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A CONVENIENT $S_{RN}1$ SYNTHESIS OF AROMATIC NITRILES FROM DIAZONIUM SALTS VIA DIAZOSULFIDES

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Abstract. - Properly substituted diazosulfides XC_6H_4-N=N-SPh (1) (either isolated or generated in situ from arenediazonium tetrafluoroborates and sodium benzenethiolate) react with tetrabutylammonium cyanide, in Me_2SO under photon or electron stimulation, leading to nitriles XC_6H_4CN (2). Satisfactory yields of 2, comparable with those of the Sandmeyer reaction, are obtained when X = 3- or 4-CF_3, 2-, 3-, or 4-CN, 4-F, 4-MeCO, 3-MeO, 4-NO_2, 4-PhCO, and 4-$PhSO_2$. For different reasons, the reaction practically fails as a useful nitrile synthesis when X = H, 4-MeO, 2-, or 3-NO_2. The collected evidences agree well with the intervention of an $S_{RN}1$ mechanism, to which diazosulfides 1, given their easy reducibility followed by a prompt fragmentation of the C-N and N-S bonds, are convenient participating substrates. An important consequence of the mechanism involved is the behaviour of bromo and chloro derivatives (1: X = Br, Cl) which lead, through the contemporaneous introduction of two cyano functionalities, to more than satisfactory yields of the corresponding dicyanobenzenes.

The synthetic utility of the functionalisation of aromatic substrates with cyano groups justifies the continuous application of organic chemists to the attainment of facile and convenient nitrile syntheses. This effort is evidenced by the substantial number of papers appeared in the latest literature, dealing with either the transformation[1] or the replacement[2] of pre-existent functionalities. Replaceable moieties have proven to be, e.g., thallium bis(trifluoroacetate) in arylthallium derivatives by action of cuprous cyanide,[2a] or iodine in a Pd-catalysed process with trimethylsilyl cyanide.[2b]

However, the most common substitution reactions to aromatic nitriles are undoubtedly represented by the Rosenmund-von Braun[3] and the Sandmeyer[4] reactions, which classically take advantage of the catalytic action of copper salts on haloarenes and arenediazonium salts respectively. The exploitation of diazonium salts as synthetic intermediates is actually appealing, given their reactivity and the easy availability of the parent arylamines, but, nonetheless, in the classical Sandmeyer reaction such advantages are somewhat offset, on the practical ground, by awkward procedures, coupled with sometimes unsatisfactory yields.[4d] Accordingly, new methodologies have been published, dealing with non-aqueous systems[5] and/or more sophisticated catalytic species,[6] which do not always achieve overall substantial improvements.

We have preliminarily reported[7] that suitably activated diazosulfides 1, (either isolated or generated in situ from arenediazonium tetrafluoroborates and sodium benzenethiolate) promptly react with tetrabutylammonium cyanide in Me_2SO under photon or electron stimulation leading to nitriles (eq i) with yields that compare successfully with those reported for the Sandmeyer reaction.[4]

$$\underset{1}{XC_6H_4\text{-N=N-SPh}} + CN^- \xrightarrow[Me_2SO]{h\nu \text{ or } e} \underset{2}{XC_6H_4CN} + N_2 + PhS^- \qquad \text{i}$$

Herein we present the results of the work carried out since in order to better define both the mechanism and scope of the reaction in the benzene series, with particular regard to its application, stemming from the very nature of the mechanism itself, as a convenient one-pot synthesis of phthalo-, isophthalo-, and terephthalonitrile from properly halosubstituted diazosulfides (eq ii).

$$\underset{1}{XC_6H_4\text{-N=N-SPh}} + 2CN^- \xrightarrow[Me_2SO]{h\nu} C_6H_4(CN)_2 + N_2 + X^- + PhS^- \qquad \text{ii}$$

$X = Cl, Br$

Results and Discussion

The results are collected in Tables 1 to 3, the last two Tables separately dealing with derivatives (namely halo- and nitroderivatives) whose behaviour results to be quite characteristic and deserving, for different reasons, of particular attention.

