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Synthesis and Reactions of Some Dinitrodiazoquinones

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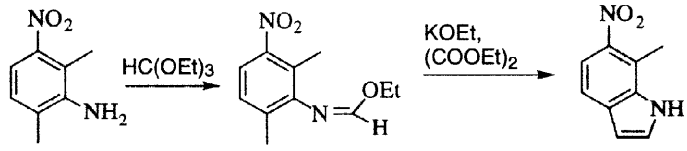
Abstract: Some novel highly substituted diazoquinones have been synthesised in one step from simple anilines by treatment with nitric acid in sulfuric acid solution. The reaction is proposed to proceed *via* an *N*,3,4,5-tetranitroaniline which on its reaction pathway undergoes a nitro-nitrito rearrangement.

Introduction: Some time ago we reported[1] that a variety of nitroindoles can be conveniently prepared at ambient temperature by treatment of *e.g.* *N*-(2-alkyl-3-nitrophenyl)imidates with alkoxides in the presence of dialkyl oxalates. The imidates were made from the appropriate alkylnitroanilines. Thus, *e. g.* 2,6-dimethyl-aniline was nitrated with nitric acid to give 2,6-dimethyl-3-nitroaniline **1** which in turn was condensed with refluxing triethyl orthoformate yielding the imidate **2**, which could be cyclized to 7-methyl-6-nitroindole (**3**), (Scheme 1).



1 2 3

Scheme 1: Synthesis of nitroindoles from nitroanilines.

Attempts to prepare 2,6-dimethyl-3,5-dinitroaniline (**4**), a known compound,[2] from 2,6-dimethylaniline by a similar nitration (3 eq. HNO_3 instead of 1 eq.) gave a yellow substance that decomposed violently at approximately 150 °C. The product showed an intense IR-absorption at 2145 cm^{-1}, only one ^{1}H-NMR signal at 2.36 ppm and five ^{13}C-NMR signals at 161, 144, 137, 85 and 14 ppm. This information pointed towards the structure **5**, which was later confirmed by X-ray

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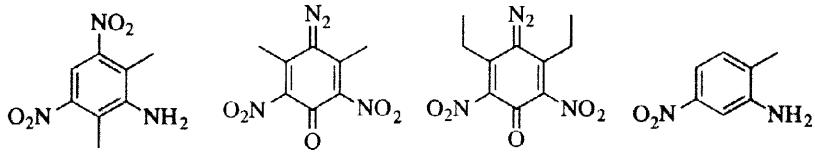
crystallography (Figure 1). 3,5-Diethyl-2,6-dinitro-*p*-diazoquinone **6**, also a crystalline compound, could be prepared by a similar procedure.



4 **5** **6** **7**

Most organic chemists are familiar with both aromatic and aliphatic diazo compounds. Perhaps a little less known are the diazoquinones[3] (also called quinone diazides, diazo anhydrides, diazo oxides), a class of substances that takes an intermediate position between their aromatic and aliphatic relatives. Thus, they may undergo the same reactions as diazonium salts, aliphatic diazoketones and diazoalkanes, depending upon the structure of the diazoquinone and the conditions used.

Diazoquinones[3] are energetic, usually yellow substances that are sensitive towards heat[4] light[5,6] and shocks.[7] Diazoquinones have found applications in diverse areas like primary explosives,[7] stabilizers in polymers,[8] photolithographic technology[3] and photoaffinity probes for enzymes[9,10] etc.[3]

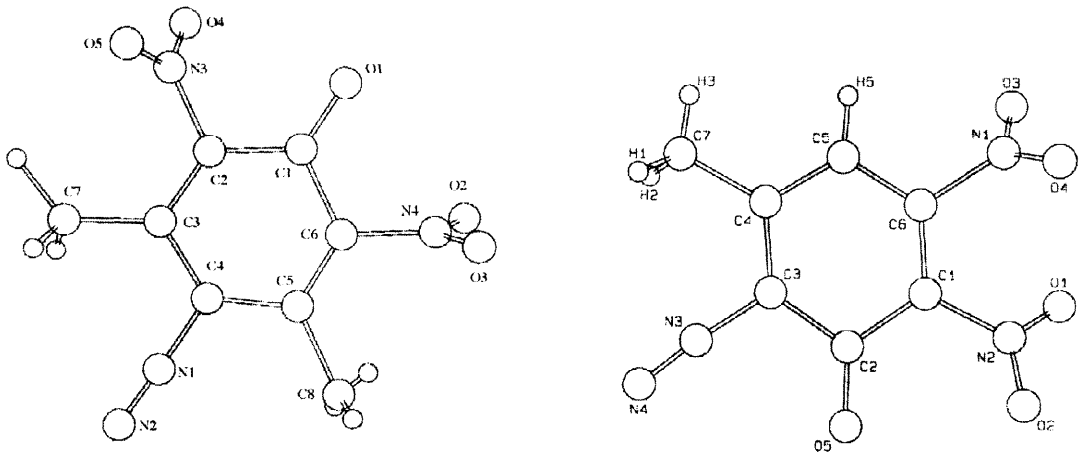
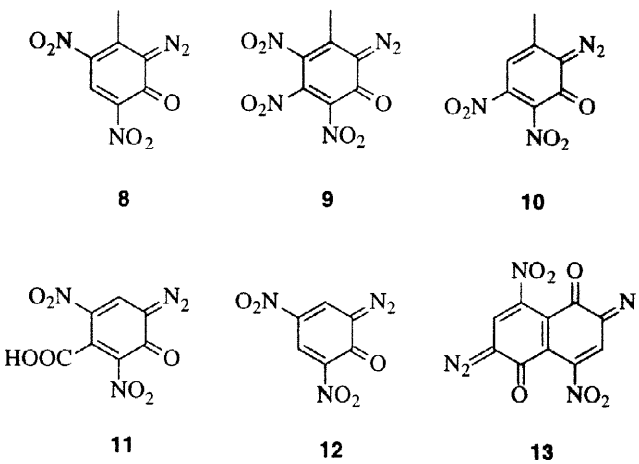


