

## By-products in the Rearrangement of *N*-Methyl-*N*-phenylnitramine.

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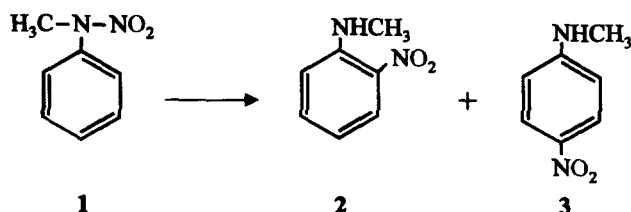
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**Abstract:** *N*-Methyl-*N*-phenylnitramine was rearranged in the aqueous dioxane – sulphuric acid mixture to 2-nitro- and 4-nitro-*N*-methylanilines. The isomer ratio was independent of the acidity within the range of  $-0.3 > H_0 > -2.8$ . Some by-products were isolated and identified *e.g.* *N*-methyl-*N*-nitrosoaniline, its 2-nitro and 4-nitro derivatives, nitrosobenzene and 4',4''-bis-(*N*-methylanino)-3',3''- dinitrodiphenylmethane. The mechanism of the nitramine rearrangement is discussed.

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### INTRODUCTION

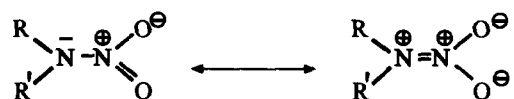
The mechanism of the nitramine rearrangement has been the subject of controversy almost from the first discovery of nitramines by Bamberger.<sup>1</sup> Nowadays, the White's theory of the solvent-caged-pair is considered to be a satisfactory explanation of the rearrangement. The mechanism involves protonation of the nitramine molecule on the nitrogen atom, homolytic cleavage of the N–N bond and migration of the NO<sub>2</sub> radical in the solvent cage which is responsible for the intramolecularity of the rearrangement. Recombination of radical and cation-radical gives *ortho* and *para*  $\sigma$ -complexes, and then – corresponding nitroanilines. Detection of anilines and nitrous acid as the side products is perceived to be the argument in favour of this theory.<sup>2</sup>



There are, however, some reactions involving analogous nitro group migrations, to which the solvent-caged-pair mechanism cannot be applied. 2,3-Dinitroaniline isomerizes to the mixture of 3,4-dinitroaniline and 2,5-dinitroaniline under the influence of hot, concentrated sulphuric acid.<sup>3</sup> 2,5-Dimethyl-2-nitrocyclohexa-3,5-dienone, obtained by nitration of 2,5-xyleneol, rearranges at ambient temperature to the mixture of 4-nitro-2,5-dimethylphenol and 2-nitro-3,6-dimethylphenol in 1:2 ratio.<sup>4</sup> 3,4-Dimethyl-4-nitrocyclohexa-2,5-dienone also rearranges at room temperature in hexane solution to 2-nitro and 6-nitro-3,4-xyleneols; the activation energy (23 kcal/mol)<sup>5</sup> seems to be too low to suggest a dissociative mechanism, with homolytic cleavage of the C–N

bond. Anomalous behaviour of the acetanilide-type compounds in the nitration<sup>6</sup> can be explained if we assume preliminary *N*-nitration with subsequent migration of the nitro group according to the same mechanism as in the nitramine rearrangement.<sup>7</sup> There are also some aromatic rearrangements of intramolecular character, for which the free radical mechanism has been ruled out (e.g. benzidine and Claisen rearrangement) and it is known that migration of a substituent from heteroatom to the ring follows the sigmatropic shift path. On the other hand, in some intermolecular transformations, as the Fischer-Hepp rearrangement of *N*-nitroso-anilines and isomerization of *N*-phenylhydroxylamines into 4-aminophenol, a cage effect has never been observed.<sup>8</sup> In this context, it seems obvious that the mechanism of nitramine rearrangement requires a reconsideration.

