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Nitration of 4-Acetylamino-4'-nitro-, 4-Acetylamino-2'-nitrodiphenyl Sulfides and 4-Acetylamino-2'-nitrodiphenyl Ether

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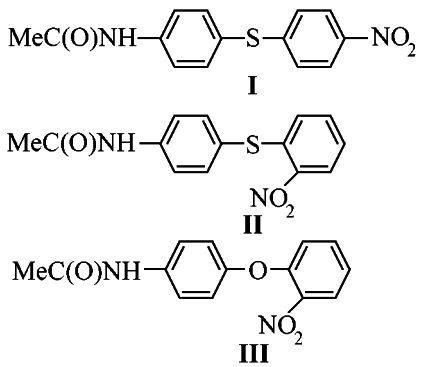
Abstract—Nitration of 4-acetylamino-4'-nitrodiphenyl sulfide, 4-acetylamino-2'-nitrodiphenyl sulfide, and 4-acetylamino-2'-nitrodiphenyl ether yields respectively 4-acetylamino-3,4'-dinitrodiphenyl sulfide, 4-acetylamino-2',3-dinitrodiphenyl sulfide, and 4-acetylamino-2',3-dinitrodiphenyl ether.

4-Acetylamino-4'-nitrodiphenyl sulfide (**I**), 4-acetylamino-2'-nitrodiphenyl sulfide (**II**), 4-acetylamino-2'-nitrodiphenyl ether (**III**), and obtained therefrom by nitration respectively 4-acetylamino-3,4'-dinitrodiphenyl sulfide (**IV**), 4-acetylamino-2',3-dinitrodiphenyl sulfide (**V**), and 4-acetylamino-2',3-dinitrodiphenyl ether (**VI**) are important semiproducts in the synthesis of quite a number of helminthicides from the series of 2-aminobenzimidazole derivatives [1–3]. The demand on these preparations is fairly high, and therefore the development of reliable synthetic methods for them is urgent.

The present study was aimed at investigation of compounds **I**–**III** nitration to obtain the corresponding dinitro derivatives **IV**–**VI** and to optimize the nitration conditions.

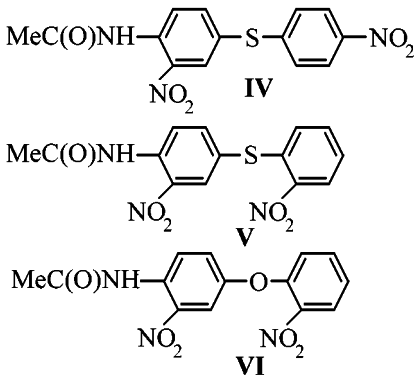
The nitration mechanism in the aromatic series is considered in detail in numerous publications [4–8].

In the molecules of substrates **I**–**III** in *para*-position with respect to each other are present two groups capable to affect the orientation of nitration: MeC(O)NH and $SC_6H_4NO_2$, MeC(O)NH and $OC_6H_4NO_2$. Therefore the direction of nitration may be predicted by analysis of the electronic effects of these substituents [6].



The groups $SC_6H_4NO_2$ in compounds **I** and **II** and $OC_6H_4NO_2$ in substrate **III** possess overall negative effects (–*I* and –*E*) and decrease the electron density in the second benzene ring impeding its nitration and orienting the new substituent into the *meta*-position with respect to these groups. On the other hand, the MeC(O)NH group possesses an electropositive effect and directs the nitro group entering into this ring into *ortho*- and *para*-positions.

Therefore obviously in this case occurs correlated orientation, and it is possible to expect selective formation from compounds **I**–**III** respective dinitro derivatives **IV**–**VI**.



Nitrocompound **IV** was obtained in [9] by nitration of sulfide **I** by the mixture of acetic and nitric acids. The nitric acid used was of density 1.4 g cm^{-3}. Regretfully, the yield of the product was not indicated, but it was stated that the reaction is accompanied by

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oxidation of compound **IV** into sulfoxide and sulfone. Under more stringent conditions, when nitration was performed with the use of a mixture of equal volumes of nitric and sulfuric acids, sulfone was the main reaction product.