Figure 1: X-Ray structure of diazoquinones **5** and **10**.

The most important synthetic routes towards diazoquinones are diazotation of hydroxy anilines[11] and treatment of toluenesulfohydrazones with base.[12,13] Other routes include nitrosation of phenols[14] and hydroxylation of diazonium compounds.[15] It has been shown that phenolics in food react with nitrite under gastric conditions to produce mutagenic diazoquinones.[16]

This paper will describe formation of diazoquinones by nitration of anilines. In the literature only a few examples of this synthetic route to diazoquinones has been reported. Thus Wilson, Nielsen and coworkers prepared some nitrated *o*-diazoquinones **8-13**.[17,18] The 3-methyl-4,6-dinitro-*o*-diazoquinone (**8**) had previously been prepared by Glowiak[19] in one of the earlier investigations of the structures of *o*-diazoquinones.

Results and discussion: Nitration of 2-methyl-5-nitroaniline (**7**), wherein only one *ortho* position is blocked, gave a product in good yield, that also crystallised well. This product had previously been synthesized by Nielsen *et al.* in a low yield and was originally assigned the structure **8**[18] but later studies suggested it to be the 3-methyl-5,6-dinitro-*o*-diazoquinone (**10**),[7] which has now been confirmed by X-ray crystallography (Figure 1). The nitration of **7** was originally reported by Kapil[20] who incorrectly claimed to have obtained 2-amino-4,6-dinitrotoluene.



The X-ray crystallographic data now obtained for the diazoquinones **5**, **6** and **10** correspond well with data obtained by other workers[21-24] and support the general structures shown below as valid descriptions of these compounds (Figure 2).

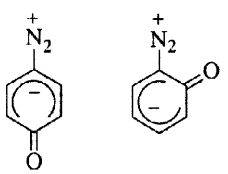
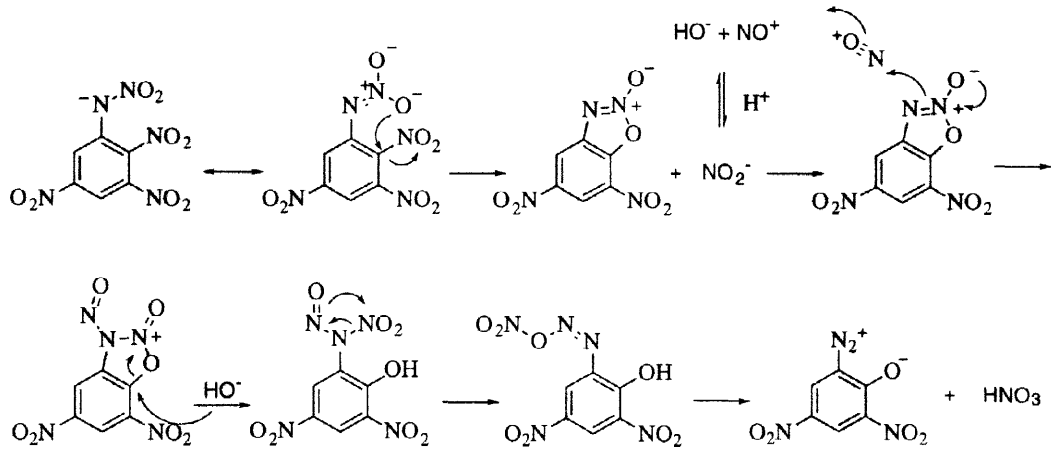


Figure 2: Structures of diazoquinones.