The reactions as displayed in eqs i and ii smoothly occur at room temperature, with somewhat better yields when starting from isolated diazosulfides. In photostimulated (sunlamp) experiments the irradiation time for reactions pushed to completion was generally prolonged to 60 min, exhaustion of substrate being ensured by ceasing of nitrogen evolution and/or TLC analysis. More details are to be found in the Experimental section.

General mechanistic and synthetic aspects. - In the preliminary communication[7] we suggested that the reaction under examination be yet another example of the nowadays well recognised $S_{RN}1$ substitution.[8] The chain-propagation cycle can be represented by equations P1-P3, that is, respectively,

$$\underset{1^{\bullet-}}{[XC_6H_4\text{-N=N-SPh}]^{\bullet-}} \longrightarrow XC_6H_4^{\bullet} + N_2 + PhS^- \qquad \text{P1}$$

$$XC_6H_4^{\bullet} + CN^- \longrightarrow \underset{2^{\bullet-}}{[XC_6H_4CN]^{\bullet-}} \qquad \text{P2}$$

$$2^{\bullet-} + 1 \rightleftharpoons 2 + 1^{\bullet-} \qquad \text{P3}$$

fragmentation (P1) of the radical anion of the substrate, coupling (P2) between the resulting σ aryl radical and the negatively charged nucleophile, and (P3) single-electron transfer to regenerate the reactive $1^{\bullet-}$ species[9] with formation of the overall substitution product 2. It must be pointed out that the actual sequence of such propagation steps depends on the nature of the initiation to be discussed later.

The most straightforward piece of evidence to support our hypothesis is represented by the need for photostimulation[10] if appreciable yields of nitrile are to be obtained in reasonable times (cf. expts 1 and 10 with expts 2 and 11 respectively in Table 1). Of course, photostimulation is a diagnostic test for single-electron transfer processes only if backed by further relevant

Table 1. Photon or electron stimulated reactions between diazosulfides XC$_6$H$_4$-N=N-SPh and tetrabutylammonium cyanide in Me$_2$SO at room temperature.

Expt No	X	Compd No	Conditions[a]	CN$^-$/substr. molar ratio	E_{pc} (V)[b]		Yield(%)[c]			
					1	**2**	**1**	**2**	**3**	XC$_6$H$_5$
1	4-PhCO	**1a**	D, 66 h	5	-1.25	-1.61	9	27	21	20
2	"	"	I	5				35	40	15
3	"	"	I, 13 min	5			78	11	6	5
4	"	"	I	0					25	45
5	"	"	E, 0.25 F mol^{-1}	5				40	36	18
6	"	"	I[d]	5				4		6
7	"	"	I	10				52	29	15
8	"	"	I	20				69	21	12
9	"	"	I[e]	20				64	22	11
10	4-MeCO	**1b**	D, 184 h	10	-1.28	-1.77	16	19	3	13
11	"	"	I	10				40	25	16
12	"	"	I	20				50	19	11
13	2-CN	**1c**	I, 45 min	20				63	13	[f]
14	3-CN	**1d**	I	20				75	17	[f]
15	4-CN	**1e**	I	5	-1.23	-1.82		50	38	[f]
16	"	"	I	20				71	19	[f]
17	"	"	I[e]	20				46	26	[f]
18	"	"	E, 0.07 F mol^{-1}	20				71	20	[f]
19	4-PhSO$_2$	**1f**	I	20	-1.23	-1.75		74	16	8
20	"	"	E, <0.06 F mol^{-1}	20				72	15	12
21	3-CF$_3$	**1g**	I	20				61	13	[f]
22	4-CF$_3$	**1h**	I	20	-1.42	-2.11		60[g]	22	[f]
23	H	**1i**	I	20	-1.61	-2.56		traces	33	[f]
24	3-MeO	**1j**	I	20				35	21	[f]
25	4-MeO	**1k**	I	20				9	20	[f]
26	"	"	I[e]	20				7	12	[f]

