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Aprotic Diazotization in the Presence of Cuprous Cyanide

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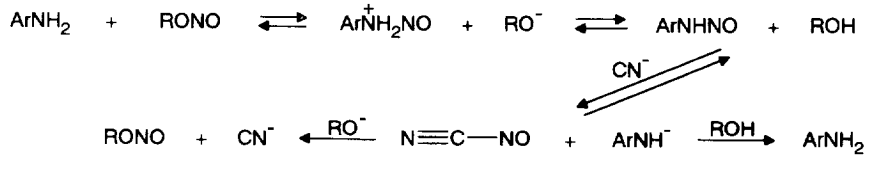
Abstract: In a procedure of extreme simplicity and rapidity a mixture of an aromatic primary amine, copper (I) cyanide and an alkyl nitrite in dimethyl sulphoxide yielded fair to moderate yields of the corresponding nitriles. Side processes observed were reduction ($NH_2 \rightarrow H$), nitration ($NH_2 \rightarrow NO_2$) and hydroxylation ($NH_2 \rightarrow OH$). In the case of polyhaloanilines halogen dance products could be detected. Copyright © 1996 Elsevier Science Ltd

One batch aprotic diazotization with eventual Sandmeyer type reaction is a process of great interest for the inherent simplicity of the operations involved, the limitation of the chemicals used and the lesser need for temperature and pH control of the reactions. Time and reagents saving can also be extensive.

By working on a number of aromatic amines (**1**) having different electronic and steric features we are now able to describe the phenomenological pattern of the aprotic diazotization-cyanation reaction. All of the methods so far reported employed at least one molecular equivalent excess of soluble cyanide ion over stoichiometry, an unpleasant problem to deal with especially at the workup and disposal stages.

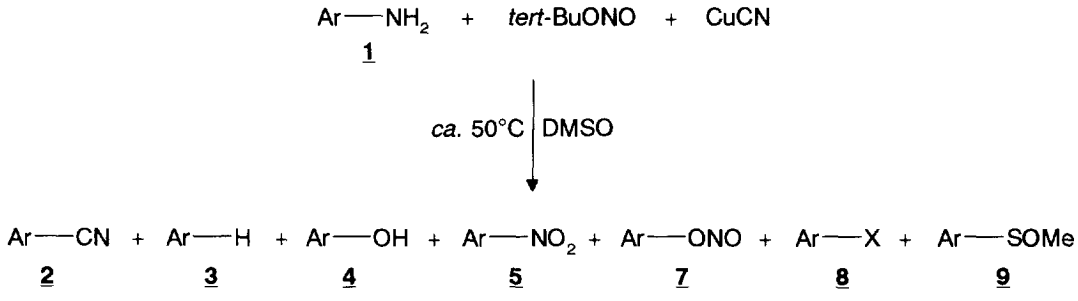
RESULTS AND DISCUSSION

When using the system arylamine/*tert*-butyl nitrite in dimethyl sulphoxide (DMSO), sodium cyanide alone was unable to produce the corresponding nitrile (**2**) in any amount. The diazotization reaction itself was completely inhibited, the amine is fully recovered in these experiments. This behaviour may be ascribed to a negative catalysis of the free cyanide ion, causing regression of the initial step of the diazotization sequence.

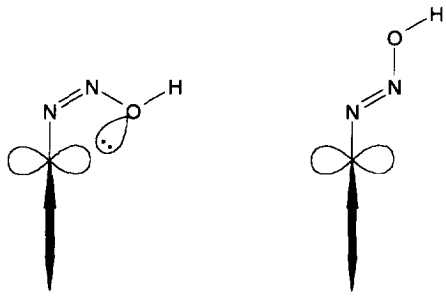


The unexpected process may be also favoured by the properties of DMSO.

The same observation was made when the complex $Cu(CN)_2^-$ was substituted for sodium cyanide. The first problem to solve was that of keeping a good concentration of CuCN in solution at all times without the use of an alkali cyanide. The solvent of choice appeared to be DMSO, in which - possibly thanks to its complexing properties - the copper salt is moderately soluble at *ca.* 50°C, a temperature quite suitable for the process. When a stoichiometric amount of CuCN was used, the system promptly reacted with the organic nitrite and further underwent substitution to a number of products, among which the corresponding nitrile (**2**) was usually the main one.



