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NITRATION OF ACYLATED SUBSTITUTED METHYLENEDIAMINES
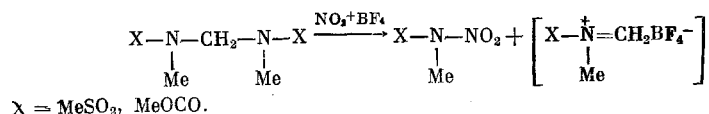
O. A. Luk'yanov, T. G. Mel'nikova, and V. A. Tartakovskii   UDC 542.958.1:547.415.1

Previously, we showed that during nitration of linear alkylimides by nitronium tetrafluoroborate, the acetyl and methanesulfonyl groups can be replaced by a nitro group [1].
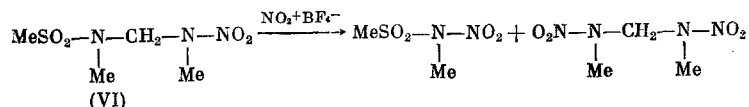
In the present paper, we studied the reaction of nitronium tetrafluoroborate with N', N-diacylated and N,N'-disulfonylated dialkyl-substituted methylenediamines and also monosulfonylated tri- or N,N-dialkyl-substituted methylenediamines. The literature data on nitration of this type of compound are fragmentary [2-4] and do not make it possible to make any generalizations.

We found that the direction of the reactions of these compounds depended significantly on the nature of the acid groups. In addition, one or both acetyl groups were replaced by a nitro group. The ratio of the products depended significantly on the ratio of the starting reagents (Table 1). In going from acetyl to methanesulfonyl and carbomethoxy derivatives, we observed cleavage of the methylenediamine fragment with formation of the corresponding N-alkyl-N-nitroamides

$$X-\underset{\underset{Me}{|}}{N}-CH_2-\underset{\underset{Me}{|}}{N}-X \xrightarrow{NO_2^+BF_4^-} X-\underset{\underset{Me}{|}}{N}-NO_2 + \left[X-\overset{+}{\underset{\underset{Me}{|}}{N}}=CH_2BF_4^-\right]$$

$$X = MeSO_2, MeOCO.$$

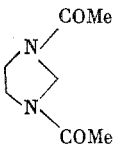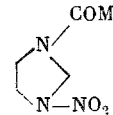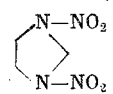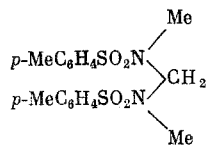In this case, the role of the leaving group was performed not by acid groups, but by methyleneamidonium cations.

Nitration of p-toluenesulfonyl derivatives of methylenediamine proceeded in both possible directions. This fact apparently indicates that during nitration the p-toluenesulfonyl group tended more to act as a leaving group than the methanesulfonyl group. It is logical to assume that the direction of the reaction could be changed, at least partially, by a decrease in the thermodynamic stability of the resulting methyleneamidonium cations. Indeed, during nitration of (VI) the expected N,N'-dimethyl-N,N'-dinitromethylenediamine was formed:

$$\underset{(VI)}{MeSO_2-\underset{\underset{Me}{|}}{N}-CH_2-\underset{\underset{Me}{|}}{N}-NO_2} \xrightarrow{NO_2^+BF_4^-} MeSO_2-\underset{\underset{Me}{|}}{N}-NO_2 + O_2N-\underset{\underset{Me}{|}}{N}-CH_2-\underset{\underset{Me}{|}}{N}-NO_2$$

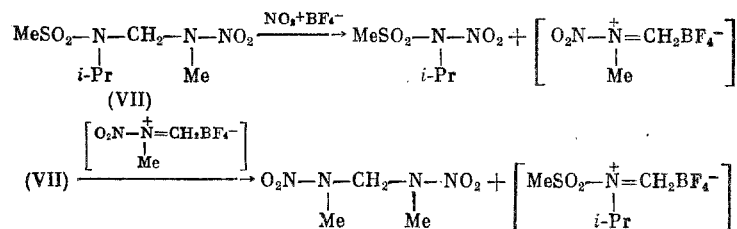However, this same methylenedinitroamine was obtained in high yield in the reaction of nitronium tetrafluoroborate with (VII), and the desired N-methyl-N'-isopropyl-N,N'-dinitromethylenediamine was not formed at all. This could be explained with the following scheme:

