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THE REACTIVITY OF SULFUR NUCLEOPHILES TOWARDS ARENEDIAZONIUM TETRAFLUOROBORATES IN APROTIC SOLVENTS: SYNTHESIS OF S-ARYL THIOACETATES

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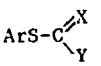
Abstract: Various S-aryl thioacetates are prepared in 40-60% yield by treatment of arenediazonium tetrafluoroborates with commercial potassium thioacetate in DMSO at room temperature.

S-Aryl thioesters such as 1a-c have recently attained to a remarkable importance as



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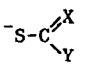

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a: X = O or S; Y = R or Ar
b: X = O or S; Y = OR, OAr, or SAr
c: X = O or S; Y = NR_2

intermediates both in biochemistry[1] and in the synthesis of simple organosulfur compounds.[2] Accordingly, a good deal of preparative routes have been developed, mainly involving modifications of the nucleophilic attack of thiolates on carboxylic acid derivatives.[3]

On the other hand, alternative methods are required when either thiols do not represent easily available substrates or they are themselves the target compounds (through either hydrolysis or reduction of thioesters[2a,4]). In this respect, beside the thermal rearrangement of O-aryl thioesters,[2a,5] methods employing both organometals[4b,6a] and electrophilic substrates such as diaryliodonium salts[6b] or aryl halides (either activated[6c] or unactivated in rather drastic conditions[6d]) have been sparingly reported.[7] Aqueous arenediazonium salts have also been repeatedly used[4a,8,9] [a classical example being represented by the Leuckart synthesis of thiols[4a,9] through ethyl xanthates (1b: X = S, Y = OEt)] although yields not always satisfactory often couple with the hazard of heating reaction mixtures[8,9b] of covalent derivatives of diazonium salts.

Our recent interest in the chemistry of arenediazonium tetrafluoroborates towards sulfur nucleophiles in polar aprotic solvents[10] has led us to test (both from a preparative and a mechanistic point of view) their reactivity towards some selected nucleophiles 2 in DMSO and preliminary results on the synthesis of S-aryl thioacetates (1a: X = O, Y = Me) are reported in the Table.

Typically, a DMSO solution of crude diazonium tetrafluoroborate[11] is dropped into a well stirred solution of 1.2 mol. equiv. of commercial potassium thioacetate kept under a positive pressure of argon. Gas evolution almost immediately occurs, while the colour darkens and the

temperature rises to about 40°C. Work-up involves pouring of the mixture into brine and extraction with Et_2O. Column chromatography [silica gel, proper CH_2Cl_2 - petroleum ether (b.p. 40-70°C) mixtures as eluants] affords pure thioesters. Beside the hydrodediazoniation products (ArH), by-products are generally represented by the relevant sulfide (ArSAr) and disulfide (ArSSAr); identification and quantification of by-products has been performed only in some significant cases (see Table).

The method herein represents a convenient synthetic approach to S-aryl thioacetates: mild conditions and short reaction times couple with yields which can be regarded as satisfactory. In particular, (a) both electron-withdrawing and -releasing substituents seem compatible, and (b) steric hindrance on the electrophilic site by two ortho methyl groups (entries 4 and 5) or by a peri hydrogen (entry 9) does not dramatically depress the yield.

As to the mechanistic implications of the present reaction, the initial formation of the covalent diazothioacetate Ar-N=N-SCOMe (3) is reasonable.[12] On the other hand, the occurrence

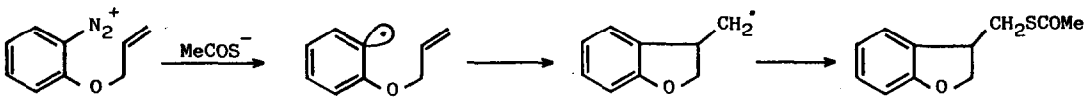
Table. S-Aryl thioacetates (**1a**: X = O, Y = Me) from arenediazonium tetrafluoroborates and potassium thioacetate in DMSO.[a]

Entry	Ar	Reaction time (min)	Yield (%)[b] ArSCOMe	ArSAr	ArSSAr	Others
1a	C_6H_5	30	58	5	4	C_6H_6: [c]
1b	C_6H_5[d]	30	60	2	5	C_6H_6: [c]
2	4-MeC_6H_4	40	55	4	tr.	
3	2-MeC_6H_4	30	60	5		
4	2,6-$Me_2C_6H_3$	30	48[e]			
5	2,4,6-$Me_3C_6H_2$	30	39			
6	4-$MeOC_6H_4$	30	60			
7	4-$O_2NC_6H_4$	45	47			$C_6H_5NO_2$: [c]
8	4-IC_6H_4[f]	90	41	tr.	8	7: 3
9	1-naphthyl	50	60			naphthalene: 8
10	2-naphthyl	30	60			naphthalene: [c]
11	4-$^+N_2C_6H_4$[g]	60	7: 34			C_6H_5SCOMe: 8
12	2-(2-propenyloxy)C_6H_4[h]	60				5: 41[i]