The most incomprehensible aspect of the mechanism is the role of an acidic catalyst. *N,N*-Dimethylnitramine molecule is planar and the bond length (N—N, 132 pm) indicates a high bond order.<sup>9</sup> Computational studies have demonstrated a high (10–14 kcal/mol) rotational energy barrier of the N—NO<sub>2</sub> bond in aliphatic nitramines.<sup>10</sup> There is no data for *N*-methyl-*N*-phenylnitramine, but the nitramino group has always been considered to be the resonance hybrid of two mesomeric forms:



The scheme given above presents a molecule containing a set of four  $\pi$ -orbitals occupied by three electron pairs. There is no unshared electron pair on the nitrogen atom, so the site of protonation is not self-evident since it has been shown that oxygen may be a basic center as well.<sup>11</sup> Even the influence of an acidic catalyst on isomer distribution remains ambiguous. It is known that the transformation of *N*-phenylnitramine in concentrated sulphuric or perchloric acid gives 2-nitroaniline, while the transformation in diluted aqueous solutions also produces significant amounts of 4-nitroaniline.<sup>12</sup> In the rearrangement of **1** in water–glycerol mixture, a marked increase in *ortho/para* ratio is observed with the increased proportion of glycerol in the solution. White has interpreted this effect as a result of viscosity changes,<sup>13</sup> however it is known that in the case of ternary systems their acidity is dependent on the solvent ratio. Our primary aim was to establish the acidity profile of the *N*-methyl-*N*-phenylnitramine (**1**) rearrangement *i.e.* dependence of the *ortho/para* ratio vs. acidity. We employed aqueous dioxane (60% v/v) - sulphuric acid system for which the Hammett's acidity scale was elaborated.<sup>14</sup> The results were rather confusing, they indicated that transformation of a nitramine under the influence of an acid was a more complex process than it had been assumed to be.

## RESULTS

Small (1–3 mmoles) samples of **1** were dissolved in dioxane, tenfold excess of aqueous sulphuric acid was added and the mixtures were left in the dark at room temperature until all the nitramine rearranged. The solutions were diluted with cold water, neutralised and extracted with methylene chloride. The extracts were dried and analysed on a gas chromatograph, equipped with a capillary column and flame ionisation detector. Compounds **2** and **3** were identified by the addition of standards, the responses of FID were converted into 1/2 *ortho/para* ratios and plotted *versus* acidity expressed as H<sub>0</sub>. When the acidity increased from –0.3 to –2.8 the 1/2 *o/p* ratio decreased from nearly 10 to *ca.* 2 and levelled off at a higher concentration of sulphuric acid. The

plot was a mirror reflection of an analogous diagram for *N*-phenylnitramine based on the literature data.<sup>12</sup> Such a difference in behaviour of the primary and secondary nitramine seems inexplicable, however a typical chromatogram presented on the figure below shows that our results are questionable: the reaction mixture contains several compounds in comparable concentrations.

