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$S_{RN}1$ SYNTHESES OF BIS(PHENYLTHIO)- AND DICYANO-NAPHTHALENES VIA DIAZOSULFIDES

M. Novi, G. Garbarino, G. Petrillo, and C. Dell'Erba
Istituto di Chimica Organica,
C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni,
Corso Europa 26, 16132 Genova, Italy

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Summary: The reactions of bromonaphthalenediazonium tetrafluoroborates (**6a,b** and **11a,b**) with sodium benzenethiolate in DMSO give, through the preliminary formation of the corresponding diazosulfides (**7a,b** and **12a,b**), bis(phenylthio)naphthalenes (**8a,b** and **13a,b**) deriving from substitution of both the diazo group and the bromine. Isolated diazosulfides (**7a,b** and **12a,b**) likewise furnish satisfactory yields of dinitriles (**9a,b** and **14a,b**) by reaction with excess tetrabutylammonium cyanide in DMSO under photostimulation by a sunlamp. The intervention of an $S_{RN}1$ process accounting for the formation of the disubstitution products is postulated.

Diazosulfides ArNNSAr' (1) are covalent adducts of arenediazonium salts whose applications in synthesis[1] are under investigation in our laboratories. In particular, compounds (1) showed[1b,e] to be convenient substrates in $S_{RN}1$ processes[2] owing to: (a) an easy initiation of the chain reaction by either thermal or photochemical fragmentation (eq. 1) as well as by electron-transfer-catalyzed decomposition (eq. 1') of (1) to give in any case aryl radicals; (b) a relatively high efficiency of the $S_{RN}1$ propagation cycle because of the favourable reduction potential of (1). In other words the (arylthio)azo group as a whole can be regarded as an easily accessible and good leaving group for $S_{RN}1$ processes, and relevant examples are the syntheses, from diazosulfides either isolated or formed in situ, of diaryl sulfides,[1a,b] bis(arylthio)benzenes,[1b] aromatic nitriles,[1d,e] and isomeric phthalonitriles[1d,e] recently reported by us.

$$\underset{1}{\mathrm{Ar{-}N{=}N{-}SAr'}} \longrightarrow \mathrm{Ar^{\cdot}} + \mathrm{N_2} + \mathrm{Ar'S^{\cdot}} \qquad (1)$$

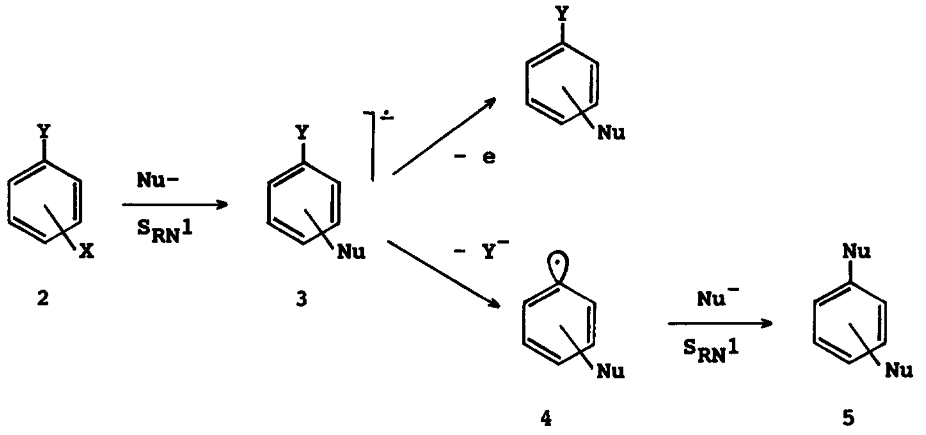
$$\underset{1}{\mathrm{Ar{-}N{=}N{-}SAr'}} \xrightarrow{+e} 1^{\dot{-}} \longrightarrow \mathrm{Ar^{\cdot}} + \mathrm{N_2} + \mathrm{Ar'S^{-}} \qquad (1')$$

$$\mathrm{Ar^{\cdot}} + \mathrm{Nu^{-}} \longrightarrow \mathrm{Ar{-}Nu^{\dot{-}}} \qquad (2)$$

$$\mathrm{Ar{-}Nu^{\dot{-}}} + 1 \longrightarrow \mathrm{Ar{-}Nu} + 1^{\dot{-}} \qquad (3)$$

The cited formation[1b,e] of the bis-substituted products derives from a well known[2] peculiarity of the $S_{RN}1$ process, by which, when the arene moiety bears two nucleofugic groups (X and Y in 2), the radical anion of the monosubstitution product, e.g. (3), can extrude a Y^- ion with formation of an aryl radical (4) which starts a new propagation cycle leading to the disubstitution product (5) (Scheme 1).