TABLE 1. Products of the Reaction of the N,N'-Diacyl-Substituted Methylenediamines with Nitronium Tetrafluoroborate (NTFB)

Compound undergoing nitration	Compound undergoing nitration: NTFB (molar)	Reaction time at 20°C, h	Products	Yield, *%
MeCONCH₂NCOMe, Me, Me (I)	1:1	1	MeCONCH₂NNO₂, Me, Me	33 (36)
			O₂NNCH₂NNO₂, Me, Me	38 (45)
N–COMe / N–COMe ring (II)	1:1 / 1:2	1	N–COMe / N–NO₂ ring	28 / 23
	1:1 / 1:2	1	N–NO₂ / N–NO₂ ring	38 / 53
MeSO₂NCH₂NSO₂Me, Me, Me (III)	1:1 / 1:2	15 / 2	MeSO₂NNO₂, Me	71 (89) / 88
MeO₂CNCH₂NCO₂Me, Me, Me (IV)	1:1	1	MeO₂CNNO₂, Me	77 (100)
p-MeC₆H₄SO₂N(Me)–CH₂–N(Me)SO₂C₆H₄Me-p (V)	1:1	1	p-MeC₆H₄SO₂NNO₂, Me	75 (94)
			p-MeC₆H₄SO₂NCH₂NNO₂, Me, Me	24 (30)
			O₂NNCH₂NNO₂, NO₂, NO₂	31 (40)
MeSO₂NCH₂NNO₂, Me, Me (VI)	1:1	1	MeSO₂NNO₂, Me	52
			O₂NNCH₂NNO₂, Me, Me	22
MeSO₂NCH₂NNO₂, i-Pr, Me (VII)	1:1	1	MeSO₂NNO₂, i-Pr	23
			O₂NNCH₂NNO₂, Me, Me	80

*The yield based on the starting compound which actually reacted is given in parentheses.

$$MeSO_2\!-\!N(i\text{-}Pr)\!-\!CH_2\!-\!N(Me)\!-\!NO_2 \xrightarrow{NO_2^+BF_4^-} MeSO_2\!-\!N(i\text{-}Pr)\!-\!NO_2 + \left[O_2N\!-\!\overset{+}{N}(Me)\!=\!CH_2BF_4^- \right]$$

$$\left[O_2N\!-\!\overset{+}{N}(Me)\!=\!CH_2BF_4^- \right] \xrightarrow{(VII)} O_2N\!-\!N(Me)\!-\!CH_2\!-\!N(Me)\!-\!NO_2 + \left[MeSO_2\!-\!\overset{+}{N}(i\text{-}Pr)\!=\!CH_2BF_4^- \right]$$

This scheme apparently also can explain the formation of methylenedinitroamine during nitration of (VI).

The basicities of both N atoms in (III), (V), (VI), and (VII) are equal or comparatively close. It seemed of interest to elucidate the directions of nitration of the methylenediamine derivatives with N atoms significantly differing in basicity. Therefore, we studied the nitration of monosulfonylated methylenediamine derivatives (VIII) and (IX). Electrophilic attack at the amine-N atom in (VIII) and (IX) should be favored by the high basicity of the atom, and attack at the amide N should be favored by the possibility of formation of the more stable methyleneimmonium cation. It was elucidated that nitration of (VIII) and (IX) by nitronium tetrafluoroborate led to a mixture of the corresponding nitrosulfonamides and nitromorpholine with significant predominance of the latter. In our opinion, this fact indicates that the determining step in the nitration of the methylenediamine derivatives was the step of formation of the N-nitronium cation.

