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Frontier Orbital Interactions in the Regioselectivity of the Amination of Nitroquinolines by Liquid Ammonia/Potassium Permanganate[1]

Marian Woźniak, Andrzej Barański, and Krystyna Nowak

Institute of Organic Chemistry and Technology, Polytechnical University, Kraków, Poland

Henk C. van der Plas*

Laboratory of Organic Chemistry, Agricultural University, De Dreijen 5, 6703 BC Wageningen, The Netherlands

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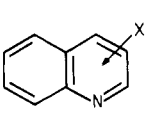
5-Nitro-, 6-nitro-, 7-nitro-, 8-nitro-, and 2-nitroquinoline and 5,7-dinitro- and 6,8-dinitroquinoline were aminated in a liquid ammonia solution of potassium permanganate. 8-Nitro- and 2-nitroquinoline were found to be unreactive. The intermediary σ-adducts, formed between 5,7-dinitro- and 6,8-dinitroquinoline and liquid ammonia, could be detected by ^{1}H NMR spectroscopy. FMO calculations nicely confirm the experimentally observed regioselectivity of the amination.

We recently reported that 3-nitroquinoline (**1a**) on treatment with liquid ammonia and potassium permanganate at −35 °C is converted into 4-amino-3-nitroquinoline (**2a**) and that 4-nitroquinoline (**1b**), when treated with the same reagents under identical conditions, gave 3-amino-4-nitroquinoline (**2b**).[2,3] This last-mentioned result shows that the replacement of hydrogen on the carbon adjacent to that of the nitro group is more favored than replacement of the hydrogen in the α-position of the ring nitrogen. Also kinetic studies show that nitro activation is of more importance than aza activation.[4] These results induced us to study the amination of the nitroquinolines more extensively. For that purpose we investigated the behavior of all the remaining nitroquinolines, i.e., the 5-nitro- (**1c**), 6-nitro- (**1d**), 7-nitro- (**1e**), 8-nitro- (**1f**), and 2-nitroquinoline (**1g**) toward liquid ammonia/potassium permanganate.

Results

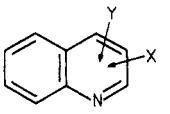
Mononitroquinolines. To a solution of each of the compounds **1c–g** in liquid ammonia was added potassium permanganate, and this solution was stirred for 10 h. Each of the reaction mixtures was found by TLC to contain only the aminonitroquinoline and starting material (Scheme I).

Scheme I



1

a: X = 3-NO_2
b: X = 4-NO_2
c: X = 5-NO_2
d: X = 6-NO_2
e: X = 7-NO_2
f: X = 8-NO_2
g: X = 2-NO_2



2

a: X = 3-NO_2, Y = 4-NH_2
b: X = 4-NO_2, Y = 3-NH_2
c: X = 5-NO_2, Y = 6-NH_2
d: X = 6-NO_2, Y = 5-NH_2
e: X = 7-NO_2, Y = 8-NH_2

After workup, **1c** was found to be converted into 6-amino-5-nitroquinoline (**2c**, 33%, recovered **1c**, 62% (GLC)), **1d** gave 5-amino-6-nitroquinoline (**2d**, 10%, recovered **1d**, 84% (GLC)), and **1e** yielded 8-amino-7-nitroquinoline (**2e**, 7%, recovered **1e**, 90% (GLC)). The 8-nitro compound **1f** was found to be completely inactive; the starting material could be recovered from the reaction mixture in an almost quantitative yield. From 2-nitroquinoline (**1g**) only a small amount of 2-aminoquinoline was formed. No indication for the formation of an amino-2-nitroquinoline was found.

On the basis of the yields of products and recovered material, the reactivity order in this series of compounds is 5-NO_2 > 6-NO_2 > 7-NO_2 ≫ 8-NO_2 ~ 2-NO_2. Both amino compounds **2d**[5] and **2e**[6] were prepared previously

(1) Part 47 on σ-adduct formation between azines and liquid ammonia. For part 46, see: Buurman, D. J.; Van der Plas, H. C. *J. Heterocycl. Chem.* **1986**, *23*, 1015.
(2) Tondys, H.; Van der Plas, H. C.; Woźniak, M. *J. Heterocycl. Chem.* **1985**, *22*, 353.
(3) For a recent review on Chichibabin amination, see: Van der Plas, H. C.; Woźniak, M. *Croat. Chem. Acta* **1986**, *59*, 33.
(4) Illuminati, G. *Adv. Heterocycl. Chem.* **1964**, *4*, 285.
(5) Huisgen, R. *Liebigs Ann. Chem.* **1948**, *559*, 142.