Scheme 1



In spite of numerous studies on simple halogenated derivatives,[3] the extension of the synthetic strategy above to polycyclic arenes with two potential nucleofugic groups has received little attention and no example of disubstitution via $S_{RN}1$ reaction is so far known in this field: the only relevant report[4] concerns the rections of 5-chloro-7-iodo-8-isopropoxy-quinoline where replacement of the iodine alone was observed. The present investigation was undertaken to test whether and to what extent disubstitutions via the $S_{RN}1$ mechanism could be extended to appropriate naphthalene derivatives and we report herein on the successful preparation of bis(phenylthio)- and dicyano-naphthalenes from some bromonaphthalenediazonium tetrafluoroborates and the corresponding diazosulfides.

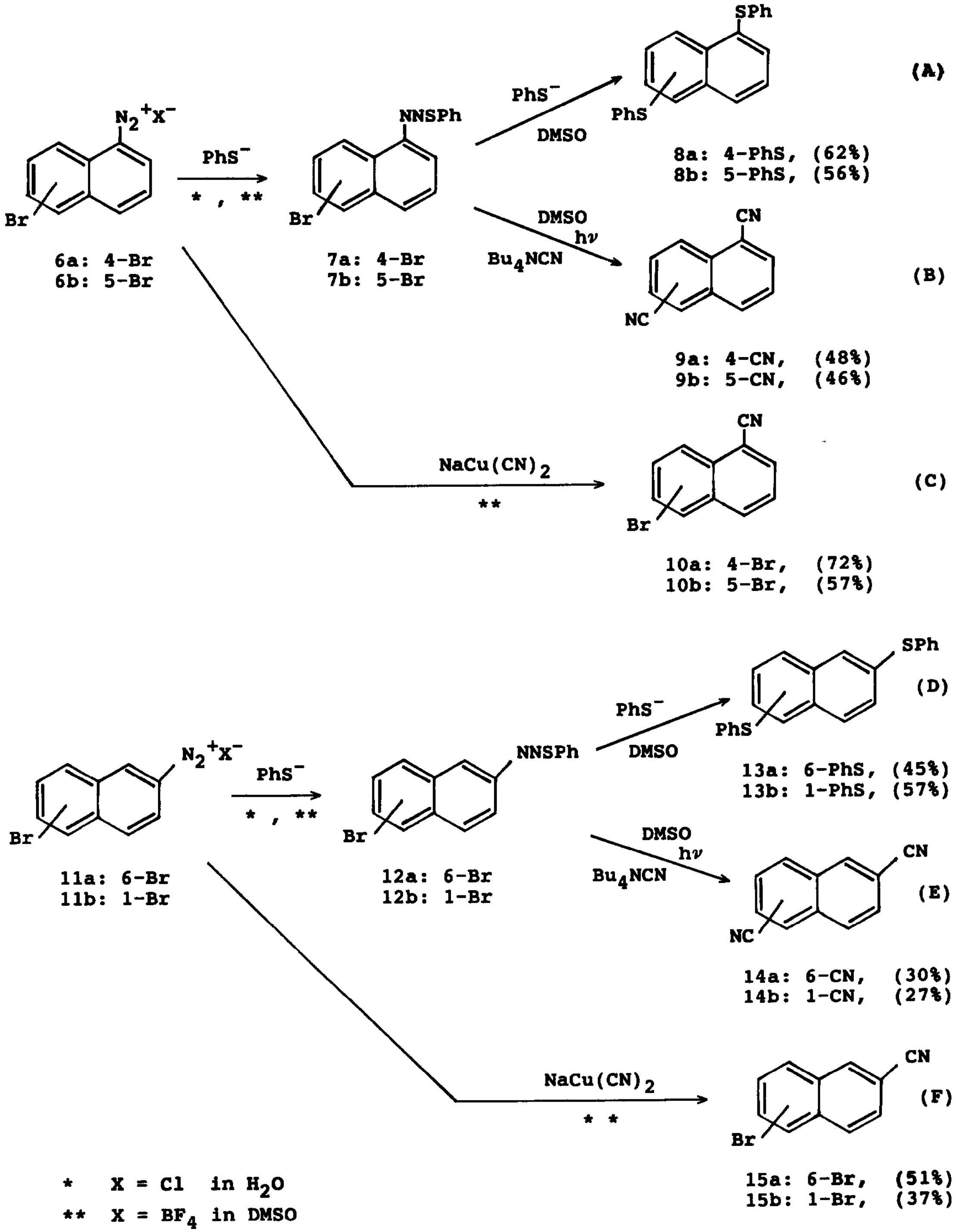
RESULTS AND DISCUSSION

As summarized in paths A and D of Scheme 2, the reactions of bromonaphthalenediazonium tetrafluoroborates (**6a,b** and **11a,b**) with sodium benzenethiolate in DMSO furnish the bis(phenylthio) derivatives **8a,b** and **13a,b** via the preliminary formation[1a,b] of diazosulphides **7a,b** and **12a,b**. Similarly (paths B and E), when isolated diazosulphides **7a,b** and **12a,b** are reacted with excess tetrabutylammonium cyanide, in DMSO and under photostimulation by a sunlamp, substitution of both the bromine and the (arylthio)azo group occurs with formation of dinitriles **9a,b** and **14a,b**.

Thus the method herein offers a simple and straightforward access to the shown bis-substitution products under mild conditions and without any troublesome procedure. It is worth remembering on this regard that neither the Ziegler (for thioethers)[5,6] nor the Sandmeyer (for nitriles)[6,7] reactions can afford bis-substituted products from halogenoarenediazonium salts. By sake of comparison, the results obtained from the reactions of arenediazonium tetrafluoroborates (**6a,b** and **11a,b**) and sodium cuprocyanide in DMSO (a Sandmeyer-like reaction[7b]) are also reported (paths C and F): as expected, bromonitriles (**10a,b** and **15a,b**) are invariably formed without any trace of bis-substitution products and in analogy with the same processes carried out in aqueous medium. Therefore the results reported here and previously,[1b,e] show that starting from a halogenoarylamine, the possibility exists of choosing between two alternative pathways depending on the desired product: the simple arylthio- or