The yields were not good (Table 1), but it should be noticed that it was possible to quickly and easily obtain the nitriles from heavily hindered amines like 2,6-diisopropylbenzenamine (**1a**) and pentachlorobenzenamine (**1b**). Side products observed are those typically encountered in these aprotic reactions,[1] namely hydro- (**3**), hydroxy- (**4**) and nitro- (**5**) dediazotization compounds. Interestingly, phenol formation was observed only and always with *ortho* substituted substrates. Water is stoichiometrically formed in the diazotization stage and may be present in the DMSO used: it is usually assumed that water reacts with the aryl cation, produced by the dissociation of the arenediazonium cations. This reaction may be accelerated by steric compression by the *ortho* substituents against the diazo group: some evidence for this hypothesis came from the comparison with the behaviour of the less hindered 2,4,6-tribromobenzenamine (**1c**), which in the end gave little phenol (**4c**). In contrast with this rationale is 2,6-diisopropylbenzenamine (**1a**): notwithstanding the very bulky groups no phenol was formed. Rather than with this hardly likely incursion of a polar route with the capture of the little water present in the system, we propose the hydroxyl radical interception directly in the final stages of the radical breakdown of the hydroxydiazotate (**6**), facilitated by the prevalent configuration of this species, which should exhibit a reasonable population of the molecules having the NNOH group at right angle with respect to the plane of the ring (*syn*- and *anti*-**6**). The *syn*-**6** conformer, though, is the suitable one for the hydroxylation reaction, but is unfavoured in the case of very large *ortho*-substituent(s).



syn-**6** *anti*-**6**

Table 1. Products of the Reactions between Aromatic Amines (**1**), *tert*-Butyl Nitrite and Cuprous Cyanide in DMSO.[a]

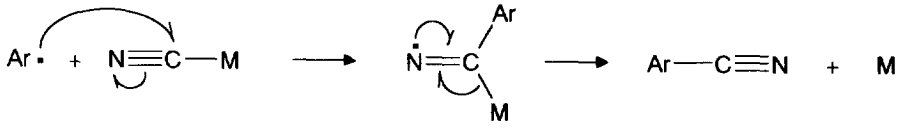
$ArNH_2$ **1**	ArCN **2**, %	ArH **3**, %	ArOH **4**, %	$ArNO_2$ **5**, %	ArX **8**, %
2,6-(*iso*-$C_3H_7)_2C_6H_3$ (**1a**)	**2a**, 52	**3a**, 13	----	**5a**, 9	----
Cl_5C_6 (**1b**)	**2b**, 48	**3b**, 30	----	**5b**, 6	**8b**, 7
2,4,6-$Br_3C_6H_2$ (**1c**)	**2c**, 20	**3c**, 37	**4c**, 4	**5c**, 4	**8c**, 7
2-$NO_2C_6H_4$ (**1d**)[b]	**2d**, 38	**3d**, 16	**4d**, 6	**5d**, 8	----
2-$NO_2C_6H_4$ (**1d**)[c]	**2d**, 39	**3d**, 11	**4d**, 20	**5d**, 9	----
2-$NO_2C_6H_4$ (**1d**)[d]	**2d**, 40	**3d**, 5	**4d**, 10	**5d**, 4	----
3-$NO_2C_6H_4$ (**1e**)	**2e**, 33	**3d**, 4	----	**5e**, 7	----
4-$NO_2C_6H_4$ (**1f**)	**2f**, 24	**3d**, 3	----	**5f**, 9	----
2-$COOMeC_6H_4$ (**1g**)	**2g**, 35	**3g**, 4	**4g**, 6	**5g**, 8	----
4-$COOMeC_6H_4$ (**1h**)	**2h**, 33	**3g**, 3	----	**5h**, 8	----

[a]Conditions and quantitative determinations of individual reaction as indicated in the Experimental Part. [b]Procedure A of Experimental Part. [c]Procedure B of Experimental Part. [d]Procedure C of Experimental Part.

Amine **1a** gave two GC well separated compounds, whose mass spectra exhibited isobaric parent ions, corresponding to $C_{12}H_{17}NO_2$. This composition leads to two NO_2 derivatives of the hydrocarbon 1,3-diisopropylbenzene: one was found to be 2,6-diisopropylnitrobenzene (**5a**) and the other a rare aryl nitrite, namely 2,6-diisopropylphenyl nitrite (**7**). The former, separated by absorption chromatography, was identified by the combined mass spectrometric and spectroscopic properties: moreover, its reduction with Zn and hydrochloric acid in acetic acid gave **1a**, identified on the basis of GC retention properties and mass fragmentation pattern. The nitrite is assumed to be formed by the interception of nitrogen dioxide at one of the extremities of this radical, a behaviour classically shown by carbon radicals crowded about the reactive site, as in the reaction of isobutene with nitrogen dioxide, where the first molecule adds uniquely at the nitrogen atom using the methylene carbon, but the second exhibits a two faced reactivity, yielding both a second nitrated carbon as well as a nitrite ester.[2] Nitrogen dioxide is usually present in these reactions from the hydrolysis of the nitrite ester with forming water.