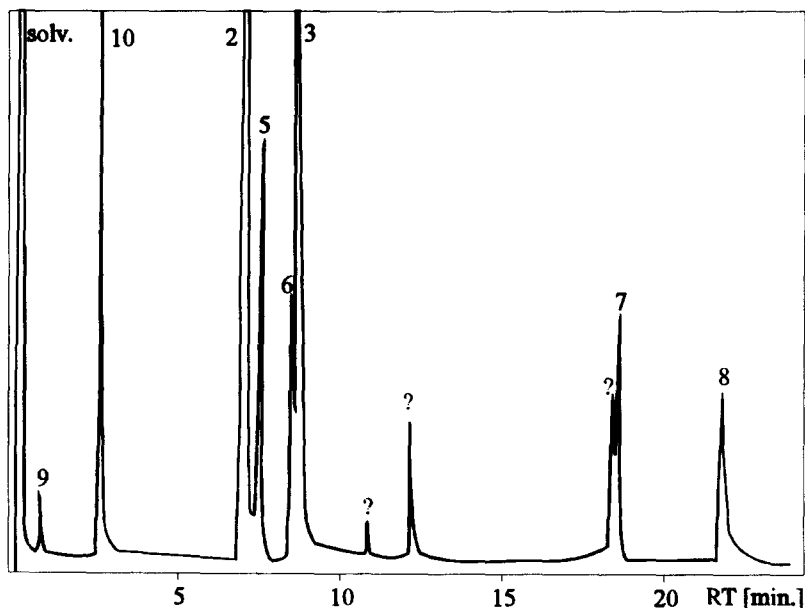


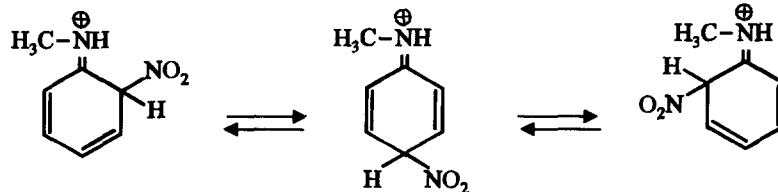
Fig. 1. Products of *N*-methyl-*N*-phenylnitramine rearrangement in aqueous dioxane - sulphuric acid mixture; (29% H<sub>2</sub>SO<sub>4</sub>, H<sub>0</sub> = -1.5): 9, nitrosobenzene (0.3%); 10, *N*-methylaniline (3%); 2, *N*-methyl-2-nitroaniline (75%); 5, *N*-methyl-*N*-nitroso-2-nitroaniline (2%); 6, *N*-methyl-*N*-nitroso-4-nitroaniline (1.3%); 3, *N*-methyl-4-nitroaniline (12%); 7, 4',4''-bis-(methylamino)-3',3''-dinitrodiphenylmethane (2%); 8, 2,4-bis-(4-methyl-amino-3-nitrobenzyl)-*N*-methyl-6-nitroaniline (3%).

Selected samples were separated by the preparative layer chromatography, the compounds were purified by crystallisation and identified by spectroscopic methods. The structures of *N*-methyl-*N*-nitrosoaniline (4) and its 2-nitro- (5) and 4-nitro- (6) derivatives were confirmed by independent syntheses and compounds used as the standards for GC analyses. The compound RT = 19 min. was identified as 4',4''-bis-(methylamino)-3',3''-dinitrodiphenylmethane (7). Its structure seemed to be important for understanding of the course of the reaction. The proton NMR spectra indicated the presence of 1,2,4-trisubstituted aromatic ring; chemical shifts were similar to those observed in the spectra of para-substituted *N*-methyl-2-nitroanilines. The signal at 2.94 ppm, assigned to the *N*-methyl group, was a doublet (<sup>3</sup>J = 5 Hz); after addition of CH<sub>3</sub>OD to the solution of the sample in DMSO-*d*<sub>6</sub>, multiplet at 8.11 ppm disappeared and the signal of the *N*-methyl group turned into a singlet. The proton on the heteroatom was very sensitive to the solvent and its signal in acetone-*d*<sub>6</sub> solution appeared at 2.76 ppm. Infrared spectra confirmed the presence of a nitro group (1352, 1525 cm<sup>-1</sup>) *ortho* to the methylamino substituent. In the mass spectrum, strong peaks at *m/z* 316 and 195 revealed that the molecule consisted of two *N*-methyl-2-nitroaniline residues joined with a methylene group. The presence of the bridge

was observed in the carbon NMR spectrum as the peak at 38.9 ppm, next to the signal (29.8 ppm) of *N*-methyl group. By analogy, the structure of 2,4-bis-(4-methylamino-3-nitrobenzyl)-*N*-methyl-6-nitroaniline (**8**, *m/z* 480) was assigned to the compound forming yellow crystals having the m.p. 223°C.

