Tetrahedron Vol. 45, No. 23, pp. 7411 to 7420, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

THE REACTION BETWEEN ARENEDIAZONIUM TETRAFLUOROBORATES AND ALKALINE THIOCARBOXYLATES IN DMSO: A CONVENIENT ACCESS TO ARYL THIOLESTERS AND OTHER AROMATIC SULFUR DERIVATIVES.

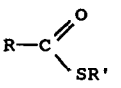
Giovanni Petrillo,* Marino Novi, Giacomo Garbarino, and Marcos Filiberti

Istituto di Chimica Organica dell'Università,
C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni,
Corso Europa 26, I-16132 Genova, Italy.

(*Received in UK* 31 *August* 1989)

Summary - The reaction between potassium thioacetate or sodium thiobenzoate and arenediazonium tetrafluoroborates in DMSO leads to the corresponding aryl thiolesters **1** which can either be isolated or further reacted providing a convenient one-pot access to a number of other aromatic sulfur derivatives.

Thiolesters **1** are useful intermediates in organic chemistry due to the electronic



1

R, R' = alkyl, aryl

distribution within the functional group, which makes both the carbonyl carbon more electrophilic and the α-hydrogens in R more acidic with respect to the fully oxygenated analogue.[1] Compounds **1** have thus been exploited as either electrophiles in acyl-transfer processes[2] or as carbanion precursors in condensation reactions,[1,3] both mimicking biological counterparts of utmost importance involving e.g. the S-acetyl-coenzime-A.[4] Furthermore, besides the long-standing transformation into thiols via alkaline hydrolysis or hydride reduction,[5] thiolesters **1** provide a convenient access to a number of other different functionalities, through either reduction[6] or oxidation processes.[7,8]

In agreement with the usefulness of **1**, a great variety of synthetic methods have been set up,[9] the two main general strategies being represented by the introduction of the sulfur atom (a) from a thiol, through nucleophilic attack onto a carboxylic acid derivative,[10] or (b) from a thiocarboxylic acid, in turn reacting with suitable electrophiles such as epoxides[11] or alkyl[12a] and activated aryl[12b] haloderivatives: the literature offers only a recent example relevant to unactivated aryl halides in rather drastic conditions.[12c] Thus, if one excludes the thermal rearrangement of thionobenzoates,[13] the synthesis of aryl thiolesters (**1**, R' = aryl) is almost exclusively confined to the employment of aromatic thiols [according to case (a) above], clearly leaving a gap when the latter are not easily available or represent themselves the target products.

Arenediazonium salts are well-known versatile 'electrophilic' intermediates for the preparation of aromatic derivatives *via* ionic or radical pathways.[14] We have recently shown[15,16] that, *in polar aprotic solvents, arenediazonium tetrafluoroborates or their covalent adducts such as the diazothioethers ArN=NSPh represent suitable substrates for* the $S_{RN}1$[17] syntheses of diaryl sulfides[15] and aromatic nitriles[16] respectively. We have also preliminarily reported[18] that the reaction of the same arenediazonium tetrafluoroborates with potassium thioacetate in DMSO results in the smooth formation of aryl thiolacetates (1, R = Me) (eq i), and further significance to the reaction has been

$$ArN_2^+ + RCOS^- \xrightarrow{DMSO} \underset{1}{RCOSAr} + N_2 \qquad (i)$$

more recently added through the successfull application to hindered substrates.[19]

The main intents herein are to extend the applicability range of eq (i) to aromatic thiocarboxylate anions (1, R = Ph), and to provide some examples of convenient one-pot syntheses of other sulfur derivatives from diazonium tetrafluoroborates through **1**. Besides such practical aspects, some results, although not conclusive, relevant to the mechanism of reaction (i) are also presented.

Results and Discussion

Reactions between arenediazonium tetrafluoroborates and alkaline thiocarboxylates.