cyano-dediazoniation by the Ziegler[5,6] or the Sandmeyer[6,7] reaction or the substitution of both the diazo and the halogen via electron-transfer processes involving diazosulphides as substrates in dipolar aprotic solvents. The obtained results represent, to our knowledge, the first example of disubstitution via the $S_{RN}1$ reaction in polycyclic arenes, which moreover shows that such disubstitution can be also accomplished when the two leaving groups are on different aromatic nuclei belonging to the same π-electron system:[8] the yields of disubstitution products appearing to be practically the same irrespective of the reciprocal position of the two leaving groups (cf. yields of **8a** and **8b**, **9a** and **9b**, **13a** and **13b**, and **14a** and **14b**).

With regard to the synthesis of dinitriles, the yields reported in Scheme 2 could appear somehow less than satisfactory, at least in some cases.

Scheme 2



* X = Cl in H_2O

** X = BF_4 in DMSO

Actually, because of the nature of the $S_{RN}1$ process operative in these reactions,[1,2] competitive paths lead to the formation of by-products such as bromo-cyano-, phenylthio-cyano-, and even bis(phenylthio)-naphthalenes (see Experimental Section). As already pointed out,[1e] the formation of such by-products is, in part, bound to the competition, set up in our systems, for the aryl radical intermediates between cyanide and the benzenethiolate ion formed via cleavage of diazosulfide radical anions (eq. 1', Ar'= Ph); the intrinsic lower ability of the cyanide ion to couple with aryl radicals[9] represents therefore a rationale for the concomitant formation of phenylthio derivatives in the studied reactions. Anyway, in spite of the above drawback, the herein reported synthetic approach to aromatic dinitriles, starting from easily accessible arylamines, can be considered an alternative and complementary method to those involving ,e.g., the treatment of dihaloarenes with either cuprous cyanide[10] or trimethylsilyl cyanide under catalysis of Pd-triphenylphosphine[11].

EXPERIMENTAL

Melting points were taken on a Buchi 535 apparatus. ^1H NMR spectra were recorded on a Varian FT80 instrument with Me_4Si as internal standard and chemical shifts are expressed as δ (ppm) values. Column chromatography was performed on silica gel using as eluants light petroleum bp 30-50 °C or proper mixtures with dichloromethane.
Unknown compounds gave satisfactory microanalytical data (C ± 0.4, H ± 0.1, N ± 0.1, S ± 0.2).