[a] D = in the daylight; I = irradiation (60 min, unless otherwise stated) with a 300-W Osram sunlamp in a Pyrex flask; E = controlled-potential electrolysis at a Pt-flag cathode. Substrate concentration 13-15 mM in any set of conditions. [b] Cathodic peak potentials in Me$_2$SO-0.1 M Bu$_4$N$^+$BF$_4^-$ on a Pt-bead cathode vs. Ag/AgNO$_3$ 0.01 M in Me$_2$SO. Scan rate 100 mV sec^{-1}. Cyclic voltammetry of **1** showed irreversible peaks up to the maximum sweep rate (1 V sec^{-1}) allowed by the pen-to-chart recording method. [c] Isolated yield, unless otherwise stated. [d] The diazonium tetrafluoroborate was employed, in the absence of benzenethiolate. [e] The diazosulfide was generated in situ from equimolar amounts of diazonium tetrafluoroborate and sodium benzenethiolate prior to addition to the cyanide solution. [f] Detected (HPLC or GC) but not quantified. [g] Determined by GC.

evidence,[10] as will be presented hereinafter. Anyway it must be pointed out that diazosulfides have been recently shown in our laboratories to willingly participate in $S_{RN}1$ chain processes in the presence of suitable electron sources such as thiolate anions or a cathode.[11]

Herein, the detection, throughout the whole series of experiments carried out, of variable amounts of XC_6H_5 represents a further hint as to the intermediacy of the $XC_6H_4^{\cdot}$ radical. Termination steps such as reduction (T1) of the radical followed by protonation (by e.g., the tetrabutylammonium ion used as the counterion of cyanide, or adventitious water), or H-atom transfer (T2) to the radical (from the solvent or the tetrabutylammonium cation) are generally invoked[8,12] in order

$$XC_6H_4^{\cdot} \xrightarrow{e} XC_6H_4^{-} \xrightarrow{H^+} XC_6H_5 \qquad \text{T1}$$

$$XC_6H_4^{\cdot} + SH \longrightarrow XC_6H_5 + S^{\cdot} \qquad \text{T2}$$

to justify the occurrence of such reduction products within the $S_{RN}1$ pathway.

Strong substantiation of the proposed mechanism comes from the electrochemical experiments reported in Table 1. While cyclic voltammetry of diazosulfides **1a,b,e,f,h,i** provides clear evidence for an irreversible substrate reduction, the controlled-potential electrolyses in the presence of tetrabutylammonium cyanide (expts 5, 18, and 20) enlighten, through a very low current consumption (0.1—0.2 F mol^{-1}) the electrocatalytic nature of the process[13] and, accordingly, the operation of an efficient propagation cycle. Furthermore, as both relative and absolute yields in the just cited electrolyses tightly match those obtained from the relevant photostimulated counterparts (cf. expts 2, 16, and 19 respectively), the involvement of a propagation cycle of similar efficiency in the latter experiments seems to be guaranteed, although initiation may well be different in the two sets of conditions. Actually, if our analysis is correct, in the electrochemically induced processes entry into the propagation cycle is straightforwardly provided by the $\mathbf{1}^{\cdot-}$ radical anion (i.e. at the P1 level), initiation being represented by single-electron transfer from the cathode to the substrate. As regards initiation under photostimulation, among a few alternatives conceivable herein,[14] we feel that homolytic photodissociation of the diazosulfide (step I1)[15] (and hence entry into the propagation cycle through $XC_6H_4^{\cdot}$ at the P2 level) represents a pre

$$\underset{\mathbf{1}}{XC_6H_4\text{-}N{=}N\text{-}SPh} \xrightarrow{h\nu} XC_6H_4^{\cdot} + N_2 + PhS^{\cdot} \qquad \text{I1}$$

ferable route to, e.g., photostimulated reduction of substrate by the cyanide ion, a reportedly poor electron donor.[16] It is noteworthy that, in the absence of cyanide ions, the 4-benzoylderivative **1a** (X = 4-PhCO) disappears within the usual irradiation time to give products likely to derive from the 4-benzoylphenyl radical (expt 4), an outcome which represents clear evidence of the fact that cyanide ions are not required in order to generate reactive intermediates.