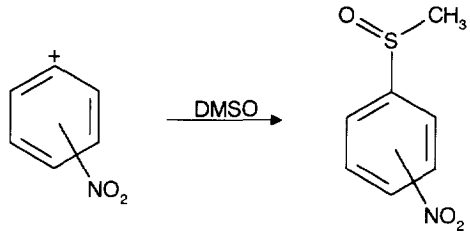
The role of copper in Sandmeyer reactions, especially as far as cyanide introduction is concerned, still appears unclear. Certainly, against the too capricious illation that the mechanism might be similar or identical to that leading to halogenation using cuprous halides, stand some facts. Redox chain mechanisms have been invoked for the latter, but cyanide is a group, not a single nucleus and, moreover, the end attached to the coordinating center is a carbon. By and large, complexes of Cu (II) were successfully used and in some cases Ni (II) cyano complexes were found more effective than the former. The role of complexation, as was uncovered[3] in the case $C_6H_6N_2^+/Cu_2Br_3^-$, was ruled out for the cationic arylazo group, but nothing is known about it as a neutral radical species. Arylazo radicals may be generated both in a redox reaction between the arylazo cation and Cu (I) and by homolytic decomposition of covalently bound arylazo groups, a reaction observed previously by others.[4]

The reactions leading to hydrocarbons, nitriles and nitro derivatives appear to be radicalic in nature. Hydrogen donors could be the alkyl nitrite itself or formed alcohol, also in the transient form of alcoxy radical. It is to be noticed that use of *n*-butyl nitrite caused a large occurrence of the reduction reaction, which, though, was very effective even with the *tert*-butyl nitrite. Formation of nitro arenes may be rationalized by the reaction of aryl radicals with nitrogen dioxide, produced by the slow partial hydrolysis of alkyl nitrites. A mechanistic likehood for nitrile formation is the attack of an aryl radical to the π-bond carbon end of metal coordinated cyano group followed by expulsion of a nitrile molecule.



The heavy involvement of aryl radicals in our process is inferred also from a radical halogen dance, observed with pentachlorobenzenamine (**1b**) and 2,4,6-tribromobenzenamine (**1c**) which yielded hexachlorobenzene (**8b**) and 1,2,3,5-tetrabromobenzene (**8c**), respectively.

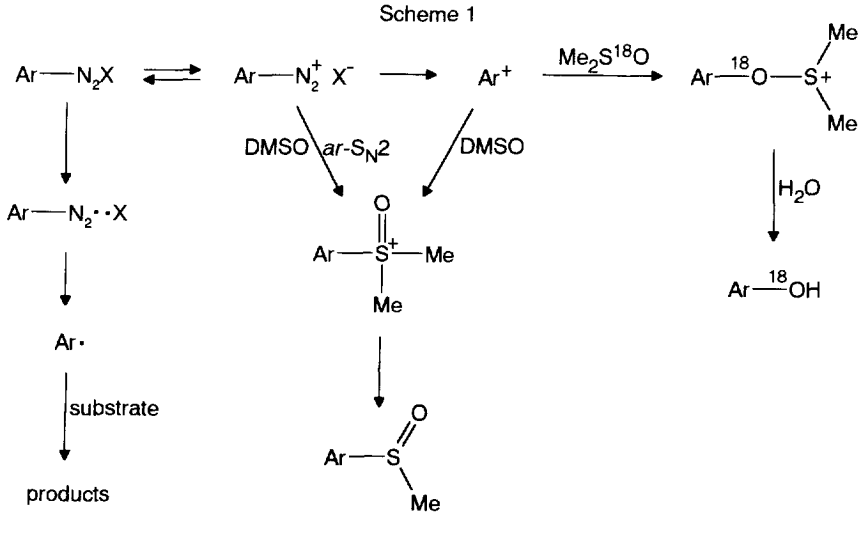
On the other hand, even *ortho-* and *para*-nitrobenzenediazonium cations, whose existence is probably favoured by the properties of the very polar solvent, may yield aryl carbocations, as inferred by their reaction with DMSO, to yield 2-nitrophenyl methyl sulfoxide (**9d**) and 4-nitrophenyl methyl sulfoxide (**9f**), respectively, in an unprecedented reaction.



9d and **9f**

This behaviour is at variance with previous observations of the decomposition of preformed *para*-nitrobenzenediazonium salts in DMSO,[5] where a dual mechanism was acknowledged. In the presence of aromatic substrates radical arylations were favoured, but, when no such radical acceptors were at hand, a cationic reaction involving the *para*-nitrophenyl cation became prevalent as shown by the formation of phenol, via reaction with DMSO. Of course, this incursion may partly take place even in our systems. Another alternative mechanism may envisage a direct *ipso* attack of the *ar*-S_N2 type by the sulphur atom of DMSO. The results of the quoted work and ours could be accomodated by the overall picture offered in Scheme 1.

Scheme 1



^{1}H NMR monitoring of the process in the case of 3-nitrobenzenamine (**1e**), allowed to observe the intermediate formation of 1,3-bis(3-nitrophenyl)triazene (**10**): preformation of the triazene and its reaction with CuCN and *tert*-butyl nitrite, though, did not improve the yield of the cyanation reaction.