Chemicals. Commercial pure grade dimethylsulfoxide was used as received after storage over molecular sieves (type 4Å). Sodium benzenethiolate was prepared as described[12] while tetrabutylammonium cyanide was from commercial origin and used as received. The aqueous diazonium chlorides of the following amines: 1-amino-4-bromo- (commercial), 1-amino-5-bromo-,[13] 2-amino-6-bromo-,[14] and 2-amino-1-bromo-[15] were transformed into the corresponding tetrafluoroborates[16] or covalent diazosulfides[1e] and used for the successive reactions as crude materials.

Reactions of Bromonaphthalenediazonium Tetrafluoroborates with Sodium Benzenethiolate in DMSO.
Preparative runs were carried out under argon and worked up following the general synthethic procedure already reported.[1b]
The reaction of the 4-bromo-1-diazonio derivative **6a** (25°, 6h) gave: (a) 62% of 1,4-bis(phenylthio)naphthalene **8a**, mp 116-117 °C (EtOH), δ (CD_3COCD_3) 8.42 (2H, m), 7.63 (2H, m), 7.51 (2H, s), 7.31 (10H, m); (b) 20% of 4-bromo-1-(phenylthio)naphthalene as a waxy oil which was characterized as sulfone after oxidation with hydrogen peroxide in glacial acetic acid: the 4-bromo-1-(phenylsulfonyl)naphthalene had mp 171-172 °C (EtOH), δ (CD_3COCD_3) 8.73 (1H,

m), 8.44 and 8.39 [2H in all, d (*J* 8.0 Hz) and m partly overlapped], 8.15 (1H, d, *J* 8.0 Hz), 8.02 (2H, m), and 7.67 (5H, m); (c) 5% of 1-(phenylthio)-naphthalene identified by comparison (NMR, IR) with an authentic sample.[1b]

From the reaction of the 5-bromo-1-diazonio derivative **6b** (25°, 2h) the following products were isolated: (a) 1,5-bis(phenylthio)naphthalene **8b** (56% yield), mp 143 °C (EtOH), δ (CD_3SOCD_3) 8.44 (1H, m), 7.75 (2H, m), and 7.37 (5H, m); (b) 5-bromo-1-(phenylthio)naphthalene (22%), obtained as an oil contaminated by traces (TLC) of other by-products, characterized as sulfone: the 5-bromo-1-(phenylsulfonyl)naphthalene had mp 156 °C (EtOH), δ (CD_3COCD_3) 8.88 (1H, d, *J* 8.7 Hz), 8.76 (2H, m), 8.10 (4H, m), and 7.72 (4H, m).

The reaction on the 6-bromo-2-diazonio derivative **11a** (1h at 25° and 3h at 60°) gave: (a) 45% of 2,6-bis(phenylthio)naphthalene **13a**, mp 132 °C (petroleum bp 80-100 °C), δ ($CDCl_3$) 7.74 (1H, br s), 7.63 (1H, d, *J* 8.6 Hz), and 7.34 (6H, m); (b) 19% of 6-bromo-2-(phenylthio)naphthalene, mp 104-105 °C (light petroleum bp 30-50 °C), δ ($CDCl_3$) 7.94 (1H, br s), 7.63 (4H, m), and 7.36 (6H, m).

In the reaction of the 1-bromo-2-naphthalenediazonium tetrafluoroborate **11b** (25°, overnight) no attempt was made to identify by-products and only the main component, 1,2-bis(phenylthio)naphthalene **13b**, was isolated in 57% yield, mp 108-110 °C (EtOH), δ (CD_3COCD_3) 8.43 (1H, m), 7.88 (2H, m), 7.50 (7H, m), and 7.13 (6H, m).

Photoinduced Reactions of Bromonaphthylazo Phenyl Sulfides with Tetrabutylammonium Cyanide in DMSO.

