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REACTIONS OF 3-NITRO-1,2,4-TRIAZOLE DERIVATIVES WITH ALKYLATING AGENTS. 5.* SELECTIVE SYNTHESIS OF 1,4-DIALKYL- AND 1,4,5-TRIALKYL-3-NITRO-1,2,4-TRIAZOLIUM SALTS FROM 1-ALKYL- AND 4,5-DIALKYL-3-NITRO-1,2,4-TRIAZOLES AND DIALKYL SULFATES

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Interaction of $N_{(1)}$-alkyl-substituted 3-nitro-5-R-1,2,4-triazoles with dialkyl sulphates proceeds selectively and results in the respective salts of 1,4-dialkyl-, 1,4,5-trialkyl-3-nitro-1,2,4-triazoliums. The reaction of $N_{(4)}$-alkyl-substituted 3-nitro-5-R-1,2,4-triazoles yields the mixtures of the salts of 1,4-dialkyl-, 1,4,5-trialkyl-3-nitro-1,2,4-triazoliums and 1,4-dialkyl-, 1,3,4-trialkyl-1,2,4-triazol-5-ones with predominance of quaternary salts.

Keywords: N-alkyl-3-nitro-5-R-1,2,4-triazoles, 3-nitro-5-R-1,2,4-triazoles, quaternization, selectivity.

The probability and rate of quaternization increase with increasing basicity of the heterocycle [2]. 1,2,4-Triazoles with electron-donor substituents readily form quaternary and even diquaternary salts [3]. The introduction of a nitro group at $C_{(3)}$ or $C_{(5)}$ in the heterocycle leads to a considerable change in the atomic charges and significantly decreases the effective negative charge [4]. Thus, the major problem in the quaternization of nitroazoles is the low basicity of the ring nitrogen atoms due to the effect of the electron-withdrawing nitro group in the heterocycle and the regioselectivity of this reaction related to the ambident nature of the nitrotriazole ring. We have attempted to determine the optimal conditions for this reaction. Furthermore, charged species are formed in this reaction, leading to the question of charge localization in these products.

We studied the following N-alkyl-3-nitro-5-R-1,2,4-triazoles:

$N_{(1)}$-alkyl isomers: 1-methyl- (**1**), 1-ethyl- (**2**), 1,5-dimethyl- (**3**), and 1-ethyl-5-methyl-3-nitro-1,2,4-triazoles (**4**);

$N_{(4)}$-alkyl isomers: 4-methyl- (**5**), 4-ethyl- (**6**), 4,5-dimethyl- (**7**), and 4-ethyl-5-methyl-3-nitro-1,2,4-triazoles (**8**).

In a continuation of a study of the reaction of nitrotriazole derivatives with alkylating agents [4-6], we studied the effect of the position of the N-substituent on the selectivity of quaternization of N-alkyl-3-nitro-1,2,4-triazoles.

* Communication 4, see ref. [1].

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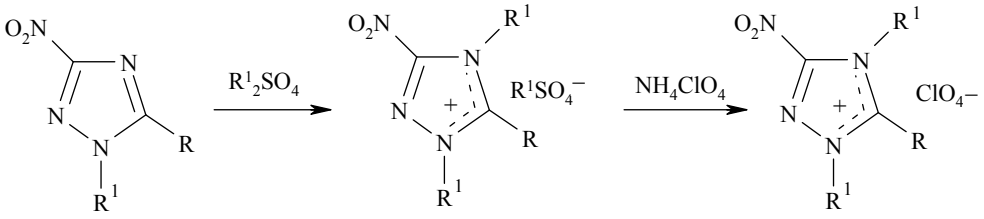
According to our previous findings [5, 6], a complex mixture is formed in the reaction of N-unsubstituted 3-nitro- (**9**) and 5-methyl-3-nitro-1,2,4-triazoles (**10**) with excess dialkyl sulfate (DAS) including products of N-monoalkylation and 1,4-dialkylation of the 3-nitro-5-R-1,2,4-triazoles and 1,4-dialkyl-5-R-1,2,4-triazol-5-ones. The major products of the alkylation of nitrotriazoles **9** and **10** by dimethyl sulfate (DMS) are N-monomethyl-3-nitro-5-R-1,2,4-triazoles (the overall yield of the isomer mixture is 53-73% and the ratio of the products, $N_{(1)}$-, $N_{(2)}$-, and $N_{(4)}$-methyl-3-nitro-5-R-1,2,4-triazoles is, on the average, 0.035:1.0:7.75). The fraction of 1,4-dimethyl- and 1,3,4-trimethyl-1,2,4-triazol-5-ones in the product mixture is 3-6%, while the yield of 1,4-dimethyl- and 1,4,5-trimethyl-3-nitro-1,2,4-triazolium salts is only 8-12% [5].

