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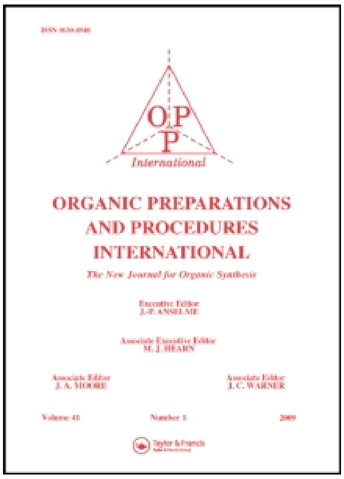

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REDUCTION OF AROMATIC SULFONYL CHLORIDES TO DISULFIDES

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REFERENCES

1. a) C. J. Cooksey, E. J. Land, P. A. Riley, T. Sarna, and T. G. Truscott, *Free Radical Res. Commun.* **4**, 131, (1987); b) E. J. Land, C. J. Cooksey and P. A. Riley, *Biochem. Pharmacol.*, **39**, 1133 (1990); c) C. J. Cooksey, K. Jimbow, E. J. Land and P. A. Riley, *Melanoma Res.*, **2**, 283 (1992); d) C. J. Cooksey, E. J. Land, C. A. Ramsden and P. A. Riley, *Anti-Cancer Drug Design*, **10**, 119 (1995).

2. S. Naish-Byfield, C. J. Cooksey, A. M. Latter, C. I. Johnson and P. A. Riley, *Melanoma Res.*, **1**, 273 (1991).

3. P. Capdevielle and M. Maumy, *Tetrahedron Lett.*, **23**, 1577 (1982).

4. H. Bretschneider, K. Hohenlohe-Oehringen, A. Kaiser and U. Wolcke, *Helv. Chim. Acta.*, **56**, 2857 (1973).

5. a) **3a** from the aldehyde, G. W. Kabalka, N. K. Reddy and C. Narayana, *Tetrahedron Lett.* **33**, 865 (1992); b) **3** (R = octyloxy and R = decyloxy, in 4 steps from 3,4-dihydroxybenzaldehyde), Y. Naito, M. Sugiura, Y. Yamaura, C. Fukaya, K. Yokoyama, Y.Nakagawa, T. Ikeda, M. Senda and T. Fujita, *Chem. Pharm. Bull. Jpn*, **39**, 1736 (1991); c) **3d** by pyrolysis of a dimethylsulfonium salt, A. Winkler, *Ger. Offen.* DE 2644591 (1978); *Chem. Abstr.*, **89**, 23960 (1978).

6. H. J. Teuber, *Chem. Rev.*,**71**, 229 (1971).

7. V. Balogh, M. Fetizon and M. Golfier, *J. Org. Chem.*, **36**, 1339 (1971).

8. D. H. Rosenblatt and R. W. Rosenthal, *J. Am. Chem. Soc.*, **75**, 4607 (1953).

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REDUCTION OF AROMATIC SULFONYL CHLORIDES TO DISULFIDES

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Lalancette and Arnac first reported the preparation of sodium selenated borohydride ($NaBH_2Se_3$) by the reaction of sodium borohydride and selenium powder in diglyme in 1969.[1] This reagent, similar to the sodium sulfurated borohydride ($NaBH_2S_3$), could be useful as a new stereoselective reducing agent.[2] However, no further reports concerning the reducing capacity of $NaBH_2Se_3$ have appeared. We now report that sodium triselenoborohydride ($NaBH_2Se_3$)[1] reduces aromatic sulfonyl chlorides to the corresponding diaryl disulfides in moderate to good yields (Table 1).

$$\mathbf{NaBH_4} + \mathbf{3Se} \xrightarrow[\text{70-80°}]{\text{MeCN, } N_2} \mathbf{NaBH_2Se_3} \xrightarrow[\text{MeCN, } \Delta]{ArSO_2Cl\ (\mathbf{1})} \underset{\mathbf{2}}{\mathbf{Ar{-}S{-}S{-}Ar}}$$

a) Ar = C_6H_5 b) Ar = p-ClC_6H_4 c) Ar = o-ClC_6H_4 d) Ar = p-BrC_6H_4
e) Ar = m-$NO_2C_6H_4$ f) Ar = p-$CH_3C_6H_4$ g) Ar = o-$CH_3C_6H_4$ h) Ar = p-$Ch_3OC_6H_4$
i) Ar = o-$CH_3OC_6H_4$ j) Ar = 2,5-$(CH_3)_2C_6H_3$ k) Ar = α–$C_{10}H_7$) Ar = β-$C_{10}H_7$

All products were identified by comparison with authentic specimens. Although some arenesulfonyl chlorides can be successfully reduced to disulfides using sodium borohydride alone, the yields were lower than the yields of obtained under the same reaction conditions with sodium triselenoborohydride. Thus, this one-pot procedure using sodium triselenoborohydride provides a new method for the conversion of arenesulfonyl chlorides into disulfides under especially mild, non-aqueous conditions.