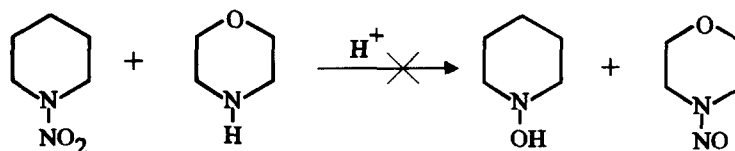


The nitramine rearrangement is accompanied with some side reactions irrespective of the acidity, however the relative rates of the rearrangement as well as subsequent processes are influenced by the acid concentration. *N*-Methyl-*N*-nitrosoaniline is detected (1 – 6%) only at lower ( $H_0 > -1$ ) acidities while an unidentified compound RT = 11 min. appears when the acidity of the reaction medium exceeds  $H_0 = -1.5$ . In diluted acid, **3** and **6** are present in nearly the same concentration, hence 1/2 *ortho/para* ratios are too high (e.g. 6.25 for 10.5%  $H_2SO_4$ ). We have assumed that the compounds **5** and **6** as well as **7** and **8** are the artefacts formed from the rearrangement products (**2**, **3**). The isomer distributions were re-counted considering also correction factors (0.7 to 1.4) for GC estimations. It turned out that the acidity, within the interval of  $-0.3 > H_0 > -2.8$ , had no influence on the proportion of isomers since the 1/2 *o/p* ratios were scattered in the range of 2 – 3.5 (e.g. 2.54 for 10.5%  $H_2SO_4$ ). The simplest explanation involves equilibrium of the Wheland's intermediates:



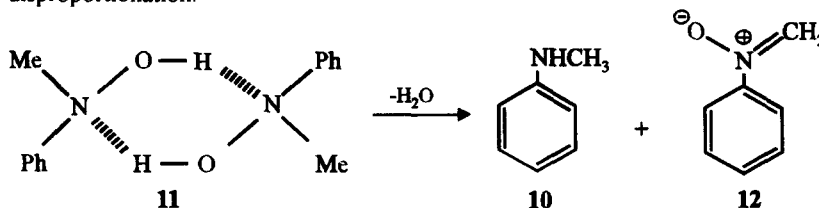
It seems that under the conditions employed, the nitro substituent migrates around aromatic ring several times until the expulsion of the C-proton fixes its position. White has rearranged isotopically labeled **1** ([2,6- $H_2$ ]-*N*-methyl-*N*-phenylnitramine) and found that the isomer distribution is exactly the same as obtained by the rearrangement of an ordinary **1**.<sup>15</sup> The absence of the heavy atom kinetic isotope effect in the rearrangement of [4- $^{14}C$ ]-**1** and [2- $^{14}C$ ]-**1**<sup>16</sup> also militates in favour of this concept. It is inferred from the aforementioned results that the proportion of the *ortho* and *para* isomers reflects relative stabilities of the corresponding  $\sigma$ -complexes. Their interconversion by the simple sigmatropic shift of the nitro group seems to be improbable. The analysis of by-products provides some information on the nature of this migration.

The only possible source of the nitroso group present in **4**, **5** and **6** is *N*-methyl-*N*-phenylnitramine. In fact, the rearrangement of **1** in the presence of aniline gives benzenediazonium cation which has been coupled with 2-naphthol; we isolated benzene-azo- $\beta$ -naphthol and the rearrangement products **2** and **3**. The experiment was repeated with the use of 4-methanesulphonylaniline as the scavenger of nitrosating species; again nitroanilines **2** (62 %) and **3** (18 %) were isolated as well as the dye (5 %). The cross-nitrosation can be separated from the rearrangement in a simple way, by using aliphatic nitramines as the substrates. We have tried to "rearrange" *N*-nitropiperidine in the presence of morpholine.



Under typical conditions employed in the rearrangement of **1**, the mixture remains unchanged. After several hours at an elevated temperature, GC analyses indicated formation of *N*-nitrosomorpholine in minute amounts (up to 8%) but 1-hydroxypiperidine was not detected. The nitrosoamine might have been formed on a different path involving *e.g.* intermediacy of nitrogen(IV) oxide formed by the thermally induced homolytic cleavage of the N-N bond. Considering much more severe conditions required for the cross nitrosation in this case, it seems evident that the nitrosating properties of a nitramine are observed when the nitramino group is bonded to an aromatic system.