0022-3263/87/1952-5643$01.50/0

Table I. Chemical Shifts (δ) of Ring Hydrogens in the Compounds 3 and 6 in Various Solvents[a]

compd	solvent	H-2	H-3	H-4	H-5	H-6	H-7	H-8
3	DMSO-d_6	9.27	8.02	8.90		9.01		9.14
	NH_3	8.32	7.32	9.04		8.78		5.27
	$\Delta\delta$	−0.95	−0.70	+0.14		−0.23		−3.87
6	DMSO-d_6	9.23	7.90	8.89	9.07		9.36	
	NH_3	8.44	6.18	7.85	5.17		8.75	
	$\Delta\delta$	−0.79	−1.72	−1.04	−3.90		−0.61	

[a] $J_{H_8-H_4}$ = 1.1 Hz; $J_{H_5-H_7}$ = 2.8 Hz.

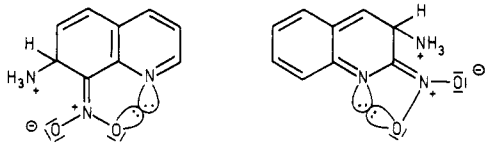


Figure 1.

from **1d** and **1e**, respectively, by treatment with hydroxylamine hydrochloride in ethanol, containing potassium hydroxide. Interestingly, **1c** has been reported[6] to give the hydroxylamine hydrochloride in basic medium 8-amino-5-nitroquinoline, while with our aminating system **1c** only yields the 6-amino compound **2c**.

In the conversion of **1a,1b** into **2a,2b** the intermediate covalent σ-amino adducts were detected by ^{1}H NMR spectroscopy.[2] In order to establish whether σ-adduct formation could also be observed between the substrates **1c–g** and liquid ammonia, we measured solutions of the compounds **1c–g** in liquid ammonia (thus solutions that do not contain potassium permanganate) by ^{1}H NMR spectroscopy. At −35 °C as well as at +10 °C in each of these solutions no absorptions that could be attributed to the presence of covalent σ-adducts could be identified. If these adducts are present, apparently their concentrations are too low to be detectable by the NMR technique.

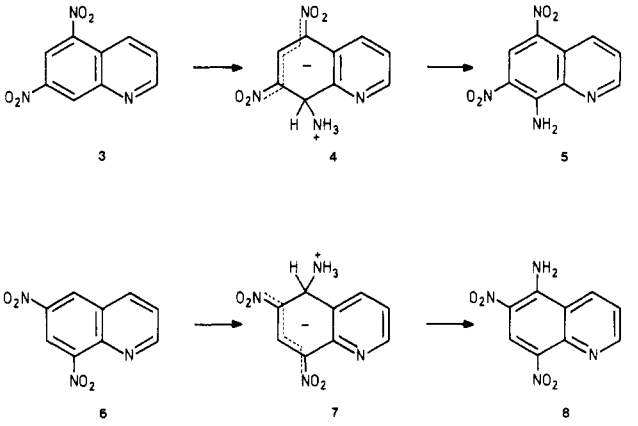
From these and previous NMR measurements it is clearly shown that the presence of a nitro group in the pyridine ring (**1a**, **1b**) leads to a stable, easily detectable covalent σ-adduct but that in the case where the nitro group is present in the benzene ring, the electrophilicity of the benzene ring is apparently too low to allow adduct formation. In the kinetic scheme usually presented for

$$1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \sigma\text{-adduct} \xrightarrow{k_2} \text{product } 2$$

nucleophilic replacement reactions, it means that in liquid ammonia for **1a,b** k_1/k_{-1} is large and k_2 small compared to k_{-1}, but that for **1c,e** k_1/k_{-1} is very small and also k_2 small compared to k_{-1}.[3] In the presence of an oxidant the rate of formation of product **2** is strongly enhanced, shifting the equilibrium 1 $\rightleftharpoons$ σ-adduct to the right in the case of **1c–e**. The reason why the 2- and 8-nitro compounds do not give adducts is not clear but is possibly due to an electronic repulsion between the sp^2 electrons on the nitrogen of the pyridine ring and the developing negative charge on the oxygen of the nitro group during adduct formation (Figure 1).