The formation of *o*-diazoquinones as by-products during nitrations of aniline derivatives has been accounted for in terms of *N*-nitration followed by intramolecular displacement of a nitro group. The following mechanism has been proposed by Scilly (Scheme 2).[25] Later Wilson found some support for such a formulation. They could isolate the intermediate nitramines and transform them into the corresponding *o*-diazoquinones by heating them in ethyl acetate.[7]

An analogous formulation seemed unlikely for the easy formation of the *p*-diazoquinones now observed and to elucidate this mechanism these reactions were studied in more detail. By slightly altering the reaction conditions (using HNO_3 d=1.48 rather than HNO_3 d=1.52) it was possible to isolate a colourless inter-mediate, which under mild conditions *e. g.* heating to 50-60 °C in benzene, could be converted to the *p*-diazoquinone **5**. This transformation also gradually occurs when storing the intermediate for a few weeks at room temperature.



Scheme 2: (from reference 21).

Treatment of the crude reaction mixture from the nitration of 2,6-dimethylaniline with methanol gave a somewhat more stable methylated nitramine derivative, which after analysis with NMR and MS, was considered to be the *O*-methyl derivative **14**, isolated as a mixture of the two stereoisomers **14a** and **14b** in a ratio of 84:16. Similar behaviour was observed if the reaction mixture was treated with ethanol, thus **15a** and **15b** were obtained in a 80:20 ratio. These derivatives were stable at room temperature, but could be converted to the diazoquinone **5** by heating them in a solvent *e. g.* benzene.

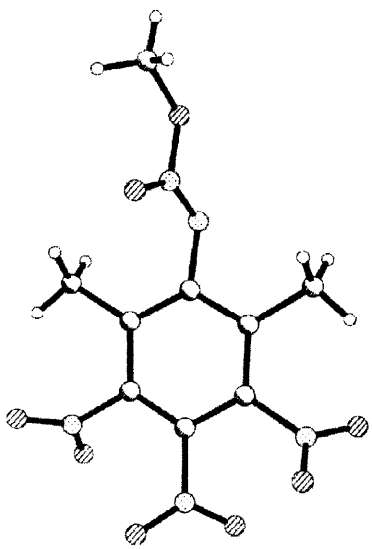


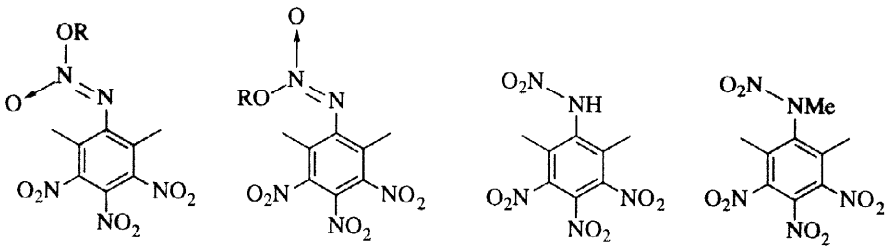
Figure 3: X-Ray structure of **14a**.

O-Alkylnitramines have been known since the late 19th century when Franchimont and Umbgrove alkylated silver salts (sodium or potassium salts give the *N*-methylated nitramines) of aliphatic nitramines with methyl iodide,[26-29] whereas Bamberger observed the same chemistry with aromatic nitramines.[30-32] Soon thereafter alkylations were also performed using diazomethane,[33] a reaction later more thoroughly studied by Unterhalt et al.[34] The reaction of nitramines with dicyclohexyl carbodiimide also produces *O*-alkylated nitramines as byproducts.[35]

Although already discussed by Bamberger,[31] and Franchimont,[29] it was not until the early 60's that proof for the existence of *E/Z* isomerism of the *O*-alkylated nitramines appeared.[36] Lamberton rationalized how to distinguish the two isomers using NMR,[37] and Avakyan *et al.* did the same using IR.[38] The assignments of isomers from our reactions were consistent with both methods.

The crystals of **14a**, obtained by treating a benzene solution of the isomer mixture of **14a** and **14b** with isooctane, were good enough to allow determination of the structure by X-ray crystallography, which confirmed the assignment as an *E*-*O*-methyl nitramine (Figure 3). From the similarity of the NMR data of the intermediate with those of **14**, it was concluded that it had the structure **16** and that it

was a true intermediate in the pathway leading to *p*-diazoquinones. To our knowledge this is the first report of a 'normal' acid catalysed esterification of a nitramine.