Transfer of the nitroso group from the nitramine **1** to the aniline must give the unstable *N*-methyl-*N*-phenylhydroxylamine (**11**). It is well known that methylation of *N*-phenylhydroxylamine gives unidentified products of higher molecular weight, although other *N*-alkyl-*N*-phenylhydroxylamines can be prepared by simple alkylations in aqueous pyridine solutions. It has also been demonstrated that these compounds are very susceptible to disproportionation.<sup>17</sup>



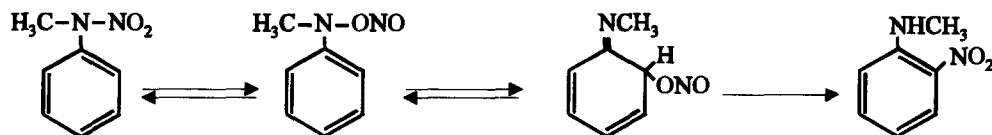
This process accounts for the instability of **11** and its transformation into **10** and *N*-phenylnitrene whose hydrolytic cleavage must give formaldehyde. We have found that condensation of formaldehyde with **2** in acidic, aqueous dioxane gives the same compound **7** which was found among the products of rearrangement. The reaction is rather slow at  $H_0 = -0.9$  but very efficient, and after a few days **7** has been isolated in a high yield. The result may be considered as indirect evidence for the involvement of **11** in the nitramine rearrangement.

A doubtful point of the White's theory is the concept of the solvent cage. Obviously, the solvent effect accounts for the facilitated recombination of radicals generated by photolysis or thermal, homolytic dissociation in solutions. It seems questionable whether it can also be responsible for the intramolecularity of the  $\text{NO}_2$  radical migration, considering that the cage is made of mobile water molecules which react readily with nitrogen(IV) oxide. We carried out rearrangements of neat **1** exposing the crystalline substrate to anhydrous hydrogen fluoride or vapours of trifluoroacetic acid, and to ammonia after the reaction. There was no solvent and solvent cage, but the results were quite similar. Again **2** was the main product, compounds **3**, **6**, **7** and **8** were isolated and the remaining ones were detected chromatographically. The yields of rearrangement products (**2**, **3**), their *N*-nitroso derivatives (**5**, **6**) and condensation products (**7**, **8**) were 39, 20 and 18% respectively; the corrected 1/2 *ortho/para* ratio was 2.0. The result indicates that the **1** molecule can transform intramolecularly without any assistance of solvent molecules.

## DISCUSSION

Nitramine rearrangement involves not only the migration of the *N*-nitro group to aromatic ring, but also some other transformations. By analogy, benzidine rearrangement designates the isomerization of hydrazobenzene into benzidine, however semidines, diphenylines, azobenzene and some other compounds are produced simultaneously.<sup>8</sup> A reliable theory should account for the formation of all of them. In some cases it is possible and instructive to suppress side reactions and investigate only one of all the possible transformations e.g. it has been shown that the Wallach rearrangement under kinetic conditions is quantitative. On the other hand, it is known that at preparative concentrations of the substrate, 4-hydroxyazobenzene is contaminated with significant amounts of azobenzene, aniline and a polymeric compound of an unknown structure.<sup>18</sup> The kinetic approach to mechanistic problems gives sometimes surprising results. *N*-Methyl-*N*-nitrosoaniline in ethanolic solution rearranges to *N*-methyl-4-nitrosoaniline under the influence of hydrogen chloride, however under kinetic conditions only denitrosation has been observed.<sup>19</sup> Alternatively, the mechanisms of reactions can be investigated under conditions that are usually employed in preparative experiments with the use of chromatographic methods. Detection and identification of side products provides important information on reactive intermediates and, consequently, on the mechanism of the reaction.