Dinitroquinolines. Whereas, as we have seen above, the presence of *one* nitro group in the benzene ring does not lead to a detectable amount of σ-amino adducts, *two* nitro groups in the benzene ring have been found to make the ring sufficiently electrophilic to give easily detectable adducts. As seen from the Table I, 5,7-dinitroquinoline (**3**) gives, when dissolved in liquid ammonia (−45 °C), the 8-amino adduct **4** ($\Delta\delta$(H-8) = 3.87 ppm) and 6,8-dinitroquinoline (**6**) yields the 5-amino adduct **7** ($\Delta\delta$(H-5) = 3.90 ppm). These spectra did not change when raising the temperature of these solutions from −45 °C to +10 °C. The assignments of the hydrogens in **3**, **4**, **6**, and **7** were supported by measurements of deuteriated derivatives of **3** and **6** in DMSO-d_6 and in liquid ammonia. Addition of potassium permanganate to these solutions lead to the formation of the corresponding 8-amino-5,7-dinitroquinoline (**5**, 40%) and 5-amino-6,8-dinitroquinoline (**8**, 43%) (Scheme II).

Scheme II



FMO Calculations Concerning the Regioselectivity of the Amination of Nitroquinolines. Regioselectivity in nucleophilic substitutions of organic compounds can be predicted by means of the theory of pertubation of molecular orbitals. According to this theory the reaction between an organic compound A and a nucleophile N are considered as a second-order pertubation. This pertubation involves "mixing" occupied MO's of N with unoccupied MO's of A. Usually not all interactions are considered, only those which give the most important contributions for the stabilization energy (ΔE) of the reacting system. As a rule it involves interactions between the highest occupied orbitals (HOMO) of nucleophile N and the lowest unoccupied orbitals (LUMO) of starting material A. Using approximate calculations, it is sufficient to consider only the LUMO orbital or the LUMO and LUMO + 1 orbitals of A.[7] Within the framework of second-order pertubation theory the total stabilization energy (ΔE) can be written as the sum of HOMO/LUMO and HOMO/(LUMO + 1) pertubation energies (eq 1). C_r

$$\Delta E_{AN} = C_r^2(\text{HOMO})\beta_{rs}^2\left[\frac{2C_s^2(\text{LUMO})}{E^N_{\text{HOMO}} - E^A_{\text{LUMO}}} + \frac{2C_s^2(\text{LUMO}+1)}{E^N_{\text{HOMO}} - E^A_{\text{LUMO}+1}}\right] \quad (1)$$

is the HOMO coefficient of the nucleophile N; C_s is the

(6) Colonna, M.; Montanari, F. *Gazz. Chim. Ital.* **1951**, *81*, 744; *Chem. Abstr.* **1952**, *46*, 70934.

(7) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: Chichester, Sussex, England, 1976.

Table II

mononitroquinoline	values of coefficients of LUMO and LUMO + 1 at atoms								$E_{LUMO+1} - E_{LUMO}$ [eV]
	N-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	
1a	−0.210	−0.095	0.419	−0.509	0.278	−0.030	−0.334	0.187	−1.66
	0.259	−0.511	0.068	0.270	−0.231	0.426	−0.086	−0.278	−1.07
1b	0.370	−0.216	−0.446	0.467	−0.232	0.220	0.156	−0.251	−1.69
	0.046	−0.413	0.362	−0.014	0.051	0.335	−0.341	−0.041	−0.96
1c	0.228	−0.163	−0.252	0.281	−0.422	0.411	0.217	−0.458	−1.61
	−0.013	0.391	−0.327	−0.052	0.011	−0.370	0.361	0.006	−0.94
1d	−0.187	0.369	0.048	−0.316	0.466	−0.410	0.084	0.274	−1.58
	0.221	0.103	−0.446	0.280	−0.237	−0.087	0.481	−0.278	−1.09
1e	−0.235	0.021	0.365	−0.253	0.279	0.078	−0.418	0.460	−1.55
	−0.219	0.453	−0.050	−0.309	0.289	−0.482	0.093	0.233	−1.08
1f	0.229	−0.259	−0.198	0.332	−0.469	0.232	0.399	−0.427	−1.53
	0.017	0.374	−0.350	−0.004	−0.007	−0.355	0.375	−0.003	−0.94
1g	−0.390	0.459	−0.068	−0.319	0.207	−0.354	−0.018	0.291	−1.56
	−0.191	−0.111	0.507	−0.343	0.293	0.051	−0.414	0.231	−1.13