EXPERIMENTAL SECTION

Melting points are uncorrected. Elemental analyses were carried out on a Carlo Erba 1106 apparatus. Commercial aromatic sulfonyl chlorides were purified by recrystallization or distillation. Compounds **1b**, **1c**, **1h**, **1i** and **1j** were prepared by literature procedures[4,5] Selenium powder (99.999%) and NaBH4 were commercially obtained. Acetonitrile was distilled from small amounts of P_2O_5. All reactions should be performed in a good hood.

General Procedure.- A solution of the sulfonyl chloride **1** (1 mmol) in dry acetonitrile (about 2-3 mL) was added over a period of 45 minutes to a solution of sodium selenated borohydride (2mmol) [prepared by heating selenium powder (6mmol) and $NaBH_4$ (2mmol) in dry CH_3CN (6-8 mL) at 70-80° under nitrogen for 0.5-1 hr] The resulting mixture was kept at reflux for the periods listed in TABLE 1. The progress of the reaction was monitored by TLC (10:1 v/v), hexane-ethyl acetate). After heating, the resulting mixture was stirred at room temperature in the open air for 1-2 hrs. The reaction mixture was then quenched by the addition of a saturated aqueous NH_4Cl (1 mL) and the resulting mixture aerated to oxidize the resulting thiol. The deposited selenium was filtered off and the filtrate was partitioned three times between ethyl acetate (30 mL) and water (30 mL). The organic phases were separated, combined, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed over silica gel using hexane-ethyl acetate (10:1 v/v) to give the disulfide **2**, recrystallized from 95% ethanol if necessary.

TABLE 1. Disulfides, Time of reaction, Yields, Mps and Elemental Analyses

cmpd	Time	Yield[a]	mp.	lit. mp.[b]	Elemental Analysis (Found)			
	(hrs)	(%)	(°C)	(°C)	C	H	S	N
2a	3	88	56-58	61	66.01(65.85)	4.62(4.58)	29.37(29.45)	
2b	2.5	55	67-68	70-71	50.18(50.08)	2.81(2.79)	22.33(22.39)	
2c	2.5	60	86-88	89-90	50.18(50.25)	2.81(2.83)	22.33(22.28)	
2d	2	50	89-91	93.5	38.54(38.44)	2.14(2.10)	17.05(17.11)	
2e	1	45	80-81	84	46.74(46.65)	2.62(2.59)	20.80(20.85)	9.09(9.13)
2f	4	67	42-44	48	68.25(68.16)	5.73(5.70)	26.03(26.08)	
2g	4	75	35-37	38	68.25(68.13)	5.73(5.69)	26.03(26.11)	
2h	3.5	60	40-41	44-45	60.40(60.28)	5.07(5.10)	23.03(22.98)	
2i	3.5	67	116-117	119-120	60.40(60.25)	5.07(5.03)	23.03(23.10)	
2j	4	78	41-43	46-47	70.02(69.85)	6.61(6.58)	23.37(23.41)	
2k	6	53	87-88	91	75.43(75.31.)	4.43(4.39)	20.14(20.20)	
2l	6	48	136-137	139	75.43(75.36)	4.43(4.40)	20.14(20.18)	

a) No attempts were made to optimize the yields. b) Ref. 3

REFERENCES

1. J. M. Lalancette and M. Arnac, *Can. J. Chem.*, **47**, 3695 (1969).
2. J. M. Lalancette and A. Frêche, *ibid.*, **47**, 739 (1969).
3. Beilstein, **H6**, 324, 330, 326, 334, 339, 425, 372, 863, 795, 498, 625, 663.
4. *Chem. Abs.*, **55**, 23411f (1961); **63**, 11410f (1965); **55**, 23411e (1961); **52**, 9003a (1958).
5. H. Gilman and A. H. Blatt, *Org. Syn., Coll. Vol. 1*, 2nd Ed., 85 (1951).

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