Direct thioalkylation of nitroquinolines with alkanethiolate anions *via* nucleophilic displacement of a ring hydrogen atom

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Nitroquinolines readily react with alkanethiols in tetrahydrofuran in the presence of excess sodium hydride to give the corresponding alkylthio derivatives *via* the preferential displacement of a ring hydrogen atom adjacent to the nitro group. After an induction period, the reaction starts and completes within a short time even at low temperature, suggesting the involvement of a radical species as an intermediate. Using this methodology, a series of thioalkylation products have been prepared from 5-, 6-, 7- and 8-nitroquinolines in good to moderate yields.

Introduction

Sulfur-based anions are generally known as good nucleophiles in the nucleophilic substitution of haloarenes.[1-3] A great number of papers have been published to date on the introduction of sulfur functionalities into aromatic rings *via* the displacement of halogens by sulfur nucleophiles. However, there are very few reports about the direct nucleophilic displacement of a ring hydrogen by thioanions.[1,4] One recent article has mentioned briefly that 3-chloronitrobenzene reacts with the ethanethiolate anion so as to displace a hydrogen atom, leading to the formation of some thioalkylation products.[1] However, the amount of such products was too small to indicate the preparative potential of this substitution reaction.[5] This would probably be due to the high ability of thiolate anions to act as a reducing agent for the nitro group.[6] Besides, thioanions often tend to displace the nitro group itself of nitroarenes in polar solvent systems.[3,7]

We have recently reported that a strong base such as sodium hydride promotes the direct displacement of a hydrogen atom in nitroarenes by nucleophilic species, which included a range of carbon-,[8] nitrogen-[9] and oxygen[10]-based nucleophiles. In this paper, we report the facile displacement reaction of a ring hydrogen of nitroquinolines by alkanethiolate anions, which involves treatment of nitroquinolines with alkanethiol in the presence of an excess of sodium hydride in tetrahydrofuran (THF) at low temperature in air.
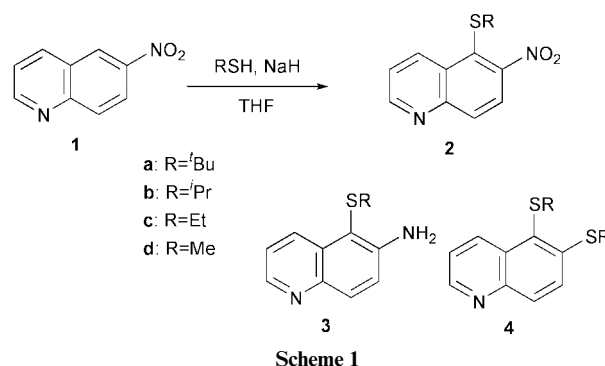
Results and discussion

When 6-nitroquinoline **1** was reacted with 1,1-dimethylethanethiol in THF in the presence of excess sodium hydride under ambient conditions, 5-*tert*-butylthio-6-nitroquinoline **2a** was obtained in 54% yield (Table 1). Similarly, the reaction with 1-methylethanethiol gave 5-isopropylthio-6-nitroquinoline **2b** (33%), together with 6-amino-5-isopropylthioquinoline **3b** (11%) and 5,6-bis(isopropylthio)quinoline **4b** (3%) as by-products (Scheme 1). Under similar conditions, however, the reaction with ethanethiol did not afford 5-ethylthio-6-nitro-quinoline **2c** but gave 6-amino-5-ethylthioquinoline **3c** (17%) and 5,6-bis(ethylthio)quinoline **4c** (4%) as the only isolated products. Attempted reaction with methanethiolate anion only led to a complex mixture of products as a tarry material. These results suggested that the primary and secondary thiolate anions are too reactive and therefore less effective for the nucleophilic displacement of a ring hydrogen atom as compared with the tertiary thiolate anion. When compound **1** was reacted with ethanethiol at −10 °C, the expected product **2c** was obtained in 46% yield. At this temperature, the yields of other thiolation products also improved; the yield of **2b** rose to 56%. When the reaction of **1** and 1,1-dimethylethanethiolate was allowed to run at −50 °C, the reaction came to show an induction period (*ca.* 1.5 h), but the yield of **2a** was not much affected. Other aprotic, polar solvents such as *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP) and diethyl ether may also be used as the reaction media, but the yields of products were somewhat lowered. Moisture in solvent was found to exert a noticeable effect on the product composition, and the amount of side products **3** and **4** increased at the expense of the main product **2**. We could not detect both 6-aminoquinoline and

