Aromatic nucleophilic substitution of hydrogen: reactions of 6-nitroquinoline with potassium cyanide and nitroalkanes

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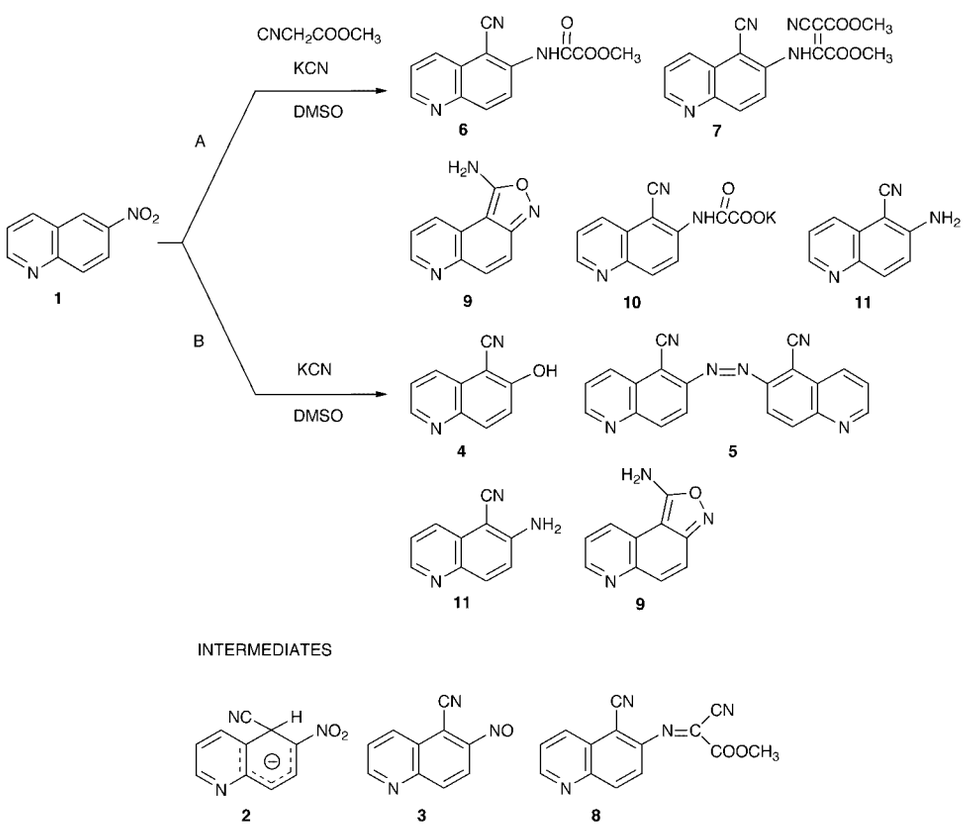
The reactions of 6-nitroquinoline **1** and potassium cyanide with methyl nitroacetate, nitroethane, 1-nitropropane, and 2-nitropropane have been carried out in the medium of dimethyl sulfoxide. ^{1}H NMR has been used to identify the reaction products from 6-nitroquinoline **1** with methyl nitroacetate and potassium cyanide and to determine the proportions of products in the reaction mixture. The main reaction products are 6-(methoxalylamino)quinoline-5-carbonitrile **6** and 1-aminoisoxazolo[4,3-*f*]quinoline **9**. The reactions of 6-nitroquinoline **1** with potassium cyanide and primary nitroalkanes give, as the main products, 3-substituted pyrido[3,2-*f*]quinazolin-1(2*H*)-ones **12a**,**b**. The reaction of 6-nitroquinoline **1** and potassium cyanide with 2-nitropropane produces 3-(1-cyano-1-methylethyl)-2,3-dihydro-1*H*-pyrazolo[4,3-*f*]quinolin-1-one **14** as the chief product. In all cases the reaction involves substitution of the 5-hydrogen of quinoline skeleton with concomitant lowering of oxidation number of the nitrogen atom in the original nitro group of **1**. A mechanism is suggested for the reactions investigated involving 6-nitrosoquinoline-5-carbonitrile **3** as a likely common intermediate.