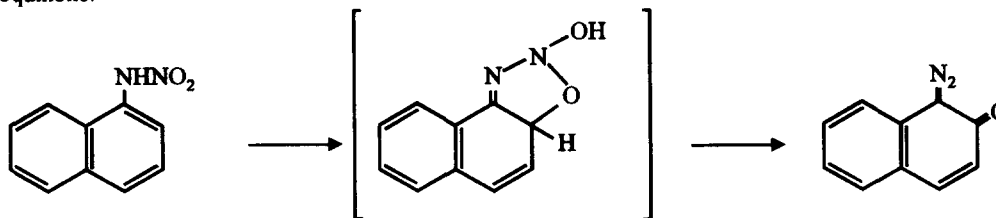
*N*-Methylaniline and nitrous (not nitric) acid were detected by White as the side products which were formed during rearrangement of **1** in diluted perchloric acid. According to his solvent-caged-pair theory, the compounds came into being as the result of the decomposition of the cage and reduction of the radical and radical-cation. The nature of the reducing agent is unknown,<sup>20</sup> and its presence in perchloric acid solutions seems rather doubtful for us. In fact, White never detected nitrous acid in the reaction mixture. He reported that during **1** rearrangement, carried out in the presence of 4-nitroaniline, 4-nitrobenzenediazonium cation was formed and detected spectrophotometrically after coupling with 1-dimethylaminonaphthalene.<sup>2</sup> The result indicated that either **1** or an intermediate formed thereof had nitrosating properties. Nitrous acid is not the only possible nitrosating or diazotating species. It is well known that nitroso group transfer from *N*-nitrosoamine to amine can occur directly, without the intermediacy of nitrous acid.<sup>21</sup> The structure of the nitrosating intermediate and its source is a very important problem. The most probable candidate is the *N*-nitrito form of **1**, as postulated by Ingold.<sup>22</sup>



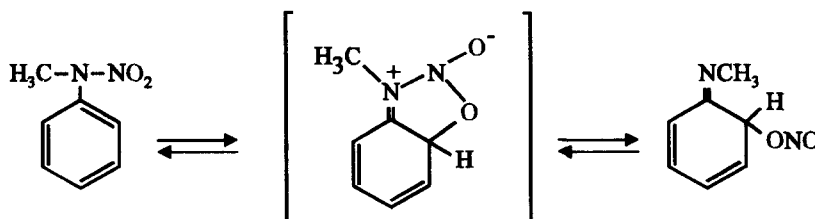
The N-O-N-O sequence is encountered in the furoxan structure where it forms a part of the aromatic system, but simple *O*-nitrosohydroxylamines are not known. The reversible transformation of the *C*-nitro group into *C*-nitrito form has been demonstrated by Ridd with the use of a spectroscopic method.<sup>23</sup> Hartshorn *et al.* have observed that *O*-nitrosation can occur, and 4-hydroxydienones are converted into 4-nitrodienones *via* the corresponding 4-nitritodienones.<sup>24</sup> An analogous nitro–nitrito transformation may occur with aromatic nitramines, however its nature is not clear. At least two possibilities must be taken into consideration: a concerted rearrangement involving three-membered, cyclic transition state or a homolysis–recombination pathway. A molecular orbital study of reversible transformation of organic nitrates into peroxyxynitrites reveals

a large barrier for concerted rearrangement (60 kcal/mol) as compared with a free radical path (11 kcal/mol).<sup>25</sup> In the case of nitramines the second mechanism is not so self-evident since activation energy for the N-NO<sub>2</sub> homolytic cleavage (46 kcal/mol) is much higher than in the case of O-NO<sub>2</sub> bond in nitrates.<sup>26</sup> According to our observations, transformation of **1** into nitrosating species requires assistance of the aromatic system.

In 1922 Bamberger described transformation of *N*-(1-naphthyl)-nitramine into relatively stable diazoquinone.<sup>27</sup>



The reaction proceeds smoothly under mild conditions; a hypothetical intermediate may possess a benzo-1,2,3-oxadiazole structure. The nature of the nitro–nitrito transformation finds a simple explanation if we assume an analogous structure for the intermediate in the nitramine rearrangement.



The *C*-nitrito group can migrate to the *para* position or return to the nitrogen atom by [3, 3] sigmatropic shift. There is no need to presume a strained transition state or homolytic cleavage of the N-N bond. The scheme above presents valence tautomerism of *N*-methyl-*N*-phenylnitramine.