The highest yield of dinitrosulfide **IV** (45%) we obtained at nitrating with dilute nitric acid (ρ 1.35 g cm^{-3}) and at the ratio substrate–HNO_3–AcOH 1:3:10. The nitric acid was added to the dispersion of the initial compound **I** in AcOH at room temperature, and then the reaction mixture was heated to 35–40°C for 3–4 h. In the course of the process a liberation of nitrogen oxides as brown vapor was observed. The addition of small amount of urea did not prevent oxidation, and at large quantities of urea the nitration decelerated up to total inhibition of reaction when 1 mole of urea per 1 mole of substrate **I** was used.

The data obtained support the mechanism of nitration with dilute nitric acid [10] as "catalytic nitration", and the process in the dilute nitric acid proceeds only in the presence of nitrogen(IV) oxides. The side oxidative processes result in increasing concentration of nitrogen(IV) oxides in the course of nitration. The molecules of nitric acid here serve as a source of nitrogen dioxide.

Nitrogen oxides play dual role in nitration of sulfide **I**. On the one hand, no nitration occurs when they are absent; on the other hand, they oxidize sulfur in sulfide **I** into sulfoxide and sulfone. We observed that if the reaction mixture was not stirred, the removal of excessive nitrogen oxides was hampered, and the oxidative processes increased.

To reduce the excess of nitrogen(IV) oxides and therewith the oxidation processes the nitration of sulfide **I** should be performed in less polar medium that acetic acid. Therefore we carried out the nitration in mixtures of acetic acid with aprotic solvents for instance, with dichloromethane, dichloroethane, chloroform, chlorobenzene etc. The nitration was performed in a mixture of acetic acid with chloroform (1:3 by volume) using nitric acid of ρ 1.35 g cm^{-3}. This procedure resulted in decreased oxidation and increased yield of dinitrosulfide **IV** up to 60%.

In 2–3 h after adding nitric acid in the reaction mixture were no found either initial compound **I** and its oxidation products (according to the data of TLC and HPL chromatography). However the isolated reaction product had lower melting point that 4-acetylamino-3,4'-dinitrodiphenyl sulfide [9]. Some difference was also observed in the IR and NMR spectra of the compound. We presume that similar to [11, 12] the nitration of 4-acetylamino-4'nitrodiphenyl sulfide proceeds through N-nitro compound that under mild conditions is the main reaction product.

To support the assumed mechanism of nitration of 4-acetylamino-4'-nitrodiphenyl sulfide we attempted to nitrate 4-(*N*-dimethylamino)-4'-nitrodiphenyl sulfide in the mixture of acetic acid with chloroform by dilute nitric acid (ρ 1.35 g cm^{-3}) for 6 h at 18–20°C. The analysis of the reaction mixture showed that no nitration occurred. 4-(*N*-dimethylamino)-4'-nitrodiphenyl sulfide was prepared by methylation of 4-amino-4'-nitrodiphenyl sulfide with dimethyl sulfate in a water-dioxane mixture in the presence of $NaHCO_3$ [13] and analyzed by NMR and HPLC methods.

The rearrangement of N-nitro compound into a C-nitro compound we succeeded to perform by boiling the reaction mixture in acetic acid or by stirring at room temperature in acetic acid with addition of sulfuric acid. In a mixture of acetic and nitric acid the rearrangement required a moderate heating. This rearrangement was accompanied by appearance of oxidation products, and their amount is greater in the presence of nitric acid.

Therefore after adding the mixture of nitric and acetic acids the reaction mixture was stirred for 1 h at 15–25°C, and then gradually into the reaction mixture was added separately prepared mixture of sulfuric and acetic acid in a definite required ratio. Then the reaction mixture was vigorously stirred at 15–25°C for 4–5 h more.

On completion of nitration into the reaction mixture water was added in amount necessary for separating acids from the solvent. After layers separation the organic layer was twice washed with hot water. To a solution obtained of compound **IV** in the chloroform–acetic acid mixture was added water, and the main part of solvents was distilled off in a vacuum. The dispersion of dinitrosulfide **IV** thus obtained was filtered, the product was washed on the filter with 2-propanol, water, and dried. The results of compound **I** nitration in the mixture of chloroform and acetic acid are listed in Table 1.

