Tetrahedron Letters,Vol.26,No.51,pp 6365-6368,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

A SIMPLE PREPARATION OF SYMMETRICAL AND UNSYMMETRICAL DIARYL SULFIDES FROM ARENEDIAZONIUM TETRAFLUOROBORATES

Giovanni Petrillo,* Marino Novi, Giacomo Garbarino, and Carlo Dell'Erba
Istituto di Chimica Organica dell'Università,
C.N.R. Centro di Studio sui Diariloidi e loro Applicazioni,
Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy

Abstract: The reaction between arenediazonium tetrafluoroborates and arenethiolates in Me_2SO *represents a mild, efficient, and safe alternative to the Ziegler synthesis of diaryl sulfides.*

The continuing interest in the synthesis of diaryl sulfides has led to a number of different approaches to the problem.[1-9] Besides methods involving the reduction of sulfur compounds at higher oxidation levels,[1] and those exploiting the electrophilic attack of sulfur reagents on arenes,[2] and the homolytic[3] or nucleophilic[4] attack on the sulfur atom of disulfides, the substitution pathway by sulfur nucleophiles on unactivated aromatic derivatives has been made practicable mainly through the generation of aryne intermediates[5] and the employment of metal[6] or electron-transfer[7] catalysis.

A further approach, that is the utilisation of diazonium salts as precursors, dates back to the nineteenth century[8] and involves the aqueous thermal decomposition of the diazosulfides (1), generated by treatment of diazotised amines with the alkaline solution of a thiol:

$$ArN_2^+ \xrightarrow{Ar'S^-} \underset{(1)}{Ar{-}N{=}N{-}SAr'} \xrightarrow[-N_2]{\Delta} ArSAr'$$

This synthesis, known as the Ziegler reaction, has been widely used,[9] with only minor modifications (such as the use of copper powder at low temperature to prevent decomposition of the diazonium salts to phenols[9f]) although yields are not always satisfactory and the reaction is hazardous if cumulation of the intermediate diazosulfide should occur.[10] On the other hand, the ready availability of arylamines and of the intermediate diazonium salts makes this approach quite appealing, and justifies, in our opinion, efforts to further substantial improvements.

We report herein that the reaction of arenediazonium tetrafluoroborates[11] with excess arenethiolates in Me_2SO at room temperature provides a mild, efficient, and safe access to diaryl sulfides (see Table). As TLC analysis showed, in agreement with the expected high rate of the cation-anion combination[12] diazosulfides (1) are preliminarily formed, but, due to the mild conditions employed, in no occasion hazard[10,13] occurred during reaction. The intermediacy of (1) is further supported by the reaction of the independently prepared p-nitrophenyl phenyldiazosulfide with 2 mol. equiv. of benzenethiolate, which yielded 93% p-nitrophenyl phenyl sulfide (15 min, 25°C; cf expt 2).

As a representative example of the experimental procedure, a solution of 1-naphthalenediazonium tetrafluoroborate (1.0 g, 4.1 mmol) in Me_2SO (10 cm^3) was dropped under argon into a stirred solution of PhSNa (1.6 g, 12.3 mmol) in Me_2SO (20 cm^3) kept in a water bath at 25°C. Gas evolution immediately began while the colour of the solution darkened. When the reaction was complete, as judged by the ceasing of gas evolution and by the disappearance (TLC) of the intermediate diazosulfide,[13] the mixture was poored into brine and extracted with Et_2O. Evaporation of the dried extracts at room temperature and column chromatography (silica gel-hexane) afforded the pure 1-naphthyl phenyl sulfide (0.8 g, 82%).

As to the synthetic efficiency and versatility of the reaction, from the examination of the data in the Table the following main points emerge. (a) The method is applicable to a variety of diazonium salts, and both electron-releasing and electron-withdrawing substituents seem to be compatible (expts 1, 2, 3, and 4). (b) Steric hindrance in the diazonium salt favours the reaction (cf expts 4, 5, and 6) thus overcoming the limitations reported for the $S_{RN}1$ process of aryl iodides with arenethiolates.[7a] On the other hand, steric hindrance in the arenethiolate appears to be a disfavouring factor (longer reaction times with somewhat lower yields; cf expts 1 and 9 with 10).

As far as the mechanism of the decomposition of (1) is concerned, both the shorter reaction time required for the p-nitroderivative (expt 2) and the inhibition observed by addition of a good electron acceptor such as m-dinitrobenzene[14] (cf expts 8a and 8b) suggest an electron transfer from $Ar'S^-$ as the main, if not the exclusive, activation step.[15] However, any hypothesis about the real nature of the follow-up chemical reactions would be at the moment highly speculative. Further studies are in progress to clarify this aspect as well as to better define scope and limitations of this synthetic method.