Table 1 Reaction of 6-nitroquinoline **1** with thiolate anions[a]

			Yield (%)[b]		
Entry	Thiolate anion	Temp./ °C	**2**	**3**	**4**
1	$^tBuS^-$	rt	54	—	—
2	$^iPrS^-$	rt	33	11	3
3	$^iPrS^-$	−10	56	Trace	—
4	EtS^-	rt	—	17	4
5	EtS^-	−10	46	7	—
6	$PhCH_2S^-$	−10	—[c]	—	—
7	PhS^-	−10	—[c]	—	—

[a] All reactions were carried out in air using 6-nitroquinoline (1.7 mmol), thiol (2.5 mmol) and NaH (5.0 mmol) in THF (10 mL). [b] Isolated yield. [c] Disulfide was obtained; the substrate was recovered mostly unchanged.
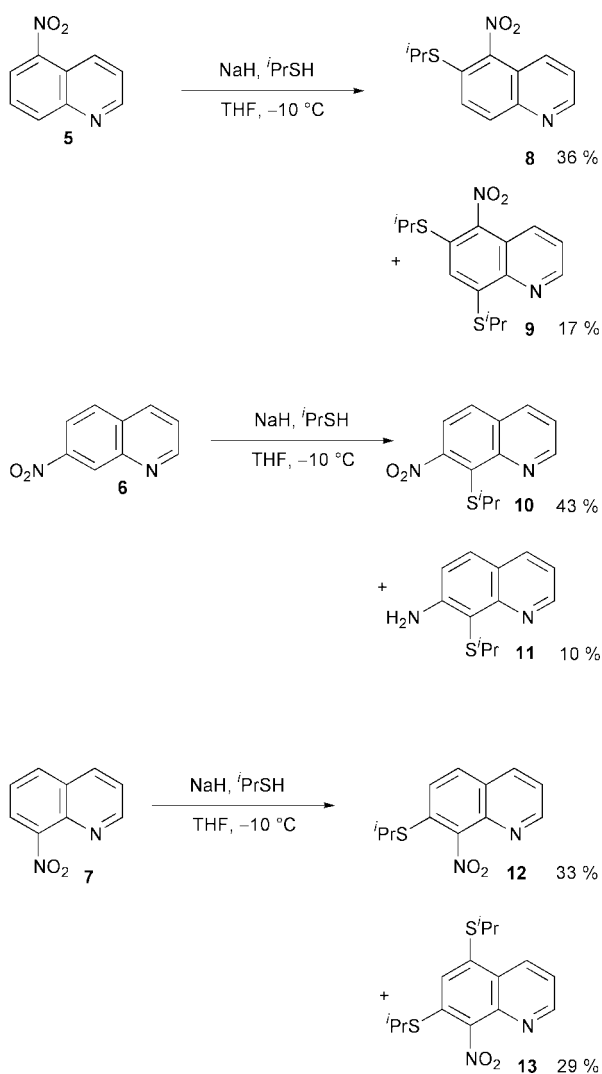

Scheme 1

6-alkylthioquinoline in the product mixture. These observations indicate the preference for nucleophilic displacement of a ring hydrogen atom in **1** over the reduction or displacement of the nitro group. Interestingly, the situation was reversed at the second substitution stage, the reaction with ethanethiolate or 1-methylethanethiolate anion leading to the corresponding 5-alkylthio-6-aminoquinoline **3b,c** and 5,6-bis(alkylthio)-quinoline **4b,c** as the major products. Benzenethiolate and phenylmethanethiolate anions failed to react with 6-nitroquinoline **1**. The stability of the thio radicals derived from thiolate anions *via* oxidation decreases in the order of PhS$^\bullet$ > PhCH$_2$S$^\bullet$ >> ^{t}BuS$^\bullet$ > ^{i}PrS$^\bullet$ > EtS$^\bullet$. In accordance with this trend, benzenethiol and phenylmethanethiol were simply transformed to the corresponding disulfides under the conditions employed (Table 1, entries 6 and 7). With the last three alkylthio radicals, the disulfide formation was not significant.