Introduction

Earlier described[1–4] aromatic nucleophilic substitution reactions of hydrogen by cyanide ion in 6-nitroquinoline **1** were presumed[1] to involve the Meisenheimer adduct **2** as an unstable intermediate followed by 6-nitrosoquinoline-5-carbonitrile **3**. Unless the reaction mixture contains a nucleophilic reagent which could react further with the nitroso group, the main reaction products are 6-hydroxyquinoline-5-carbonitrile **4** and [6,6′-azodiquinoline]-5,5′-dicarbonitrile **5** (Scheme 1, B).[1] If there is also methyl cyanoacetate in the reaction mixture beside 6-nitroquinoline **1** and potassium cyanide (Scheme 1, A), then the chief reaction products are 6-(methoxalylamino)quinoline-5-carbonitrile **6** and dimethyl 2-cyano-3-(5-cyanoquinolin-6-ylamino)butenedioate **7**.[1,2] Azomethine **8** is the intermediate of this reaction (Scheme 1, A).[1] The cyano group bound to the carbon atom of the azomethine group plays the role of a good leaving group in the subsequent nucleophilic addition reactions to the C=N bond and the following nucleophilic substitution. This leads to a presumption that analogous reactions of azo-



Scheme 1

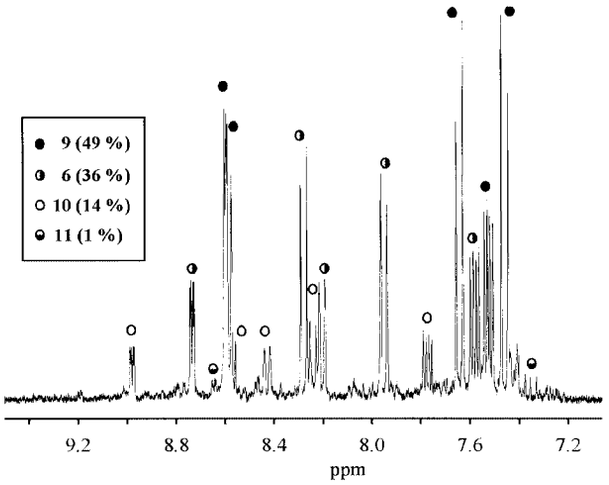


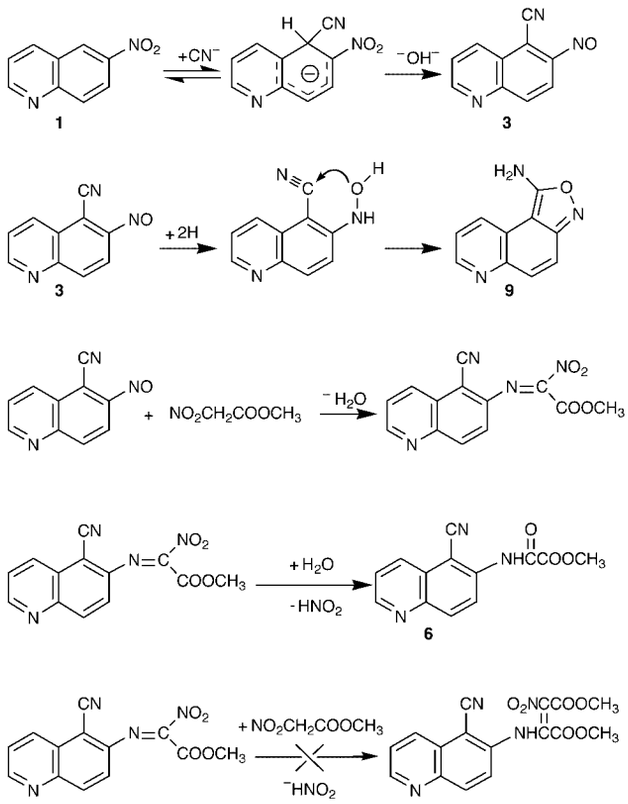
Fig. 1 ^{1}H NMR spectrum of reaction mixture of 6-nitroquinoline, methyl nitroacetate, and potassium cyanide in [$^2H_6$]dimethyl sulfoxide measured 24 h after mixing the starting substances (detail of aromatic region).

methines with nucleophilic reagents will proceed even if the cyano group is replaced by some other suitable leaving group, *e.g.*, a nitro group.[5–7] That is why the reactions of 6-nitroquinoline **1** with some aliphatic nitro compounds (methyl nitroacetate, nitroethane, 1-nitropropane, and 2-nitropropane) and potassium cyanide have been studied in the present work under experimental conditions similar to those in the previously described reaction of 6-nitroquinoline **1** with potassium cyanide and methyl cyanoacetate.