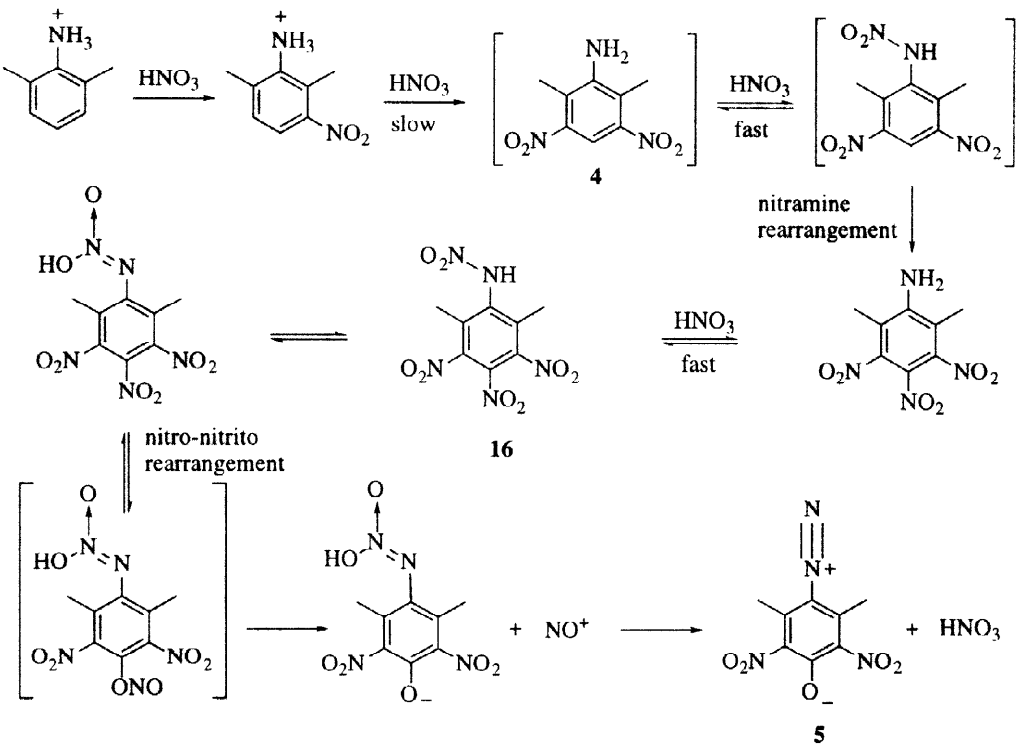
14a: R=Me
15a: R=Et

14b: R=Me
15b: R=Et

16

17

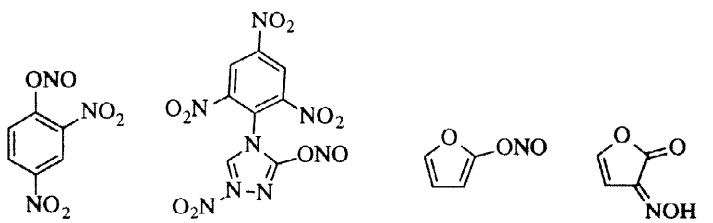
Reaction of **16** with diazomethane gave the same methylated derivative **14a** alongside the stereoisomer **14b** and minor amounts of the *N*-methylated nitramine **17** as well. Unterhalt and Thamer have reacted methyl-nitramine with diazomethane and obtained a similar mixture of *N,N*-dimethylnitramine and *N,O*-dimethyl-nitramine.[39,34]



Scheme 3: Proposed mechanism of the formation of *p*-diazoquinones *via* a nitro-nitrito rerrangement.

To account for the ready formation of **16** and its transformation to the *p*-diazoquinone **5**, we propose a mechanism as outlined in Scheme 3. Initially, nitration of the protonated aniline gives 2,6-dimethyl-3-nitroaniline[1] which is subsequently nitrated once more to form **4**, an intermediate that

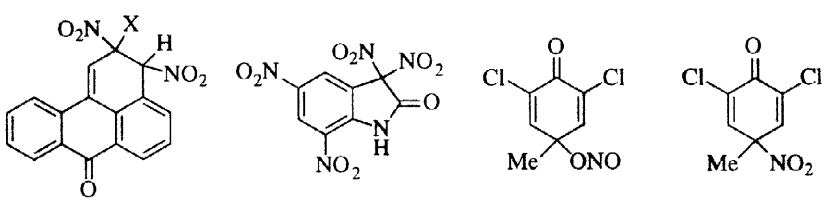
could not be isolated. The third step, which therefore probably is faster than the second (nitration of 2,6-dimethylaniline with two equivalents of nitric acid in sulfuric acid gave only traces of **4**), is a *N*-nitration leading to 2,6-dimethyl-*N*,3,5-trinitroaniline which undergoes a nitramine rearrangement[40] leading to 2,6-dimethyl-3,4,5-trinitroaniline. This intermediate undergoes a second *N*-nitration forming the isolated intermediate **16** that readily transforms to **5** *via* a nitro-nitrito rearrangement in the crucial step. It should be noted that although the mechanism is debated, nitrito intermediates are also believed to be intermediates in the nitramine rearrangement, at least according to the 'cartwheel' hypothesis[40] which is similar to the well established mechanism of the Claisen rearrangement. The most accepted rationalisation of the mechanism of the nitramine rearrangement is however that of White *et al.*, which involves a radical pair. Substrates that carries powerful electronwithdrawing substituents probably rearrange *via* heterolytic processes.[41]