Thus from the data obtained for nitration of sulfide **I** the following conclusions may be drawn. Firstly, the limiting stage of sulfide **IV** formation is obviously the rearrangement of N-nitrocompound into C-nitrocompound. Secondly, the side oxidation processes occur at the rearrangement stage or after. Thirdly, in the presence of sulfuric acid the rearrangement proceeds under milder conditions and with less oxidation.

Table 1. Nitration of 4-acetylamino-4'-nitrodiphenyl sulfide (**I**) in a mixture of chloroform with acetic acid by 57% nitric acid

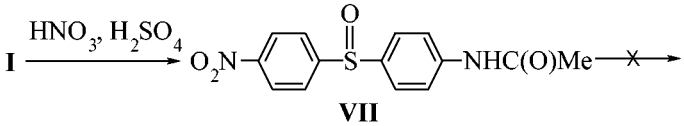
Ratios of reagents				Dinitrosulfide (**IV**) yield, %[c]
(**I**) : HNO_3[a]	CH_3COOH : HNO_3[a]	HNO_3 : H_2SO_4[a]	$CHCl_3$: (**I**)[b]	
1.0 : 3.46	[d]	4.38 : 1.0	[e]	21 (93)
1.0 : 6.97	33.9 : 1.0	2.38 : 1.0	3.46 : 1.0	20 (93)
1.0 : 6.93	22.5 : 1.0	2.40 : 1.0	3.46 : 1.0	55 (72)
1.0 : 6.97	33.9 : 1.0	2.40 : 1.0	3.46 : 1.0	56 (75)
1.0 : 6.00	29.2 : 1.0	2.77 : 1.0	3.00 : 1.0	56 (76)
1.0 : 1.29	1.32 : 1.0	8.58 : 1.0	3.00 : 1.0	56 (92)
1.0 : 1.30	1.32 : 1.0	9.00 : 1.0	3.00 : 1.0	58 (93)
1.0 : 1.30	1.32 : 1.0	9.00 : 1.0	3.00 : 1.0	58 (94)
1.0 : 1.30	1.32 : 1.0	8.58 : 1.0	3.00 : 1.0	57 (93)
1.0 : 1.58	1.32 : 1.0	8.58 : 1.0	3.00 : 1.0	69 (91)
1.0 : 1.60	1.32 : 1.0	8.50 : 1.0	3.00 : 1.0	70 (92)
1.0 : 1.40	1.30 : 1.0	9.00 : 1.0	3.00 : 1.0	69 (92)
1.0 : 1.23	1.94 : 1.0	8.77 : 1.0	3.00 : 1.0	46 (89)

[a] Molar reagents ratio.
[b] Weight ratio.
[c] Yield of crude reaction product (**IV**); the content of the main product in the sample, wt%, is given in parentheses.
[d] Without acetic acid.
[e] Without solvent.

The latter conclusion seems to contradict the data [9] on sulfone formation as the main product in the nitration process with the use of sulfuric acid in the nitrating system. However in [9] were used concentrated nitric and sulfuric acids, and in this case the nitration apparently occurred by an other mechanism.

To elucidate the effect of sulfuric acid on the nitration with a dilute nitric acid we carried out a series of experiments and established that at the ratio initial sulfide **I**–nitric acid (ρ 1.35 g cm^{-3})–acetic acid–sulfuric acid 1 : 3 : 5 : 0.5, providing the sulfuric acid be added after the nitric acid, then the nitration occurred with high rate, the rearrangement did not require heating, and the whole process could be carried out at room temperature. However in this case the content of oxidation products did not decrease.

If at the same ratio of reagents the sulfuric acid is added before the nitric acid, then arises a significant amount of compound originating from oxidation of the initial sulfide at the sulfur atom (compound **VII**);



VII

this substance cannot be nitrated under the given reaction conditions.

The formation of sulfoxide derivative **VII** is also unwelcome because it impedes the isolation of the target dinitro compound **IV** at the stage of nitration. Since the source of excess nitrogen oxides was the nitric acid, we further decreased its amount in the reaction mixture. At the ratio initial sulfide **I**–nitric acid (ρ 1.35 g cm^{-3})–acetic acid–sulfuric acid 1 : (1.3–1.5) : 5 : 1.0, providing the sulfuric acid was added after the nitric acid, we carried out the reaction at room temperature and increased the yield of the target dinitro compounds **IV** to 50%. If the reaction is carried out in a less polar medium, i.e. in the mixture of acetic acid with chloroform, then the yield of compound **IV** can be raised to 70%.