EXPERIMENTAL SECTION

Materials. All aromatic amines, CuCN *n*- and *tert*-butyl nitrite were secured from commercial sources and purified before use, when deemed necessary. Silica gel (60-120 mesh) and alumina (active neutral Brockmann Grade I) were obtained from BDH (Milano, Italy). Preparative thick layer chromatography was performed on silica gel (Kieselgel 60 F_{254}, 2 mm thickness, Merck, Darmstadt, D). Solvents were used as received.

Equipment. GC-MS analyses were performed with a Fisons TRIO 2000 gaschromatograph-mass spectrometer, working in the positive ion 70 eV electron impact mode. Injector temperature was kept at 260°C and the column (Supelco® SE-54, 30 m long, 0.32 mm i.d., coated with a 0.25 μm phenyl methyl silicone rubber film) temperature was programmed from 80°C to 300°C with a gradient of 10°C/min. Direct inlet mass spectra (DI-MS) were obtained on the same instrument: temperatures between 50 and 200°C were found suitable to volatilize all the compounds into the ion source. GC quantitative determinations were performed by means of suitable internal standards after independent determinations of area/weight calibration factors.

IR spectra were obtained with a Nicolet FT-IR Magna 550 spectrophotometer using the KBr technique for solids.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker AC-F 200 spectrometer at 200 and 50 MHz, respectively. NMR peak locations are reported as δ-values from TMS (^{1}H NMR) and the central peak of $CDCl_3$ (^{13}C NMR). Some ^{1}H multiplets are characterized by the term *app* (apparent): this refers only to their appearance and may be an oversimplification.

Elemental analyses were performed with a Carlo Erba Mod. 1106 elemental analyzer and were in satisfactory agreement with calculated values with the exception of **11** (vide infra).

Melting points were determined with an automatic Mettler (Mod. FP61) apparatus and are not corrected.

Boiling points refer to the center cut of small distillations and are uncorrected.

*2-Nitrobenzenamine (**1d**), tert-butyl nitrite and CuCN.* Procedure A. - The amine (**1d**, 20.3 mmol) dissolved in DMSO (10 mL) was added during 90 min to a well stirred solution of CuCN (26.3 mmol) and *tert*-butyl nitrite (60.0 mmol) in DMSO (20 mL) kept at 50-55°C, under inert atmosphere. A prompt reaction set in with gas evolution. After an additional period of 90 min at 60°C, the chilled mixture was poured onto water (*ca.* 100 mL), freed from a separating solid by filtration and thoroughly extracted with dichlorometha-

ne. The organic brown solution was washed with water, dried (Na_2SO_4) and concentrated to yield a solid (2.52 g). GC-MS analysis separated and allowed the preliminary identification of the following products (in brackets are the percentiles of the total ion current): nitrobenzene (**3d**, 12%), 2-nitrophenol (**4d**, 13%), 2--nitrobenzonitrile (**2d**, 55%), 1,2-dinitrobenzene (**5d**, 7%) and two more components **9d** and **11**, whose highest mass ions appeared respectively at 185 and 152 u. Only traces of the starting amine were present. Absorption chromatography, performed on silica gel using cyclohexane with increasing concentration of methyl *tert*-butyl ether as eluent, of the total reaction mixture yielded the following results in order of elution: **3d**, 16%, **4d**, 6%, **5d**, 8% and **2d**, 38%. Melting points and spectral characteristics as well as the GC retention properties of the separated products confirmed their nature. Compounds **9d** and **11** could be obtained and identified as single products in the experiment described right below. When *tert*-butyl nitrite was replaced with *n*-butyl nitrite the qualitative product pattern was unchanged, but the reduction product **3d** formed to a greater extent.

Procedure B. When the former experiment was repeated with the addition of powdered copper (6.0 mmol) all the products other than **3d** showed up at a much higher concentration in the reaction mixture. The reaction mixture was treated with much water and dichloromethane and insoluble matter filtered and discarded. The green organic layer was dried over Na_2SO_4 and the solvent removed to leave 3.30 g of a brown solid, which was extracted with diethyl ether to leave behind a greenish solid, 0.98 g, MS apparent molecular ion at 152 u, other peaks at 138(20), 136(21), 120(26), 94(16), 92(33), 90(34), 76(58), 74(25), 64(55), 63(67), 51(61), 50(86) and 39(52). This mass spectrum, obtained with the DI-MS technique, was identical with that obtained for product **11** in the former experiment by GC-MS. IR (KBr) 3108w, 3095w, 1605m, 1588m, 1528vs, 1484m, 1358vs, 1314s, 1264s, 1182vs, 1162s, 1149m, 1108m, 931vs, 856m, 783s, 744vs, 721s, 696m, 645m, 618m, 600m, 559m cm^{-1}. The compound recrystallized from ethanol-ethyl acetate decomposed at 165°C and showed the following elemental analysis: C, 33.53; H, 1.74 and N, 19.08. This composition could not be reconduced to any likely organic material. Copper could be precipitated from it as the sulphide by treatment with ammonium sulphide in water. Reduction with Zn and hydrochloric acid in acetic acid gave aniline and 2-phenylenediamine. A significant ^1H NMR spectrum of **11** could not be obtained, because of an enormous widening of the resonances.