In the light of the proposed scheme the synthetic limitations clearly emerging from the inspection of Table 1 are next to be discussed. As a matter of fact, in appropriate reaction conditions, electron-attracting X substituents (with halogens, to be discussed in a following section, lining up nicely in this respect) lead to nitrile yields which are better or anyway comparable with those obtained with the Sandmeyer procedure.[4] On the contrary, the unsubstituted diazosulfide **1i** (expt 23) and the 4-methoxyderivative **1k** (X = 4-MeO) (expts 25, 26) fail to give appreciable amounts of nitrile. In principle, a differential reactivity within the proposed chain mechanism can originate from any of the steps involved (initiation, propagation, and/or termination). Anyway, we can reasonably assume that initiation is relatively uninfluent in the overall economy of the process, so that reactivity differences are to be explained mainly within the efficiency of the chain.

At this regard, it must be first of all recalled that scanty literature reports on the involvement of the cyanide ion in $S_{RN}1$ reactions agree in assigning it a low rank in a reactivity scale of nucleophiles.[12a,c,13,17] Such a low reactivity has been attributed to the slowness of the P3 electron transfer[17a] (which, depending on the nature of the substrate, can be thermodynamically disfavoured and therefore slow), but a more recent report[12c] stresses the role played by the radical/anion P2 coupling: at variance with nucleophiles such as benzenethiolate, diethyl phosphite, or acetone enolate,[12b,18] such coupling does not approximate the diffusion limit but suffers a retardation which can amount up to several powers of ten. The doubt is left,[12c] though, wether this differential behaviour be attributable, in the employed conditions (sodium or potassium cyanide in liquid ammonia at -40 °C), to a low intrinsic reactivity of cyanide or rather to ion pairing with the countercation.

The employment of diazosulfides **1** herein offers the advantage that, as shown by the voltammetric data in Table 1, the reduction potential (E_{pc}) of **1** is positive with respect to that of **2**, the unsubstituted diazosulfide **1i** (which gives poor yields of nitrile) making no exception. This occurrence is likely to guarantee an invariably fast P3 electron transfer, and reasonably leaves major responsibility for the abovementioned poor results to the radical/anion coupling, the radicals preferentially undergoing diverse competitive pathways. It is noteworthy that the analogous $S_{RN}1$ reaction of diazosulfides with benzenethiolate[11a,b] is hardly affected by the X substituent, pointing to a faster, and accordingly less selective, coupling between aryl radicals and PhS^-.

As to the rationalisation, within the P2 step, of the herein observed reactivity differences, it must be pointed out that, although the electrophilicity of an aryl radical should conceivably be slightly influenced by substituents,[19] any substituent effect is undoubtedly bound to show up when a radical ion is formed as the result of a radical/ion coupling,[20] unless the transition state very closely resembles the reactants.[19] As a matter of fact, the coupling rate between the cyanide ion and some aryl radicals in liquid ammonia has been determined and found to approximately correlate with the standard potential of the $ArCN/ArCN^{\bullet-}$ couple, the radical anions of more easily reducible nitriles being more rapidly formed.[12c]

The intrinsic low ability of the cyanide ion to couple with aryl radicals represents also a rationale for the concomitant formation, in the studied reaction, of aryl phenyl sulfides (XC_6H_4SPh, **3**). In fact, if we recall that the benzenethiolate ion is one of the fragments resulting from the P1 propagation step, the formation of **3** can be readily explained as a consequence of the effective competition between benzenethiolate and cyanide ions for the $XC_6H_4^{\bullet}$ radical.[12c] Accordingly, a new propagation cycle (P1 + P2' + P3') is triggered, which, given also the higher radical/anion coupling rate, is more efficient than the one relevant to nitrile formation.

$$XC_6H_4^{\bullet} + PhS^- \longrightarrow \underset{\mathbf{3}^{\bullet-}}{\left[XC_6H_4SPh\right]^{\bullet-}} \qquad \text{P2'}$$

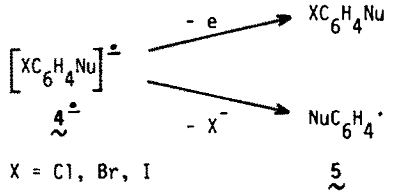
$$\mathbf{3}^{\bullet-} + \mathbf{1} \rightleftharpoons \mathbf{3} + \mathbf{1}^{\bullet-} \qquad \text{P3'}$$

On synthetic grounds, the incidence of such competition can be considerably depressed if the lower coupling ability of the cyanide ion is kinetically enhanced through a concentration effect.