Thus the optimal parameters of the process are as follow: the temperature of the main process 15–25°C, the temperature to the end of the process 20–25°C, stirring of reaction mixture after nitric acid addition till the start of sulfuric acid addition for 60 min, the duration of the process after addition of all acids 4–5 h, weight ratio of chloroform and acetic acid in the solvent (3.14–5.24) : 1, weight ratio chloroform–substrate **I** (2.0–3.1) : 1, molar ratio nitric acid–sulfide **I** 1.30 : 1.00, the volume ratio of nitric and

Table 2. Nitration of 4-acetylamino-2'-nitrodiphenyl sulfide (**II**) in a mixture of chloroform with acetic acid by 57% nitric acid

Ratios			Yield of crude producta, %[c]
$CHCl_3 : CH_3COOH$[a]	Sulfide **II** : HNO_3[b]	$H_2SO_4 : HNO_3$[b]	
2.00 : 1.0	1.0 : 2.90	1.0 : 65.00	60 (92)
2.50 : 1.0	1.0 : 2.90	1.0 : 65.00	62 (93)
3.00 : 1.0	1.0 : 2.90	1.0 : 65.00	72 (96)
3.33 : 1.0	1.0 : 2.86	1.0 : 64.96	73 (98)
3.33 : 1.0	1.0 : 2.86	1.0 : 64.96	73 (99)
3.96 : 1.0	1.0 : 2.44	1.0 : 49.27	67 (95)
3.96 : 1.0	1.0 : 2.44	1.0 : 49.27	67 (94)

[a] Volume ratio.

[b] Molar ratio of reagents.

[c] Yield of unpurified reaction product **V**; the content of the main product in the sample, wt%, is given in parentheses.

Table 3. Nitration of 4-acetylamino-2'-nitrodiphenyl sulfide (**II**) in a mixture of chlorobenzene with acetic acid by 57% nitric acid

Ratios				Yield of crude product, %[c]
chlorobenzene : acetic acid[a]	sulfide **II** : HNO_3[b]	$H_2SO_4 : HNO_3$[b]	$CH_3COOH : HNO_3$[b]	
4.48 : 1.0	1.0 : 2.6	1.0 : 40.0	1.0 : 1.76	54 (93)
7.27 : 1.0	1.0 : 2.6	1.0 : 40.0	1.0 : 1.56	51 (94)
3.96 : 1.0	1.0 : 4.0	1.0 : 40.0	1.0 : 1.36	55 (94)
2.00 : 1.0	1.0 : 2.5	1.0 : 60.0	1.0 : 1.35	56 (94)
2.00 : 1.0	1.0 : 2.4	1.0 : 65.0	1.0 : 1.35	56 (95)
2.00 : 1.0	1.0 : 2.6	1.0 : 60.0	1.0 : 1.35	55 (95)
1.00 : 1.5	1.0 : 2.6	1.0 : 60.0	1.0 : 0.75	54 (95)
1.00 : 1.5	1.0 : 2.0	1.0 : 60.0	1.0 : 0.70	54 (93)

[a] Volume ratio.

[b] Molar ratio of reagents.

[c] Yield of unpurified reaction product **V**; the content of the main product in the sample, wt%, is given in parentheses.

acetic acids in the nitrating mixture 2.0 : 1.0, the volume ratio of sulfuric and acetic acids 1.0 : 2.0, the molar ratio of nitric and sulfuric acids 1.3 : 1.0, weight concentration of the initial nitric acid 57% (free of oxides).

The nitration of sulfide **II** differs from that of sulfide **I** because the nitro group in ortho-position with respect to sulfur hampers sulfur oxidation into sulfoxide and sulfone apparently due to steric hindrances. This fact simplifies the nitration. The nitration is also performed with dilute nitric acid.

The nitration of sulfide **II** was studied using as solvent mixtures of acetic acid with chloroform or chlorobenzene.