Quantitative GC-MS, using a suitable standard, showed the following products: **3d**, 11%, **4d**, 20%, **2d**, 39% and **5d**, 9%. The solid residue from which **11** had been removed was dissolved completely in the cold with benzene-cyclohexane: slow addition of more cyclohexane allowed to obtain an orange solid admixed with an oily material. Upon standing the solution yielded a red solid **12**, identified as 2,2'-dinitrodiphenylamine (not eluted in GC): yield 6%; mp 169°C, lit.[6] 169°C; DI-MS m/z 259(M^+, 100), 212(10), 196(42), 180(10), 179(11), 169(23), 168(56), 167(50), 166/39), 157(16), 154(26), 140(30), 139(33), 92(24), 64(29), 63(32); IR (KBr) 3308w, 1608s, 1584m, 1540m, 1517vs, 1335vs, 1321s, 1293vs, 1263vs, 1164s, 1149s, 858m, 732vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.04-7.16 (2H, *app* m, H_{arom}), 7.47-7.66 (4H, *app* m, H_{arom}), 8.06 (1H,

broad s, NH), 8.22 (2H, dd, J_o = 8.6 Hz, J_m = 1.4 Hz, H_{arom}); Anal. Calcd for $C_{12}H_9N_3O_4$: C, 55.59; H, 3.50; N, 16.22. Found: C, 55.61; H, 3.51; N, 16.24.

Thick layer chromatography on silica gel of the material of the mother liquour from the crystallization of **12** allowed to separate pure 2-nitrophenyl methyl sulphoxide (**9d**): yield 4%; mp 101°C, lit.[7] 101-102°C; MS m/z 185(M^+, 51), 169(11), 135(9), 109(99), 96(20), 93(26), 91(33), 81(27), 80(43), 78(56), 76(43), 63(41), 52(30), 51(100), 50(58); IR (KBr) 3085w, 3009w, 2924m, 1517vs, 1347vs, 1108s, 1064vs, 1033vs, 973s, 852m, 791s, 740s, 711m, 681m cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.94 (3H, s, $SOCH_3$), 7.68-7.78 (1H, *app* m, H_{arom}), 7.94-8.05 (1H, *app* m, H_{arom}), 8.33 (1H, dd, J_o = 8.1 Hz, J_m = 1.2 Hz, H_{arom}) and 8.39 (1H, dd, J_o = 8.1 Hz, J_m = 1.5 Hz, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 43.75, 125.08, 126.09, 131.46, 135.69, 144.59, 145.32; Anal. Calcd for $C_7H_7NO_3S$: C, 45.40; H, 3.81; N, 7.57. Found: C, 45.38; H, 3.82; N, 7.57.

Procedure C.- When *tert*-butyl nitrite was dropwise added during 60 min to the solution of the other reagents (all other things being equal), the reaction mixture was simplified, containing **3d**, 5%, **4d**, 10%, **2d**, 40% and **5d**, 4% (GC quantitative determination, using a suitable standard, on the reaction mixture after workup).

*3-Nitrobenzenamine (**1e**), tert-butyl nitrite and CuCN.* The reaction carried out according to the procedure A described for **1d** gave the following GC profile (in brackets are the percentiles of the total ion current): nitrobenzene (**3d**, 14%), 3-nitrobenzonitrile (**2e**, 63%) and 1,3-dinitrobenzene (**5e**, 23%), which were separated as homogeneous materials by absorption chromatography (alumina, cyclohexane-dichloromethane). Separated yields (in order of elution): **3d**, 4%, **5e**, 7% and **2e**, 33%. All of the products were confirmed by comparison of their properties with authentic materials.

*4-Nitrobenzenamine (**1f**), tert-butyl nitrite and CuCN.* Procedure A described for **1d** was followed. Alumina was used in order to separate the reaction products (eluants: cyclohexane-dichloromethane): nitrobenzene (**3d**), 3%, 4-nitrobenzonitrile (**2f**), 24% and 1,4-dinitrobenzene (**5f**), 9%, which are the only products detected by GC-MS on the whole mixture.

When a solution of the cyanide and *tert*-butyl nitrite in DMSO was added to a solution of the amine **1f** in DMSO at 50°C, in addition to the above described products (the overall recovery was poorer) the GC-MS trace of the whole mixture revealed the presence of 4-nitrophenyl methyl sulphoxide (**9f**), identified on the basis of its mass spectrum [MS m/z 185(M^+, 100), 170(39), 169(10), 140(25), 139(13), 124(20), 112(15), 108(8), 96(13), 92(12), 76(23), 63(25), 50(28), 45(15)] by library comparison.