In all discussions on the mechanism of the nitramine rearrangement it is presumed without any evidence that protonation of the substrate begins the transformation. The catalytic effect of an acid does not necessarily mean that proton is bonded to the intact nitramine molecule, in the preliminary step of the rearrangement. It is well known that amides are weak bases and protonation occurs on the oxygen not nitrogen atom; amides of nitric acid probably behave similarly. In our opinion, intermediates in the nitramine rearrangement can be formed without any intervention of proton. Thermal rearrangement of nitramines of various types<sup>28</sup> militates in favour of this idea. Protonation can occur when positive charge disappears from the amino nitrogen *i.e.* *C*-nitrito forms of **1** react as proton acceptors. *N*-Protonation facilitates the expulsion of a ring proton and reconstruction of the aromatic sextet. It has been demonstrated by White that ring substituents influence strongly the rate of the rearrangement; the second-order rate constants vary within the six orders of magnitude<sup>29</sup> and so does the basicity constants of ring substituted anilines; such a convergence cannot be incidental.

## EXPERIMENTAL

Preparation of *N*-methyl-*N*-phenylnitramine (**1**) was described previously.<sup>30</sup> *N*-Methylnitroanilines, their *N*-nitroso derivatives and other reference compounds were obtained according to the well known procedures. The samples were analysed on the Hewlett-Packard HP 5890/II gas chromatograph equipped with HP-1 capillary column (poly-dimethylsiloxane, 10 m × 0.53 mm × 0.88 μm) to estimate the retention times (RT) and correction factors. Satisfactory separation without decomposition of the compounds was achieved when the temperature was raised from 40°C to 90°C at the rate of 10°C/min. and then to 200°C at the rate of 20°C/min. The nitramine **1** was rearranged in 25 runs varying in the concentration of sulphuric acid from 7.6 to 46.2%. A typical run is described below.

*Rearrangements in solutions:* *N*-Methyl-*N*-phenylnitramine (151 mg, 1 mmol) was dissolved in 2.3 ml of dioxane. Sulphuric acid (0.56 ml of 96% H<sub>2</sub>SO<sub>4</sub>, 10 mmol) was diluted with 1.55 ml of water and the solutions were combined. The mixture (*H*<sub>0</sub> = −0.95) was maintained in the dark, at room temperature for 5 days. It was diluted with 50 ml of ice and water, and extracted with five portions (10–15 ml) of chloroform. The extract was diluted with *n*-hexane, dried over anhydrous magnesium sulphate, concentrated and chromatographed. The compounds detected and identified by addition of standards, are listed in the order of appearance on chromatograms: **9** (0.5%), **10** (8.2%), **4** (0.7%), **2** (67.9%), **5** (4.1%), **6** (4.5%), **3** (7.2%), **7** (1.9%) and **8** (4.2%).

*Rearrangement of 1 in the presence of 4-methanesulphonylaniline:* Concentrated sulphuric acid (10.2 g of 96% H<sub>2</sub>SO<sub>4</sub>) was dissolved in 20.4 g of cold water and 4-methanesulphonylaniline (1.71 g, 0.01 mol) was added to the solution. *N*-Methyl-*N*-phenylnitramine (1.52 g, 0.01 mol) was dissolved in 31 ml of dioxane and the cold solutions were combined. The mixture was left in the dark at room temperature for 6 h and cooled to −5°C. It was poured into the solution of 2-naphthol (0.72 g, 5 mmol) in aqueous potassium hydroxide (100 ml of 3N KOH). The mixture was maintained at room temperature for 2 h and extracted (3 × 50 ml) with methylene chloride. GC analyses indicated the presence of 2-nitro (24%) and 4-nitro-*N*-methylaniline (7%). The products were separated by the preparative layer chromatography. *N*-Methyl-2-nitroaniline (0.95 g, 62%) and *N*-methyl-4-nitroaniline (0.27 g, 18%) were isolated and identified by their mixed melting points. The crude dye was crystallised from acetic acid and 1-(4-methanesulphonylphenylazo)-2-naphthol (0.17 g) was obtained as red needles m.p. and mixed m.p. 227–229°C.