In these experiments into a solution of sulfide **II** in the mixed solvent was added a mixture of acetic and sulfuric acids. Then into the reactor at temperature not exceeding 30°C was gradually added the nitric acid (ρ 1.35 g cm^{-3}). After the end of nitric acid addition the reaction mixture was vigorously stirred for 4–5 h. After completion of the process the separation of the acid layer and isolation of dinitrosulfide **V** from the organic layer was carried out similarly to the workup described for dinitrosulfide **IV**.

In Table 2 are given the data on the nitration of sulfide **II** in the mixture of chloroform and acetic acid. The optimal parameters of dinitrosulfide **V** synthesis are as follows: reaction temperature of the

Table 4. Nitration of 4-acetylamino-2'-nitrodiphenyl ether **III** with 90% nitric acid at 40–45°C

Ratios			Concentration of nitric acid %	Duration of process, h	Yield of crude product, %[c]
ether **III**: HNO_3[a]	acetic acid: HNO_3[a]	HNO_3:acetic anhydride[a]			
1.0 : 3.12	1.0 : 3.11	1.0 : 2.35	57	5.0	92 (97)
1.0 : 3.12	1.0 : 3.11	1.0 : 2.35	57	5.5	92 (96)
1.0 : 3.10	1.0 : 2.09	1.0 : 2.04	57	7.0	84 (91)
1.0 : 3.00	1.0 : 4.94	1.0 : 2.65	57	8.0	76 (99)
1.0 : 3.01	1.0 : 2.77	1.0 : 2.65	57	9.0	75 (99)
1.0 : 2.94	1.0 : 4.73	1.0 : 0.34	90	3	90 (99)
1.0 : 2.87	1.0 : 5.13	1.0 : 0.37	90	1.0	93 (97)
1.0 : 2.75	1.0 : 5.11	1.0 : 0.37	90	1.5	94 (98)
1.0 : 2.74	1.0 : 5.11	1.0 : 0.36	90	1.0	79 (98)
1.0 : 2.74	1.0 : 5.11	1.0 : 0.36	90	1.5	93 (99)
1.0 : 2.74	1.0 : 5.11	1.0 : 0.36	90	2.0	95 (99)
1.0 : 2.77	1.0 : 5.12	1.0 : 0.36	90	1.75	93 (99)
1.0 : 2.70	1.0 : 5.13	1.0 : 0.37	90	1.5	92 (98)
1.0 : 2.70	1.0 : 5.13	1.0 : 0.37	90	1.5	92 (98)
1.0 : 2.68	1.0 : 2.12	1.0 : 2.10	57	7.0	85 (99)
1.0 : 2.65	1.0 : 2.12	1.0 : 1.77	57	4.5	96 (96)
1.0 : 2.65	1.0 : 2.12	1.0 : 1.77	57	5.5	95 (97)
1.0 : 2.65	1.0 : 2.13	1.0 : 1.77	57	6.5	95 (98)
1.0 : 2.64	1.0 : 2.12	1.0 : 2.09	57	7.0	86 (99)
1.0 : 2.64	1.0 : 2.12	1.0 : 1.76	57	6.5	85 (98)

[a] Molar ratio of reagents.

[b] Yield of crude dinitroether **VI**, wt% of main compound in the samples is given in parentheses.

[c] Nitration temperature 32°C.

main process 25–30°C, temperature to the end of the process 30–35°C, temperature during evaporation of chloroform in a vacuum not higher than 45°C, duration of the process 5–6 h, molar ratio initial sulfide **II**–nitric acid 1.0 : (2.6–2.9), molar ratio nitric acid–sulfuric acid (50–65) : 1.0, volume ratio chloroform–acetic acid in the solvent (3.0–4.0):1.

In nitration carried out in a mixture of chlorobenzene and acetic acid the yield and quality of the target product **V** are somewhat worse than in reaction performed in a mixture of chloroform and acetic acid.

In this case after the end of nitration and washing of the reaction mixture from oxides and acids the solution of compound **V** in chlorobenzene was cooled with brine to 0–5°C, filtered, the product on filter was washed with 2-propanol and water, and dried.

The results obtained at nitration of sulfide **II** in the mixture of acetic acid with chlorobenzene are presented in Table 3.

The best parameters of the process are as follows: volume ratio chlorobenzene–acetic acid in the solvent (2.0–4.0) : 1.0, molar ratio initial sulfide **II**–nitric acid 1.0 : (2.4–2.6), molar ratio nitric acid–sulfuric acid (60–65) : 1.0, molar ratio acetic acid–nitric acid 1.00 : 1.35, the process temperature and duration are the same as in nitration of sulfide **II** in the mixture of chloroform and acetic acid.