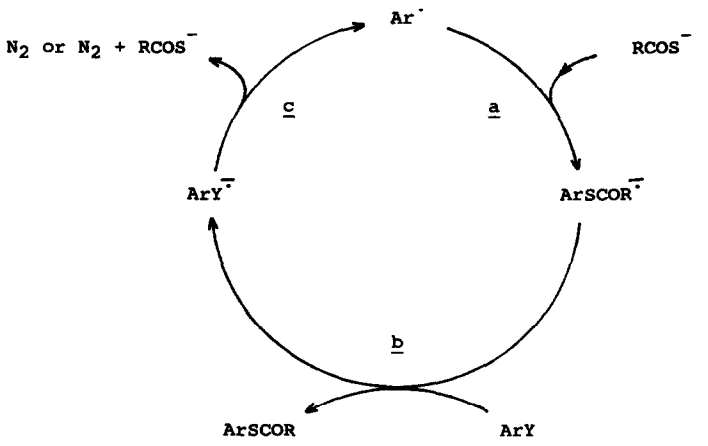
The figures of Table 1 provide, together with previous data,[18,19] clear evidence that the reaction (i), (R = alkyl, aryl) represents a general approach to aryl thiolesters which couples mild experimental conditions and short reaction times with consistently satisfactory yields: both electron-withdrawing and -releasing substituents on the diazonium cation are compatible, while steric hindrance on the electrophilic centre causes minor or anyway acceptable yield depressions.

From a mechanistic point of view, by analogy with our cited previous work,[15,16] reaction (i) seemed an obvious candidate for the occurrence of the $S_{RN}1$ propagation cycle (*Scheme 2*).[17] *It should be noticed, though, that the involvement of sulfur nucleophiles in* $S_{RN}1$ processes is, to our knowledge, so far limited to alkane- and arene-thiolates:[15,17b,20] among others, potassium thiocyanate or ethylxanthate proved to be unreactive towards haloarenes in $S_{RN}1$ conditions.[17b]

As already reported in the preliminary communication,[18] the intermediacy of σ aryl radicals along the main pathway to thiolesters 1 is strongly suggested by the cyclization test carried out on the 2-(2-propynyloxy)benzenediazonium salt 2 which affords the cyclic 3-[(acetylthio)methyl]-2,3-dihydrobenzofuran 4, most likely through exo-cyclization of the intermediate radical 3[21] (Scheme 2).

Herein aryl radicals can conceivably be formed through either outer-sphere electron transfer from the sulfur anion to the diazonium cation or *via* cation/anion coupling

Scheme 1

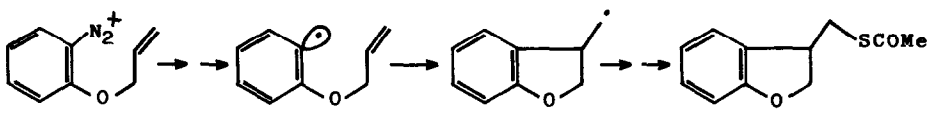


ArY = ArN_2^+ or ArN=NSCOR

$ArY^{\cdot-}$ = $ArN_2^{\cdot}$ or $ArN=NSCOR^{\cdot-}$

R = Me, Ph

Scheme 2



2 3 3' 4

followed by homolytic cleavage (overall inner-sphere electron transfer) of the resulting diazothiolester ArN=NSCOR. The initial rapid formation of such covalent adducts upon mixing of the reactants is actually hinted by the presence of transient coloured spots when monitoring the reaction progress by TLC and would be in line with our observation[15a] (successively confirmed by others[22]) that the reactions of the same diazonium salts with arenethiolates in analogous conditions proceed via the diazothioethers ArN=NSAr'. At this regard, control experiments have been carried out on the independently synthesized, relatively stable, 4-cyanophenylazo thiolbenzoate (4-NCC_6H_4N=NSCOPh, 5). Interestingly enough, while 5 slowly decomposes in DMSO to furnish only traces of 4-cyanophenyl thiolbenzoate 1c (Table 1, entry 3b),[23] the addition of 0.2 molar equivalents of sodium thiobenzoate effectively drives the decomposition towards a 66% yield of 1c (entry 3c) within a time which is comparable to that required by the reaction of the corresponding