Results and discussion

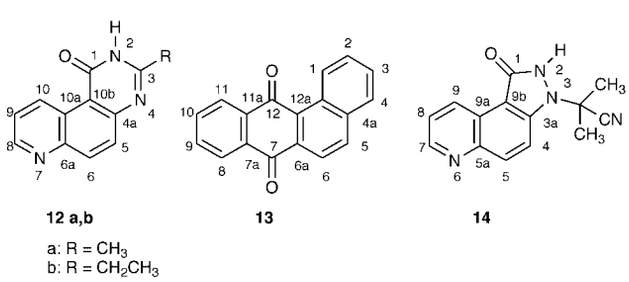
Using ^{1}H NMR spectroscopy, we analyzed the products of the reaction of 6-nitroquinoline **1** with methyl nitroacetate and potassium cyanide in [$^2H_6$]dimethyl sulfoxide medium (Fig. 1). The reaction products did not need to be isolated because their structure could be determined by comparing the ^{1}H NMR spectra of standards with that of the reaction mixture, *e.g.*, by the method of addition of each pure component to the reaction mixture. The reaction of 6-nitroquinoline **1**, methyl nitroacetate and potassium cyanide (Scheme 2), at the molar proportions of the starting substances which are given in the Experimental section, produces 1-aminoisoxazolo[4,3-*f*]quinoline **9** (49%), 6-(methoxalylamino)quinoline-5-carbonitrile **6** (36%), potassium salt of *N*-(5-cyanoquinolin-6-yl)oxamic acid **10** (14%), and 6-aminoquinoline-5-carbonitrile **11** (1%). The products given are identical with those formed in the reaction of 6-nitroquinoline **1** with potassium cyanide and methyl cyanoacetate (Scheme 1, A).[1] The proportions of individual components (calculated from integral intensities of proton signals, neglecting products present in amounts below 1%) are distinctly different as compared with the previous reaction. In addition, the reaction mixture completely lacks an analogue of butenedioic acid **7**, which means that the reaction of the imine similar to **8** with the anion of methyl nitroacetate does not take place. The formation of main products of the reaction of 6-nitroquinoline **1** with methyl nitroacetate and potassium cyanide is presented in Scheme 2.

Furthermore, we studied reactions of 6-nitroquinoline **1** with nitroethane, 1-nitropropane, and 2-nitropropane taking place with participation of potassium cyanide in the medium of dimethyl sulfoxide. ^{1}H NMR spectra of the reaction mixtures (Fig. 2A and C) are relatively complex, nevertheless they provide valuable information about products of the individual reactions. In the cases of the primary nitroalkanes, the spectra of the corresponding mixtures exhibit a multiplet for the chief component with a characteristic, high value of chemical shift



Scheme 2

at about 10.2 ppm. This signal is completely absent from the spectra of the reaction mixture of 6-nitroquinoline **1** with 2-nitropropane, where, on the other hand, we observed another characteristic multiplet with the chemical-shift-value of 9.4 ppm. As the structure of compounds with the above-mentioned chemical shifts was not known, it was necessary to carry out isolation of products from the reaction mixtures and to determine their structure. The syntheses of necessary compounds were carried out under reaction conditions similar to those for the reaction performed in NMR tubes but on a larger scale. The isolation procedure consisted in distilling off the solvent together with excess of nitroalkane under reduced pressure, chromatographic separation of the distillation residue, and recrystallization of the separated components. In this way it was possible to obtain, in high purity, the main products of reaction of 6-nitroquinoline **1** with nitroethane, 1-nitropropane, and 2-nitropropane.



The described procedure applied to the dimethyl sulfoxide–nitroethane mixture gave 3-methylpyrido[3,2-*f*]quinazolin-1(2*H*)-one **12a**, which exhibits in its ^{1}H NMR spectrum (Fig. 2, B) an abnormally high chemical shift for the H-10 hydrogen atom (10.16 ppm). Comparison of the spectrum of isolated substance **12a** with that of the reaction mixture (Fig. 2, A and B) showed that the isolated compound **12a** is identical with the main reaction product from 6-nitroquinoline **1** and nitroethane

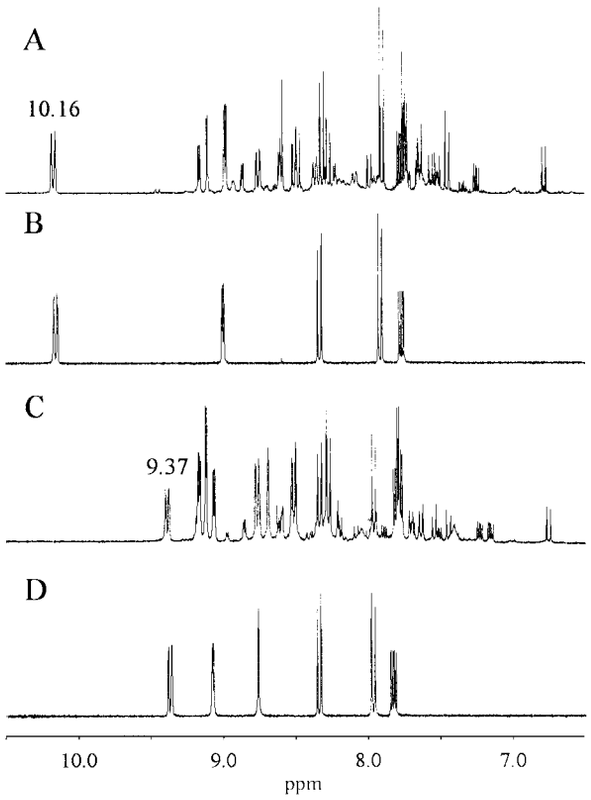


Fig. 2 A, ^{1}H NMR spectrum of reaction mixture after reaction of 6-nitroquinoline, KCN and nitroethane in [$^2H_6$]dimethyl sulfoxide. B, ^{1}H NMR spectrum of compound **12a**. C, ^{1}H NMR spectrum of reaction mixture after reaction of 6-nitroquinoline, KCN and 2-nitropropane in [$^2H_6$]dimethyl sulfoxide. D, ^{1}H NMR spectrum of compound **14**.