Other isomeric nitroquinolines **5**–**7** were similarly treated with alkanethiols in the presence of an excess of sodium hydride. 7-Nitroquinoline **6** behaved similarly to 6-nitroquinoline **1**, giving 8-isopropylthio-7-nitroquinoline **10** and its descendant 7-amino-8-isopropylthioquinoline **11** (Scheme 2).

Scheme 2

Noteworthy is that 5-nitro- and 8-nitroquinolines **5** and **7** formed a significant amount of dithioalkylation products **9** and **13** under similar conditions, in addition to the expected monothioalkylation products **8** and **12**. The monothioalkylation and dithioalkylation of these substrates proceeded in parallel, although their relative importance varied appreciably depending on the conditions employed. A remarkable color change
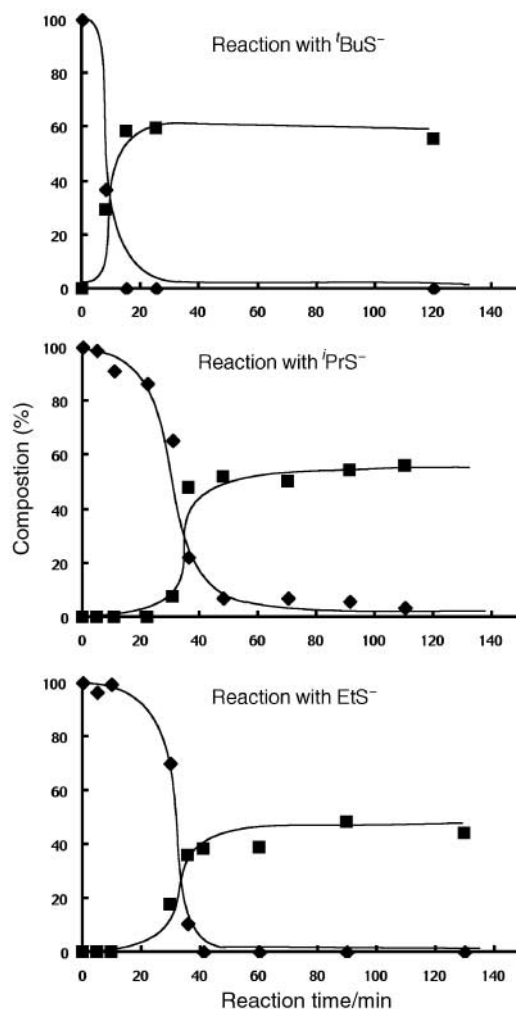
Fig. 1 Time–course observed in the reaction of 6-nitroquinoline with alkanethiolate anions, determined by GLC using cyclododecane as an internal standard. Conditions: temperature, −10 °C; solvent, THF (20 mL); substrate, 1.7 mmol; thiol 2.5 mmol; NaH: 5.0 mmol. ◆ 5-Alkylthio-6-nitroquinoline; ■ 6-nitroquinoline.

was observed during the course of the reaction; the initial yellow suspension gradually deepened to dark green as the reaction proceeded and it turned dark brown at the final stage. The time–course diagrams for the reactions of **1** with 1,1-dimethylethanethiolate, 1-methylethanethiolate, and ethanethiolate anions at −10 °C are shown in Fig. 1. For all reactions, the induction period was observed clearly and it was found to shorten in the order ^{t}BuS > ^{i}PrS ≈ EtS. This order parallels the ease with which the alkylthio radicals are generated from the alkanethiolate anions,[11] but inversely parallels the ease of oxidative coupling of the thiolate anions to disulfides. This would probably be the reason why the reaction worked best with the 1,1-dimethylethanethiolate anion. There are some papers that have suggested the possibility that the reaction of nitroarenes with thiolate anions may proceed *via* a thio radical species as intermediate.[12,13]