In addition to nitronium tetrafluoroborate, conc. HNO_3 was used in the nitration of (VIII) and (IX). It should also be noted that nitromorpholine either was not formed at all in case (VIII) or was formed in insignificant amounts in

## TABLE 2. Products of the Reaction of Monosulfonylated Tri- and N,N-Dialkyl-Substituted Methylenediamines with Nitronium Tetrafluoroborate and HNO_3

| Compound undergoing nitration	Nitrating agent	Nitrating reagent: compound undergoing nitration (molar)	React. time at 20°C, h	Reaction products	Yield, %
p-MeC₆H₄SO₂NCH₂N⟨ ⟩O (VIII) Me	NO₂⁺BF₄⁻	1:1	1	p-MeC₆H₄SO₂NNO₂ Me · p-Me(NO₂)C₆H₃SO₂NNO₂ Me	18—20
				O⟨ ⟩N—NO₂	50—55
MeSO₂NCH₂N⟨ ⟩O Me (IX)	NO₂⁺BF₄⁻	1:1	1	MeSO₂NNO₂ Me	15
				O⟨ ⟩N—NO₂	38
(VIII)	HNO₃	29:1	0,5	p-Me(NO₂)C₆H₃SO₂NNO₂ Me	5
				p-Me(NO₂)C₆H₄SO₂NH Me	61
(IX)	HNO₃	24:1	1	MeSO₂NNO₂ Me	21
				O⟨ ⟩N—NO₂	3
ArSO₂NHCH₂N⟨ ⟩O Ar = Ph (X), p-MeC₆H₄ (XI)	NO₂⁺BF₄⁻	1:1	0,5	O⟨ ⟩N—NO₂	42—51

case (IX). The main reaction products were N-alkyl-N-nitrosulfonamides and also N-alkylsulfonamides, which could be obtained during decomposition of the starting compounds in a strongly acid medium (Table 2).

On the basis of the results of nitration of (VIII) and (IX), it was assumed that (X) and (XI) would be at least partially nitrated at the amide N. It was found, however, that only the amine N atom underwent electrophilic attack. This was possibly because of the formation of a transition state in which the nitronium cation attacked the most basic N atom, and a proton acted as the leaving group

$$ArSO_2—N \cdots \overset{+}{C}H_2 \cdots N⟨ ⟩O$$
$$\quad\quad\quad H \quad\quad\quad NO_2$$
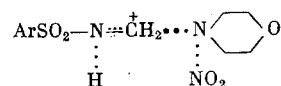
EXPERIMENTAL

General Procedure for Nitration with Nitronium Tetrafluoroborate. The appropriate (see Tables 1 and 2) amount of NO_2BF_4 was added to a solution of 10 mmoles of the compound undergoing nitration in 20 ml of abs. MeCN with stirring and cooling to −25°C. The whole was stirred for a certain time at $\sim$20°C, poured into 2 ml of water, extracted with CH_2Cl_2, and dried with Na_2SO_4. The solvent was evaporated. The mixture of products was separated by thin-layer chromatography on silica gel, and the individual substances were identified by means of IR and PMR spectra and data of elemental analysis.

General Procedure for Nitration by HNO_3. With intensive stirring at 0-5°C, the necessary amount (see Table 2) of $XSO_2NMeCH_2N⟨ ⟩O$ was added to HNO_3 (sp. gr. 1.5) in small portions. The mixture was kept at $\sim$20°C for 1 h, poured into a 10-fold amount of ice, extracted with CH_2Cl_2, and dried with Na_2SO_4. The solvent was evaporated in vacuo, and the mixture of products was separated by thin-layer chromatography on silica gel.

N-Alkyl-N-(nitroaminomethyl)methanesulfonamides. To a solution of 20 mmoles of $MeSO_2N(R)CH_2Cl$ in 30 ml of abs. ether was added in small portions with cooling by ice water 20 mmoles of $MeNHNO_2$ and then dropwise a solution of 20 mmoles of Et_2N in 10 ml of abs. ether. The mixture was stirred for 3 h at $\sim$20°C. The ether was evaporated in a

stream of air. The dry solid residue was treated with 40 ml of cold water and the undissolved residue was filtered, washed with water, and dried in air. Obtained: R = Me, 3 g (76%) of (VI), mp 80-81°C (from H_2O). PMR spectrum ($CDCl_3$, δ, ppm): 2.85 singlet ($MeSO_3$) 2.97 singlet ($MeNSO_2$), 3.39 singlet ($MeNNO_2$), and 5.18 singlet (CH_2). IR spectrum (KBr, ν, cm^{-1}): 1585, 1295 (NNO_2), 1375, 1180 (S = O). Found: C 24.42; H 5.59; S 16.14%. $C_4H_{11}O_4N_3S$. Calculated: C 24.35; H 5.59; S 16.25%. R = iso-Pr, 2.75 g (61%) of (VII), mp 82.5-83°C (from H_2O). PMR spectrum ($CDCl_3$, δ, ppm): 1.25 doublet (2 MeCH), 2.9 singlet ($MeSO_2$), 3.4 singlet ($MeNNO_2$), 4.0 multiplet (CHN), and 5.39 singlet (CH_2). IR spectrum (KBr, ν, cm^{-1}): 1520, 1310 (NNO_2), 1325, 1177 (S = O). Found: C 32.21; H 6.82; S14.17%. $C_6H_{15}N_4O_3S$. Calculated: C 32.03; H 6.72; S 14.23%.