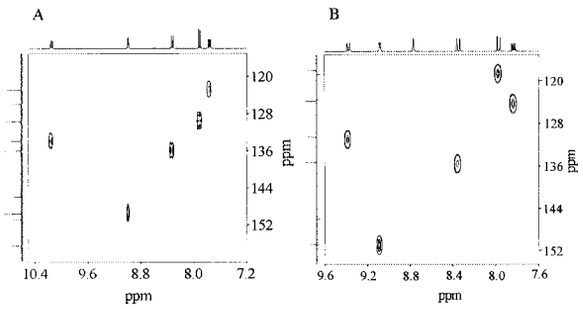


Fig. 3 A, 2D ^{1}H–^{13}C reverse-detected NMR spectrum of compound **12a**. B, 2D ^{1}H–^{13}C reverse-detected NMR spectrum of compound **14**.

and potassium cyanide in dimethyl sulfoxide medium. Compound **12a** was identified on the basis of elemental analysis, mass spectrometry, and ^{1}H and ^{13}C NMR spectroscopy. Mass spectrometry gave the mass of the molecular ion ($M^+ = 211$, 100%), and the measurement of high resolution gave the molecular formula as $C_{12}H_9N_3O$, which was confirmed by elemental analysis. The greatest amount of information on the structure of compound **12a** was obtained from NMR spectra. The ^{1}H NMR spectrum is characteristic of a 5,6-disubstituted quinoline (Fig. 2B) but for the unusually high chemical shift of the proton bound at the 4-position of quinoline skeleton (*i.e.*, H-10 here). Moreover, we detected a singlet for the methyl group at 2.50 ppm and a very broad signal for the NH hydrogen at 12.73 ppm. An unambiguous assignment of chemical shifts for carbon atoms of CH type in the ^{13}C NMR spectrum of compound **12a** was achieved with the help of the heterocorrelated spectrum measured with inverse detection (Fig. 3, A). The assignment of quaternary carbon atoms was carried out with the use of a ^{13}C selective INEPT experiment with selective transmissions of polarization from H-10, H-5, and H-6 protons.

The above described treatment of the reaction mixture of 6-nitroquinoline **1**, 1-nitropropane and potassium cyanide in dimethyl sulfoxide led to the isolation of 3-ethylpyrido[3,2-*f*]-quinazolin-1(2*H*)-one **12b**. The structure of compound **12b** was verified in the same way as described above for compound **12**a. The very high value of the chemical shift of the H-10 proton in pyridoquinazolinones **12a**,**b** is due to the shielding effect by the carbonyl oxygen atom, the C=O group being close in space to the shielded H-10 nucleus. The same effect was observed also in the case of substituted benz[*a*]anthracene-7,12-diones,[8] where the spatial arrangement of carbonyl oxygen atom and aromatic hydrogen is analogous. Thus *e.g.* the ^{1}H NMR spectrum of benz[*a*]anthracene-7,12-dione **13** exhibits[8] a signal for the H-1 proton at 9.62 ppm, whereas the signals of other protons are found in the interval 7.50–8.30 ppm.

The side products of the reaction of 6-nitroquinoline **1** with primary nitroalkanes with participation of potassium cyanide include 6-hydroxyquinoline-5-carbonitrile **4** and 1-amino-isoxazolo[4,3-*f*]quinoline **9**. Both these substances are also formed in the reaction of 6-nitroquinoline **1** with potassium cyanide (Scheme 1, B).[1] These compounds were identified by comparing the spectra of reaction mixtures with those of pure compounds. Due to the considerable overlap of signals in the ^{1}H NMR spectra of reaction mixtures (Fig. 2, A) it was impossible to determine the proportions of the individual products.

The isolation carried out from the mixture of dimethyl sulfoxide–2-nitropropane gave 3-(1-cyano-1-methylethyl)-2,3-dihydro-1*H*-pyrazolo[4,3-*f*]quinolin-1-one **14** whose ^{1}H NMR spectrum exhibits a characteristic signal at 9.4 ppm (Fig. 2, D). Comparison of the spectrum of pure component **14** with those of 6-nitroquinoline **1**, 2-nitropropane, and potassium cyanide in [$^2H_6$]dimethyl sulfoxide medium (Fig. 2, C) confirmed that the isolated substance is identical with the chief product of the respective reaction. For determination of the structure of compound **14** we again used the results of elemental analysis, mass spectrometry and especially NMR spectroscopy.