Table III

mononitroquinoline	values of ΔE when a molecule of NH_3 attacks position								preferable position for NH_3 attack
	N-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	
1a	0.023	0.054	0.038	0.069	0.027	0.036	0.025	0.023	C-4 > C-2 > C-6
1b	0.029	0.043	0.067	0.046	0.012	0.032	0.028	0.014	C-3 > C-4 > C-2
1c	0.011	0.035	0.034	0.017	0.037	0.062	0.035	0.044	C-6 > C-8 > C-5
1d	0.017	0.030	0.040	0.036	0.056	0.036	0.047	0.031	C-5 > C-7 > C-3
1e	0.021	0.041	0.028	0.032	0.033	0.047	0.038	0.055	C-8 > C-6 > C-2
1f	0.011	0.041	0.032	0.023	0.046	0.036	0.060	0.038	C-7 > C-5 > C-2
1g	0.039	0.046	0.052	0.045	0.026	0.027	0.034	0.028	C-3 > C-2 > C-4

Table IV

no.	formal charge at the atom								preferable position for NH_3 attack
	N-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	
2-NO_2	−0.1538	*0.0575*	−0.0608	*0.0029*	−0.0421	−0.0355	−0.0520	−0.0118	C-2 > C-4
3-NO_2	−0.2199	*0.1250*	−0.1577	*0.1080*	−0.0167	−0.0600	−0.0259	−0.0389	C-2 > C-4
4-NO_2	−0.1791	*0.0508*	−0.0405	−0.0093	−0.0331	−0.0456	−0.0468	−0.0230	C-2 > C-4
5-NO_2	−0.2160	*0.0795*	−0.1131	0.0119	−0.0598	*0.0329*	−0.0886	*0.0306*	C-2 > C-6 > C-8
6-NO_2	−0.2237	*0.0990*	−0.1263	*0.0262*	*0.0634*	−0.0869	−0.0055	−0.0344	C-2 > C-5 > C-4
7-NO_2	−0.2063	*0.0779*	−0.1028	*0.0000*	−0.0373	−0.0160	−0.0729	*0.0639*	C-2 > C-8 > C-4
8-NO_2	−0.2031	*0.0980*	−0.1205	*0.0148*	*0.0210*	−0.0937	0.0454	−0.0603	C-2 > C-7 > C-5 > C-4

LUMO (or LUMO + 1) coefficient of the different reaction centers of the organic compound A; β_{rs} is the resonance integral, featuring the interaction between the reaction centers r and s. Since $C_r^2(\text{HOMO})\beta_{rs}^2$ is constant in the reaction series under consideration, eq 1 can be simplified to eq 2. When the starting material A has several potential reaction centers, nucleophile N will most favorably attack that position in A that leads to the highest stabilization energy. To calculate the values of ΔE for the several positions in the nitroquinolines, we had to calculate the LUMO and LUMO + 1 energy levels of the mononitroquinolines studied and to determine the value of the coefficients at the carbons and ring nitrogen in the LUMO and LUMO + 1 for each mononitroquinoline. Quantum-chemical calculations of mononitroquinolines were carried out by the MNDO method. In each case bond lengths and bond angles were optimized. Initial values of bond lengths and angles were those given by Beveridge and Pople.[8] We reasonably assumed that the mononitroquinolines have a flat molecular structure. The values obtained for the LUMO and LUMO + 1 energy levels and the respective values of coefficients C_s are presented in Table II. For