18 **19** **20** **21**

Aryl nitrite intermediates have been invoked previously by several authors. Thus in the formation of picric acid from 2,4-dinitrobromobenzene in melts of quaternary ammonium nitrates, Gordon invoked 2,4-dinitro-benzenenitrite **18** as the key intermediate, which was supposed to arise from nucleophilic displacement of bromide by a nitrite ion.[42] A very similar mechanism was presented by Sitzmann in the reactions of 3,5-dinitrotriazoles with picryl chloride, which produced 1-picryl-3-nitro-1,2,4-triazol-5-one, and was proposed to proceed via the nitrito-triazole **19**.[43] Similarly, Reid proposed **20** as an intermediate during the photochemical transformation of 2-nitrofuran to the oxime derivative **21**.[44] Recently Suzuki *et al.* have reacted benzanthrone with NO_2 in carbon tetrachloride and obtained evidence for the involvement of the nitrito derivative **22**, on the reaction pathway leading to **23**.[45]

Decomposition of *gem*-dinitro compounds, *e. g.* 2,2-dinitropropane to acetone,[46] or 3,3,5,7-tetranitro-oxindole (**24**) to 5,7-dinitroisatin[47] and polynitro-fullerenes to polyhydroxy-fullerenes[48] also seem to involve nitro-nitrito rearrangements.

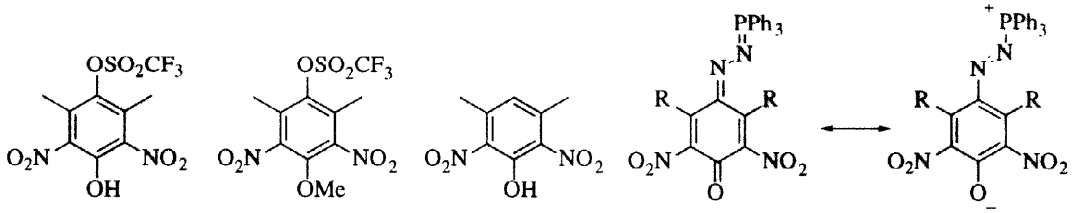


22: X = ONO
23: X = OH

24 **25** **26**

Although several theoretical calculations[49-51] of the nitro-nitrito rearrangement have been published, no such nitrito-intermediates have been isolated so far. Ridd *et al.* however, could observe what seem to be such an intermediate **25** when they dissolved the ^{15}N-labelled *ipso*-derivative **26** in chloroform and monitored the reaction using ^{15}N NMR.[52]

Benzenediazonium ions with flanking alkyl substituents are good sources of indazoles.[53-55] Thus *e. g.* heating the 2-methyl-5-nitrodiazonium ion in acid solution will give rise to 6-nitroindazole in 85 % yield.[56] In view of accomplishing this transformation the diazoquinones were therefore treated with strong acids, such as sulfuric or trifluoromethane sulfonic acid (TfOH).



27 **28** **29** **30**: R = Me **31**: R = Et

However, instead of the expected formation of indazoles, the diazoquinones were either decomposed, as in the case when using sulfuric acid, or the diazo group was substituted for a trifluoromethane sulfonate group as in the case with TfOH and compound **27** was isolated as the sole product in good yield. This compound was characterized as its *O*-methyl derivative prepared by treating **27** with diazo-methane. This methyl derivative gave ^{1}H-, ^{13}C-, ^{19}F-NMR and mass spectra that fully satisfied the requirements of structure **28**.

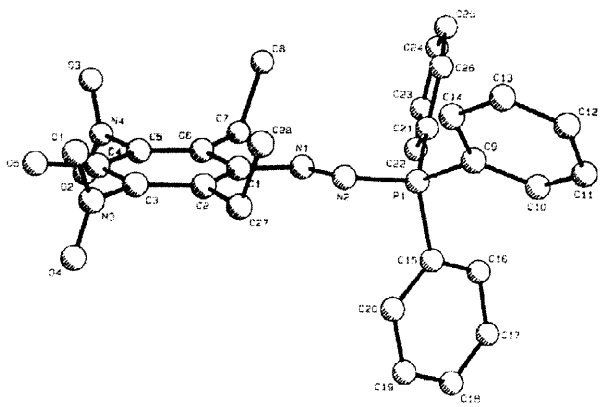


Figure 4: X-Ray structure of **31**.