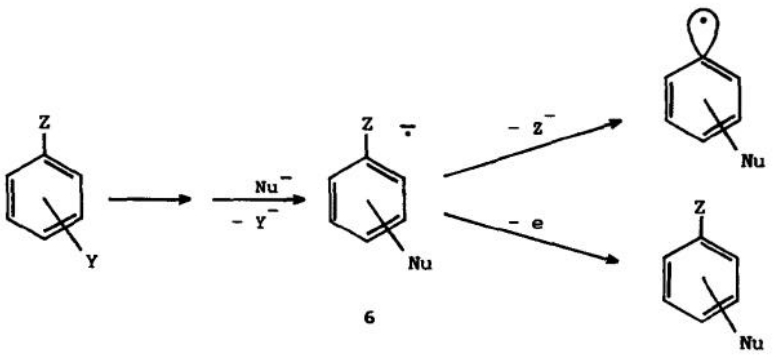
Table 1. Reactions of arenediazonium tetrafluoroborates and of 4-cyanophenylazo thiolbenzoate (**5**) with sodium thiobenzoate in DMSO.

Entry	Substrate	[Substrate] (M)	$PhCOS^-$/Substr. molar ratio	Reaction time (min)	Yield (%)[a]	
					ArSCOPh	$1,4-(PhCOS)_2C_6H_4$
1	$C_6H_5N_2^+$	0.26	1.2	60	**1a**: 62	
2	$2,6-(Me_2CH)_2C_6H_3N_2^+$	0.26[b]	1.2[b]	60	**1b**: 57[b]	
3a	$4-NCC_6H_4N_2^+$	0.26	1.2	30	**1c**: 87	
3b	**5**	0.12	[c]	100	**1c**: <5	
3c	**5**	0.12	0.2	25	**1c**: 66	
3d	**5**	0.12	1.0	22	**1c**: 76	
3e	**5**	0.08	0.2	1.3	**1c**: 51	
3f	**5**[d]	0.08	0.2	1.3	**1c**: 40	
3g	**5**[e]	0.08	0.2	1.3	**1c**: 38	
4	$4-IC_6H_4N_2^+$	0.26	3.0	60	**1d**: 74	6
5	$1,4-C_6H_4(N_2^+)_2$	0.26	3.0	120		30
6	$1-naphthyl-N_2^+$	0.26	1.2	240	**1e**: 70	

[a]Yield of isolated product. [b]Calculated with respect to the parent arylamine. [c]In the absence of added thiobenzoate. [d]*p*-Dinitrobenzene (0.3 mol. equiv. with respect to substrate) also present. [e]*p*-Dinitrobenzene (1.0 mol. equiv. with respect to substrate) also present.

diazonium salt with 1.2 molar equivalents of nucleophile (entry 3a).[24] Thus, if on one side the intermediacy of diazothiolesters along the main reaction pathway finds strong support, the presence of catalytic[25] amounts of thiocarboxylate anions seems to play a fundamental role as to the formation of the expected product. Although a coupling between aryl radicals and free thiocarboxylate anions (Scheme 1, step a) represents a conceivable event, no substantial evidence of the presence of radical anions along the main reaction flow could be reached by means of two commonly accepted $S_{RN}1$ recognition tests,[17,26] namely inhibition by electron scavengers and disubstitution on suitably substituted substrates. Actually, up to 1 molar equivalent of p-dinitrobenzene (E_{pc}[27] = -0.87 V) exerted on the reaction of thiobenzoate with 5 (E_{pc}[27] = -1.07 V) only a meagre retardation (Table 1, entries 3e-g) which can possibly be regarded as a rough indication as to the incidence of the $S_{RN}1$ pathway among competitive routes. As far as the second abovementioned test is concerned, it is a nowadays well assessed peculiarity of the $S_{RN}1$ process that an aromatic substrate with two suitable leaving groups (Y and Z) can undergo competitive mono- and di-substitution: the latter occurs via an 'enlarged' $S_{RN}1$ cycle triggered by the expulsion of Z^- from the radical anion of the monosubstitution product (6)[17] (Scheme 3). As far as $S_{RN}1$ dediazoniation reactions are concerned (Y = N_2^+ or

Scheme 3



6

N=NSPh), disubstitution proved to be the long-preferred pathway with both PhS^- and CN^- as nucleophiles when Z = Cl, Br, I.[15,16] In the present case, the 4-iodobenzenediazonium tetrafluoroborate predominantly furnishes, with both thioacetate[18] and thiobenzoate (Table 1, entry 4), substitution of the diazogroup alone; if, on one hand, the formation of some disubstitution product can be regarded as a clue for the presence of radical anions such as 6 (Nu = PhCOS, MeCOS; Z = 4-I), the high mono- to di-substitution ratio could find different explanations, not necessarily excluding the $S_{RN}1$ pathway if one assumes a slow fragmentation of 6 which would favour the competitive electron transfer to substrate.