The mechanism for the thioalkylation of nitroquinolines with alkanethiolate anions *via* a ring hydrogen displacement has not yet been clarified, but it may be explained in terms of the reaction sequence depicted in Scheme 3, taking the thioalkylation reaction of **5** as an example. Compound **5** reacts with alkanethiolate anion to form a Meisenheimer complex **14**, which undergoes the removal of an *ipso* hydrogen by an alkylthio radical to form a radical anion **15**. The alkylthio radical would probably come from the oxidation of alkanethiolate anion by nitroquinoline as well as by molecular oxygen in the air. Aromatic nitro compounds are known to oxidize alkanethiolate anions *via* a one-electron transfer process to form

Table 2 Thiolato–thiolato exchange reaction of 5-alkylthio-6-nitroquinolines **2a,b**[a]

Entry	Substrate	Temp./°C	Reagent	Product **2** R =	Yield (%)[b]
1	**2a**	0	K_2CO_3–[i]PrSH	[i]Pr	92
2	**2a**	0	K_2CO_3–EtSH	Et	95
3	**2a**	−10	MeSNa	Me	87
4	**2a**	−10	K_2CO_3–PhSH	Ph	—[c]
5	**2a**	0	K_2CO_3–PhCH$_2$SH	PhCH$_2$	95
6	**2a**	0	NaSH	H	—[c]
7	**2a**	0	K_2CO_3–HOCH$_2$CH$_2$SH	CH$_2$CH$_2$OH	65
8	**2a**	0	K_2CO_3–MeO$_2$CCH$_2$SH	CH$_2$CO$_2$Me	72
9	**2a**	0	KSCN	CN	—[c]
10	**2a**	0	K_2CO_3–PhCOSH	PhCO	—[c]
11	**2b**	0	K_2CO_3–[t]BuSH	[t]Bu	98

[a] All reactions were carried out under air by stirring a mixture of substrate (0.38 mmol), reagent (3.8 mmol) and THF (10 mL) for 15 h. [b] Isolated yield. [c] The reaction did not take place and the substrate was recovered mostly unchanged.
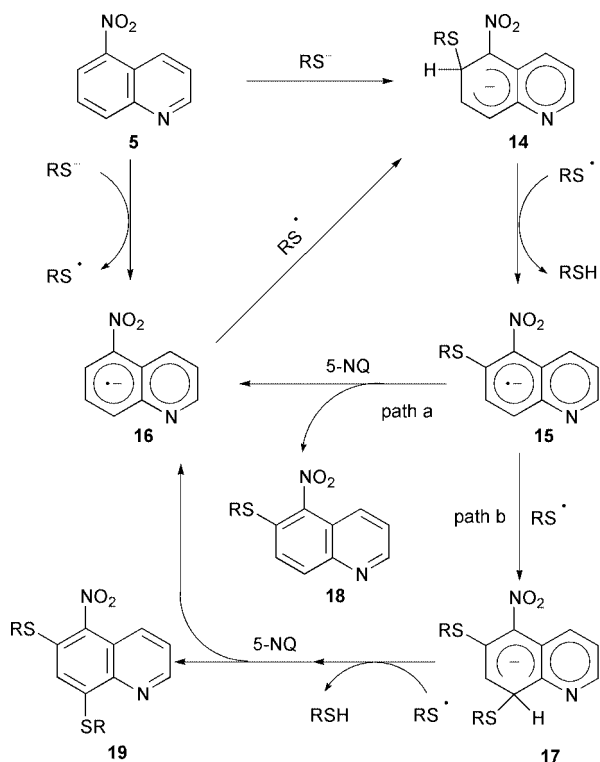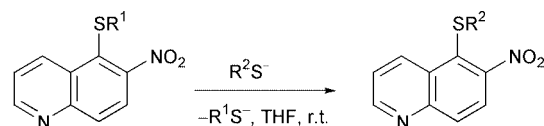

Scheme 3

disulfides.[14] Thus, under an atmosphere of argon, 6-nitroquinoline **1** reacted with 1,1-dimethylethanethiolate anion to produce 5-*tert*-butylthio-6-nitroquinoline **2a**, 6-aminoquinoline and di-*tert*-butyl disulfide in 32, 10 and 11% yields, respectively. In air, the yield of **2a** improved to 54% and the aminoquinoline disappeared, suggesting the important role of molecular oxygen as the oxidant for alkanethiolate anions. Therefore, it is evident that nucleophilic substitution by the thiolate anion was considerably favored and the reduction to the amine was suppressed in the presence of atmospheric oxygen.