In fact, higher initial CN^- to diazosulfide molar ratios (cf. expts 2, 7, and 8, expts 11 and 12, or expts 15 and 16) do lead to increased nitrile yields: this is accompanied, though, by a decrease in the sulfide yield which is less than linear, pointing to a non-zero limit. We feel that a concentration-independent solvent-cage coupling between aryl radicals and PhS^- (or the $PhS^\cdot$ thiyl radical generated by any photostimulated homolytic fragmentation of diazosulfide) could also play a role. Therefore, the competitive formation of **3** seems unavoidable. On the other hand, it must be noted that the direct reaction of an arenediazonium tetrafluoroborate with tetrabutylammonium cyanide in our experimental conditions affords meagre yields of nitrile (expt 6), possibly due, inter alia, to the formation of the stable covalent diazocyanide XC_6H_4-N=N-CN.

Behaviour of halosubstituted diazosulfides (**1**: X = Hal). - It is nowadays a tenet of organic chemistry that, to the exclusion of the unreactive fluoroderivatives, dihaloarenes, when subjected to $S_{RN}1$ processes, can afford mixtures of mono- and disubstitution products,[8] the crucial point of the overall system being represented by the partitioning of the radical anion of the monosubstitution product (**4**$^{\cdot-}$ in Scheme 1) between oxidation and halide ion cleavage. The latter choice leads to the σ radical **5**, from which the disubstitution product eventually derives. Such choice is almost precluded to fluorosubstituted radical anions given the slower fragmentation of the C-F bond.[8,21]

Scheme 1



Herein, as already experienced in the recently reported sulfide synthesis from haloarenediazonium salts,[11b,c] the expectation above is completely fulfilled, to further substantiate the proposed mechanism: thus (see Table 2), the fluoroderivative **1l** exclusively yields the monosubstitution product (4-fluorobenzonitrile),[21] while bromo (**1m**,**n**) or chloro (**1o**) derivatives regiospecifically lead, irrespective to the relative position of the halogen and the diazothio group, to more than satisfactory yields of the corresponding dinitriles; the concomitant formation of the by-products reported in Table 2 (expts 28—30) is readily rationalisable within the proposed mechanism.

Table 2. Photostimulated reactions between halosubstituted diazosulfides XC_6H_4-N=N-SPh and tetrabutylammonium cyanide in Me_2SO at room temperature.[a]

Expt No	X	Compd No	Isolated yield (%)				
			2	**3**	$C_6H_4(CN)_2$	CNC_6H_4SPh	$C_6H_4(SPh)_2$
27	4-F	**1l**	37	20			
28	4-Br	**1m**		8	54	15	3
29	3-Br	**1n**		5	50	20	5
30	2-Cl	**1o**		[b]	53	10	3

[a] Irradiation (60 min) was performed with a 300-W Osram sunlamp in a Pyrex flask; substrate concentration 16 mM; initial CN^- to substrate molar ratio 20. [b] Detected (HPLC) but not quantified.

Besides the mechanistic implications of this result, its synthetic meaning should also be stressed. Our reaction, allowing the contemporaneous introduction of two cyano functionalities, represents a mild and convenient access to dicyanobenzenes from bromo- or chloroanilines (alternative to reported methods from dihalobenzenes[2b,3b]) whereas the Sandmeyer reaction of halobenzene diazonium salts exclusively yields the corresponding halobenzonitriles.

Behaviour of nitrosubstituted diazosulfides (1: X = NO_2). - Within the range of the diazosulfides whose participation to the present $S_{RN}1$ reaction has been tested, the nitroderivatives present a peculiar behaviour (Table 3).

