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LETTERS TO THE EDITOR

SYNTHESIS OF 3,4-BIS(1,3,5-TRIAZINYL)-1,2,5-OXADIAZOLE N-OXIDES

V. V. Bakharev, A. A. Gidaspov, and E. V. Peresedova

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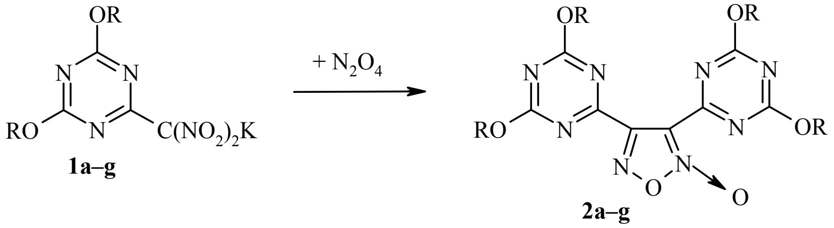
We have not found any data in the literature on reaction of salts of dinitromethyl derivatives of 1,3,5-triazine with nitrogen tetroxide. We have established that the reaction of the potassium salts of 2,4-dialkoxy(aryloxy)-6-dinitromethyl-1,3,5-triazines **1a-g** with nitrogen oxides in a medium of organic solvents is accompanied by formation of previously undescribed 3,4-bis(2',4'-dialkoxy(aryloxy)-1,3,5-triazin-6'-yl)-1,2,5-oxadiazole N-oxides **2b-g** (for **2a**, see [1]) in 60-85% yield, according to the following scheme.



1, **2** **a** R = Me, **b** R = Pr, **c** R = *i*-Pr, **d** R = Bu, **e** R = *cyclo*-C_6H_{11},
f R = *p*-C_6H_4Br, **g** R = *p*-C_6H_4COOMe

The reaction, starting with rapid nitrosation of the dinitromethyl anion and formation of the nitroso-dinitro derivative (as indicated by the blue–green color typical of monomers of nitroso compounds, which gradually disappears as the reaction proceeds) and potassium nitrate (which precipitates), then probably occurs with formation and subsequent dimerization of nitrile oxide, similarly to [2].

The IR spectra were recorded on an Avatar spectrophotometer in KBr disks (except for **2b** and **2d**, which were run in a liquid film); the ^{1}H NMR spectra were taken on a Bruker AM-300 spectrometer(300 MHz) in acetone-d_6 (compound **2a**) and $CDCl_3$ (compounds **2b-g**), internal standard TMS.

3,4-Bis(2',4'-dialkoxy(aryloxy)-1,3,5-triazin-6'-yl)-1,2,5-oxadiazoles 2a-g. Nitrogen dioxide (N_2O_4) (0.37 ml, 0.006 mol) in an organic solvent (dichloroethane, dichloromethane, chloroform, diethyl ether) (5 ml) was added to a suspension of the potassium salt of 2,4-dialkoxy(aryloxy)-6-dinitromethyl-1,3,5-triazine **1a-g** (0.005 mol) in the same organic solvent (10 ml). The reaction mixture was held at a temperature of 20-25°C for 48 h (for dialkoxy derivatives **1a-e**) and 96 h (for diaryloxy derivatives **1f-g**). After the holding time was ended,

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Samara State Technical University, Samara 443100, Russia; e-mail: knil@sstu.smr.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 635-636 April, 2006. Original article submitted March 18, 2006.

the potassium nitrate precipitate was filtered out and the organic solvent was distilled off from the filtrate under reduced pressure. From the residue we isolated the target 3,4-bis(2',4'-dialkoxy(aryloxy)-1,3,5-triazin-6'-yl)-1,2,5-oxadiazole N-oxide **2a-g** by column chromatography on silica gel, with dichloroethane as the eluent.

Compound 2a. Yield 0.78 g (85%); mp 148-150°C. IR spectrum, ν, cm^{-1}: 3022, 2960, 2919, 2885, 2852, 1629, 1591, 1548, 1481, 1367, 1311, 1230, 1201, 1105, 1018, 1004, 931, 819, 779, 759. ^1H NMR spectrum, δ, ppm: 3.84 (12H, s, OCH_3). Found, %: C 39.62; H 3.41; N 30.44. $C_{12}H_{12}N_8O_6$. Calculated, %: C 39.57; H 3.32; N 30.76.