*Rearrangement of neat 1:* *N*-Methyl-*N*-phenylnitramine (3.02 g, 20 mmol) and trifluoroacetic acid (1.5 ml) in separate, open vessels were maintained in a desiccator for five days. A brown, tarry mixture was dissolved in methylene chloride, extracted with aqueous sodium bicarbonate and dried over magnesium sulphate. The solvent was evaporated, the residue was dissolved in acetone and chromatographed on twenty glass plates (20 × 20 × 0.1 cm, Kieselgel 60 G) using toluene as an eluent. Coloured zones were collected and extracted with acetone. The solvent was evaporated and products purified by crystallisation. The compounds **2** (1.10 g), **3** (70 mg) and **6** (0.35 g) were isolated and identified by their mixed melting points with original samples. 4',4''-bis-(*N*-Methylamino)-3',3''-dinitrodiphenylmethane (**5**, 0.45 g) was identified on the basis of spectral data. Elemental analysis: C, 60.03%; H, 5.17%; N, 17.90%. Calculated for C<sub>15</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>: C, 59.95%; H, 5.10%; N, 17.71%. MS, *m/z* (int.): 316 (*M*<sup>+</sup>, 100), 299 (4), 286 (4), 236 (15), 223 (13), 165 (29), 119 (35), 118 (57). IR (KBr): 1325, 1525 (NO<sub>2</sub>); 1400, 1417 (N-CH<sub>3</sub> deformations); 1570, 1631 (1,2,4-substituted ring stretching); 2814, 2852, 2916 (CH<sub>2</sub> and N-CH<sub>3</sub> stretch); 3985 (N-H stretching vibrations). <sup>1</sup>H-NMR

(DMSO- $d_6$ ):  $\delta$  8.11, q  $^3J = 5$  Hz, 2H (NH); 7.93, d  $^4J = 2$  Hz, 2H (H-2' and H-2''); 7.44, dd  $^3J = 8$  and  $^4J = 2$  Hz, 2H (H-6' and H-6''); 6.94, d  $^3J = 8$  Hz, 2H (H-5' and H-5''); 3.83, s, 2H (CH<sub>2</sub>); 2.94, d  $^3J = 5$  Hz, 6H (CH<sub>3</sub>).  $^{13}\text{C-NMR}$  (Pyr- $d_5$ ): 145.6 (C-4); 137.7 (C-6); 132.1 (C-3); 128.2 (C-1); 126.2 (C-2); 114.8 (C-5); 338.9 (-CH<sub>2</sub>-); 29.8 (-CH<sub>3</sub>).

The compound **8** of the highest RT value was isolated in smaller (100 mg) yield and identified as 2,4-bis-(4-methylamino-3-nitrobenzyl)-*N*-methyl-6-nitroaniline. Elemental analysis: C, 57.57%; H, 5.10%; N, 17.40%. Calcd. for C<sub>23</sub>H<sub>24</sub>N<sub>6</sub>O<sub>6</sub>: C, 57.49%; H, 5.03%; N, 17.49%. MS, *m/z* (int.): 480 (M<sup>+</sup>, 7), 465 (98), 450 (10), 329 (84), 315 (77), 178 (91), 167 (63), 105 (100). IR (KBr): 1354, 1524 (NO<sub>2</sub>), 2855, 2918 (CH<sub>2</sub> and CH<sub>3</sub> groups); 3392 (NH).

The neat nitramine **1** was rearranged analogously under the influence of hydrogen fluoride, obtained in desiccator from calcium fluoride and sulphuric acid. The reaction mixture was worked up and analysed by GC as described above. The results were the same within an experimental error.

*Condensation of 2 with formaldehyde:* *N*-Methyl-2-nitroaniline (1.52 g, 0.01 mol) and formalin (1.0 g) were dissolved in the mixture of water (13.8 g), sulphuric acid (10.2 g) and dioxane (22.4 g). The solution was stirred at 40°C for 70 h. A red precipitate was collected by filtration, washed with water and dried. After crystallisation from toluene 1.40 g (90%) of 4',4''-bis-(methylamino)-3',3''-dinitrodiphenylmethane (**7**); m.p. and mixed m.p. with the afore mentioned specimen 193–195°C.

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