Increasing the excess of DMS to two- or three-fold reduces the yield of the products of the N-monomethylation of the nitrotriazoles to 15-24% and enhances the yield of the 1,4-dimethyl- and 1,4,5-trimethyl-3-nitro-1,2,4-triazolium methyl sulfate salts **11** and **12** or perchlorate salts **13** and **14** to 45-60%.

When diethyl sulfate (DES) was used [6], the N-monosubstituted 3-nitro-5-R-1,2,4-triazoles gave only $N_{(2)}$-isomers, namely, 1-ethyl-5-nitro- and 1-ethyl-3-methyl-5-nitro-1,2,4-triazoles, and $N_{(4)}$-isomers **6** and **8** (the overall yield of the mixture was 26.3 and 45.3% and the ratio of the $N_{(2)}$- and $N_{(4)}$-isomers was 1.0:2.7 and 1.0:2.3, respectively). The yield of the ethylated triazolones, 1,4-diethyl- (36.7%) and 1,4-diethyl-3-methyl-1,2,4-triazol-5-ones (29.4%) was much greater when compared to the methyl analogs. The yield of the 1,4-diethyl- (**15**) and 1,4-diethyl-5-methyl-3-nitro-1,2,4-triazolium ethyl sulfate salts (**16**) and the corresponding perchlorate salts (**17** and **18**) was low, as in the case of using DMS as the quaternizing agent (9.7 and 5.5%).

The use of mild alkylating agents such as methyl iodide and ethyl bromide for quaternization of the alkylnitrotriaozoles was unsuccessful. Thus, in light of the rather high activity of dialkyl sulfates in the formation of quaternary salts from N-unsubstituted nitrotriazoles [5, 6], it appeared desirable to employ these alkylating agents for the further study of the quaternization of the indicated N-alkylnitrotriazoles.

The question of selectivity arises in the study of the quaternization of N-monosubstituted alkylnitrotriazoles. The position of the alkyl substituent at the ring nitrogen atoms of $N_{(1)}$- and $N_{(4)}$-monosubstituted 5-nitro-5-R-1,2,4-triazoles has a significant effect on the reaction conditions required and the yield, structure, and properties of the products obtained (Table 1). Two nonequivalent atoms are available for attack by the electrophilic agent in derivatives of 1-alkyl- ($N_{(2)}$ and $N_{(4)}$) and 4-alkyl- 3-nitro-5-R-1,2,4-triazoles ($N_{(1)}$ and $N_{(2)}$). Nitrotriazoles with substituted nitrogen atoms, in particular, $N_{(1)}$-substituted derivatives, probably cannot be quaternized in the α-position to the substituent due to reduced nucleophilicity and steric hindrance. Thus, quaternization of 1-alkylnitrotriazoles **1-4** by dialkyl sulfates proceeds selectively at the most basic $N_{(4)}$ atom and leads to 1,4-dimethyl-, 1,4,5-trimethyl- (**11-14**) and 1,4-diethyl-, 1,4-diethyl-5-methyl-3-nitro-1,2,4-triazolium methyl sulfates and perchlorates **15-18**:

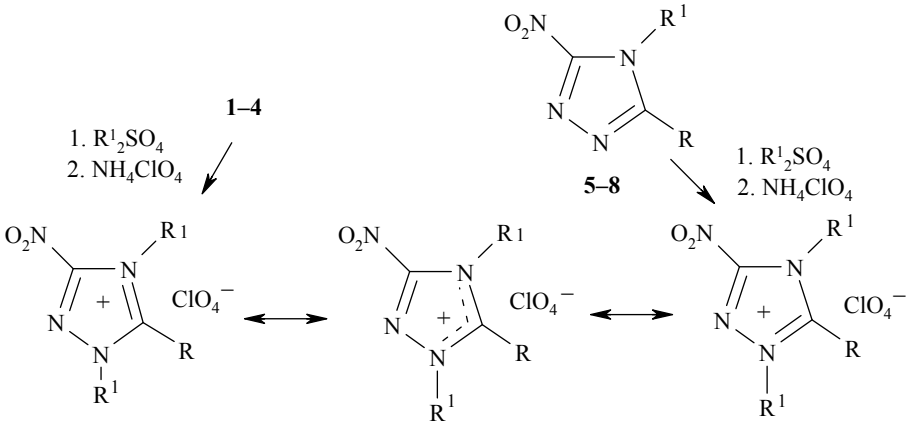


1–4 **11**,**12**,**15**,**16** **13**,**14**,**17**,**18**

1, **11**, **13** R = H, R^1 = Me; **2**, **15**, **17** R = H, R^1 = Et;
3, **12**, **14** R = R^1 = Me; **4**, **16**, **18** R = Me, R^1 = Et

The formation nitrotriazolium salts **11, 12, 15,** and **16** from 1-substituted nitrotriazoles **1-4** proceeds through the following scheme. The electrophilic reagent attacks the nitrotriazoles at the unshared electron pair of $N_{(4)}$, which is available for coordination, or at the π-bond of this atom with localization of the substituent at

$N_{(4)}$. The reaction of $N_{(1)}$-alkyl-substituted 3-nitro-1,2,4-triazoles **1-4** with DMS or DES proceeds smoothly below 100°C. 1,4-Dimethyl- (**11, 12**) and 1,4-diethyl-3-nitro-5-R-1,2,4-triazolium alkyl sulfates **15** and **16** are quite soluble in the reaction media and water and are hygroscopic. Thus, they were separated in high yield (85-90% relative to starting alkylnitrotriazole) by an exchange reaction as the corresponding perchlorate salts **13, 14, 17,** and **18**.



5 R = H, R^1 = Me; **6** R = H, R^1 = Et; **7** R = R^1 = Me; **8** R = Me, R^1 = Et

The finding that N-alkyl-3-nitro-1,2,4-triazoles substituted at $N_{(1)}$ or at $N_{(1)}$ and $C_{(5)}$ are quaternized at $N_{(4)}$ is in good accord with the results of the reaction of isomeric $N_{(1)}$-methyl-3-nitro-1,2,4-triazoles with a proton, which is the simplest electrophile [7].

As a consequence of their lower solubility and hygroscopicity, trialkylnitrotriazolium alkyl sulfate salts may be isolated as pure products by dilution of the reaction mixture with acetone. In particular, 1,4,5-trimethyl-3-nitro-1,2,4-triazolium methyl sulfate (**12**) was isolated by this procedure.

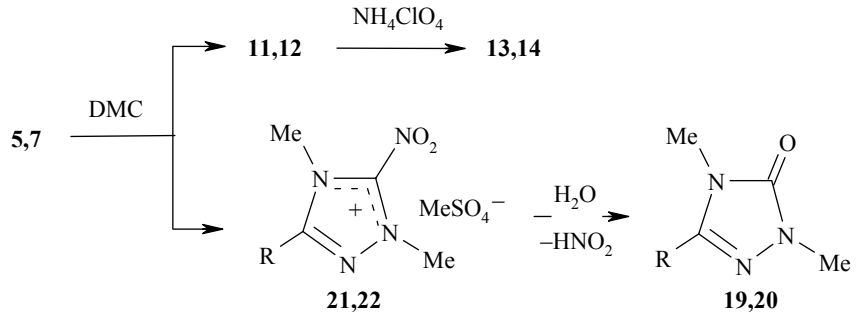
On the whole, the quaternization sites in the exhaustive alkylation of unsaturated heterocyclic compounds do not always coincide with the subsequent localization of positive charge. Delocalization of positive charge has been demonstrated for several examples of isomeric tetrazolium salts [8, 9]. We obtained similar results in the synthesis of 1,4-dialkyl-3-nitro-5-R-1,2,4-triazolium salts. For example, nitrotriazolium salts **13, 14, 17,** and **18** were obtained by convergent synthesis from $N_{(1)}$- (**1-4**) and $N_{(4)}$-isomeric nitrotriazoles (**5-8**) in varying yield (Table 1).