A significant piece of information about the structure of **14** was obtained from the NOESY spectrum (Fig. 4) wherefrom it follows that the methyl hydrogen atoms and the aromatic proton at the 4-position are close to each other in space; on the other hand, no cross-peak was detected with the H-2 proton. Another piece of information about the structure of compound **14** was obtained from measurements of ^{13}C NMR spectra of the reaction mixture of 6-nitroquinoline **1**, 2-nitropropane, and K^{13}CN (99.5% + ^{13}C) which confirmed that both the carbonyl carbon atom (159.6 ppm) and the cyano group carbon atom (118.9 ppm) in compound **14** come from the labelled cyanide (Fig. 5). The signal at 166.8 ppm is due to 1-aminoisoxazolo-[4,3-*f*]quinoline **9**; the other signals lying in the interval 113–123 ppm (the region of cyano groups) are due to minor reaction products.

An unambiguous assignment of chemical shifts of carbon atoms of the CH type in the ^{13}C NMR spectrum of compound **14** was similar to that of compound **12a**, *i.e.* it was carried out with the help of a heterocorrelated spectrum measured with inverse detection (Fig. 3, B). The assignment of quaternary carbon atoms was carried out by adopting the ^{13}C selective INEPT experiment with the selective transmissions of polarization from H-4, H-5, H-9 and protons of methyl groups. The ^{15}N NMR spectrum of compound **14** (enriched with ^{15}N isotope at the 3-position to a level of 10%+) was measured by the INEPT technique. The values found for N-2 and N-3 are δ_N −190.0 [^1J(NH) 61.4] and −180.6 [^2J(NH) 7.3], respectively. In the case of measurements of spectra of the unlabelled compound **14** we detected only the signal of N-2 nitrogen with the values of δ_N and J(NH) equal to those of the enriched compound.

The side products of reaction of 6-nitroquinoline **1** with potassium cyanide with participation of 2-nitropropane include (as

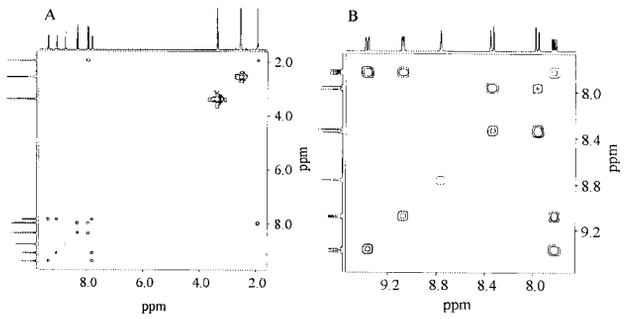


Fig. 4 NOESY spectrum of **14**. A, The spectrum in the whole range measured. B, Detailed representation of aromatic section.

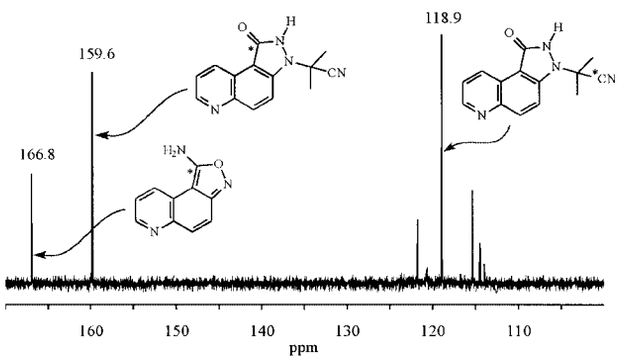
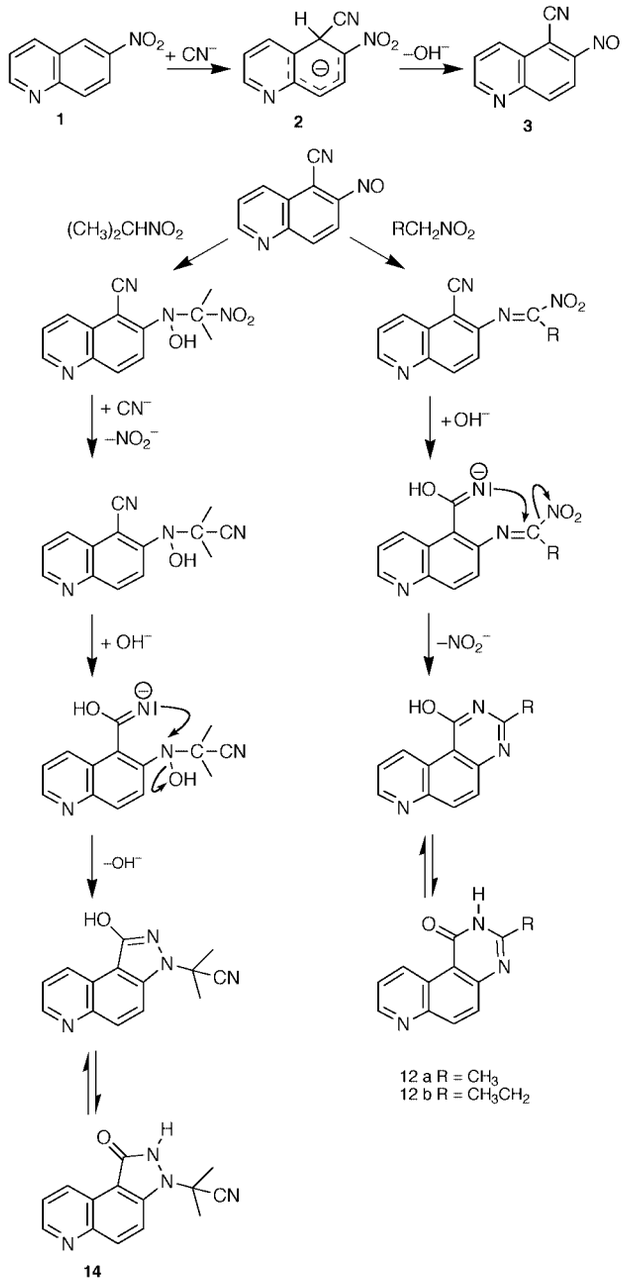