Compound 2b. Yield 0.93 g (78%), light yellow oil. IR spectrum, ν, cm^{-1}: 2969, 2939, 2879, 1629, 1554, 1484, 1454, 1419, 1355, 1330, 1301, 1218, 1122, 1056, 987, 931, 827, 790, 755. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.00 (16H, m, CH_3); 1.78 (8H, m, CH_2); 4.25 and 4.34 (8H, two t, *J* = 7.8, OCH_2). Found, %: C 50.35; H 6.00; N 23.50. $C_{20}H_{28}N_8O_6$. Calculated, %: C 50.41; H 5.92; N 23.52.

Compound 2c. Yield 0.97 g (81%); mp 72-74°C. IR spectrum, ν, cm^{-1}: 2983, 2935, 2875, 1625, 1560, 1544, 1473, 1459, 1400, 1388, 1319, 1218, 1180, 1145, 1099, 985, 962, 948, 906, 825, 784, 755. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.48 (24H, t, *J* = 7.5, CH_3); 5.18 and 5.26 (4H, two m, OCH). Found, %: C 50.48; H 5.79; N 23.61. $C_{20}H_{28}N_8O_6$. Calculated, %: C 50.41; H 5.92; N 23.52.

Compound 2d. Yield 1.01 g (76%), light yellow oil. IR spectrum, ν, cm^{-1}: 2960, 2935, 2873, 1629, 1556, 1484, 1457, 1417, 1338, 1216, 1108, 1064, 1018, 985, 935, 825, 781. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.94 (12H, t, *J* = 8.2, CH_3); 1.45 (8H, m, CH_2); 1.76 (8H, m, CH_2); 4.25 and 4.37 (8H, two t, *J* = 7.6, OCH_2). Found, %: C 54.16; H 6.75; N 20.97. $C_{24}H_{36}N_8O_6$. Calculated, %: C 54.12; H 6.81; N 21.04.

Compound 2e. Yield 1.18 g (74%); mp 159-161°C. IR spectrum, ν, cm^{-1}: 2941, 2856, 1637, 1560, 1533, 1465, 1415, 1357, 1338, 1313, 1261, 1214, 1122, 1097, 1035, 1008, 985, 931, 894, 825, 786. ^1H NMR spectrum, δ, ppm: 1.35, 1.60, 1.82, and 1.94 (40H, four m, CH_2); 4.96 (4H, m, OCH). Found, %: C 60.43; H 7.05; N 17.54. $C_{32}H_{44}N_8O_6$. Calculated, %: C 60.36; H 6.97; N 17.60.

Compound 2f. Yield 1.5 g (65%); mp 200-201°C. IR spectrum, ν, cm^{-1}: 3091, 3066, 1625, 1587, 1550, 1483, 1436, 1400, 1361, 1317, 1226, 1197, 1164, 1097, 1066, 1012, 985, 931, 906, 860, 819, 775, 752. ^1H NMR spectrum, δ, ppm (*J*, Hz): 7.07 and 7.53 (16H, two d, *J* = 8.8, *p*-C_6H_4). Found, %: C 41.38; H 1.69; N 12.14. $C_{32}H_{16}Br_4N_8O_6$. Calculated, %: C 41.41; H 1.74; N 12.07.

Compound 2g. Yield 1.31 g (62%); mp 104-106°C. IR spectrum, ν, cm^{-1}: 3112, 3070, 2998, 2952, 1724, 1629, 1554, 1502, 1436, 1359, 1280, 1238, 1207, 1193, 1164, 1112, 1016, 929, 864, 821, 773, 700. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.83 (12H, s, $COOCH_3$); 7.34 and 8.00 (16H, two d, *J* = 9.6, *p*-C_6H_4). Found, %: C 56.82; H 3.39; N 13.25. $C_{40}H_{28}N_8O_{14}$. Calculated, %: C 56.88; H 3.34; N 13.27.

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