TABLE 1. Reaction Conditions for Quaternization of N-Alkyl-3-nitro-5-R-1,2,4-triazoles **1-8** by Dialkyl Sulfates and Data for the Resultant 1,4-Dialkyl- and 1,4,5-Trialkyl-3-nitro-1,2,4-triazolium Salts **12-14, 17,** and **18**

Starting reagents			Reaction condition		3-nitro-5-R-1,2,4-triazolium salt	mp., °C	Yield, %
Azole	DAS	Azole: DAS, mol/mol	Time, h	T, °C			
1	DMS	1:2	1	78–80	**13**	171-173	90
5	DMS	1:2	2	25–30	**13**		60
3	DMS	1:3	3	90–95	**12**	160-164	83
3	DMS	1:3	3	90–95	**14**	196-198	90
7	DMS	1:2	2	25–30	**14**		55
2	DES	1:3	8	92–97	**17**	150-151	86
6	DES	1:4	3	25–30	**17**		54
4	DES	1:3	8	92–97	**18**	168-170	79
8	DES	1:2	3	25–30	**18**		56

The quaternization products are identical in their physicochemical and spectral data and correspond to 1,4-dimethyl-3-nitrotriazolium salts **13, 14, 17,** and **18** also obtained by alkylation of N-unsubstituted nitrotriazoles **9** and **10** by DAS [5, 6].

The quaternization of $N_{(4)}$-substituted alkylnitrotriazoles by dialkyl sulfates has special features. The quaternization reaction proceeds well at room temperature and is complete after a few hours for monosubstituted nitrotriazoles **5-8** as indicated by gas-liquid chromatography. Raising the temperature to 40°C leads to an uncontrollable exothermic reaction. Atoms $N_{(1)}$ and $N_{(2)}$ are free for attack by electrophilic agents in 4-alkylnitrotriazoles. Hence and in contrast to $N_{(1)}$-substituted nitrotriazoles, quaternization of the $N_{(4)}$-isomers by DAS proceeds nonselectively. For example, the attack of the electrophilic agent at $N_{(1)}$ in 4-methylnitrotriazoles **5** and **7** gives 1,4-dimethyl- or 1,4,5-trimethylnitrotriazolium salts in 60% yield, which are identical to salts **13** and **14** also obtained by quaternization of $N_{(1)}$-substituted nitrotriazoles **1** and **3** with analogous substituents. Furthermore, as in the alkylation of the neutral heterocycle [5], gas-liquid chromatography with a standard and ^{1}H NMR spectroscopy showed that the alkylation of 4-alkylnitrotriazoles gives 1,4-dimethyl- (**19**) and 1,3,4-trimethyl-1,2,4-triazol-5-ones, whose precursors are 1,4-dimethyl- (**21**) and 1,3,4-trimethyl-5-nitro-1,2,4-triazolium salts (**22**) formed by attack by the electrophilic agent at $N_{(2)}$.



19, **21** R = H; **20**, **22** R = Me

The structure of triazoles **12-14, 17,** and **18** as 1,4-dialkyl- and 1,4,5-trialkyl-3-nitro-1,2,4-triazoleium salts was supported by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy (Table 2). The IR spectra of nitrotriazolium salts**12-14, 17,** and **18** retain the characteristic nitro group bands for nitrotriazoles [10, 11] and nitrotriazolum salts [5, 6], bands for symmetrical antiphased stretching vibrations at 1565-1550 cm^{-1}, and the analogous synphased vibrations at 1340-1320 cm^{-1} and show new strong bands for the perchlorate anion in the vicinity of 1100 cm^{-1} (**13, 14, 17, 18**) or the methyl sulfate anion at 1238 cm^{-1} (**12**). The ^{1}H NMR spectra of quaternizates **13** and **17** show characteristic signals for the protons at $C_{(5)}$ in the heterocycle at 10.31 and 10.42 ppm, respectively, a pair of equal singlets for the protons of the two methyl groups at 4.16 and 4.21 ppm of salt **13** and two triplets (1.52 and 1.55 ppm) and quartets (4.53 and 4.57 ppm) of the ethyl groups in salt **17**. The ^{1}H NMR spectrum of triazolium salt **14** shows three singlets of equal intensity (two signals at 4.05 and 4.15 ppm for protons of the methyl groups at $N_{(4)}$ and $N_{(1)}$) and a singlet for the protons of the methyl groups at ring atom $C_{(5)}$ at 2.89 ppm. The signals for the three methyl groups attached to the heterocycle in nitrotriazolium salt **12** and of the above-mentioned salt **14** are virtually identical in form and frequency (Table 2).