As it is known that protonated diazoquinones behave as normal diazonium salts, the formation of **27** under the conditions used, cannot be considered as unexpected. Although no diazonium salts seem to have been converted to triflates,[57] the somewhat related transformation of diazonium salts to fluoro-sulfonates is however known.[58] We therefore applied the conditions to a more simple reactant, that is *p*-nitrodiazonium tetrafluoroborate, and could isolate a product that in every way corresponded with the known[59,60] compound *p*-nitrophenyl triflate.

The diazo functionality of **5** could easily be reduced by heating in dilute hypophosphorous acid (H_3PO_2), which yielded 3,5-dimethyl-2,6-dinitrophenol (**29**).

In the Staudinger reaction, diazoquinones **5** and **6** reacted with triphenylphosphine to yield the expected[61] quinone phosphazines **30** and **31**. The latter was fully characterized by X-ray crystallography (Figure 4).

Experimental:

Melting points were measured on a **Reichert VME Kofler bench**, IR-spectra recorded with a **Perkin Elmer 1600 FTIR**, NMR-spectra with a **Bruker AM400** or **DPX300** spectrometer and mass spectra with a **Finnigan MATSSQ710** instrument with direct inlet at 70 eV. CHN-Analyses were purchased from **H. Kolbe Mikroanalytisches Laboratorium**, Mülheim an der Ruhr, Germany. CAUTION Most of the compounds described below are energetic materials and appropriate precautions should be taken in their preparation and handling.

3,5-Dimethyl-2,6-dinitro-*p*-diazoquinone (5): To an ice cooled solution of 2,6-dimethylaniline (24.2 g, 200 mmol) in sulfuric acid (160 ml, d=1.88), fuming nitric acid (30 ml, d= 1.52, 710 mmol) was added dropwise during 2 h, keeping the temperature between 5-10 °C. After stirring the mixture additionally 4 h at 0-10 °C, it was poured out on lots of ice (if it is quenched to early or with smaller amount of ice a very exo-thermic reaction will take place in the ice-mixture). The crude product (actually containing a mixture of nitramide **16** and diazoquinone **5**) was collected and left to dry over night. Then the product was dissolved in the minimum volume of acetonitrile. This gave a two-phase system, consisting of a dark brown organic phase and a clear aqueous phase that was discarded. The organic phase was then heated to boiling and then upon standing the diazoquinone **5** crystallized as large yellow flakes, 14.7 g (31 %). Mp (dec. viol.): 150-170°C (depending upon purity of the sample). IR (KBr) : 2145, 1610, 1527, 1367, 1317, 1193, 776 cm^{-1}, ^{1}H-NMR (DMSO-d6): 2.36 (s). ^{13}C-NMR (DMSO-d6) 160.7 (s), 143.9 (s), 136.5 (s), 84.5 (s), 14.0 (q) ppm.

3,5-Diethyl-2,6-dinitro-*p*-diazoquinone (6): Fuming nitric acid (16 ml, d=1.52, 400 mmol) was added dropwise to a solution of 2,6-diethylaniline (15.0 g, 100 mmol) in sulphuric acid (20 ml, d=1.88) at a temperature between 0-15°C. The mixture was stirred 4 h and then allowed to reach ambient temperature whereupon it was poured onto lots of ice. The crude diazoquinone was collected, dried and recrystallized from acetonitrile yielding 13.33 g (50 %) as yellow flakes. Mp (dec. viol.): 150-180°C, IR (KBr): 2152, 1600, 1524, 1182 cm^{-1}, ^{1}H-NMR (DMSO-d6): 2.63 (2H, q, J=7.6 Hz), 1.21 (3H, tr, J=7.6 Hz) ppm. ^{13}C-NMR (DMSO-d6) 160.9 (s), 143.5 (s), 141.5 (s), 82.5 (s), 21.9 (t), 13.0 (q) ppm. The structure of **6** was also confirmed by X-ray chrystallography (structure not shown).

3-Methyl-5,6-dinitro-*o*-diazoquinone (10): 2-Methyl-5-nitroaniline (15.2 g, 0.100 mol) was dissolved in sulfuric acid (120 ml, d=1.84) and nitric acid (15 ml, d=1.52) was added during 5 min. to the well stirred solution, at 0-3°C. The reaction mixture was then allowed to assume room temperature, and the then poured into an ice/water mixture. The dark semi-solid material obtained was collected and stirred with 2-propanol during 1 h at 15°C. The orange solid obtained was collected, washed with cold 2-propanol and dried. Yield 10.5 g (47 %). Mp (dec.) 150-160°C. IR (KBr): 2195, 1619, 1558, 1519, 1397, 1372, 1343, 1254, 1122, 876 cm^{-1}. ^{1}H-NMR (DMSO-d6): 6.83 (1H, s), 2.52 (s, 3H) ppm. ^{13}C-NMR (DMSO-d6):164.6 (s), 147.7 (s), 146.0 (s), 133.9 (s), 104.7 (d), 101.9 (s), 18.7 (q) ppm.