Table 3. Reaction between nitrosubstituted diazosulfides Ar-N=N-SPh and tetrabutylammonium cyanide in Me_2SO at room temperature.[a]

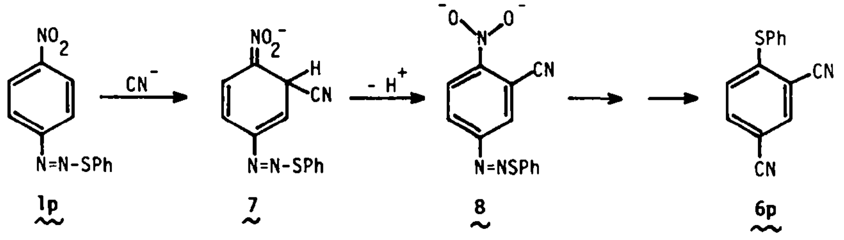
Expt No	Ar	Compd No	CN^-/substr. molar ratio	Isolated yield (%) ArCN	ArSPh	ArH	others
31	$4\text{-}NO_2C_6H_4$	1p	3.3[b]	36	40	traces	6p: 8
32	"	"	5	48	28	"	" : 12
33	"	"	20	33	16	"	" : 28
34	$3\text{-}NO_2C_6H_4$	1q	5	4	15	⩾13	
35	$2\text{-}NO_2C_6H_4$	1r	5	14	22	⩾31	
36	$2,6\text{-}Me_2\text{-}4\text{-}NO_2C_6H_2$	9a	5	46	27	traces	10: 7
37	$3,5\text{-}Me_2\text{-}4\text{-}NO_2C_6H_2$	9b	20[c]	60	19	"	

[a] In the daylight (60 min) unless otherwise stated; substrate concentration 14 mM. [b] Reaction time 90 min. [c] Irradiation (60 min) with a 300-W Osram sunlamp in a Pyrex flask.

Most strikingly, for the initially tested[7] 4-nitroderivative 1p nitrogen evolution readily takes off without photostimulation upon mixing of the reactants. Furthermore, besides the expected nitrile 2p, 4-nitrophenyl phenyl sulfide (3p), and nitrobenzene, the reaction affords (TLC) a few side-products, among which it has been possible to isolate a compound whose yield increases as the initial cyanide ion to diazosulfide molar ratio is enhanced (expts 31—33). Such compound, which has been identified as the 2,4-dicyanophenyl phenyl sulfide 6p on the grounds of both elemental and spectral analyses, seems to form competitively with 2p.

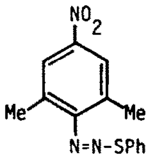
A rationale for the above described behaviour could in our opinion be represented by a von Richter-type[22] reactivity of the cyanide ion towards the diazosulfide 1p, initially leading to negatively charged intermediates such as 7 and, possibly, 8 (Scheme 2). These presumably rapidly formed intermediates (or reactive species hence derived) could act as effective one-electron reductants towards the substrate,[23] triggering the chain process leading to 2p without the need for

Scheme 2

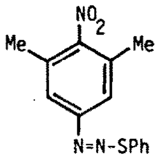


photostimulation. The formation of 2p through an $S_{RN}1$ pathway is not in disagreement with the observation that the yield of the concomitantly formed sulfide 3p decreases with increasing initial cyanide ion to diazosulfide molar ratios in a way which is similar to that previously reported herein. Several pathways accounting for the formation of the isolated 6p from intermediates like 7 or 8 can be envisaged, although a more detailed discussion in this respect is beyond the scope of the present work. It could be relevant that the reaction between 4-nitrobenzophenone and KCN in Me_2SO leads to 3-cyano-4-methoxy- or 3-cyano-4-hydroxybenzophenone (with or without added methanol respectively),[23b] a displacement pattern which somehow recalls the present result.

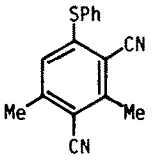
Further insight into the matter is provided by the reactivity of the dimethyl-4-nitrodiazosulfides 9a,b (Table 3). Actually, 9a behaves much like 1p, needing no photostimulation and leading to the isolation of compound 10, which is structurally similar to 6p. Conversely, the reaction on 9b (where both the *ortho* positions to the nitro group are engaged) requires photostimulation; furthermore, side-products structurally correlated to 6p or 10 are not formed and the yield of the desired 3,5-dimethyl-4-nitrobenzonitrile rises to a more satisfactory figure (expt 37).