Clearly, a deeper insight is needed in order to attain sounding conclusions on the mechanism of reaction (i). Unfortunately, the relatively fast decomposition of diazothiolesters in DMSO did not even allow other significant electrochemical experiments

such as constant-potential electrolyses and chronocoulometries to be reliably carried out. On the other hand, further efforts on the mechanistic side have not been pursued herein as they go well bejond the synthetic significance of the reaction.

Use of commercial potassium thioacetate as sulfur-transfer agent. One-pot synthesis of some aromatic sulfur derivatives

As outlined in the introduction, thiolcarboxylate esters are routinely employed as precursors of thiols through either reduction or hydrolysis.[5] The basic hydrolysis of the reaction mixture from the dediazoniation process with potassium thioacetate revealed to be a convenient one-pot access to arenethiolate anions and hence to a number of other sulfur derivatives through the following treatment with suitable electrophiles (Scheme 4). The

Scheme 4

$$ArN_2^+ \xrightarrow{RCOS^-} ArSCOR \xrightarrow[\text{or } MeO^-/MeOH]{OH^-/H_2O} ArS^- \xrightarrow{EHal} ArSE$$

E = H, R, Ar, CN

yields of the various ArSE products (Table 2) are generally comparable to those of the corresponding thiolester precursors also in the case of hindered substrates. While the isolation of thiols is straightforward, the reactions with benzyl chloride, methyl iodide, or chloro-2,4-dinitrobenzene represent just some selected examples of thioether syntheses. Much interest should on the other hand be attached to the one-pot access to aryl thiocyanates [28] starting from arenediazonium tetrafluoroborates, particularly as the long exploited synthesis from diazonium salts and metal thiocyanates in aqueous solvent is always complicated mainly by the formation of by-products.[30]

Experimental section

Melting points were taken on a Büchi 535 apparatus and are uncorrected. Liquids were distilled bulb-to-bulb in a Büchi GKR-50 Kugelrohr apparatus and boiling points are referred to the air-bath temperature. ^1H NMR Spectra were recorded on a Varian FT80 instrument ($CDCl_3$ as solvent, Me_4Si as internal standard). Column chromatography was performed on silica gel, using hexane or proper hexane-dichloromethane mixtures as eluant.

Unknown compounds gave satisfactory microanalytical data (C ± 0.4, H ± 0.1, N ± 0.1, S ± 0.2).

Materials. Dimethylsulfoxide (Fluka AG) was used as received after storage over molecular sieves (type 4 Å). Potassium thioacetate was a commercial product (Janssen) while sodium thiobenzoate was prepared before use from thiobenzoic acid in MeONa/MeOH. Arylamines were commercial products used without further purification.

Arenediazonium tetrafluoroborates (always used as crude materials) were generally prepared by diazotization in HCl followed by addition of $NaBF_4$;[31] 1,4-bis(diazonio)benzene

Table 2. One-pot synthesis of aromatic sulfur derivatives from $ArN_2^+BF_4^-$ in DMSO *via* hydrolysis of intermediate aryl thiolacetates.[a]

Entry	Ar	Yield(%)[b]					
		ArSCOMe[c]	ArSH[d,e]	ArSMe[f,g]	$ArSCH_2Ph$[f,g]	ArS-(2,4-DNP)[f,g]	ArSCN[f,h]
1	C_6H_5	58	62		58		50
2	$3\text{-}MeC_6H_4$	47[i]	38				
3	$2,6\text{-}(Me_2CH)_2C_6H_3$[j]	36		31[k]	42	34	32
4	$4\text{-}MeOC_6H_4$	60	40		52		36
5	$4\text{-}{}^+N_2C_6H_4$	34	20[l]		38[m]		
6	1-naphthyl	60	38		66		48