Fig. 5 ^{13}C NMR spectrum of reaction mixture after reaction of 6-nitroquinoline, 2-nitropropane and $K^{13}CN$ measured 70 min after mixing the starting substances.

in the previous reactions with primary nitroalkanes) 6-hydroxyquinoline-5-carbonitrile **4** and 1-aminoisoxazolo[4,3-*f*]quinoline **9**. Due to the considerable overlap of signals in the ^1H NMR spectra of reaction mixtures (Fig. 2, C), it was again impossible to precisely determine the proportions of individual products. The main products of reactions of 6-nitroquinoline **1** with cyanides with the participation of nitroalkanes are heterocyclic compounds **12a**,**b** and **14**, whose skeletons include both a carbon atom coming from cyanide (two carbon atoms in the case of **14**) and that coming from the nitroalkane. In the products, the carbon atom coming from cyanide always replaced a hydrogen atom originally bound at the 5-position of 6-nitroquinoline **1**. The α-carbon atom of the starting nitroalkane is, in compounds **12a**,**b** and **14**, always bound to the nitrogen atom of the original nitro group of compound **1**. In the case of compound **14**, a bond was formed between two nitrogen atoms, which is relatively rare in syntheses of pyrazole and indazole derivatives.[9–11] The formation of main products in the reaction of 6-nitroquinoline **1** with potassium cyanide and nitroalkanes is explained in Scheme 3.

Conclusions

Reactions of 6-nitroquinoline **1** with cyanides and aliphatic nitro compounds in polar aprotic solvent produce complex mixtures of products. All the products show a common feature in that they are formed by nucleophilic substitution reaction of hydrogen atom by cyanide ions at the 5-position of the quinoline skeleton with concomitant lowering of the oxidation number of nitrogen of the original nitro group. The main products contain the carbon skeleton coming from the aliphatic nitro compounds, however, without the original nitro group. These findings support the idea of a mechanism typical in reactions of some aromatic nitro compounds with cyanide ion. The Meisenheimer adduct **2** is formed at first. Its properties are distinctly affected by the cyano group, which increases the acidity of the hydrogen atom bound to the sp^3-carbon atom. The following reduction–oxidation processes lead to reduction of the nitro



Scheme 3

group to a nitroso group and simultaneous oxidation of the sp^3-carbon atom of the Meisenheimer adduct. Thus the net process is an aromatic substitution reaction of hydrogen and formation of a very reactive intermediate—6-nitrosoquinoline-5-carbonitrile **3**. It is only the competitive reactions (particularly those with nucleophilic reagents) of compound **3** which lead to the compounds identified in the individual reaction mixtures. These competitive reactions involve aliphatic nitro compounds reacting with the nitroso group. Hence the composition of reaction mixtures strongly depends on the type of the nucleophilic reagent added, an aliphatic nitro compound in this case.