$$\Delta E \sim 2\left[\frac{C_s^2(\text{LUMO})}{E^N_{\text{HOMO}} - E^A_{\text{LUMO}}} + \frac{C_s^2(\text{LUMO}+1)}{E^N_{\text{HOMO}} - E^A_{\text{LUMO}+1}}\right] \quad (2)$$

the molecule of ammonia a full optimization was carried out and the value $E^N_{\text{HOMO}} = -11.19$ eV was found. With use of these data, the ΔE values for each position of the studied mononitroquinolines are calculated (see Table III). The calculations nicely confirm the experimental results obtained with the compounds **1a–e**. In each of these compounds the highest contribution of stabilization energy is the position adjacent to the one occupied by the nitro group. Moreover, those calculations also predict that the order of reactivity is 3-NO_2 ~ 4-NO_2 > 5-NO_2 ≃ 8-NO_2 > 6-NO_2 > 7-NO_2 > 2-NO_2. With the exception of the 8-NO_2 and 2-NO_2 compounds, this order of reactivity is also in agreement with the experiments. The fact that the calculations show that the 8-NO_2 compound is more susceptible to amination than the 7-NO_2, while experimentally the reverse is observed (8-NO_2 compound is complete unreactive), strongly suggests that the formation of the initial adduct at C-7 in the 8-NO_2 compound is not inhibited for kinetic reasons but due to factors discussed above. We have also calculated, for comparison, the formal charges/electron densities on all annular carbon and nitrogen atoms (see Table IV). In general, these data do not confirm the results of experiments. Therefore, it seems that the electron density is not a suitable parameter for predicting the regiospecific S^H_N substitution in nitroquinolines.

Experimental Section

Melting points are uncorrected and were determined on a Kofler plate. The ^{1}H NMR spectra were recorded on a Tesla BS-80 or

(8) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

a Varian EM-390 spectrometer equipped with a Varian EM-3940 variable temperature controller. Tetramethylsilane was used as internal standard; in liquid ammonia the solvent peak was used as the standard. Mass spectra were carried out with a LKB GC/MS 9000 or AEI MS 902 spectrometer.

Synthesis of Starting Material and Reference Compounds. 5-, 6-, 7-, and 8-Nitroquinolines[9] and 6,8-dinitroquinoline[10] were obtained by Skraup reactions from the respective aminonitrobenzenes. 6-Amino-5-nitro-,[11] 5-amino-6-nitro-,[5] and 8-amino-7-nitroquinolines[6] were prepared according to published procedures.

5,7-Dinitroquinoline (3). A mixture of 2 g (11.5 mmol) of 5-nitroquinoline, 20 mL of fuming nitric acid (d = 1.51), and 20 mL of fuming sulfuric acid containing 25% sulfur trioxide was heated at 150 °C under reflux for 30 h. The solution was poured on ca. 150 g of ice and neutralized with a water solution of ammonia. A yellow precipitate was filtered off, washed with water, dried, and recrystallized twice from methanol to give 0.55 g (22%) of **3**: light-yellow needles, mp 185–186 °C (lit. mp 179 °C,[12] 182–183 °C[13]). The compound showed identical properties with those obtained by Skrauping of 3,5-dinitroaniline.[13] For the ^{1}H NMR data, see Table I.

2-Nitroquinoline. The compound was obtained according to a somewhat modified prescription given in the literature.[14,15] A mixture of 1.5 g (6 mmol) of 2-iodoquinoline,[18] 2 g (30 mmol) of anhydrous sodium nitrite, and 10 mL of anhydrous dimethyl sulfoxide was heated at 145–150 °C for 3 h. After cooling the mixture was diluted with 100 mL of water and a dark-yellow precipitate was obtained, which was filtered off and washed with water. The precipitate was then suspended in 50 mL of 2% aqueous solution of sodium hydroxide and stirred for 10 min. The decolorized mixture was extracted with chloroform (ca. 50 mL), the chloroform solution was dried with anhydrous sodium sulfate, and the solvent was removed. The residue was twice recrystallized from methanol to give 0.22 g (22%) of 2-nitroquinoline: light-yellow needles at mp 126–127 °C (lit. mp 121–122 °C,[14] 125 °C[9]); MS, m/e (relative intensity) 174 (M^+, 12), 144 ($M^+ - NO$, 3.5), 128 ($M^+ - NO_2$, 100). Anal. Calcd for $C_9H_6N_2O_2$: C, 62.07; H, 3.45; N, 16.09. Found: C, 62.15; H, 3.62; N, 16.22.