*Methyl 2-aminobenzoate (**1g**), tert-butyl nitrite and CuCN.* Procedure A described for **1d** was followed. Absorption chromatography (silica gel, cyclohexane-dichloromethane) of the reaction mixture after workup yielded methyl 2-hydroxybenzoate [**4g**, 6%; bp 100°C at 1600 Pa, lit.[8] 101 at 12 mm Hg; MS m/z 152(M^+,

59), 121(30), 120(100), 93(20), 92(94), 65(29), 64(18), 63(16), 39(38); IR (neat) 3189s, 2956m, 1679vs, 1615vs, 1586s, 1487vs, 1442vs, 1329vs, 1306vs, 1254vs, 1217vs, 1159vs, 1135s, 1091vs, 1033m, 964m, 849s, 758vs, 702vs, 667s, 530m cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.95 (3H, s, $COOCH_3$), 6.88 (1H, ddd, J_o = 8.1 Hz, J_o = 7.2 Hz, J_m = 1.2 Hz, H_{arom}), 6.98 (1H, ddd, J_o = 8.5 Hz, J_m = 1.2 Hz, J_p = 0.4 Hz, H_{arom}), 7.41-7.51 (1H, *app* m, H_{arom}), 7.84 (1H, ddd, J_o = 7.9 Hz, J_m = 1.8 Hz, J_p = 0.4 Hz, H_{arom}), 10.77 (1H, s, OH); ^{13}C NMR ($CDCl_3$) δ 52.96, 113.04, 118.24, 119.83, 130.56, 136.37, 162.24, 171.25; Anal. Calcd for $C_8H_8O_3$: C, 63.14; H, 5.30. Found: C, 63.11; H, 5.30], methyl benzoate (**3g**, 4%), methyl 2-nitrobenzoate (**5g**, 8%) and methyl 2--cyanobenzoate [**2g**, 35%; mp 51°C, lit.[9] 50°C; MS m/z 161(M^+, 24), 131(17), 130(100), 103(19), 102(65), 76(16), 75(23), 51(10), 50(9); IR (KBr) 3043w, 3019w, 2959m, 2228s, 1725vs, 1592vs, 1576vs, 1488vs, 1454s, 1427vs, 1273vs, 1193vs, 1187vs, 1138vs, 1082vs, 957vs, 831vs, 761vs, 691vs, 661s, 556vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.01 (3H, s, $COOCH_3$), 7.66-7.75 (2H, m, H_{arom}), 7.80-7.87 (1H, m, H_{arom}), 8.12-8.19 (1H, m, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 53.39, 113.43, 118.08, 131.71, 132.89, 133.09, 133.31, 135.37, 165.03; Anal. Calcd for $C_9H_7NO_2$: C, 67.06; H, 4.38; N, 8.69. Found: C, 67.10; H, 4.36; N, 8.71], corresponding to the GC-MS detected products in the reaction mixture.

*Methyl 4-aminobenzoate (**1h**), tert-butyl nitrite and CuCN.* Procedure A described for **1d** was followed. Absorption chromatography (silica gel, cyclohexane-dichloromethane) of the reaction mixture after workup yielded methyl benzoate (**3g**, 3%), methyl 4-nitrobenzoate (**5h**, 8%) and methyl 4-cyanobenzoate (**2h**, 33%) with a full correspondence to the GC-MS profile of the reaction mixture.

*2,6-Diisopropylbenzenamine (**1a**), tert-butyl nitrite and CuCN.* According to procedure A the corresponding nitrile **2a** was obtained in 52% separated pure product [bp 125°C at 1600 Pa, lit.[10] 122-3°C at 12 Torr; MS m/z 187(M^+, 38), 172(100), 157(39), 156(17), 155(30), 144(17), 130(18), 128(18), 115(19), 77(16); IR (neat) 2966vs, 2931s, 2873s, 2217m, 1593m, 1463s, 1386m, 1366m, 1061m, 804s, 756s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (12H, d, J = 6.8 Hz, CH_3), 3.33 (2H, sept, J = 6.8 Hz, CH), 7.10-7.48 (3H, m, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 23.29, 32.55, 111.11, 117.03, 123.07, 132.73, 152.74; Anal. Calcd for $C_{13}H_{17}N$: C, 83.36; H, 9.16; N, 7.48. Found: C, 83.31; H, 9.17; N, 7.48] from absorption chromatography (alumina, cyclohexane) on the whole reaction mixture as produced from workup which enable to recover also some 13% of the hydrocarbon 1,3-diisopropylbenzene (**3a**). In addition, GC-MS profile of the reaction mixture revealed the presence of 2,6-diisopropylnitrobenzene (**5a**, separated yield 9%; bp 110°C at 680 Pa, lit.[11] 105°C at 5 mm Hg; MS m/z 207(M^+, 9), 150(100), 175(12), 174(16), 162(22), 148(47), 132(65), 117(47), 115(40), 91(51), 77(32), 43(94); IR (neat) 2970vs, 2934s, 2874m, 1526vs, 1478m, 1465s, 1385s, 1375vs, 1061m, 1042m, 850s, 803s, 764s, 76m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (12H, d, J = 6.8 Hz, CH_3), 2.82 (2H, sept, J = 6.8 Hz, CH), 7.20-7.46 (3H, m, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 23.77, 29.11, 124.12, 130.16, 138.97, 150.34; Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.52; H, 8.27; N, 6.76. Found: C, 69.49; H, 8.25; N, 6.74] and another product **7**,