The experimental conditions and procedures were the same as those described previously.[1e]

The reaction on the diazosulfide **7a** gave: (a) 48% of 1,4-dicyanonaphthalene **9a**, mp 208 °C (lit.,[17] mp 208 °C), δ (CD_3COCD_3) 8.32 and 8.26 (4H in all, A_2 of A_2B_2 and s partly overlapped) and 8.01 (2H, B_2 of A_2B_2); ν_{CN} (nujol) 2240 cm^{-1}; (b) 21% of 1-cyano-4-(phenylthio)naphthalene, mp 115-116 °C (light petroleum bp 30-50 °C/toluene), δ (CD_3COCD_3) 8.42 and 8.17 (2H, two m partly overlapped), 7.87 (3H, m), 7.52 (5H, m), and 7.24 (1H, d, *J* 7.8 Hz); ν_{CN} (nujol) 2215 cm^{-1}; (c) 3% of 4-bromo-1-cyanonaphthalene which was identified by comparison (NMR, IR) with an authentic sample (see below).

The reaction on the diazosulfide **7b** furnished: (a) 46% of 1,5-dicyanonaphthalene **9b**, mp 266 °C (lit.,[17] mp 263 °C), δ (CD_3COCD_3) 8.54 (2H, d, *J* 9.0 Hz), 8.33 (2H, d, *J* 7.2 Hz), and 8.02 (2H, two d partly overlapped, *J* 7.2 and 9.0 Hz), ν_{CN} (nujol) 2226 cm^{-1}; (b) 22% of 1-cyano-5-(phenylthio)naphthalene, mp 81 °C (petroleum bp 60-80 °C), δ (CD_3COCD_3) 8.69 (1H, d, *J* 7.0 Hz), 8.20 (2H, m), 7.78 (3H, m), and 7.32 (5H, m); ν_{CN} (nujol) 2218 cm^{-1}; (c) 5-bromo-1-cyano- (8%) and 1,5-bis(phenylthio)-naphthalene (3%) which were identified by comparison (NMR, IR) with authentic samples.

From the reaction on 6-bromo-2-naphthylazo phenyl sulfide **12a** the following products could be identified: (a) 2,6-dicyanonaphthalene **14a** (30% yield), mp 295 °C (lit.,[17] mp 293 °C), δ (CD_3COCD_3) 8.63 (2H, s), 8.31 (2H, d, *J* 8.4 Hz), and 7.94 (2H, d, *J* 8.4 Hz); ν_{CN} (nujol) 2288 cm^{-1}; (b) 2-cyano-6-(phenylthio)naphthalene (17% yield), mp 112-113 °C (petroleum bp 80-100 °C), δ (CD_3COCD_3) 8.39 (1H, br s), 7.99, 7.95, 7.81, 7.70 [4H in all, partly overlapped signals: d (*J* 8.7 Hz), d (*J* 8.6 Hz), br s, and dd (*J* 8.7 and 1.6

Hz)], and 7.48 (6H, m); ν_{CN} (nujol) 2226 cm^{-1}; (c) 2-cyanonaphthalene (11%) identified by mixed mp with an authentic sample from our laboratories.
The rather complex mixture of by-products coming from the reaction carried out on the 1-bromo-2-naphthylazo phenyl sulfide 12b was not exhaustively investigated. Only the main product (27%) was isolated and identified as 1,2-dicyanonaphthalene **14b**, mp 190 °C (lit.,[17] mp 190 °C), δ (CD_3COCD_3) 8.50 (1H, d, *J* 8.7 Hz), 8.26 (2H, m), and 7.98 (3H, m); ν_{CN} (nujol) 2230 cm^{-1}.

Reactions of Bromonaphthalenediazonium Tetrafluoroborates with Sodium Cuprocyanide in DMSO.
The diazonium tetrafluoroborates **6a,b** and **11a,b** were reacted with sodium cuprocyanide via reported[7b] experimental procedures. The following bromocyanonaphthalenes, whose ^1H NMR spectra were in agreement with the proposed structure, were obtained: 4-bromo-1-cyanonaphthalene **10a** (72%), mp 100 °C (lit.,[18] mp 102-103 °C); 5-bromo-1-cyanonaphthalene **10b** (57%), mp 147 °C (lit.,[19] mp 147 °C); 6-bromo-2-cyanonaphthalene **15a** (51%), mp 158-160 °C (lit.,[20] mp 160-162 °C); 1-bromo-2-cyanonaphthalene **15b** (37%), mp 90-91 °C (lit.,[21] mp 93 °C).

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8 Interestingly enough, preliminary results show higher ratios between mono- and di-substitution when the reactions with benzenethiolate and cyanide anions are carried out on 4-bromo-4'-diazonio- or 4-bromo-4'-(phenylthio)-azo-biphenyl respectively, where the overlapping of the π-electron systems of the two rings is only partial.

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