9a



9b



10

The negative results obtained from the 3- (1q) and the 2-nitroderivative (1r) are finally to be mentioned. Here again photostimulation is not needed and complex product mixtures result, with very meagre nitrile yields coupled to appreciable amounts of nitrobenzene.

Conclusions. - The work herein represents, to our knowledge, the first systematic investigation on the involvement of the cyanide ion in aromatic $S_{RN}1$ processes. Furthermore, from a synthetic point of view, notwithstanding the described limitations, the reaction between tetrabutylammonium cyanide and aryl phenyl diazosulfides represents, in our opinion, not only a valid alternative to, *e.g.*, the Sandmeyer approach to aromatic nitriles, but indeed an appealing and unprecedentedly mild access to isomeric phthalonitriles from easily available haloanilines. If it is recalled that the benzenethiolate ion, consumed for the formation of the covalent diazosulfides from the corresponding diazonium salts, is regenerated within the propagation cycle to the final nitriles, the $S_{RN}1$ synthesis herein can be well classified as an overall benzenethiolate-catalysed cyanodediazoniation, as described in eq iii.

$$\mathrm{ArN_2^+ + CN^- \xrightarrow{PhS^-} ArCN + N_2} \tag{iii}$$

Experimental

M.P.s were taken on an Electrothermal melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian FT 80 instrument (Me_4Si as internal standard). IR spectra (neat or nujol mull) were recorded on a Perkin-Elmer 881 Infrared Spectrophotometer. GC was performed on a Carlo Erba HRGC chromatograph equipped with a flame ionisation detector and an Alltech fused-silica capillary column (30 m x 0.25 mm; liquid phase RSL 150). HPLC was performed on a Waters Model ALC-202 chromatograph equipped with a Model 440 UV detector and using a 3.9 x 300 mm μ-Porasil column.

Materials. - Dimethylsulfoxide (Fluka AG) was used as received after storage over molecular sieves (type 4Å). Tetrabutylammonium cyanide and tetrafluoroborate (the supporting electrolyte in the electrochemical experiments) were Fluka AG reagents, used without further purification.

4-Benzoyl-, 4-cyano-, and 4-methoxybenzenediazonium tetrafluoroborates[24] and diazosulfides 1a-r and 9a,b[25] were prepared (yield ≥80%) according to reported procedures from the corresponding amines. 2,6-[26] And 3,5-dimethyl-4-nitroaniline[27] were synthesized, the other parent arylamines being commercial products used without further purification. Crude arenediazonium tetrafluoroborates were purified by insolubilisation with diethyl ether from a methanolic solution and stored in the refrigerator. Crude diazosulfides were flash-chromatographed (silica gel; hexane or hexane-dichloromethane mixtures as eluant). The yellow-orange compounds obtained were stored in the refrigerator and used without further purification, the structure being confirmed in every case by IR[25] and ^1H NMR spectroscopy. CAUTION.[28]

General synthetic procedure. - The experiments were carried out under argon, the apparatus being deaerated using five freeze-pump-thaw cycles. Reactions were started by dropping the Me_2SO solution of substrate into a double volume of a magnetically stirred solution of tetrabutylammonium cyanide in the same solvent, to obtain an overall 13-16 mM initial substrate concentration. Irradiation was performed with a 300-W Osram sunlamp placed ca. 15 cm from the reaction vessel (Pyrex flask). An appropriately positioned fan served to maintain the reaction temperature around 25 °C. For reactions pushed to completion the irradiation time was generally prolonged to 60 min, exhaustion of substrate being judged by ceasing of nitrogen evolution and/or TLC analysis. Usual workup involved dilution with brine (5-6 vol.) and 4-fold extraction with diethyl ether, followed by washing of the combined extracts with 10% NaOH and brine. The organic layer was dried (Na_2SO_4) and the solvent removed under reduced pressure at room temperature. Column chromatography on silica gel (hexane or proper hexane—dichloromethane mixtures as eluant) yielded pure nitriles. By-products were sometimes mixtures further analysed by GC or HPLC.