Experimental

The ^1H, ^{13}C, and ^{15}N NMR spectra were measured at 360.14, 90.57, and 36.51 MHz, respectively, using a Bruker AMX 360 spectrometer. The chemical shifts δ_H and δ_C measured for the solutions of substances in [$^2H_6$]dimethyl sulfoxide (approximately 10 mg substance per 0.5 ml solvent) were referenced to the central multiplet of the solvent (δ_H 2.55 and δ_C 39.6). *J*-Values are given in Hz. The assignment of signals in NMR

spectra of compounds **12a** and **14** was carried out with the help of H,H COSY experiments, heterocorrelated 2D spectra with inverse detection (HMQC) optimized with respect to one-bond interaction J(H,C) 155 Hz, and several ^{13}C selective INEPT experiments for assigning the signals of quaternary carbon atoms. With compound **14** we also measured the NOESY spectrum (mixing time 700 ms). The ^{15}N NMR spectrum of compound **14** enriched at N-3 with ^{15}N isotope to a level of 10%+ was measured by the INEPT method [$\tau(1/4J_{NH})$ 2.78 ms]. The ^{15}N NMR spectrum of nonlabelled compound **14** was measured in the same way. The chemical shifts δ_N are referenced to the signal of external nitromethane (δ_N 0.0). The mass spectrum of compound **12a** was measured with a ZAB-EQ, VG Analytical spectrometer (Manchester, UK) at high resolution with EI ionization; those of compounds **12b** and **14** were measured on a LC MS VG-Platform apparatus allowing APCI (atmospheric pressure chemical ionisation) or ESP (electrospray) ionization in both positive and negative mode.

NMR analyses of reaction mixtures of 6-nitroquinoline, potassium cyanide and aliphatic nitro compounds

The ^1H and ^{13}C NMR spectra of reaction mixtures were measured at 360.14 and 90.57 MHz, respectively, using the Bruker AMX 360 spectrometer. Measurements were carried out in a 5 mm NMR probe at a temperature of about 21 °C. The chemical shifts δ_H and δ_C measured for the solutions of substances in [$^2H_6$]dimethyl sulfoxide were referenced to the central signal of the solvent multiplet (δ_H 2.5 and δ_C 39.6). The ^1H NMR spectrum of the reaction mixture of 6-nitroquinoline **1** (10 mg, 0.06 mmol), methyl nitroacetate (0.10 ml, 1.1 mmol), and potassium cyanide (50 mg, 0.77 mmol) in [$^2H_6$]dimethyl sulfoxide (0.5 ml) was measured 24 h after mixing of the starting components. The ^1H NMR spectra of reaction mixtures of 6-nitroquinoline **1** (10 mg, 0.06 mmol) and KCN (10 mg, 0.15 mmol) in [$^2H_6$]dimethyl sulfoxide (0.5 ml) with the addition of nitroalkane (nitroethane, 1-nitropropane, or 2-nitropropane, always 1.1 mmol) were measured 70 min and 24 h after mixing of the reaction components. The ^{13}C NMR spectrum of the reaction mixture of 6-nitroquinoline **1** (10 mg, 0.06 mmol), 2-nitropropane (0.1 ml, 1.1 mmol), and K^{13}CN (10 mg, 99.5%+ ^{13}C, 0.15 mmol) in [$^2H_6$]dimethyl sulfoxide (0.5 ml) was measured 70 min after mixing the starting substances.

Preparation of 3-methylpyrido[3,2-*f*]quinazolin-1(2*H*)-one 12a

0.5 g (2.9 mmol) of 6-nitroquinoline **1** was dissolved in 25 ml of dimethyl sulfoxide. The solution was added to a mixture of 0.5 g (7.7 mmol) of finely ground potassium cyanide and 15 ml (0.21 mmol) of nitroethane. The reaction mixture was vigorously stirred for 3 h. Then the dimethyl sulfoxide was distilled off *in vacuo* together with the residual nitroethane, and the distillation residue was treated with chloroform (200 ml) and water (100 ml). The mixture was shaken and the chloroform extract was concentrated and submitted to column chromatography (silica gel; chloroform–acetone 9 : 1 v/v). The first fraction contained 95 mg (15.5%) of compound **12a**. After recrystallization from ethanol, *compound* **12a** had mp 300–301 °C (Found: C, 68.0; H, 4.3; N, 19.8. $C_{12}H_9N_3O$ requires C, 68.2; H, 4.3; N, 19.9%); δ_H[(CD$_3$)$_2$SO] 2.50 (3H, s, CH$_3$), 7.77 (1H, dd, *J* 8.6 and 4.3, H-9), 7.92 (1H, d, *J* 9.1, H-5), 8.33 (1H, dd, *J* 9.1 and 0.8, H-6), 9.00 (1H, dd, *J* 4.3 and 1.7, H-8), 10.16 (1H, m, *J* 8.6, 1.7 and 0.8, H-10), 12.73 (1H, br, NH); δ_C[(CD$_3$)$_2$SO] 21.4 (CH$_3$), 113.2 (C-10b), 123.1 (C-9), 126.1 (C-10a), 129.8 (C-5), 134.0 (C-10), 136.1 (C-6), 146.0 (C-6a), 149.7 (C-8), 151.0 (C-4a), 156.6 (C-3), 162.7 (C-1); *m*/*z* 211.0741 (M^+, 100%. $C_{12}H_9N_3O$ requires *M*, 211.0746), 196 ($M^+ - CH_3$, 4), 183 ($M^+ - CO$, 9.3), 170 ($M^+ - C_2H_3N$, 15.2), 142 ($M^+ - C_3H_3NO$, 13), 127 ($M^+ - C_3H_4N_2O$, 6.5), 105.5 (M^{2+}, 5.1).