In comparison with the spectrum of salt **14**, the spectrum of salt **12** additionally has a singlet for the methyl group of the methyl sulfate anion at 3.32 ppm.

The ^{13}C NMR spectra of nitrotriazolium salts **12-14, 17,** and **18** (Table 2) display characteristic signals for $C_{(3)}$ at the nitro group, ring atom $C_{(5)}$-H (at 145.78 and 147.17 ppm for salts **13** and **17**) and ring atom $C_{(5)}$ attached to a methyl group at 9.98-10.43 ppm (salts **12, 14,** and **18**) as well as the corresponding signals of

TABLE 2. Spectral Data for N,N-Dialkyl-3-nitro-5-R-triazolium Salts **12-14, 17,** and **18**

Compound	IR spectrum, ν, cm^{-1}		UV spectrum, λ_{max}, nm	^{1}H NMR spectrum, δ, ppm. (*J*, Hz)*	^{13}C NMR(DMSO-d_6), ppm
	λ, NO_2	ClO_4, (SO_4)			
12	1550, 1340	1238 (SO_4)	238	2.86 (3H, s, C<u>CH$_3$</u>); 3.32 (3H, s, CH_3SO_4); 4.03 (3H, s, NCH_3); 4.12 (3H, s, NCH_3)	10.43 (CCH_3); 35.68 (N<u>CH$_3$</u>); 38.83 (NCH_3); 53.06 (CH_3SO_4); 150.38 ($C_{(3)}$); 156.29 ($C_{(5)}$)
13	1565, 1340	1085	229	4.16 (3H, s, NCH_3); 4.21 (3H, s, NCH_3); 10.31 (1H, s, CH) [4.17 (3H, s, NCH_3); 4.18 (3H, s, NCH_3); 9.55 (1H, s, CH)]	37.09 (NCH_3); 40.22 (NCH_3); 147.17 ($C_{(5)}$); 150.99 ($C_{(3)}$)
14	1550, 1335,	1100	240	2.89 (3H, s, CCH_3); 4.05 (3H, s, NCH_3); 4.15 (3H, s, NCH_3) [2.78 (3H, s, CCH_3); 4.08 (3H, s, NCH_3); 4.02 (3H, s, NCH_3)]	10.38 (C<u>CH$_3$</u>); 35.67 (NCH_3); 38.93 (NCH_3); 150.38 ($C_{(3)}$); 156.18 ($C_{(5)}$)
17	1562, 1325	1080	—	1.52 (3H, t, *J* = 7.2, CH_3); 1.55 (3H, t, *J* = 7.2, CH_3); 4.53 (2H, q, *J* = 7.2, CH_2); 4.57 (2H, q, *J* = 7.2, CH_2); 10.42 (1H, s, CH) [1.57 (3H, t, *J* = 7.3, CH_3); 1.60 (3H, t, *J* = 7.3, CH_3); 4.50 (2H, q, *J* = 7.3, CH_2); 4.61 (2H, q, *J* = 7.3, CH_2); 9.65 (1H, s, CH)]	13.36 (CH_2<u>CH_3</u>); 13.62 (CH<u>CH_3</u>); 46.72 (NCH_2); 49.09 (NCH_2); 145.78 ($C_{(5)}$); 150.92 ($C_{(3)}$)
18	1550, 1320	1090	—	1.44 (3H, t, *J* = 7.2, CH_3); 1.45 (3H, t, *J* = 7.2, CH_3); 2.94 (3H, s, CCH_3); 4.49 (2H, q, *J* = 7.25, CH_2); 4.53 (2H, q, *J* = 7.25, CH_2) [1.47 (3H, t, *J* = 7.3, CH_3); 1.51 (3H, t, *J* = 7.3, CH_3); 2.82 (3H, s, *J* = 7.3, CCH_3); 4.41 (2H, q, *J* = 7.3, CH_2); 4.52 (2H, q, *J* = 7.3, CH_2)]	9.98 (C<u>CH$_3$</u>); 13.11 (CH_2<u>CH_3</u>); 13.17 (CH_2<u>CH_3</u>); 44.89 (NCH_2); 47.14 (NCH_2); 150.39 ($C_{(3)}$); 155.32 ($C_{(5)}$)

* The NMR spectra were taken in DMSO-d_6; the spectra taken in CD_3CN are given in brackets.

methyl groups (salts **12-14**) and ethyl groups bound to nitrogen atoms of the nitrotriazole heterocycle (salts **17** and **18**). The signal of $C_{(3)}$ is only slightly dependent on the type and position of the alkyl substituents in the heterocycle and fall in a narrow range 150.38-150.99 ppm.