In the presence of sodium hydride, dialkyl disulfides are cleaved to alkanethiolate anion and alkanethiol, the latter reacting further with sodium hydride to give additional alkanethiolate anion and molecular hydrogen. The electron transfer from radical anion **15** to substrate **5** leads to the product **18** and another radical anion **16**; the latter would be trapped by the alkylthio radical to generate the original Meisenheimer complex **14**, thus completing a cyclic process for the nucleophilic thioalkylation of nitroarene **5**. The electron transfer pathway (path a) and the addition pathway of an alkylthio radical (path b) compete in the subsequent reaction of radical anion **15**. The nitro group at the 5-position of this intermediate favors the formation of a stabilized anion **17**, which loses an *ipso* ring

hydrogen to give the dithioalkylation product **19**. Alternatively, the radical anion **15** may combine with an alkylthio radical at the 5-position, which results in the expulsion of nitrite anion to form a disulfide **4**. With compound **7**, the nitro group at the 8-position acts favorably for the second thioalkylation at the 5-position, whereas such a structural advantage of forming the stabilized Meisenheimer intermediate is lost with compounds **1** and **6**, thus ruling out the possibility of the second ring thioalkylation.

This new type of thioalkylation is applicable to alkanethiolate anions but not to arenethiolate and arylmethanethiolate anions. A variety of alkylthio groups may also be introduced into the 5-position of nitroquinoline **1** *via* the thiolato–thiolato exchange reaction of compound **2a** with an appropriate sulfur nucleophile (Scheme 4). In the presence of an excess

Scheme 4

of a second alkanethiolate anion, the bulky *tert*-butyl group in **2a** is readily displaced by the new sulfur nucleophile to afford the corresponding 5-alkylthio-6-nitroquinoline in good yield (Table 2, entries 1–3, 5, 7, 8). Benzenethiolate anion failed to react similarly, probably due to the lower nucleophilicity and increased steric bulkiness. Prolonged reaction resulted in the reduction of initial product **2** to 5-alkylthio-6-aminoquinoline **3** as well as the displacement of the nitro group in **2** by a thiolate anion. These processes became especially prominent in the reaction of **1** with methanethiolate anion and resulted in a complex mixture of products; compound **2d** readily underwent the displacement of the nitro group adjacent to the methylthio group to give 5,6-bis(methylthio)quinoline **4d**.

In summary, we report a new methodology for the direct thioalkylation of nitroquinolines,[15] in which a ring hydrogen atom is readily displaced by an alkanethiolate anion under mild conditions. It provides a straightforward route to some multifunctionalized aza-arenes, which are otherwise laborious to prepare. The general nature of this thioalkylation suggests the involvement of an alkylthio radical species as the intermediate.

Experimental

General and materials

Melting points were determined on a Yanagimoto hot-plate apparatus and are uncorrected. ^{1}H NMR spectra were recorded in CDCl$_3$ and/or DMSO-d_6 on a Varian Gemini 200 MHz NMR spectrometer by using TMS as an internal reference, unless otherwise mentioned; coupling constants are quoted in

hertz (Hz). Infrared spectra were measured as KBr pellets or liquid films with a Shimadzu FTIR-8100S infrared spectrophotometer and only prominent peaks in the region 2000–750 cm^{-1} are recorded. EI mass spectra were determined at 70 eV on a Shimadzu GCMS-QP2000A mass spectrometer. CI mass spectra were measured on a GCMS-QP5000 mass spectrometer using isobutane (2-methylpropane) as an ionizing gas. 1,3-Dimethylimidazolidin-2-one (DMI) was distilled from CaH$_2$ under reduced pressure and tetrahydrofuran (THF) from benzophenone ketyl prior to use. All reagents were commercial products, except for 7-nitroquinoline **6** which was prepared according to the reported procedure.[16]

Direct thioalkylation of nitroquinolines 1, 5–7. General procedure

A mixture of a nitroquinoline (1.70 mmol), sodium hydride (5.80 mmol) and THF (30 mL) was stirred in air and cooled to −10 °C. To the resulting suspension was added alkanethiol (0.25 mL, 2.40 mmol) in one portion. After standing at room temperature for a while, the mixture was diluted with water (100 mL) and extracted with CH$_2$Cl$_2$ (30 mL × 3). The combined extracts were evaporated and the residue was chromatographed on silica gel using a mixture of ethyl acetate and hexane as the eluent to obtain the thioalkylation products. Under the exclusion of air, the progress of the reaction became slower and the yield of substitution products considerably decreased. The products and their yields are summarized in Table 1.

