

Table 2. Results from reductions of disulfides (5.0 g or 5.0 ml) with other electrophiles in DMF/0.5 M LiCl.

Starting material	-E (V) vs. Ag/AgCl/0.5 M Cl ⁻	Electrophile (ml)	Product yield (%)		B.p./mmHg or M.p. (°C)	n _D ²⁵
			Crude	Isolated		
[CH ₃ S-] ₂	1.2	C ₆ H ₅ CH ₂ Cl (18)	—	63	82–86/9	1.5604
[CH ₃ COS-] ₂	0.8	» (5)	87	76.5	65–75/0.25	1.5564
[C ₆ H ₅ S-] ₂	0.8	» (5.5)	98	92	41–42	
[C ₆ H ₅ CH ₂ S-] ₂	1.2	CH ₃ CHClCH ₃ (20)	90	75.5	100–104/10	1.5362
»	1.2	(CH ₃ CO) ₂ O ^a (15)	95	89.5	68–72/0.25	1.5564
[o-NO ₂ C ₆ H ₄ S-] ₂	0.2	» ^a (15)	87	68.5	118–125/0.25	1.5910
»	0.2	CH ₃ COCl (10)	—	39	110–120/0.15	1.5912
»	0.3	CH ₃ I (2.2)	89	84	68–69	
»	0.3	(CH ₃ O) ₂ SO ₂ (10)	98	91	66–68	
»	0.3	(CH ₃ CH ₂ O) ₂ SO ₂ (20)	82	76.5	115–125/0.25	1.6234
[(CH ₃) ₂ NCSS-] ₂	0.4 ^b	(CH ₃) ₂ NCOC ^c (5)	44	37	76–77	
[C ₆ H ₅ COS-] ₂	0.4	CH ₂ Br ₂ (2)	98	66 ^d	118–119	
»	0.4	CH ₂ Cl ₂ (1.2)	57	34 ^d	108–110	

^a 5 ml of pyridine added. ^b Solvent acetonitrile/0.8 M NaClO₄, sat. LiCl in the reference electrode. ^c 2 ml of pyridine added. ^d The product was di-*S*-thiobenzoylmethane.

in this particular case, but it proved to be advantageous for the reductions with acetic anhydride.

In most experiments DMF has been employed as the solvent, but acetonitrile may also be useful for reductive alkylations and acylations. In some cases, e.g. dibenzyl disulfide, the yield of methylated product was considerably lower in acetonitrile (82%) than in DMF (95%), whereas with *N,N*-dimethylcarbamoyl chloride as the electrophile the yield was higher in acetonitrile than in DMF. Ethanol and presumably other protic solvents are inferior to the aprotic solvents and a considerable amount of thiol was found as a side product in methylations with methyl chloride, but possibly dimethyl sulfide may be used instead.

Experimental. The electrolytic equipment has been described earlier.¹ The disulfides were either commercial products or prepared by literature methods. The DMF was dried over A4 molecular sieves. Boiling and melting points are uncorrected.

General procedure for electrolytic reductive alkylation and acylation. The disulfides (5.0 ml or 5.0 g) were reduced overnight at room temperature (cell surrounded by a water bath) in DMF (approx. 175 ml) containing 0.5 M lithium chloride. The reference electrode was Ag/AgCl/0.5 M LiCl in DMF, and working potentials and amounts of added electrophile are indicated in Tables 1 and 2. For some of the very easily reducible compounds the mercury cathode was polarized negatively before addition of the disulfide to avoid the formation of a black precipitate by reaction with the metal. The electricity consumption was usually very close to 2 F/mol of disulfide. After reduction an equal volume of benzene was added to the catholyte which was then washed 3 times with 1.5 l of water to remove the DMF. For experiments in

acetonitrile the solvent was evaporated *in vacuo* before the extraction with benzene. The organic layer was dried over anhydrous magnesium sulfate, the solvent removed *in vacuo*, and the residue either fractionated *in vacuo* or recrystallized from ethanol. In a few experiments with diphenyl- and dibenzyl disulfide about 600 ml of water were added to the catholyte which was then extracted continuously with petroleum ether (16–20 h) and worked up as above. The extraction procedure was checked with benzyl methyl sulfide giving 95% recovery. The prepared sulfide derivatives were known from the literature and identified by comparison with authentic specimens or literature data. Optimization of yields has not been attempted.

***S*-Methyl(2-thiomethyl)thiobenzoate.** For this compound our m.p. (53–54 °C) did not agree with the reported³ one (121–122 °C). NMR-spectrum (60 MHz, CCl₄, TMS): δ 2.35 (s, 3 H); δ 2.40 (s, 3 H); δ 6.9–7.9 (multiplet, 4 H). Strong IR-absorptions (KBr, cm⁻¹): 1660, 1205, 905. (Found: C 54.47; H 5.13; S 32.07. Calc. for C₉H₉OS₂: C 54.54; H 5.09; S 32.30). For comparison the NMR (CCl₄) *S*-methyl signals are given for *S*-methylthiobenzoate: δ 2.40 (s, 3 H) and *S*-methyl(2-methylthio)dithiobenzoate: δ 2.32 (s, 3 H) and δ 2.69 (s, 3 H).

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