[a]Initial substrate concentration *ca.* 0.26 M; 1.2 mol. equiv. of commercial potassium thioacetate with respect to the diazonium group. [b]Yield of isolated products. [c]Data from reference 18 (entries 1,4-6) or 19 (entry 3). [d]Hydrolysis was performed with *ca.* 3 M KOH/H_2O (2.5 mol. equiv. with respect to the diazonium group). [e]Yield after distillation. [f]Hydrolysis was performed with *ca.* 3 M MeONa/MeOH (1.3 mol. equiv. with respect to the diazonium group). [g]1.5 Mol. equiv. of RX [MeI, $PhCH_2Cl$, or $2,4\text{-}(O_2N)_2C_6H_3Cl$ (2,4-DNPCl)] with respect to the diazonium group. [h]3.0 Mol. equiv. of ICN with respect to the diazonium group. [i]From the present work. [j]Yields are referred to the parent arylamine. [k]Confirmed as sulfone. [l]1,4-Dimercaptobenzene, not purified and confirmed as 1,4-bis(benzylthio)benzene. [m]1,4-Bis(benzylthio)benzene.

tetrafluoroborate[32] and the hindered 2,6-diisopropylbenzenediazonium salt were prepared in aqueous HBF_4.[31] The latter proved to be rather unstable at room temperature[19] and was accordingly filtered in the cold, washed with little 50% HBF_4 and then thoroughly with cold Et_2O, and immediately used for the thiolacetate synthesis.[19]

4-Cyanophenylazo thiolbenzoate. 4-Cyanoaniline was diazotized in the usual manner.[31] The resulting clear solution was buffered with 25% MeCOONa and cautiously poored under stirring into a cold solution of commercial thiobenzoic acid (1.1 mol. equiv.) in H_2O/EtOH, according to a procedure previously reported for the synthesis of arenediazothioethers.[16] The yellow precipitate was filtered, washed with cold EtOH, dried, and purified by insolubilization with benzine (b.p. 80-100 °C) from a toluene solution: yield 88%; m.p. 123 °C with gas evolution; ^{1}H NMR, δ: 7.64 (3 H, m), 7.81 (4 H, s), 8.00 (2 H, m). CAUTION should be taken in handling potentially hazardous diazothio-derivatives,[33] especially avoiding any mass heating.

Synthesis of S-aryl thioesters.

The experiments were carried out under argon, as previously described.[16] Reactions were started by dropping a DMSO solution of substrate into a double volume of a magnetically stirred solution of the thiocarboxylate salt in the same solvent, to obtain an overall 0.26 M initial substrate concentration. The end of reaction was judged by ceasing of nitrogen evolution and/or TLC analysis: in any case the time of preparative runs was somewhat prolonged in order to insure completion of reaction. Usual workup[16] followed by column chromatography yielded pure thiolesters.

Thiolbenzoates **1a**,[34] **1c**,[13] and **1e**,[35] and 3-methylphenyl thiolacetate[36] matched reported physical constants: in any case their structure was confirmed by ^{1}H NMR spectroscopy.

2,6-Diisopropylphenyl thiolbenzoate (**1b**):b.p. 170 °C/5 mmHg; ^{1}H NMR, δ: 1.22 (12 H, d, J 7.2 Hz), 3.51 (2 H, septet, J 7.2 Hz), 7.35 (5 H, m), 8.10 (3 H, m).

4-Iodophenyl thiolbenzoate (**1d**): m.p. 89.6-90.6 °C (Et_2O); ^{1}H NMR, δ: 7.21 (2 H, BB' of AA'BB'), 7.51 (3 H, m), 7.76 (2 H, AA' of AA'BB'), 7.99 (2 H, m).

1,4-Bis(benzoylthio)benzene: m.p. 167-168 °C (ethyl acetate); ^{1}H NMR, δ: 7.53 (6 H, m), 7.60 (4 H, s), 8.03 (4 H, m).

One-pot synthesis of arenethiols, alkyl aryl or diaryl sulfides, and aryl thiocyanates.