Sulfides 3c,d,f-j, and n were identified by ^1H NMR spectroscopy and/or through m.p., microanalysis, and ^1H NMR spectroscopy of the corresponding sulfones 3c',d',f'-j', and n'. Oxidation was performed at 100 °C in glacial acetic acid with an excess of 34% hydrogen peroxide.

The m.p.s of the following compounds matched those reported in the literature, the ^1H NMR spectra being in agreement with the proposed structure: 2a,[29] 2f,[30] 3a,[31] 3b,[32] 3c',[33] 3d',[30] 3e,[17c] 3f',[34] 3g',[35] 3j',[36] 3n',[37] and 3r.[38] The following compounds, together with all the reported reduction (XC_6H_5) products, were identified by comparison (mixed m.p. for solids, GC, HPLC, and/or ^1H NMR spectroscopy for liquids) with commercial or independently synthesized (reference given) samples: 2b-e,g-l,p-r, 2,6-dimethyl-4-nitrobenzonitrile,[39] 3i',k-m,o-q,[11b] and 1,2-, 1,3-, and 1,4-bis(phenylthio)benzene.[11b] The following unknown compounds gave satisfactory microanalytical data: C ± 0.4, H ± 0.1, N ± 0.1, S ± 0.2. 1-(Phenylsulfonyl)-4-(trifluoromethyl)benzene 3h': m.p. 90-91 °C (petroleum, b.p. 80-100 °C); ^1H NMR (CD_3COCD_3): δ 8.25 (2H, AA' of AA'BB', J 8.7 Hz), 8.01 (4H, m), and 7.70 (3H, m). 2,4-Dicyanophenyl phenyl sulfide 6p: m.p. 115-116 °C (petroleum, b.p. 80-100 °C); IR (nujol): ν 2230 cm^{-1} (CN); ^1H NMR (CD_3COCD_3): δ 8.25 (1H, d, J 1.8 Hz), 7.87 (1H, dd, J 1.8 and 8.6 Hz), 7.62 (5H, m), and 7.07 (1H, d, J 8.6 Hz). 2,6-Dimethyl-4-nitrophenyl phenyl sulfide: m.p. 53.5-55 °C (petroleum, b.p. 80-100 °C); ^1H NMR (CD_3COCD_3): δ 8.08 (2H, br. s), 7.21 (3H, m), 6.95 (2H, m), and 2.52 (6H, s). 2,4-Dicyano-3,5-dimethylphenyl phenyl sulfide 10: m.p. 162-163 °C (petroleum, b.p. 80-100 °C); ^1H NMR ($CDCl_3$): δ 7.52 (5H, m), 6.57 (1H, br. s), 2.73 (3H, s), and 2.38 (3H, s). 3,5-Dimethyl-4-nitrophenyl phenyl sulfide: yellow oil; ^1H NMR (CD_3COCD_3): δ 7.45 (5H, m), 7.08 (2H, br. s), and 2.22 (6H, s). 3,5-Dimethyl-4-nitrobenzonitrile: m.p. 167-168.5 °C (ethanol); ^1H NMR (CD_3COCD_3): δ 7.75 (2H, br. s) and 2.35 (6H, s).

Controlled-potential electrolyses (CPE). - Experiments 5, 18, and 20 were conducted with an Amel Model 551 potentiostat equipped with the following Amel units: a Model 563 multipurpose unit, a Model 566 function generator, and a Model 863 x-y recorder. The working electrode, set at a potential corresponding to the first reduction wave of the substrate, was repeatedly turned on (ca. 4 min) and off (ca. 12 min) until cyclic voltammetry (CV) revealed the complete disappearance of substrate. Cells were flushed with and kept under a positive pressure of high purity argon. The weight of $Bu_4N^+BF_4^-$ was adjusted so as to attain, together with the appropriate amount (see Table 1) of $Bu_4N^+CN^-$, an overall 0.1 M solution of electrolyte. A Pt-bead and a Pt-flag were the working electrodes in CVs and CPEs respectively. A Pt wire served as a counter electrode and $Ag/AgNO_3$ 0.01 M in Me_2SO was used as a reference electrode.

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