having the same apparent molecular weight [MS m/z 207(M^+, 100), 192(34), 190(15), 179(17), 178(12), 164(71), 148(30), 146(18), 130(13), 91(25), 77(23), 67(27), 53(26), 43(19), 41(36)] as **5a**, which defied attempt of absorption chromatography separation, being irreversibly retained on the stationary phase, possibly due to its decomposition.

*Pentachlorobenzenamine (**1b**), tert-butyl nitrite and CuCN.* Procedure A described for **1d** was followed. Absorption chromatography (silica gel, tetrachloromethane) of the reaction mixture after workup yielded, in order of elution, pentachlorobenzene (**3b**, 30%), hexachlorobenzene (**8b**, 7%), pentachloronitrobenzene (**5b**, 6%), pentachlorobenzonitrile [**2b**, 48%; mp 211°C, lit.[12] 210°C; MS m/z 279(M^+, 24), 277(M^+, 64), 275(M^+, 100), 273(M^+, 72), 242(9), 240(19), 238(16), 207(4), 205(11), 204(12), 170(3), 168(5), 135(5), 133(14); IR (KBr) 2237m, 1534m, 1372s, 1356vs, 1312m, 1232s, 1133m, 721vs, 657s cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 112.41, 114.73, 133.13, 135.64, 139.15; Anal. Calcd for $C_7C_{15}N$: C, 30.79; N, 5.13. Found: C, 30.78; N, 5.11] and pentachlorophenol (**4b**, 4%).

*2,4,6-Tribromobenzenamine (**1c**), tert-butyl nitrite and CuCN.* Following procedure A allowed to obtain after separation by absorption chromatography (silica gel, tetrachloromethane) 1,3,5-tribromobenzene (**3c**, 37%), 1,2,3,5-tetrabromobenzene [**8c**, 7%; mp 98°C, lit.[13] 98.5°C; MS m/z 398(M^+, 8), 396(M^+, 33), 394(M^+, 49), 392(M^+, 33), 390(M^+, 9), 317(5), 315(16), 313(15), 311(6), 236(7), 234(12), 232(6), 198(6), 197(6), 196(4), 155(19), 153(19), 117(13), 74(100), 73(41); IR (KBr) 3089w, 3052w, 1546vs, 1534vs, 1403vs, 1383vs, 1364vs, 1349vs, 1194vs, 1170s, 1131s, 1112vs, 1066s, 1016vs, 856vs, 770vs, 739vs, 675s, 532s cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72 (2H, s, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 121.39, 126.58, 126.75, 134.86; Anal. Calcd for $C_6H_2Br_4$: C, 18.48; H, 0.52. Found: C, 18.47; H, 0.52], 2,4,6-tribromonitrobenzene [**5c**, 4%; mp 125°C, lit.[14] 124.5°C; MS m/z 363(M^+, 11), 361(M^+, 34), 359(M^+, 33), 357(M^+, 12), 333(16), 331(47), 329(47), 327(17), 317(5), 315(14), 313(14), 311(5), 305(9), 303(26), 301(26), 299(10), 252(7), 250(12), 248(6), 236(18), 234(36), 232(18), 155(41), 153(39), 74(100), 73(28); IR (KBr) 3115m, 3080m, 1555vs, 1543vs, 1371vs, 1352vs, 1106s, 855vs, 757vs, 729s, 721s, 578s, 503vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80 (2H, s, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 115.24, 125.34, 135.37, 135.88; Anal. Calcd for $C_6H_2Br_3NO_2$: C, 20.18; H, 0.56; N, 3.93. Found: C, 20.16; H, 0.55; N, 3.91], 2,4,6-tribromobenzonitrile [**2c**, 20%; mp 129°C, lit.[15] 129°C; MS m/z 343(M^+, 34), 341(M^+, 96), 339(M^+, 100), 337(M^+, 37), 262(15), 260(28), 258(15), 181(17), 180(10), 179(17), 178(9), 130(9), 100(55), 99(53), 74(18), 73(16); IR (Kbr) 3095m, 3068m, 2232s, 1558vs, 1527vs, 1440s, 1409s, 1370vs, 1352vs, 1190s, 1108s, 1086s, 1062s, 854vs, 809s, 747vs, 606s, 566s cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.83 (2H, s, H_{arom}); ^{13}C NMR ($CDCl_3$) δ 115.35, 117.73, 127.01, 128.10, 134.62; Anal. Calcd for $C_7H_2Br_3N$: C, 24.94; H, 0.60; N, 4.16. Found: C, 24.93; H, 0.60; N, 4.18] and 2,4,6-tribromophenol (**4c**, 4%).