After completion of the dediazoniation process (30-50 min) hydrolysis (30-50 min) was performed at room temperature with either KOH ca. 3 M in H_2O or MeONa ca. 3 M in MeOH, following the disappearance of the thiolester by TLC. The mixture was then acidified with 37% HCl or treated with an alkyl or aryl halide (methyl iodide, 120 min; benzyl chloride, 60-120 min; choro-2,4-dinitrobenzene, 300 min), or a DMSO solution of cyanogen halide (30-40 min) at room temperature. After the usual workup sulfides and thiocyanates were purified by column chromatography, while thiols were distilled under reduced pressure to the exception of 1,4-dimercaptobenzene which was converted into 1,4-bis(benzylthio)benzene in 1 M MeONa/MeOH (2.0 mol. equiv.) by treatment with benzyl chloride (4.0 mol. equiv.) and confirmed as such; 2,6-diisopropylphenyl methyl sulfide was further confirmed as sulfone, oxidation being performed with excess H_2O_2 in acetic acid. Known arenethiols, thioethers, and thiocyanates matched reported physical constants.

2,6-Diisopropylphenyl methyl sulfide: ^{1}H NMR, δ: 1.24 (12 H, d, J 6.9 Hz), 2.20 (3 H, s), 3.96 (2 H, septet, J 6.9 Hz), 7.20 (3 H, m). The sulfone had m.p. 102.8-103.5 °C (benzine, b.p. 80-100 °C); ^{1}H NMR, δ: 1.29 (12 H, d, J 6.7 Hz), 3.14 (3 H, s), 4.22 (2 H, septet, J 6.7 Hz), 7.40 (3 H, m).

Benzyl 2,6-diisopropylphenyl sulfide: b.p. 160 °C/0.3 mmHg; ^{1}H NMR, δ: 1.14 (12 H, d, J

6.9 Hz), 3.76 (2 H, s), 3.82 (2 H, septet, J 6.9 Hz), 7.15 (8 H, m).
2,6-Diisopropylphenyl 2,4-dinitrophenyl sulfide: m.p. 140.5-141 °C (EtOH); ^{1}H NMR, δ: 1.15 (12 H, d, J 6.8 Hz), 3.44 (2 H, septet, J 6.8 Hz), 6.80 (1 H, d, J 9.0 Hz), 7.45 (3 H, m), 8.10 (1 H, dd, J 9.0 and 1.6 Hz), 9.15 (1 H, d, J 1.6 Hz).
2,6-Diisopropylphenyl thiocyanate: m.p. 37.0-38.1 °C (EtOH/H_2O); ^{1}H NMR, δ: 1.30 (12 H, d, J 6.8 Hz), 3.78 (2 H, septet, J 6.8 Hz), 7.40 (3 H, m).

References and notes

1 M.W. Cronyn, M.P. Chang, and R.A. Wall, J. Am. Chem. Soc., 77, 3031 (1955).

2 E.J. Corey and K.C. Nicolau, J. Am. Chem. Soc., 96, 5614 (1974); T.G. Back, Tetrahedron, 33, 3041 (1977); S. Masamune, H. Yamamoto, S. Kamata, and A. Fukuzawa, J. Am. Chem. Soc., 97, 3513 (1975); A. Capperucci, A. Degl'Innocenti, C. Faggi, G. Reginato, A. Ricci, P. Dembech, and G. Seconi, J. Org. Chem., 54, 2966 (1989).

3 R.B. Baker and E.E. Reid, J. Am. Chem. Soc., 51, 1567 (1929).

4 T.C.Bruice, in «Organic Sulfur Compounds», N. Kharasch, Ed., Pergamon, Oxford, 1961, vol. 1, chapt. 35; P.R. Vagelos, in «The Enzymes», P.D. Boyer, Ed., Academic Press, N.Y., 1973, vol. VIII, chapt. 5.

5 J.L. Wardell, in «The Chemistry of the Thiol Group», S. Patai, Ed., Wiley, London, 1974, chapt. 4; G. Fuchs, Acta Chem. Scand., 19, 1490 (1965); J.J. Godfrey, U.S. Pat., 3,086,049 (1963) [Chem. Abstr., 59, 8601 (1963)]; D.A. Swann and J.H. Turnbull, Tetrahedron, 20, 1265 (1964); 24, 1441 (1968); P.A. Bobbio, J. Org. Chem., 26, 3023 (1961).