Table. ArSAr' from the reaction between $ArN_2^+BF_4^-$ and $Ar'S^-Na^+$ in Me_2SO at 25°C

expt	Ar	Ar'	$Ar'S^-/ArN_2^+$ molar ratio	Reaction time (min)	Isolated yield[a,b] (%)
1	C_6H_5	C_6H_5	3.0	210	97[c]; 78[d]
2	$4\text{-}O_2NC_6H_4$	C_6H_5	3.0	15	79
3	$4\text{-}MeOC_6H_4$	C_6H_5	3.0	210	72
3a	$4\text{-}MeOC_6H_4$	C_6H_5	1.5	330	64[e]
4	$4\text{-}MeC_6H_4$	C_6H_5	3.0	450	79
5	$2\text{-}MeC_6H_4$	C_6H_5	3.0	330	82
6	$2,6\text{-}Me_2C_6H_3$	C_6H_5	3.0	120	76
7	1-naphthyl	C_6H_5	3.0	210	82
8	2-naphthyl	C_6H_5	3.0	330	78
8a	2-naphthyl	C_6H_5	3.0	240	69[e]
8b	2-naphthyl	C_6H_5	3.0	240	23[e,f]
9	C_6H_5	$4\text{-}MeC_6H_4$	3.0	210	82
10	C_6H_5	$2,4,6\text{-}Me_3C_6H_2$	3.0	330	67

[a] Solid sulfides melted as reported in the literature; liquid sulfides were identified as sulfones.

[b] Traces of reduction products (ArH) were randomly observed (TLC); traces of $(Ar'S)_2$, Ar'SH, and unidentified by-products were generally observed (TLC).

[c] Crude product, slightly contaminated by PhSH and PhSSPh.

[d] After distillation.

[e] Quenching was performed when some gas evolution was still going on.

[f] In the presence of m-dinitrobenzene (0.3 mol. equiv. with respect to ArN_2^+).

References and notes

1 - J.Drabowicz, Y.Numata, and S.Oae, *Org.Prep.Proc.Int.*, 1977, **9**, 63; H.Burton and W.A.Davy, *J.Chem.Soc.*, 1948, 528.

2 - J.K.Bosscher, E.W.A.Kraak, and H.Kloosterziel, *J.Chem.Soc., Chem.Commun.*, 1971, 1365; F.Bottino, R.Fradullo, and S.Pappalardo, *J.Org.Chem.*, 1981, **46**, 2793.

3 - C.S.Giam and K.Kikukawa, *J.Chem.Soc., Chem.Commun.*, 1980, 756.

4 - P.Jacob, III and A.T.Shulgin, *Synth.Commun.*, 1981, **11**, 957.

5 - J.F.Bunnett and T.K.Brotherton, *J.Org.Chem.*, 1958, **23**, 904; R.B.Bates and K.D.Janda, *ibid.*, 1982, **47**, 4374.

6 - W.R.Bowman, H.Heaney, and P.H.G.Smith, *Tetrahedron Lett.*, 1984, **25**, 5821, and refs cited therein; T.Migita, T.Shimizu, Y.Asami, J.Shiobara, Y.Kato, and M.Kosugi, *Bull.Chem.Soc.Jpn.*, 1980, **53**, 1385; H.J.Cristau, B.Chabaud, A.Chene, and H.Christol, *Synthesis*, 1981, 892.

7 - (a) J.F.Bunnett and X.Creary, *J.Org.Chem.*, 1974, **39**, 3173, 3611;
(b) J.Pinson and J.M.Saveant, *J.Amer.Chem.Soc.*, 1978, **100**, 1506.

8 - J.H.Ziegler, *Chem.Ber.*, 1890, **23**, 2469; 1895, **28**, 1674.

9 - (a) W.E.Truce, D.P.Tate, and D.N.Burdge, *J.Amer.Chem.Soc.*, 1960, **82**, 2872;
(b) C.W.N.Cumper, J.F.Read, and A.I.Vogel, *J.Chem.Soc.*, 1965, 5863;
(c) G.Leandri, A.Mangini, and R.Passerini, *Gazz.Chim.Ital.*, 1954, **84**, 3;
(d) H.H.Zmant and G.Levitt, *J.Amer.Chem.Soc.*, 1954, **76**, 5459;
(e) S.Oae and Y.H.Kim, *Bull.Chem.Soc.Jpn.*, 1967, **40**, 1716;
(f) G.E.Hilbert and T.B.Johnson, *J.Amer.Chem.Soc.*, 1929, **51**, 1526.

10 - H.Spencer, *Chem.Brit.*, 1977, **13**, 240, and refs cited therein.

11 - Prepared according to A.I.Vogel, "Practical Organic Chemistry," Longmans, London, 3rd edn., 1961, pp. 610—612.

12 - C.D.Ritchie and P.O.I.Virtanen, *J.Amer.Chem.Soc.*, 1972, **94**, 1589.

13 - Although no explosions were encountered in the present work,[10] nevertheless caution should be taken in handling the reaction mixture. A careful checking for complete disappearance of the diazosulfide (TLC) is bound to guarantee a safe work-up procedure;[10] anyway, in our experiments, when the conversion was not pushed to completion, heating was rigorously avoided throughout the work up and any unreacted intermediate could be easily and safely separated by chromatography.

14 - N.Kornblum, *Angew.Chem., Int.Ed.Engl.*, 1975, **14**, 734.

15 - M.Julliard and M.Chanon, *Chem.Rev.*, 1983, **83**, 425.

(Received in UK 22 October 1985)