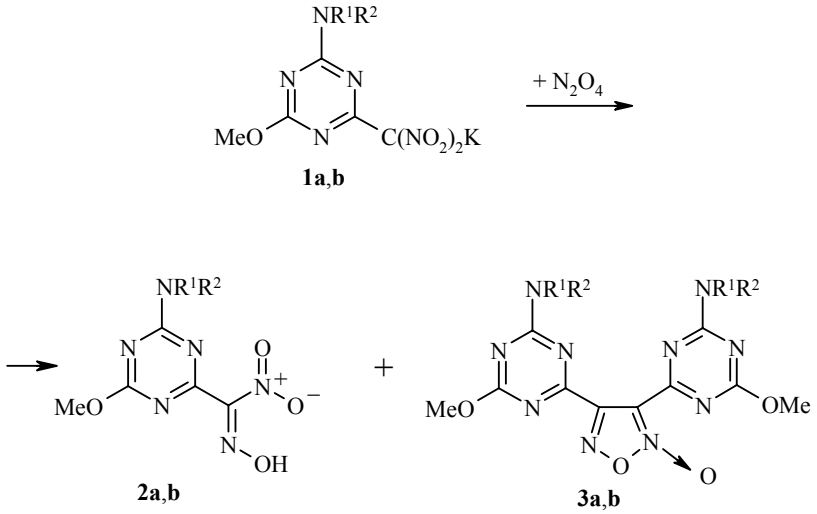
During the reaction of 2,4-dialkoxy(aryloxy)-6-dinitromethyl-1,3,5-triazine potassium salts with nitrogen tetroxide high yields of 3,4-bis[2',4'-dialkoxy(aryloxy)-1,3,5-triazin-6'-yl]-1,2,5-oxadiazole N-oxides are formed [1]. We found that the reaction of the potassium salts of 2-dimethylamino(morpholino)-4-methoxy-6-dinitromethyl-1,3,5-triazines **1a**,**b** with nitrogen tetroxide in organic solvents takes place in two directions, leading to the formation of 2-dimethylamino(morpholino)-4-methoxy-1,3,5-triazin-6-ylnitroformaldoximes (nitrolic acids) **2a**,**b** and 3,4-bis[2'-dimethylamino(morpholino)-4'-methoxy-1,3,5-triazin-6'-yl]-1,2,5-oxadiazole N-oxides **3a**,**b**.



1-3 **a** $R^1 = R^2 = Me$, **b** $R^1R^2 = (CH_2CH_2)_2O$

The introduction of the amine substituent into the molecule of the initial potassium salt probably leads to the result that the intermediate, formed as a result of nitrosation, becomes sensitive to water present as impurity in the solvent and reacts with it to form the nitrolic acid **2a**,**b**. To judge from the ratio of the yields of **2a**,**b** and **3a**,**b** this reaction path predominates over the formation of furoxans.

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The IR spectra were recorded in tablets with potassium bromide on an Avatar spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz) in acetone-d_6 (compounds **2a**,**b** and **3a**) and deuterochloroform (compound **3b**) with TMS as internal standard.

2-Dimethylamino(morpholino)-4-methoxy-1,3,5-triazin-6-ylnitroformaldoximes 2a,b and 3,4-Bis-[2'-dimethylamino(morpholino)-4'-methoxy-1,3,5-triazin-6'-yl]-1,2,5-oxadiazole N-Oxides 3a,b. To a suspension of the potassium salt **1a**,**b** (5 mmol) in organic solvent (dichloroethane, dichloromethane, chloroform, diethyl ether) (10 ml) we added N_2O_4 (0.37 ml, 6 mmol) in the same solvent (5 ml). The reaction mass was kept at 20-25°C for 30 min and cooled, and the precipitated **2a**,**b** mixed with potassium nitrate was filtered off. (To remove the potassium nitrate the product was treated with water, and the undissolved **2a**,**b** was filtered off.) The filtrate was kept at 20-25°C for 24 h. After holding the organic solvent was distilled off under vacuum. Compounds **3a**,**b** were isolated from the residue by column chromatography on silica gel with dichloroethane as eluent.

Compound 2a. Yield 0.68 g (56%); mp 109-111°C (decomp.). IR spectrum, ν, cm^{-1}: 3145, 3049, 3004, 2933, 2879, 2811, 1608, 1587, 1552, 1511, 1417, 1382, 1268, 1224, 1149, 1074, 1051, 1002, 902, 864, 806, 727, 646. ^{1}H NMR spectrum, δ, ppm: 3.16 and 3.22 (6H, two s, NCH_3, Δν = 18 Hz); 3.96 (3H, s, OCH_3); 12.48 (1H, br. s, NH). Found %: C 34.77; H 4.20; N 34.64. $C_7H_{10}N_6O_4$. Calculated %: C 34.71; H 4.16; N 34.70.

Compound 2b. Yield 0.95 g (67%); mp 110-111°C (decomp.). IR spectrum, ν, cm^{-1}: 3216, 3012, 2968, 2912, 2860, 2782, 1600, 1550, 1517, 1473, 1442, 1380, 1305, 1286, 1243, 1112, 1068, 1029, 999, 896, 840, 813, 800, 725, 642, 543. ^{1}H NMR spectrum, δ, ppm: 3.75, 3.82, and 3.92 (8H, m, OCH_2CH_2N); 3.98 (3H, s, OCH_3); 12.72 (1H, br. s, NH). Found %: C 38.10; H 4.29; N 29.51. $C_9H_{12}N_6O_5$. Calculated %: C 38.03; H 4.26; N 29.57.

Compound 3a. Yield 0.31 g (32%); mp 140-142°C. IR spectrum, ν, cm^{-1}: 3031, 2964, 2921, 2856, 1627, 1569, 1548, 1481, 1367, 1311, 1230, 1116, 1018, 1004, 931, 819, 779. ^{1}H NMR spectrum, δ, ppm: 3.08 and 3.16 (6H, two s, NCH_3, Δν = 24 Hz); 3.92 (3H, s, OCH_3). Found %: C 43.12; H 4.59; N 35.86. $C_{14}H_{18}N_{10}O_4$. Calculated %: C 43.08; H 4.65; N 35.88.

Compound 3b. Yield 0.29 g (24%); mp 180-182°C. IR spectrum, ν, cm^{-1}: 2968, 2925, 2869, 1631, 1577, 1565, 1529, 1486, 1467, 1444, 1371, 1301, 1284, 1230, 1114, 1068, 1025, 999, 989, 852, 813, 756, 636, 540. ^{1}H NMR spectrum, δ, ppm: 3.65, 3.72, and 3.96 (8H, m, OCH_2CH_2N); 3.88 (3H, s, OCH3). Found %: C 45.52; H 4.72; N 29.47. $C_{18}H_{22}N_{10}O_6$. Calculated %: C 45.57; H 4.67; N 29.52.

REFERENCES

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