6 M.L. Wolfrom and J.V. Karabinos, J. Am. Chem. Soc., 68, 1455 (1946); G.B.Spero, A.V. McIntosh, and R.H. Levin, ibid., 70, 1907 (1948); V. Prelog, J. Norymberski, and O. Jeger, Helv. Chim. Acta, 29, 360 (1946); H. Hauptmann and B. Wladislaw, J. Am. Chem. Soc., 72, 710 (1950); K. Osakada, T. Yamamoto, and A. Yamamoto, Tetrahedron Lett., 28, 6321 (1987); D.E. Bublitz, J. Org. Chem., 32, 1630 (1967), and references therein; H.-J. Liu and H.K. Lai, Canad. J. Chem., 57, 2522 (1979); Tetrahedron Lett., 1193 (1979); H.-J. Liu, H.K. Lai, and S.K. Attah-Poku, ibid., 4121 (1979).

7 J. March, «Advanced Organic Chemistry», 3rd Ed., Wiley, N.Y., 1985, p. 1087; T. Kumamoto and T. Mukaiyama, Bull. Chem. Soc. Jpn., 41, 2111 (1968).

8 S. Thea and G. Cevasco, Tetrahedron Lett., 28, 5193 (1987); 29, 2865 (1988).

9 J. Voss, in «The Chemistry of Functional Groups, Supplement B, The Chemistry of Acid Derivatives», S. Patai, Ed., Wiley, Chichester, 1979, chapt. 18.

10 K.T. Douglas, N.F. Yaggi, and C.M. Mervis, J. Chem. Soc., Perkin Trans. 2, 171 (1981); S. Kim, W.J. Lee and J.I. Lee, Bull. Korean Chem. Soc., 5, 187 (1984) [Chem. Abstr., 102, 166418s (1985)]; Y. Nagao, K. Kawabata, and E. Fujita, J. Chem. Soc., Chem. Commun., 330 (1978); D.N. Harpp, T. Aida, and T.H. Chan, Tetrahedron Lett., 2853 (1979); H.U. Reissig and B. Scherer, ibid., 21, 4259 (1980); T. Cohen and R.E. Gapinski, Tetrahedron Lett., 4319 (1978); F. Effenberger and E. Bessey, Chem. Ber., 113, 2100 (1980); S. Ohta and M. Okamoto, Angew. Chem., Int. Ed. Engl., 22, 3245 (1981); H.-J. Liu and S.I. Sabesan, Canad. J. Chem., 58, 2645 (1980); M. Ueda and H. Oikawa, J. Org. Chem., 50, 760 (1985); T. Imamoto, M. Kodera, and M. Yokoyama, Synthesis, 134 (1982); T. Kunieda, Y. Abe, and M. Hirobe, Chem. Lett., 1427 (1981); R. Berenguer, J. Garcia, and J. Vilarrasa, Synthesis, 305 (1989).

11 A.M. Jeffrey, H.J.C. Yeh, D.M. Jerina, R.M. De Marinis, C.H. Foster, D.E. Piccolo, and G.A. Berchtold, J. Am. Chem. Soc., 96, 6929 (1974); E. Vogel, E. Schmidtbauer, and H.J. Altenbach, Angew. Chem., 86, 819 (1974).

12 (a) T.M. Balthazor, J.A. Miles, and B.R. Stults, J. Org. Chem., 43, 4538 (1978); T.M. Balthazor, ibid., 45, 2519 (1980); G. Cainelli, M. Contento, F. Manescalchi, and M.C. Mussatto, Synthesis, 302 (1981); (b) A. Bhattacharya and G Thyagarajam, Chem. Rev., 81, 415 (1981); A. Ferretti, Canad. J. Chem., 50, 4056 (1972); (c) A. Osuka, N. Ohmasa, Y. Uno, and H. Suzuki, Synthesis, 68 (1983).