5-Isopropylthio-6-nitroquinoline (2b). Mp 132–133 °C. δ_H (CDCl$_3$) 1.22 (d, 6H, $J = 6.7$), 3.39 (septet, 1H, $J = 6.7$), 7.64 (dd, 1H, $J = 4.2, 8.4$), 7.88 (d, 1H, $J = 9.0$), 8.23 (d, 1H, $J = 9.0$), 9.04–9.09 (m, 2H); m/z (EI) 248 (M$^+$, 43%), 233 (27), 144 (34), 116 (83); ν_{max}(KBr)/cm^{-1} 1528 (NO$_2$), 1374 (NO$_2$), 1127, 1036, 876, 835. Found: C, 58.07; H, 4.89; N, 11.17. C$_{12}$H$_{12}$N$_2$O$_2$S requires C, 58.05; H, 4.87; N, 11.28%.

6-Isopropylthio-5-nitroquinoline (8). Mp 110–111 °C. δ_H (CDCl$_3$) 1.22 (d, 6H, $J = 6.7$), 3.39 (septet, 1H, $J = 6.7$), 7.64 (dd, 1H, $J = 4.2, 8.4$), 7.88 (d, 1H, $J = 9.0$), 8.23 (d, 1H, $J = 9.0$), 9.04–9.09 (m, 2H); m/z (CI) 249 (M$^+$ + 1, 100%), 207 (89); ν_{max} (KBr)/cm^{-1} 1524 (NO$_2$), 1487, 1362 (NO$_2$), 1304, 841, 806. Found: C, 58.01; H, 4.79; N, 11.26. C$_{12}$H$_{12}$N$_2$O$_2$S requires C, 58.05; H, 4.87; N, 11.28%.

8-Isopropylthio-7-nitroquinoline (10). Mp 166–167 °C. δ_H (CDCl$_3$) 1.19 (d, 6H, $J = 6.7$), 4.18 (septet, 1H, $J = 6.7$), 7.58 (dd, 1H, $J = 4.2, 8.3$), 7.72 (d, 1H, $J = 8.7$), 7.88 (d, 1H, $J = 8.7$), 8.25 (dd, 1H, $J = 1.8, 8.3$), 9.15 (dd, 1H, $J = 1.8, 4.2$); m/z (EI) 190 (100%), 129 (83); m/z (CI) 249 (M$^+$ + 1, 100%), 190 (15); ν_{max}(KBr)/cm^{-1} 1530 (NO$_2$), 1487, 1375, 1356 (NO$_2$), 1299, 997, 843, 806. Found: C, 58.08; H, 4.82; N, 11.13. C$_{12}$H$_{12}$N$_2$O$_2$S requires C, 58.05; H, 4.87; N, 11.28%.

7-Isopropylthio-8-nitroquinoline (12). Mp 69–70 °C. δ_H (CDCl$_3$) 1.35 (d, 6H, $J = 6.7$), 3.60 (septet, 1H, $J = 6.7$), 7.52 (dd, 1H, $J = 4.3, 8.4$), 7.68 (d, 1H, $J = 8.7$), 7.88 (d, 1H, $J = 8.7$), 8.21 (dd, 1H, $J = 1.7, 4.3$), 8.99 (dd, 1H, $J = 1.7, 4.3$); m/z (EI) 248 (M$^+$, 5.0%), 206 (31), 189 (24), 142 (100), 128 (97); ν_{max}(KBr)/cm^{-1} 1613, 1528 (NO$_2$), 1487, 1374, 1343 (NO$_2$), 1127, 1036, 876, 835, 791, 772, 656. Found: C, 58.07; H, 4.89; N, 11.17. C$_{12}$H$_{12}$N$_2$O$_2$S requires C, 58.05; H, 4.87; N, 11.28%.

