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Synthesis of 1,3,5-trisubstituted 1,2,4-triazolio-4-nitroimides

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A method for the synthesis of 1,3,5-trisubstituted 1,2,4-triazolio-4-nitroimides was developed. The method is based on the alkylation of the corresponding salts of 3,5-disubstituted 4-nitramino-1,2,4-triazoles.

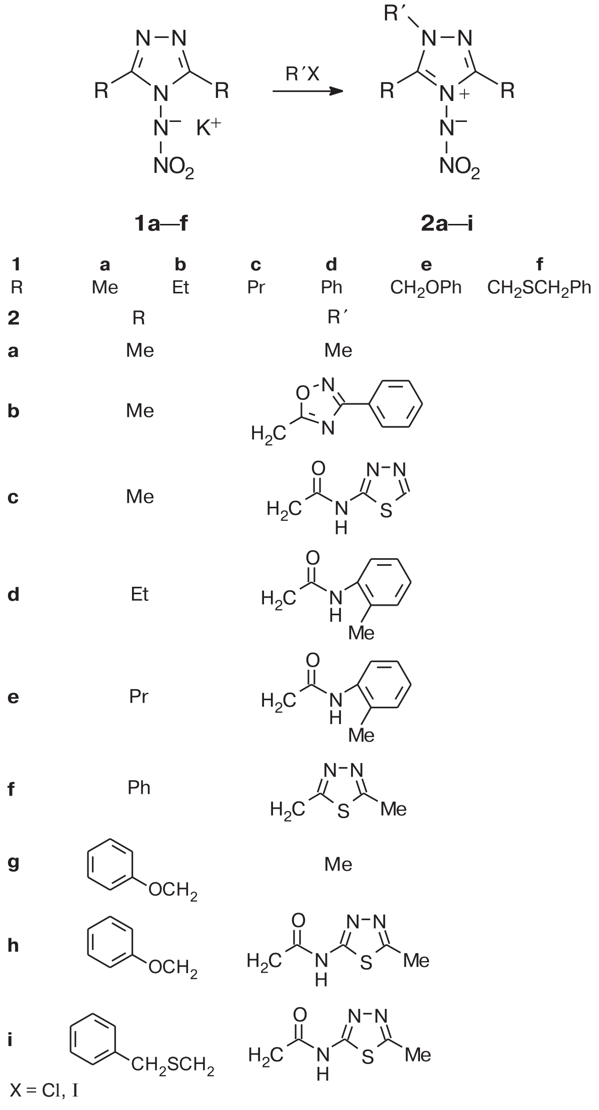
Key words: potassium salts of 3,5-disubstituted 4-nitramino-1,2,4-triazoles, 1,3,5-trisubstituted 1,2,4-triazolio-4-nitroimides, alkylating agents.

In continuation of the systematic investigations aimed at developing techniques for the introduction of an *N*-nitroimido group into *N*-heterocycles, we proposed a method for the synthesis of 1,3,5-trisubstituted 1,2,4-triazolio-4-nitroimides. The method is based on the alkylation of the previously[1] synthesized salts of 3,5-disubstituted 4-nitramino-1,2,4-triazoles, during which the *N*-nitramino group is transformed into a nitroimido group. Earlier,[2] such a transformation has been described for the alkylation of a Na salt of 4-nitramino-1,2,4-triazole with methyl tosylate in sulfolane and with benzyl chloride in ethanol. The reaction products were 1-methyl- and 1-benzyl-1,2,4-triazolio-4-nitroimides, respectively.

Insofar as the anions of the above nitramines have three centers for an electrophilic attack, are rather weak nucleophiles, and contain bulky substituents in positions 3 and 5, one could expect that the reaction would proceed ambiguously. The alkylation can occur both at the N and O atoms of the nitroimido group to give nitramines or isonitramines, respectively, and at the N atom of the triazole ring, yielding triazolionitroimides.

Salts of 3,5-disubstituted 4-nitraminotriazoles were alkylated in dimethylformamide at 60—70 °C for 8—12 h (Scheme 1).

Scheme 1



The alkylation products were stable high-melting compounds **2a—i**. Their structures were determined from IR and ^{1}H NMR data (Table 1). The IR spectra of the compounds obtained show absorption bands at 1260—1300 and 1380—1415 cm^{-1} characteristic of the aromatic *N*-nitroimido group[3] and no ν_{as} bands for the nitramino group at 1550—1620 cm^{-1}.[4] The ^{1}H NMR spectra contain only one singlet for the methylene and methyl protons in the alkyl radicals introduced, which indicates the formation of a single isomer. The protons of substituents in positions 3 and 5 become nonequivalent, and their signals are shifted downfield compared to the corresponding signals for the initial salts, which suggests

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Table 1. IR and ^{1}H NMR data for the compounds obtained