Deuteriation of 5,7-Dinitroquinoline (3) and 6,8-Dinitroquinoline (6). A mixture of 0.1 g of the appropriate dinitroquinoline and 8 mL of deuterium oxide was heated in a steel autoclave (capacity 50 mL) at 200 °C for 8 h. After cooling, deuterium oxide was removed. The dark-yellow residue was dissolved in 20 mL of acetone, the solution was filtered, and the solvent was stripped off to give 70 mg of the deuteriated product. ^{1}H NMR analysis (in DMSO) showed that the contents of deuterium in 5,7-dinitroquinoline amounted to 48% at position 2, 100% at C-6, and 83% at C-8. In 6,8-dinitroquinoline the amount of deuterium at position 2 was 31%, 39% at C-5, and 100% at C-7.

Amination of Mononitroquinolines 1c–e. To 40–45 mL of liquid ammonia were added 0.5 g (2.9 mmol) of mononitroquinoline and 1 g of potassium permanganate, and the mixture was stirred for 10 h. After evaporation of liquid ammonia, 40–50 mL of water was added and the mixture was continuously extracted with chloroform for 20 h. The residue obtained after evaporation of the solvent was worked up in the manner given below.

Amination of 5-Nitroquinoline (1c). The yellow residue was recrystallized twice from benzene to give 0.18 g (33%) of 6-amino-5-nitroquinoline: yellow-orange needles, mp 176–178 °C (lit. mp 175–176 °C,[17] 177–178 °C[11] 178 °C[18]). MS, m/e (relative intensity) 189 (100); ^{1}H NMR (in DMSO) δ 8.9 (dd, 4 H), 8.62 (dd, 2 H), 8.21 (br s, NH_2), 7.93 (d, 8 H), 7.55 (dd, 3 H), 7.41 (d, 7 H), $J_{2,3}$ = 4.2 Hz, $J_{2,4}$ = 1.5 Hz, $J_{3,4}$ = 8.4 Hz, $J_{4,8}$ = 0.6 Hz (from the extended spectrum). Anal. Calcd for $C_9H_7N_3O_3$: C, 57.14; H, 3.70; N, 22.22. Found: C, 57.15; H, 3.72; N, 22.24. The compound was fully identical (mp and ^{1}H NMR spectrum) with an authentic specimen of 6-amino-5-nitroquinoline[11] obtained from 6-bromo-5-nitroquinoline.

After evaporation of benzene from the mother liquid and crystallization of the residue from water, 0.28 g (56%) of **1c** was recovered.

Amination of 6-Nitroquinoline (1d). The yellow residue was dissolved in 30 mL of chloroform and separated on a chromatographic column filled with silica gel (Merck 60, 3 × 30 cm) and using chloroform as eluent. After separation of **1d** [0.33 g (66%) after recrystallization from petroleum ether (60–80 °C)] (ca. 500 mL of chloroform was used), further elution (ca. 250 mL of chloroform) gave 55 mg (10%) of 5-amino-6-nitroquinoline: yellow needles (from toluene) at mp 287–288 °C subl (lit. mp 283–284.5 °C[5]); ^{1}H NMR (in DMSO) δ 9.10–8.96 (multiplet, 2 H, 4 H), 8.75 (br s, NH_2), 8.22 (d, 7 H), 7.62 (dd, 3 H), 7.16 (d, 8 H, $J_{2,3}$ = 4.5 Hz, $J_{2,4}$ = 1.5 Hz, $J_{3,4}$ = 8.5 Hz. The compound showed identical properties (mp, ^{1}H NMR) with those of the reference sample.[5]