5-*tert*-Butylthio-6-nitroquinoline (2a). Mp 101–102 °C. δ_H (CDCl$_3$) 1.25 (s, 9H), 7.62 (dd, 1H, $J = 4.2, 8.7$), 7.89 (d, 1H, $J = 9.0$), 8.27 (d, 1H, $J = 9.0$), 9.05 (dd, 1H, $J = 1.7, 4.2$), 9.17 (dd, 1H, $J = 1.7, 8.7$); m/z (EI) 206 (66%), 189 (39), 142 (100); m/z (CI) 263 (M$^+$ + 1, 45%), 249 (17), 207 (100); ν_{max}(KBr)/cm^{-1} 1584, 1561, 1532 (NO$_2$), 1487, 1360 (NO$_2$), 1300, 1159, 988, 851, 804. Found: C, 59.61; H, 5.40; N, 10.62. C$_{13}$H$_{14}$N$_2$O$_2$S requires C, 59.52; H, 5.38; N, 10.68%.

6,8-Bis(isopropylthio)-5-nitroquinoline (9). Mp 44–45 °C. δ_H (CDCl$_3$) 1.38 (d, 6H, $J = 6.7$), 1.53 (d, 6H, $J = 6.7$), 3.50–3.80 (m, 2H), 7.54 (s, 1H), 7.58 (dd, 1H, $J = 4.2, 8.7$), 8.21 (dd, 1H, $J = 1.5, 8.7$), 8.95 (dd, 1H, $J = 1.5, 4.2$); m/z (EI) 322 (M$^+$, 50%), 289 (63), 248 (58), 225 (100); ν_{max}(KBr)/cm^{-1} 1565, 1530 (NO$_2$), 1468, 1341 (NO$_2$), 804. Found: C, 55.81; H, 5.67; N, 8.71. C$_{15}$H$_{18}$N$_2$O$_2$S$_2$ requires C, 55.87; H, 5.63; N, 8.69%.

5-Ethylthio-6-nitroquinoline (2c). Mp 45–46 °C. δ_H (CDCl$_3$) 1.19 (t, 3H, $J = 7.4$), 2.92 (q, 2H, $J = 7.4$), 7.65 (dd, 1H, $J = 4.9, 8.0$), 7.88 (d, 1H, $J = 9.1$), 8.23 (d, 1H, $J = 9.1$), 9.05 (dd, 1H, $J = 1.7, 4.2$), 9.07 (dd, 1H, $J = 1.7, 8.7$); m/z (EI) 234 (M$^+$, 13%), 189 (31), 169 (67), 129 (100); ν_{max}(KBr)/cm^{-1} 1530, 1489, 1368, 1304, 841, 804. Found: C, 56.30; H, 4.21; N, 11.80. C$_{13}$H$_{14}$N$_2$O$_2$S requires C, 56.39; H, 4.30; N, 11.96%.

5,7-Bis(isopropylthio)-8-nitroquinoline (13). Oil. δ_H (CDCl$_3$) 1.34 (d, 6H, $J = 6.6$), 1.37 (d, 6H, $J = 6.6$), 3.51 (h, 1H, $J = 6.6$), 3.60 (septet, 1H, $J = 6.6$), 7.54 (dd, 1H, $J = 4.2, 8.6$), 7.74 (s, 1H), 8.73 (dd, 1H, $J = 1.6, 8.6$), 8.99 (dd, 1H, $J = 1.6, 4.2$); m/z (EI) 322 (M$^+$, 6.4%), 215 (70), 173 (100); ν_{max}(KBr)/cm^{-1} 1539 (NO$_2$), 1368 (NO$_2$), 1051, 812. Found: C, 55.68; H, 5.68; N, 8.60. C$_{15}$H$_{18}$N$_2$O$_2$S$_2$ requires C, 55.87; H, 5.63; N, 8.69%.