2,6-Dimethyl-*N*,3,4,5-tetranitroaniline (16): To a solution of 2,6-dimethylaniline (6.10 g, 50 mmol) in sulfuric acid (45 ml, d=1.84) nitric acid (9.7 ml, d=1.48, 200 mmol) was added dropwise while keeping the temperature below 10°C. The reaction mixture was allowed to reach ambient temperature and after 1.5 h, it was filtered with a P2 glass filter funnel. The filtrate was poured onto a ice/water mixture, yielding diazoquinone **5**, 3.75 g (31 %). The pale beige solid obtained in the glass filter, was then treated with water and once more collected by filtration, giving **16**, 5.45 g (36 %) as a white solid. Mp: (dec.) 115-20 °C IR (KBr): 3132, 1609, 1547, 1337, 1223, 900 cm^{-1}. ^{1}H-NMR (DMSO-d_6): 10.19 (1H, s), 2.32 (6H, s) ppm. ^{13}C-NMR (DMSO-d_6): 141.7 (s), 140.4 (s), 135.3 (s), 14.3 (q) ppm.

***O*-Methyl-*N*-nitramines 14a and 14b:** To an ice cooled solution of 2,6-dimethylaniline (8.25 g, 75 mmol) in sulfuric acid (80 ml, d=1.88), fuming nitric acid (10 ml, d=1.52, 960 mmol, treated with *ca* 1g sulfaminic acid to remove any NO_X gases) diluted in sulfuric acid (10 ml, d=1.88), was added dropwise during 1 h, keeping the temperature between 5-20°C. After stirring the mixture additionally 2 h it was further cooled in a freezer to ca -10°C and then poured into MeOH (1000 ml, also cooled in a freezer to ca -35°C). Immediate filtration of the precipitate formed gave a first crop of 4.94 g. The filtrate was treated with ca 1.5 kg crushed ice. After a while another crop of 9.06 g could be isolated by filtration. ^{1}H-NMR showed that both fractions contained **14a** and **14b** in a 84:16 ratio. Overall yield 14.00 g (59 %) as a pale yellow solid. IR(KBr): 1613, 1542, 1347 cm^{-1}. M/Z: 315 (17 %), 284 (100 %), 269 (16%), 240 (9 %), 177 (14 %), 89 (29 %), 67 (17 %).

Major component: ^{1}H-NMR (DMSO-d_6): 4.24 (3H, s), 2.22 (6H, s) ppm. ^{13}C-NMR ($CDCl_3$): 146.6 (s), 142.8 (s), 134.0 (s), 128.9 (s), 59.3 (q), 13.7 (q) ppm.

Minor component: ^{1}H-NMR (DMSO-d_6): 4.02 (3H, s), 2.26 (6H, s) ppm.

***O*-Ethyl-*N*-nitramines 15a and 15b:** The same procedure as for **14a-b**, but on a 1/3 scale and with ethanol instead of methanol, was used. This afforded 4.51 g (55 %) of **15a** and **15b** in a 80:20 ratio.

Major component: ^{1}H-NMR(DMSO-d_6): 4.62 (2H, q, J=7.1 Hz), 2.24 (6H, s) 1.46 (3H, t, J=7.1 Hz) ppm. ^{13}C-NMR ($CDCl_3$): 146.3 (s), 142.8 (s), 134.0 (s), 128.3 (s), 50.6 (q), 13.5 (q) ppm.

Minor component: ^{1}H-NMR (DMSO-d_6): 4.48 (2H, q, J=7.0 Hz), 2.27 (6H, s) 1.29 (3H, t, J=7.0 Hz) ppm.

3,5-Dimethyl-2,6-dinitro-4-(trifluoromethanesulfonato)phenol (27): Diazoquinone **5**, (0.48 g, 2 mmol) was heated to 150°C for 30 minutes in trifluoromethane sulfonic acid (10 ml). Most of the acid was then recovered by distilling it off under reduced pressure. The residue was left standing 16 h and then poured into water. The product formed was filtered and washed with water, which gave a yellow-brown solid 0.33 g (46 %). IR (KBr): 1619, 1588, 1552, 1403, 1217, 1180, 1129, 907, 833 cm^{-1}. ^{1}H-NMR (DMSO-d_6): 6.81 (1H, broad), 2.24 (6H, s) ppm. ^{13}C-NMR(DMSO-d_6): 142.3 (s), 141.1 (s), 136.2 (s), 126.2 (s), 125.7-110.3 (q, J_{CF} = 322 Hz), 12.6 (q) ppm.