N-Methyl-N-(morpholinomethyl)methanesulfonamide (IX). A solution of 3.13 g (36 mmoles) of morpholine was added dropwise to a solution of 2.83 g (18 mmoles) of $MeSO_2N(Me)CH_2Cl$ in 50 ml of dry ether. The mixture was stirred for 2 h at 20°C. The precipitate was filtered, and the ether solution was evaporated in vacuo. Obtained: 2.9 g (78%) of (IX), mp 60-62°C (from Et_2O). PMR spectrum (acetone-d_6, δ, ppm): 2.52 multiplet (2-CH_2N), 2.82 singlet ($MeSO_2$), 2.86 singlet (MeN), 3.58 multiplet (2-CH_2O), and 3.79 singlet (NCH_2N). IR spectrum (KBr, ν, cm^{-1}): 1338, 1160 (S = O), 1120 (COC). Found: C 40.77; H 7.93; S 15.50%. $C_7H_{15}O_3N_2S$. Calculated: C 40.42; H 7.70; S 15.39%.

N-Methyl-N-(N'-methyl-N'-nitroaminomethyl)acetamide was obtained similarly to (VI), bp 131°C (1 mm), n_D^{25} 1.4914. PMR spectrum ($CDCl_3$, δ, ppm): 2.1 singlet (MeCO), 3.15 singlet (MeNAc), 3.4 singlet ($MeNNO_2$), and 5.25 singlet (CH_2). IR spectrum (ν, cm^{-1}): 1660 (C = 0), 1530, 1300 (NNO_2). Found: C 36.76; H 6.99; N 26.14%. $C_5H_{11}O_3N_3$. Calculated: C 37.30; H 6.84; N 26.08%.

1-Acetyl-3-nitrotetrahydroimidazole was obtained by nitration of (II), mp 51-52.5°C. PMR spectrum (DMSO-d_6, δ, ppm): 1.96 singlet (MeCO), 3.88 multiplet (CH_2CH_2) and 5.11 doublet (NCH_2N). IR spectrum (KBr, ν, cm^{-1}): 1675, 1660 (C = O), 1530, 1340 (NNO_2). Found: C 37.73; H 5.74; N 26.29%. $C_5H_9O_3N_3$. Calculated: C 37.70; H 5.66; N 26.41%.

N-Methyl-N-(N'-methyl-N'-nitroaminomethyl)-p-toluenesulfonamide was obtained similarly to (VI), mp 37-40°C. PMR spectrum ($CDCl_3$, δ, ppm): 2.34 singlet (MeC_6H_4), 2.82 singlet (MeNTS), 3.35 singlet ($MeNNO_2$), 5.10 singlet (CH_2), and 7.40 quartet (H_{arom}). IR spectrum (ν, cm^{-1}): 1598 (C=C), 1535, 1300 (NNO_2), 1345, 1165 (S=O). Found: C 45.02; H 5.57; S 2.21%. $C_{10}H_{15}O_4N_3S$. Calculated: C 44.0; D 5.50; S 11.72%.

CONCLUSIONS

1. Nitration of methylenediamine derivatives $RN(X)CH_2N(X)R$ by nitronium tetrafluoroborate was accompanied by cleavage of the N—X (X = MeCO) or N—CH_2 (X = RSO_2, RO_2C) bond and formation of N-nitro derivatives of methylenediamine or N-nitro amides, respectively.

2. During nitration of methylenediamine derivatives $RSO_2N(X)CH_2R_2$ by nitronium tetrafluoroborate, the amine nitrogen (X = H) or both nitrogen atoms (X = Me) underwent attack.

3. The direction of the nitration reaction depended on the nature of the nitrating agent (NO_2BF_4 and HNO_3).

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