Our investigation showed that nitration of ether **III** was best performed by concentrated nitric acid (90%) in a mixture of acetic acid and acetic anhydride. Into a reactor was charged the necessary amount of acetic acid, and at stirring ether **III** of technical grade. Into the mixture was poured acetic anhydride, and then at vigorous stirring and cooling with brine to 10–15°C into the reactor is gradually charged the concn. nitric acid. On completion the nitric acid addition the reaction mixture is stirred at 20–25°C for 20–25 min, and then at 40–45°C the vigorous stirring was continued for 4–6 h more.

The results obtained at nitration of ether **III** in the mixture of acetic acid and acetic anhydride are presented in Table 4.

The analysis of data obtained shows that nitration of ether **III** occurs more readily than that of sulfide **II**: the yield and quality of dinitroether **VI** are higher. Therewith the parameters of the process may be varied within relatively wide limits without hampering its outcome.

As optimal parameters of ether **III** nitration may be recommended the following: temperature 40–45°C, duration 4.5–6.5 h, 90% nitric acid, molar ratio initial ether **III**–nitric acid 1.0 : (2.7–2.9), molar ratio nitric acid–acetic acid 1.0 : (2.1–5.1), molar ratio nitric acid–acetic anhydride 1.0 : (0.3–1.7).

EXPERIMENTAL

Reaction mixtures and crude nitration products in the process of preparation of dinitro derivatives **IV**, **V**, and **VI** were analyzed by TLC (qualitatively) and HPLC (quantitatively), and identification of products was performed by IR and ^{13}C NMR spectroscopy.

IR spectra of compounds were measured on spectrometer Jasco 810-IR in the range 4000–400 cm^{-1} from solutions in CCl_4 or mulls in mineral oil. ^{13}C NMR spectra were registered on spectrometer Bruker CXP-100 in FT mode at operating frequency 22.63 MHz at full decoupling from protons or without decoupling, solvent DMSO, reference HMDS. The assignment of signals was based on chemical shifts, coupling constants, multiplicity of signals, and the intensity ratio of peaks. In interpretation of spectra were used data on chemical shifts of model compounds and calculations of magnetic shielding in aromatic ring.

TLC analyses were carried out on Silufol plates with thin layer of silica gel, spots visualized by solution of tin dichloride, diazotization of the anilines formed, and their azocoupling with α-naphthol. Eluent benzene–ethanol, 10 : 1.

HPLC analyses were performed on Altex model 330 isocratic chromatograph, pump 110, UV detector 153, loop feeders 210 of 20μl volume, Hamilton microsyringes of SNR type, volumes 30, 50, or 100 μl.

The separation and analysis of sulfide **I** and dinitrosulfide **IV** was carried out on a stainless steel column 250 × 4.6 mm with reversed phase Ultrasphere ODS, particle size 5 μ. Analysis and identification of products obtained by nitration of sulfide **I** was performed in the following eluent system: 20–30% water (by volume), 70–80% of acetonitrile, internal reference diphenyl.

Analysis of sulfide **II** and dinitrosulfide **V** was performed by separation of these compounds on a column with reversed phase Bondapac C_{18} using the following eluent system: 33.5% (by volume) of acetonitrile, 54.5% of water, 12% of 2-propanol, and 5 ml of acetic acid added per 0.5 l of eluent. The calculation of chromatograms was done by the method of internal normalization of peaks area.

Analysis of ether **III** and dinitroether **V** was performed by separation of these compounds on a column with reversed phase Rsil or Ultrasphere ODS using the following eluent system: 65% (by volume) of methanol, 35% of water, with addition 25 ml of solution of 18-crown-6 in methanol (0.1 g per 1 ml of methanol) per 1 l of eluent. The calculation of chromatograms was done by the method of internal normalization of peaks area.