Compound	IR (KBr), ν/cm^{-1}		^{1}H NMR (δ, J/Hz)
	Nitroimido group	Other groups	
2a	1404, 1290	—	2.26, 2.46 (both s, 6 H, 2 Me); 3.92 (s, 3 H, NMe)
2b	1416, 1288	—	2.34, 2.66 (both s, 6 H, 2 Me); 6.20 (s, 2 H, CH_2); 7.57—8.00 (m, 5 H, Ph)
2c	1415, 1315	1708 (C=O); 3265 (N—H)	2.31, 2.54 (both s, 6 H, 2 Me); 5.56 (s, 2 H, CH_2); 9.25 (s, 1 H); 13.40 (s, 1 H, NH)
2d	1412, 1272	1704 (C=O); 3248 (N—H)	1.16—1.25 (m, 6 H, 2 $CH_2C\underline{H}_3$); 2.26 (s, 3 H, Me); 2.65, 2.94 (both q, 4 H, 2 $C\underline{H}_2$Me, J = 7.4); 5.41 (s, 2 H, CH_2); 7.13—7.45 (m, 5 H, Ph); 9.87 (s, 1 H, NH)
2e	1408, 1264	1704 (C=O); 3272 (N—H)	0.93 (t, 6 H, $CH_2C\underline{H}_3$, J = 7.7); 1.58—1.72 (m, 4 H, 2 $C\underline{H}_2CH_3$); 2.25 (s, 3 H, Me); 2.61, 2.90 (both t, 4 H, 2 $C\underline{H}_2CH_2$, J = 7.7); 5.40 (s, 2 H, CH_2); 7.13—7.43 (m, 5 H, Ph); 9.87 (s, 1 H, NH)
2f	1416, 1272	—	2.07 (s, 3 H, Me); 5.94 (s, 2 H, CH_2); 7.65—7.92 (m, 10 H, 2 Ph)
2g	1404, 1290	—	4.16 (s, 3 H, Me); 5.49, 5.64 (both s, 4 H, 2 CH_2); 7.12—7.39 (m, 10 H, 2 Ph)
2h	1416, 1288	1702 (C=O); 3242 (N—H)	2.66 (s, 3 H, Me); 5.53, 5.70 (both s, 4 H, 2 CH_2); 5.58 (s, 2 H, NCH_2); 7.62—7.95 (m, 10 H, 2 Ph); 13.05 (s, 1 H, NH)
2i	1424, 1284	1708 (C=O); 3264 (N—H)	2.63 (s, 3 H, Me); 3.71, 4.13 (both s, 4 H, 2 $C\underline{H}_2SCH_2Ph$); 3.82, 3.84 (both s, 4 H, 2 $CH_2SC\underline{H}_2Ph$); 5.50 (s, 2 H, NCH_2); 7.26—7.30 (m, 10 H, 2 Ph); 12.97 (s, 1 H, NH)

Table 2. Physicochemical characteristics of the compounds obtained

Product	Yield (%)	τ/h	M.p./°C	Solvent	$\frac{\text{Found}}{\text{Calculated}}$ (%)			Molecular formula
					C	H	N	
2a	48	6	170—173	Pr^{i}OH	$\underline{35.23}$ 35.09	$\underline{5.36}$ 5.30	$\underline{40.71}$ 40.92	$C_5H_9N_5O_2$
2b	62	8	227—230 (decomp.)	Pr^{i}OH	$\underline{49.43}$ 49.52	$\underline{4.27}$ 4.16	$\underline{30.84}$ 31.10	$C_{13}H_{13}N_7O_3$
2c	64	8	250—253 (decomp.)	EtOH	$\underline{32.36}$ 32.21	$\underline{3.46}$ 3.38	$\underline{37.44}$ 37.57	$C_8H_{10}N_8O_3S$
2d	69	10	225—227 (decomp.)	EtOH	$\underline{54.35}$ 54.21	$\underline{6.30}$ 6.07	$\underline{25.12}$ 25.29	$C_{15}H_{20}N_6O_3$
2e	73	10	228—230 (decomp.)	EtOH	$\underline{56.74}$ 56.65	$\underline{6.68}$ 6.71	$\underline{23.36}$ 23.32	$C_{17}H_{24}N_6O_3$
2f	75	12	247—250 (decomp.)	EtOH	$\underline{57.36}$ 57.29	$\underline{4.17}$ 4.01	$\underline{25.82}$ 25.98	$C_{18}H_{15}N_7O_3$
2g	65	8	210—213 (decomp.)	Pr^{i}OH	$\underline{57.66}$ 57.46	$\underline{4.90}$ 4.82	$\underline{19.55}$ 19.71	$C_{17}H_{17}N_5O_4$
2h	78	12	243—245 (decomp.)	Pr^{i}OH	$\underline{50.93}$ 50.80	$\underline{4.12}$ 4.06	$\underline{22.48}$ 22.57	$C_{21}H_{20}N_8O_5S$
2i	75	10	198—200	Pr^{i}OH	$\underline{49.83}$ 49.62	$\underline{4.42}$ 4.35	$\underline{19.94}$ 20.13	$C_{23}H_{24}N_8O_3S_3$

that the triazole ring is alkylated at position 1 and acquires a positive charge.

Hence, the spectroscopic data (Table 1) enable us to assign an *N*-nitroimide structure to the compounds synthesized and consider the alkylation of salts of 3,5-disubstituted 4-nitramino-1,2,4-triazoles a convenient method for the synthesis of substituted 1,2,4-triazolionitroimides.

Experimental

Melting points were determined on a Boetius microscope stage. ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in DMSO-d$_6$. IR spectra were recorded on a UR-20 instrument (in pellets with KBr).

1,3,5-Trisubstituted 1,2,4-triazolio-4-nitroimides (2a—i) (general procedure). Methyl iodide or substituted methyl chloride (2.7 mmol) was added at 20 °C to a suspension of a potassium salt (3.0 mmol) of 3,5-disubstituted 4-nitramino-1,2,4-triazole (**1a—f**) in 5—7 mL of DMF. The reaction mixture was stirred for 1 h, heated to 60—70 °C, stirred at this temperature for 8—12 h, and concentrated *in vacuo*. The residue was diluted with water, and the precipitate that formed was filtered off and recrystallized from an appropriate solvent (Table 2). Compound **2a** was extracted from the residue with ethyl acetate, the solvent was removed, and the product was recrystallized.

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