The second fraction contained 5 mg of yellow 1-aminoisoxazolo[4,3-*f*]quinoline **9**, mp 199–200 °C (decomp.) (ref. 1).

Preparation of 3-ethylpyrido[3,2-*f*]quinazolin-1(2*H*)-one 12b

The procedure adopted was analogous to that for the preparation of compound **12a** with the only difference that nitroethane was replaced by 18.5 ml (0.21 mmol) of 1-nitropropane. *Compound* **12b** was obtained (80 mg, 12.2%), mp 267–268 °C (Found: C, 69.0; H, 4.9; N, 18.3. $C_{13}H_{11}N_3O$ requires C, 69.3; H, 4.9; N, 18.6%); δ_H[(CD$_3$)$_2$SO] 1.34 (3H, t, *J* 7.5, CH$_3$), 2.77 (2H, q, *J* 7.5, CH$_2$), 7.78 (1H, dd, *J* 8.7 and 4.2, H-9), 7.95 (1H, d, *J* 9.1, H-5), 8.34 (1H, dd, *J* 9.1 and 0.6, H-6), 9.01 (1H, dd, *J* 4.2 and 1.7, H-8), 10.15 (1H, m, *J* 8.7, 1.7 and 0.6, H-10), 12.76 (1H, br, NH); δ_C[(CD$_3$)$_2$SO] 11.4 (CH$_3$), 27.7 (CH$_2$), 113.4 (C-10b), 123.1 (C-9), 126.0 (C-10a), 129.9 (C-5), 134.0 (C-10), 136.2 (C-6), 146.1 (C-6a), 149.8 (C-8), 150.9 (C-4a), 160.3 (C-3), 162.7 (C-1); *m*/*z* 226 (MH^+, 100%).

Preparation of 3-(1-cyano-1-methylethyl)-2,3-dihydro-1*H*-pyrazolo[4,3-*f*]quinazolin-1-one 14

6-Nitroquinoline **1** (3 g, 0.017 mol) was dissolved in a mixture of 45 ml of dimethyl sulfoxide and 40 ml of 2-nitropropane (0.44 mol), and 3 g (0.046 mol) of finely ground KCN was added. After two days' storage at room temperature, the mixture was distilled *in vacuo* to remove 2-nitropropane and dimethyl sulfoxide. The evaporation residue obtained was dissolved in about 15 ml of chloroform and submitted to column chromatography (silica gel; chloroform–acetone 9 : 1 v/v). Distilling off the solvent from the second fraction taken gave 0.7 g (16.5%) of *compound* **14**, mp 175–177 °C (from ethanol). Compound **14** enriched with ^{15}N isotope (10%+) at the 3-position was prepared similarly in 18% yield, the starting substance being 6-nitroquinoline **1** enriched with ^{15}N isotope in the nitro group (Found: C, 66.5; H, 4.8; N, 22.3. $C_{14}H_{12}N_4O$ requires C, 66.7; H, 4.8; N, 22.2%); δ_H[(CD$_3$)$_2$SO] 1.95 (6H, s, CH$_3$), 7.83 (1H, dd, *J* 8.4 and 4.3, H-8), 7.97 (1H, d, *J* 9.2, H-4), 8.34 (1H, d, *J* 9.2, H-5), 8.77 (1H, s, NH), 9.08 (1H, dd, *J* 4.3 and 1.7, H-7), 9.37 (1H, m, *J* 8.4, 1.7 and 0.7, H-9); δ_C[(CD$_3$)$_2$SO] 25.0 (CH$_3$), 61.7 (*C*-CH$_3$), 112.9 (C-9b), 118.2 (C-4), 118.9 (CN), 123.7 (C-9a), 124.0 (C-8), 130.7 (C-9), 135.4 (C-5), 146.2 (C-5a), 151.0 (C-7), 151.1 (C-3a), 159.6 (C-1); δ_N[(CD$_3$)$_2$SO] −180.6 [^2J(NH) 7.3, N-3], −190.0 [^1J(NH) 61.4, N-2]; *m*/*z* 252 (M^+, 100%).

The preparation and spectra of compounds **4** and **9** were described in our previous paper.[1]

Acknowledgements

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