*1,3-Bis(3-nitrophenyl)triazene (**10**).* The compound, prepared according to the procedure outlined by Houston et al.,[16] is an orange solid, mp 194°C with decomposition, lit.[16] 195-6°C with violent decomposition; MS m/z 287(M^+, 2), 259(3), 167(4), 166(5), 150(61), 138(9), 122(100), 92(41), 76(37), 75(41), 64(19); IR (KBr) 3282m, 3100w, 1617m, 1529vs, 1455s, 1415s, 1350vs, 1319s, 1286vs, 1246vs, 1205s, 1166s, 1156s, 879s, 807s, 739s, 671vs, 586s cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59 (2H, *app* t, J_o = 8.1 Hz, J_o = 8.3 Hz, H_{arom}), 7.78 (2H, ddd, J_o = 8.1 Hz, J_m = 2.0 Hz, J_p = 1.0 Hz, H_{arom}), 8.07 (2H, ddd, J_o = 8.1 Hz, J_m = 2.2 Hz, J_p = 1.0 Hz, H_{arom}), 8.27 (2H, *app* t, J_m = 2.0 Hz, J_m = 2.1 Hz, H_{arom}), 9.37 (1H, broad s, NH); Anal. Calcd for $C_{12}H_9N_5O_4$: C, 50.16; H, 3.16; N, 24.39. Found: C, 50.18; H, 3.18; N, 24.41.

*Reaction of **10** with tert-butyl nitrite and CuCN.* The reaction was carried out by adding the triazene **10** (10.1 mmol) in DMSO (15 mL) to a well stirred solution of CuCN (26.5 mmol) and *tert*-butyl nitrite (40.4 mmol) in DMSO (20 mL) keeping the mixture at 50°C. After usual workup (the overall recovery was poorer), the dark solution exhibited three products in the ratio 32:55:13, recognized by mass spectrometry as nitrobenzene (**3d**), 3-nitrobenzonitrile (**2e**) and 1,3-dinitrobenzene (**5e**).

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REFERENCES

1. a) Giumanini, A. G.; Verardo, G.; Gorassini, F.; Strazzolini, P. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 311-5. b) Cadogan, I. G.; Roy, D. A.; Smith, D. M. *J. Chem. Soc.* **1966**, 1249-50.
2. March, J. in *Advanced Organic Chemistry (Reactions, Mechanisms and Structure)*; John Wiley & Sons: New York, 1992; pp. 832-833, and references cited therein.
3. Roemming, C.; Eaerstad, K. *J. Chem. Soc., Chem. Commun.* **1965**, 299-300.
4. Kuokkanen, T. *Finn. Chem. Lett.* **1989**, *16*, 19-28.
5. Gloor, B.; Kaul, B. L.; Zollinger, H. *Helv. Chim. Acta* **1972**, *55*, 1596-1610.
6. Eckert, A.; Steiner, K. *Monats. Chem.* **1914**, *35*, 1153-1155.
7. Chirasi, A.; Maccarone, E.; Parisi, G.; Perrini, G. *J. Chem. Soc., Perkin Trans. II* **1982**, 957-959.
8. Auwers, K.; Boennecke, A.; Krollpfeiffer, F.; Peters, G. *Liebigs Ann. Chem.* **1915**, *408*, 212-284.
9. Chang, P.; Chiang, K. C.; Hsu, R. C. *Hua Hsüch Hsüeh Pao* **1958**, *24*, 141-146.
10. Knorr, R.; Ruhdorfer, J.; Boehrer, P.; Bronberger, H.; Raepple, E. *Liebigs Ann. Chem.* **1994**, 433-438.
11. Kinugasa, T.; Watarai, S. *Nippon Kagaku Zasshi* **1962**, *83*, 333-338 [*Chem. Abstr.* **1963**, *59*, 3796g].
12. Merz V.; Weith, W. *Ber. Dtsch. Chem. Ges.* **1883**, *16*, 2869-2889.

13. Richter, V. *Ber. Dtsch. Chem. Ges.* **1875**, *8*, 1425-1428.
14. Jackson, C. L. *Ber. Dtsch. Chem. Ges.* **1875**, *8*, 1772-1774.
15. Buning, H. L. *Rec. Trav. Chim.* **1921**, *40*, 327-353.
16. Houston, B.; Johnson, T. B. *J. Am. Chem. Soc.* **1925**, *47*, 3011-3018.

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