3,5-Dimethyl-2,6-dinitro-4-(trifluoromethanesulfonato)anisole (28): The phenol **27** was treated with ethereal diazomethane and the mixture was then allowed to evaporate, whereupon the residual yellow solid was analysed without further purification. ^{1}H-NMR (DMSO-d6): 3.90 (3H, s), 2.33 (6H, s) ppm. ^{13}C-NMR (DMSO-d6): 143.8 (s), 143.0 (s), 140.3 (s), 129.0 (s), 124.1-111.4 (q, J_{CF} = 343 Hz), 64.5 (q), 12.6 (q) ppm. ^{19}F-NMR (DMSO-d6): 1208 (s) Hz. MS (m/z): 374 (14.9 %), 241 (100 %), 121 (42.3 %), 67 (77.0 %).

3,5-Dimethyl-2,6-dinitrophenol (29): Diazoquinone **5** (2.40 g, 10 mmol), hypophosphorous acid (20 ml, 50 % aq) and water (20 ml) was heated at a temperature of 75 °C for 72 hours, whereupon the product (1.37 g, 65 %) could be collected by filtration as a yellow powder. Recrystallization from ethanol/water gave long yellow needles. Mp: 114-115 °C. IR (KBr): 1622, 1584, 1528, 1458, 1276, 1167, 1086, 890 cm^{-1}. ^{1}H-NMR (DMSO-d6): 11.5 (1H, s), 6.90 (1H, s), 2.23 (6H, s) ppm. ^{13}C-NMR (DMSO-d6): 142.0 (s), 140.6 (s), 133.3 (s), 123.5 (d) 17.13 (q) ppm. MS (m/z): 212 (39 %), 194 (12 %), 165 (10 %), 91 (32 %), 77 (45 %), 65 (100 %), 53 (55%), 39 (60%). [Found: C, 45.06; H, 3.70; N, 13.08. $C_8H_8N_2O_5$ requires C, 45.29; H, 3.80; N, 13.20 %].

2,6-Dimethyl-3,5-dinitro-*p*-quinonetriphenylphosphazine (30): Diazoquinone **5** (1.0 g, 4.2 mmol) and triphenylphosphine (1.17 g, 4.5 mmol) were dissolved in dichloromethane (30 ml) and stirred overnight. The solvent was evaporated and the crude material chromatographed on silica gel with dichloromethane as eluent, yielding a red powder (1.75 g, 83 %). Repeated recrystallizations from acetone produced red needles with an undefined melting point (145-160 °C). IR (KBr): 1618, 1523, 1436, 1345, 1305, 1099, 776, 723, 690, 540, 483 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.80-7.74 (3H, m), 7.65-7.60 (12H, m), 2.65 (3H, s), 1.20 (3H, s) ppm. ^{13}C-NMR (CD_3CN): 165.0 (s), 136.2 (d, J_{CP}=2.9 Hz), 135.6 (d, J_{CP}=9.1 Hz), 135.2 (s), 135.0 (s), 131.4 (d, J_{CP}=12.1 Hz), 130.6 (s), 130.3 (s), 130.2 (s), 123.5 (d, J_{CP}=94.3 Hz), 19.0 (q), 13.9 (q) ppm. [Found: C, 62.26; H, 4.31; N, 11.87. $C_{26}H_{21}N_4O_5P$ requires C, 62.40; H, 4.23; N, 11.20 %].

2,6-Diethyl-3,5-dinitro-*p*-quinonetriphenylphosphazine (31): 2,6-Diethyl-3,5-dinitro-*p*-diazoquinone **6** (2.66 g, 10 mmol) and triphenylphosphine (2.62 g, 10 mmol) were dissolved in dichloromethane (30 ml, dried over $CaCl_2$) and stirred overnight, whereupon the solvent was evaporated and the crude material chromato-graphed on silica gel with dichloromethane as eluent, yielding a red powder (5.15 g, 97 %). An analytical sample was recrystallised from acetone. Mp (dec.) 200 °C. IR (KBr): 1617, 1525, 1439, 1351, 1304, 1115, 1102, 866, 798, 762, 728, 521, 488 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 7.78-7.76 (3H, m), 7.67-7.63 (9H, m), 7.33 (3H, m), 3.08 (2H, q), 2.36 (2H, q), 1.24 (3H, t), 0.70 (3H, t) ppm. ^{13}C-NMR ($CDCl_3$): 164.4 (s), 137.3 (s), 136.7 (s), 134.5 (dd, J_{CP}=2.9 Hz), 133.6 (dd, J_{CP}=8.4 Hz), 133.0 (s), 132.3 (s), 131.6 (s), 129.7 (dd, J_{CP}=12.0 Hz), 122.4 (J_{CP}=94.2 Hz), 23.7 (t), 22.0 (t), 15.3 (q), 13.8 (q) ppm. [Found: C, 63.79; H, 4.85; N, 10.54. $C_{28}H_{25}N_4O_5P$ requires C, 63.63; H, 4.77; N, 10.60 %].

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