[a]Substrate concentration ca. 0.26 M; 1.2 mol. equiv. of thioacetate if not otherwise stated; unless specified thioesters herein are known compounds, matching reported physical constants; unknown terms (boiling point and ^1H n.m.r. reported) gave correct elemental analysis; in any case the structure of thioesters was confirmed by both IR and ^1H n.m.r. spectroscopy. [b]Yield of isolated product. [c]Detected but not quantified. [d]2.5 Mol. equiv. of thioacetate. [e]Kugelrohr distilled: 140°C/0.8 mm Hg; δ($CDCl_3$, Me_4Si as internal standard) 2.34 (s, 6H), 2.39 (s, 3H), and 7.15 (br. s, 3H). [f]3.0 Mol. equiv. of thioacetate. [g]2.4 Mol.equiv. of thioacetate. [h]Prepared according to A.L.J. Beckwith and W.B. Gara, J.Chem.Soc., Perkin Trans.2, 1975, 593. [i]B.p. 106°C/0.5 mm Hg; δ($CDCl_3$, Me_4Si as internal standard) 2.35 (s, 3H), 3.16 (m, 2H), 3.67 (m, 1H), 4.39 (m, 2H), and 7.03 (m, 4H).

of aryl radicals along the main reaction pathway is definitely confirmed (beside the presence of by-products which typically derive from such species, such as ArH) by the isolation, in the reaction carried out on o-(2-propenyloxy)benzenediazonium tetrafluoroborate (4) (entry 12) of the cyclised thioester 3-[(acetylthio)methyl]-2,3-dihydrobenzofuran (5) as the main product. The formation of 5 can be easily rationalised through the sequence depicted in Scheme 1.[13]

Scheme 1



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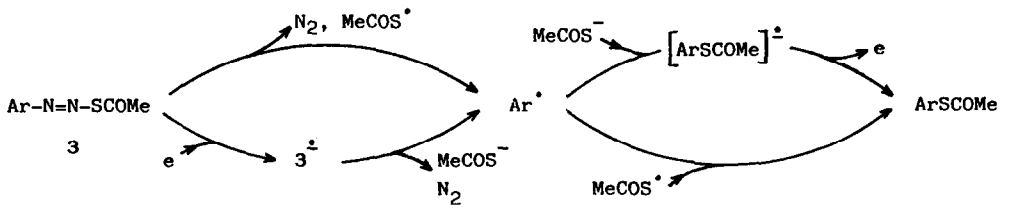
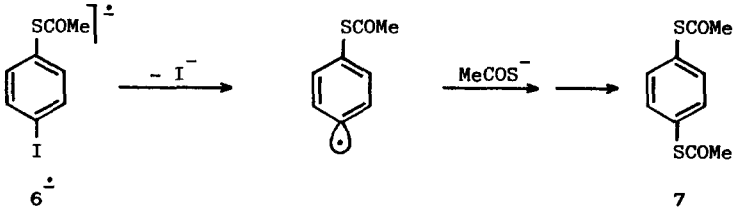
Aryl radicals can anyway be generated either by homolytic dissociation of 3 or via electron transfer to 3 followed by fragmentation of the resulting radical anion (Scheme 2). Once

Scheme 2



formed, such aryl radicals can in turn undergo either a solvent-cage recombination with the acetylthio radical or coupling with the thioacetate anion. In the latter case the so-formed radical anion would lead to S-aryl thioacetate by oxidation to the expense of, e.g., 3, within the propagation cycle of an $S_{RN}1$ pathway.[10,14] At this regard it must be pointed out that the presence of sulfide (ArSAr) and disulfide (ArSSAr) by-products is well in agreement with the involvement, at least along a secondary competitive pathway, of the radical anions of the final thioesters: independent cyclic voltammetry experiments carried out on S-phenyl thioacetate do show that its cathodic reduction is followed by CO-S bond cleavage, with the generation of benzenethiolate anion. This species could in turn be responsible of the formation of both PhSSPh (by acting[10] as an electron donor) and PhSPh (by trapping[10] of the Ph• radical, followed by oxidation of the $PhSPh^{\bullet-}$ radical anion). Furthermore, the formation of some disubstitution product 7 in the reaction with 4-iodobenzenediazonium tetrafluoroborate (entry 8) suggests the intermediacy of the anion radical $6^{\bullet-}$, which would lead to 7 through fragmentation[14] with expulsion of I^- (Scheme 3). The meagre yield of 7 with respect to the monosubstitution product 6 could be explained with either a prevalence of oxidation of $6^{\bullet-}$ over fragmentation or with the competition of an $S_{RN}1$ and a free-radical recombination pathway, the latter carrying the main reaction flow.

Scheme 3



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Further insight into the mechanistic aspects of the reaction is at present being pursued, as well as into the possibility of employing thioesters 1 for a one-pot synthesis of arenethiols and their derivatives.

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