Furthermore, the physicochemical characteristics given in Table 1, in particular, the melting points, and spectral data for nitrotriazolium salts **12-14, 17,** and **18** obtained by alkylation of N-monosubstituted nitrotriazoles and the same salts obtained from N-unsubstituted nitrotriazoles [5, 6] are identical to the data given in Tables 1 and 2, indicating that these structures are identical.

Comparative analysis of the ^{1}H NMR spectra of the starting nitrotriazoles [4, 12] and of the nitrotriazolium salts given in Table 2 shows that there is a significant downfield shift of the signal for H-5 in the spectra of nitrotriazolium salts **13** and **17** without an alkyl substituent at $C_{(5)}$ relative to the signal of the same proton in starting triazoles **2, 2, 5,** and **6**. The chemical shift depends on the solvent used and concentration of the solution (**13** and **17** in DMSO-d_6**:** 10.31 and 10.42 ppm; **13** and **17** in CD_3CN: 9.55 and 9.65 ppm). The difference in chemical shift for $N_{(1)}$-isomers **1** and **2** [4] and $N_{(4)}$-isomers **5** and **6** [5, 6] and their quaternization products (Table 2) is 1.49-1.56 and 1.49-1.64 ppm, respectively. This result indicates increased lability of the proton at the carbon atom upon quaternization and formation of hydrogen bonds with the solvent molecules. The solvent used has hardly any effect on the chemical shifts of the protons of the alkyl substituents at the carbon or nitrogen atoms (Table 2).

The alteration in the chemical shifts of the proton at the ring carbon due to formation of quaternary nitrotriazolium salts indicates a considerable increase in the CH-acidity of the N-substituted nitrotriazoles upon quaternization, which makes these salts more active in deuterium exchange and other electrophilic reactions as well as expands the scope of these reactions for obtaining new products with useful properties.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were taken on a Bruker AM-400 spectrometer at 400 and 100 MHz, respectively, with TMS as the internal standard. The IR spectra were taken on a Perkin-Elmer spectrometer for KBr pellets and the IR spectra were taken on a Specord spectrometer. The UV spectra were taken on a Specord spectrometer. The gas-liquid chromatographic analysis was carried out using an internal standard on a CHROM-5 chromatograph with a flame ionization detector and 200-mm glass column d = 3 mm) packed with SE-30 siloxane elastomer. The nitrogen gas carrier flow rate was 40 ml/min. The thermostat temperature was 180°C. The injector temperature was 220°C. The detector temperature was 220°C. The melting points were determined on a Boetius block using an RNMK-05 viewing device.

Preparation of components and reagents.

Samples of N-alkyl-3-nitro-4-R-1,2,4-tirazoles and triazolones **1-8, 19,** and **20**, which served as the starting compounds, reference compounds, and standards for the ^{1}H NMR spectra and gas-liquid chromatography were prepared according to reported procedures [4, 5, 13].

The dialkyl sulfate samples were washed with 3% aq. sodium carbonate to remove traces of acid and then distilled water, dried, and distilled in vacuum prior to use (purity ≥99.9%). The acid content relative to sulfuric acid was ≤0.1%.

Quaternization of $N_{(1)}$- and $N_{(4)}$-alkylnitrotirazoles 1-8. A rapidly stirred mixture of N-alkylnitrotriazoles **1-8** and dimethyl sulfate (in mole ratios from 1:2 to 1:4) were slowly heated to 80-95°C (for nitrotriazoles **1-4**) or 25-30°C (for nitrotriazoles **5-8**) and maintained at the indicated temperature for 1-8 h (Table 1). The reaction mixture was cooled to 30°C and water was added. Aqueous ammonium perchlorate (in 5% molar excess relative to nitrotriazoles **1-8**) was added to the aqueous layer. The precipitate formed was filtered off.

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