Thiolato–thiolato exchange reaction of 5-alkylthio-6-nitro-quinolines 2a,b. General procedure

To a stirred solution of 5-*tert*-butylthio-6-nitroquinoline (100 mg, 0.38 mmol) in THF (10 mL) was added a given thiolation reagent (3.81 mmol) in one portion and the resulting mixture was stirred at 0 or −10 °C until the substrate disappeared on a TLC film. The mixture was diluted with water (30 mL) and extracted with CH$_2$Cl$_2$ (10 mL × 3). The combined extracts were evaporated and the residue was chromatographed on silica gel using a mixture of ethyl acetate and hexane as the eluent to obtain the expected sulfide. The products and their yields are given in Table 2.

5-Methylthio-6-nitroquinoline (2d). Mp 73–74 °C. δ_H (CDCl$_3$) 2.48 (s, 3H), 7.67 (dd, 1H, $J = 4.1, 8.5$), 7.90 (d, 1H, $J = 9.0$), 8.23 (d, 1H, $J = 9.0$), 9.05 (dd, 1H, $J = 1.7, 4.1$), 9.17 (dd, 1H, $J = 1.7, 8.5$); m/z (CI) 221 (M$^+$ + 1, 100%), 191 (11); ν_{max}(KBr)/cm^{-1} 1528 (NO$_2$), 1487, 1364 (NO$_2$), 1304, 841, 804. Found: C, 54.75; H, 3.72; N, 12.48. C$_{10}$H$_8$N$_2$O$_2$S requires C, 54.53; H, 3.66; N, 12.72%.

6-Nitro-5-phenylmethylthioquinoline. Mp 87–88 °C. δ_H (CDCl$_3$) 4.08 (s, 2H), 6.97 (dd, 2H, $J = 1.6, 8.0$), 7.07–7.13 (m, 3H), 7.44 (dd, 1H, $J = 4.0, 8.8$), 7.87 (d, 1H, $J = 9.2$), 8.21 (d, 1H, $J = 9.2$), 8.73 (dd, 1H, $J = 1.6, 8.8$), 8.98 (dd, 1H, $J = 1.6, 4.0$); m/z (CI) 297 (M$^+$ + 1, 100%), 189 (10); ν_{max}(KBr)/cm^{-1} 1564, 1524 (NO$_2$), 1350 (NO$_2$), 1332, 1302, 1204, 990, 841, 806. Found: C, 64.83; H, 4.23; N, 9.42. C$_{16}$H$_{12}$N$_2$O$_2$S requires C, 64.85; H, 4.08; N, 9.45%.

5-(2-Hydroxyethylthio)-6-nitroquinoline. Mp 111–112 °C. δ_H (CDCl$_3$) 2.14 (br, 1H), 3.10 (t, 2H, $J = 5.4$), 3.70 (t, 2H, $J = 5.4$), 7.68 (dd, 1H, $J = 4.2, 8.6$), 7.87 (d, 1H, $J = 9.0$), 8.26 (d, 1H, $J = 9.0$), 9.05 (dd, 1H, $J = 1.7, 8.6$), 9.08 (dd, 1H, $J = 1.7, 4.2$); m/z (CI) 251 (M$^+$ + 1, 100%), 221 (21), 175 (99); ν_{max}(KBr)/cm^{-1} 3204 (OH), 1526 (NO$_2$), 1493, 1360 (NO$_2$), 1308, 1047, 835, 818, 808. Found: C, 52.59; H, 4.31; N, 10.56. C$_{11}$H$_{10}$N$_2$O$_2$S requires C, 52.79; H, 4.03; N, 11.19%.

Methyl (6-nitroquinolin-5-ylthio)acetate. Mp 90–91 °C. δ_H (CDCl$_3$) 3.56 (s, 3H), 3.77 (s, 2H), 7.68 (dd, 1H, $J = 3.6, 9.2$), 7.96 (d, 1H, $J = 9.2$), 8.30 (d, 1H, $J = 8.8$), 9.07–9.10 (m, 2H), 9.17 (dd, 1H, $J = 1.7, 8.7$); m/z (CI) 279 (M$^+$ + 1, 25%), 214 (65), 159 (100); ν_{max}(KBr)/cm^{-1} 1738 (C=O), 1530 (NO$_2$), 1370 (NO$_2$), 1279, 1138, 1003, 842, 806. Found: C, 51.76; H, 3.69; N, 9.92. C$_{12}$H$_{10}$N$_2$O$_4$S requires C, 51.79; H, 3.62; N, 10.07%.

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