13 Y. Araki and A. Kaji, Bull. Chem. Soc. Jpn., 43, 3214 (1970).

14 D.S. Wulfman, in «The Chemistry of Diazonium and Diazo Groups», S. Patai, Ed., Wiley, N.Y., 1978, chapt. 8; A.F. Hegarty, in «The Chemistry of Functional Groups», Supplement C, S. Patai and Z. Rappoport, Eds., Wiley, N.Y., 1983, chapt. 12.

15 (a) G. Petrillo, M. Novi, G. Garbarino, and C. Dell'Erba, Tetrahedron, 42, 4007 (1986); (b) M. Novi, G. Petrillo, and M.L. Sartirana, Tetrahedron Lett., 27, 6129 (1986).

16 G. Petrillo, M. Novi, G. Garbarino, and C. Dell'Erba, Tetrahedron, 43, 4625 (1987).

17 (a) J.F. Bunnett, Acc. Chem. Res., 11, 413 (1978); (b) R.A. Rossi and R.H. de Rossi, «Aromatic Nucleophilic Substitution by the $S_{RN}1$ Mechanism», ACS Monograph 178, American Chemical Society, Washington, D.C., 1983.

18 G. Petrillo, M. Novi, G. Garbarino, and M. Filiberti, Tetrahedron Lett., 29, 4185 (1988).

19 G. Cevasco, M. Novi, G. Petrillo, and S. Thea, Gazz. Chim. Ital., in press.

20 An example relevant to a thioamide anion as a sulfur nucleophile in a cyclization $S_{RN}1$ process has been recently reported: W.R. Bowman, H. Heaney, and P.H.G. Smith, Tetrahedron Lett., 23, 5093 (1982).

21 G.F. Meijs and A.L.J. Beckwith, J. Am. Chem. Soc., 108, 5890 (1986); A.L.J. Beckwith and G.F. Meijs, J. Org. Chem., 52, 1922 (1987).

22 A.N. Abeywickrema and A.L.J. Beckwith, J. Am. Chem. Soc., 108, 8227 (1986).

23 The main reaction product (30% yield) is represented by 4-$NCC_6H_4NHCOPh$, identified by comparison with an authentic sample. Conceivable routes for the unexpected formation of this amide (possibly involving an initial intramolecular rearrangement of 5) are under investigation.

24 The lower thiolester yield of run 3c should be mostly attributed to partial decomposition of the DMSO solution of the diazothiolester (see above in the text) prior to mixing with the nucleophile.

25 It is noteworthy, in this respect, that 1 molar equivalent of sodium thiobenzoate leads to a not much increased thiolester yield (Table 1, entry 3d).

26 M. Chanon and M.L. Tobe, Angew. Chem., Int. Ed. Engl., 21, 1 (1982).

27 Conditions: 0.1 M Bu_4NBF_4 in DMSO at room temperature; sweep rate = 100 mV/s; a Pt bead, Pt wire, and $Ag/AgNO_3$ 0.01 M in DMSO as working, counter, and reference electrodes.

28 As already reported for a synthesis of thiocyanates from differently prepared arenethiolates,[29] ICN has been found to afford better yields than BrCN within shorter reaction times.

29 L. Testaferri, M. Tingoli, M. Tiecco, D. Chianelli, and M. Montanucci, Phosphorus and Sulfur, 15, 263 (1983).

30 R.G. Guy, in «The Chemistry of the Cyanates and their Thio Derivatives», S. Patai, Ed., Wiley & Sons, N.Y., 1977, chapt. 18.

31 A. Roe, Org. React., 5, 193 (1949).

32 E.D. Bergmann, S. Berkovic, and R. Ikan, J. Am. Chem. Soc., 78, 6039 (1956).

33 (a) H. Spencer, Chem. Brit., 13, 240 (1977), and references therein; (b) ref. 15a, p. 295, and references therein; (c) Org. Synth., 47, 107 (1967) [Coll. Vol. V, 1050 (1973)].

34 H. Böhme and H. Schran, Chem. Ber., 82, 453 (1949).

35 F. Krafft and R. Schönherr, Chem. Ber., 22, 823 (1889).

36 R. Charonnat and I. Lalezari, Compt. Rend. Acad. Sci., 238, 119 (1954).