Amination of 7-Nitroquinoline (1e). The yellow residue was dissolved in 5 mL of chloroform and separated in similar way as described for the 6-nitroquinoline. The first fraction from the chromatographic column (after using ca. 100 mL of chloroform) gave 35 mg (7%) of 8-amino-7-nitroquinoline. Crystallization from toluene yielded orange needles: mp 188–189 °C subl (lit. mp 185–185.5 °C[6]); ^{1}H NMR (in $CDCl_3$) δ 8.80 (dd, 2 H), 8.12 (d, 6 H), 8.05 (dd, 4 H), 8.20–7.90 (br s, NH_2), 7.53 (dd, 3 H), 6.92 (d, 5 H), $J_{2,3}$ = 4.5 Hz, $J_{2,4}$ = 1.5 Hz, $J_{3,4}$ = 9.0 Hz, $J_{5,6}$ = 9.0 Hz. The compound had identical properties (mp and ^{1}H NMR) with those of a reference sample.[6] By further elution with a mixture of chloroform and methanol (1:1; 200 mL) 0.32 g (64%) of **1e** could be recovered after recrystallization from petroleum ether (60–80 °C).

Amination of 2-Nitroquinoline (1g). The residue obtained was extracted with $CDCl_3$ and then purified in the same way as described in the previous reaction. The first fraction gave 95 mg of starting material and the second one ca. 5 mg of 2-aminoquinoline. This compound was identified by comparison of its properties (mp, R_f) with those of a reference sample.[2]

Amination of the Dinitroquinolines 3 and 6. In 30 mL of liquid ammonia 0.2 g of the respective dinitroquinoline **3** or **6** was dissolved, and to the red solution was added 0.5 g of potassium permanganate. The mixture was stirred for 0.5 h, ammonia was evaporated off, 40–50 mL of water was added, and the mixture was continuously extracted with chloroform for 20 h. The residue after evaporation of the solvent was recrystallized twice from methanol t give the products.

8-Amino-5,7-dinitroquinoline: orange needles, mp 189–190 °C (lit.[18] mp 187–189 °C); yield 85 mg (40%); MS, m/e (relatve intensity) 234 (100). Anal. Calcd for $C_9H_6N_4O_4$: C, 46.15; H, 2.56; N, 23.93. Found: C, 46.14; H, 2.65; N, 24.19.

5-Amino-6,8-dinitroquinoline: orange needles, mp 280–283 °C dec (lit.[19] mp 273–277 °C); yield 90 mg (43%); MS, m/e (relative intensity) 234 (100); ^{1}H NMR (in DMSO) δ 9.23 (br s, NH_2), 9.17–9.07 (multiplet, 2 H, 4 H), 8.83 (s, 7 H), 7.55 (dd, 3 H), $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 9.0 Hz. Anal. Calcd for $C_9H_6N_4O_4$: C, 46.15; H, 2.56; N, 23.93. Found: C, 46.00; H, 2.60; N, 23.94.

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Registry No. **1c**, 607-34-1; **1d**, 613-50-3; **1e**, 613-51-4; **1f**, 607-35-2; **1g**, 18714-34-6; **2c**, 42606-37-1; **2d**, 35975-00-9; **2e**, 42606-35-9; **3**, 62163-05-7; **4**, 111292-07-0; **5**, 31009-29-7; **6**, 88609-20-5; **7**, 111292-08-1; **8**, 111292-06-9.

(9) Filippi, J. *Bull. Soc. Chim.* **1968**, 259.
(10) Riecke, A.; Schmilz, E.; Dietrich, P. *Chem. Ber.* **1959**, *92*, 2239.
(11) Kulka, M.; Manske, H. F. *Can. J. Chem.* **1952**, *30*, 711.
(12) Claus, A.; Hartman, G. *J. Prakt. Chem.* **1901**, *53*, 198.
(13) Kaufman, A.; Hüssy, H. *Ber.* **1908**, *41*, 1735.
(14) Fatuta, S.; Furlan, F. *Nat. Ric. Sci.* **1964**, *4*, 485.
(15) Fatuta, S.; Mauro, M.; Pasin, C. *Ric. Sci., Parte 2: Sez. A* **1965**, *8*, 736.
(16) Baker, W.; Curtius, R. F.; Edwards, M. G. *J. Chem. Soc.* **1951**, *83*; *Houben-Weyl 5/4*, p 606.
(17) Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1945**, 699.
(18) Kaufmann, A.; Zeller, O. *Ber.* **1917**, *50*, 1629.
(19) Dikshoorn, R. P. *Recl. Trav. Chim. Pays-Bas* **1929**, *48*, 244.