To a dispersion of 172.8 g (0.6 mol) of sulfide **I** in 350 ml of chloroform at 20–25°c was added 105 ml of acetic acid (11.3 g, 1.76 mol), and dropwise was added 73.7 ml (99.47 g, 0.9 mol) of nitric acid (ρ 1.35 g cm^{-3}, 57%). In 60 min after addition of nitric acid was added dropwise while stirring at room temperature a solution of 36 ml (67 g; 0.69 mol) of concn. sulfuric acid in 72 ml(76.32g, 1.2 mol) of acetic acid, and the stirring was continued for 5 h more.

In the course of nitration the reaction progress was monitored by sampling every hour and analysis by TLC for the presence of initial sulfide **I**. If the initial sulfide was still detected, to the reaction mixture was added a supplementary amount of nitric and sulfuric acids (in a mixture with acetic acid). After stirring for 1 h the reaction mixture was again analyzed for the presence of initial sulfide I. At the absence of sulfide **I** in the probe the nitration was finished.

After the end of nitration into the reactor 500 ml of water was added for washing out acids from the solution. The mixture was vigorously stirred, after separation the acid water layer was removed, and the organic layer was washed twice more with hot water. Then to the organic solution was added 500 ml of water, and the solvents were distilled off in a vacuum (at residual pressure about 100 mm Hg and at temperature not higher than 45°C). The residue was poured into a crystallization dish with cold water and after stirring was filtered. The precipitate on filter was thoroughly washed with 2-propanol and water, and dried. We obtained 139.86 g (about 70%) of 4-acetylamino-3,4'-dinitrodiphenyl sulfide **IV**, mp 140–141°C (publ. mp 140°C [9]). R_f of the initial

product 0.39, of the final product 0.60 (eluent benzene–ethanol, 10 : 1).

In nitration of 4-acetylamino-2'-nitrodiphenyl sulfide (**II**) 172.8 g (0.6 mol) of the sulfide was dissolved in a mixture of 350 ml of chloroform (or chlorobenzene) and 105 ml (111.3 g; 1.76 mol) of acetic acid. Into the reactor at cooling and stirring was charged a mixture of 72 ml (76.32 g, 1.2 mol) of acetic acid and 36 ml (0.69 mol) of concn. sulfuric acid. At vigorous stirring (with a high-speed agitator or even better, with an internal hydroacoustic device) into the reactor was gradually added dropwise 73.7 ml (99.47 g, 0.9 mol) of nitric acid (ρ 1.35 g cm^{-3}, 57%) maintaining the temperature below 30°C. After the nitric acid was added the reaction mixture was vigorously stirred for 4–5 h. In the course of nitration the reaction progress was monitored by sampling every hour and analysis by TLC for the presence of initial sulfide **II**. If the initial sulfide was still detected after 4–5 h of reaction, to the reaction mixture was added a supplementary amount of nitric acid, and the temperature was raised to 35°C; the reaction mixture at this temperature was stirred for 1/0–1.5 h more.

On completion the nitration the workup of the reaction mixture and isolation of the target nitrosulfide **V** was performed similarly to the above described procedure for nitrosulfide **IV**. The crude 4-acetylamino-2',3-dinitrodiphenyl sulfide **V** was obtained in ~73% yield; content ot the main substance was no less than 97%.

In nitration of 4-acetylamino-2'-nitrodiphenyl ether (III) to a dispersion of 163.2 g (0.6 mol) of the ether in 350 ml of acetic acid was added at 20–25°C 76 ml (82 g, 0.8 mol) of acetic anhydride, and dropwise was added 77 ml (115.5 g, 1.65 mol) of nitric acid (ρ 1.5 g cm^{-3}). The reaction mixture was stirred at room temperature for 20–25 min, and then it was heated to 40–45°C, and stirring at this temperature continued for 4–5 h. The reaction mixture was poured into water, the precipitate was filtered off, washed with water, and dried. We obtained 176 g (93%) of crude 4-acetylamino-2',3-dinitrodiphenyl ether (**VI**) with content of the main substance 98%, mp 98–99°C, R_f of nitroether **VI** 0.56, of initial ether **III** 0.30 (eluent benzene–ethanol, 10 : 2). Found, %: C 53.05; H 3.52; N 13.28. $C_{14}H_{11}N_3O_6$. Calculated, %: C 53.00; H 3.49; N 13.24.

4-Amino-4'-nitrodiphenyl sulfide was methylated with dimethyl sulfate at 35°C within 3 h by procedure [13].

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