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Synthesis of diaryl sulfides by the reactions of activated aryl halides with potassium ethyl dithiocarbonate under conditions of phase-transfer catalysis

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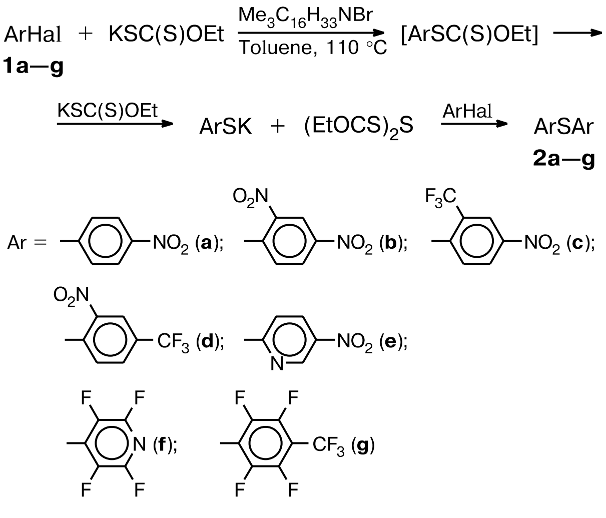
Activated aryl halides are used to synthesize diaryl sulfides by the reaction with sodium sulfide or other sulfur-containing compounds both in dipolar aprotic solvents[1] and under the conditions of phase-transfer catalysis.[2—4] The main drawback of the known routes to symmetrical diaryl sulfides is the formation of side products, *e.g.*, diaryl disulfides.[4,5] It is known that dialkyl sulfides can be obtained from alkyl halides and potassium ethyl dithiocarbonate under the conditions of phase-transfer catalysis with subsequent alkaline decomposition of substitution products.[6] We found that activated aryl halides **1a—g** react with potassium ethyl dithiocarbonate under the conditions of phase-transfer catalysis to give diaryl sulfides **2a—g** directly without the formation of diaryl disulfides as by-products (Scheme 1).

Scheme 1



Apparently, the reaction mechanism includes the formation of *S*-aryl *O*-ethyl dithiocarbonate in the first step, which reacts with the second molecule of potassium ethyl dithiocarbonate to give diethyl trithiodicarbonate (detected by mass spectrometry) and the corresponding potassium arenethiolate. The latter in turn reacts with the second molecule of aryl halide, yielding the target diaryl sulfide. The physicochemical characteristics of the known diaryl sulfides agree well with the literature data.

Synthesis of diaryl sulfides 2a—g (general procedure). A mixture of an aryl halide (**1a—g**) (1 mmol), potassium ethyl dithiocarbonate (1.1 mmol), and $C_{16}H_{33}Me_3NBr$ (0.05 mmol) in 100 mL of toluene was refluxed with vigorous stirring for 4—8 h until complete disappearance of the starting aryl halide (monitoring by TLC on Silufol UV-254 plates or GLC). In the case of volatile perfluorinated aryl halides **1f,g**, the reactions were carried out in a sealed tube. Then the reaction mixture was filtered through silica gel, and the product was eluted with toluene (TLC). The solution obtained was concentrated *in vacuo*, and the residue was recrystallized twice from light petroleum. The ^{19}F (with C_6F_6 as the internal standard) and ^{13}C NMR spectra were recorded on a Varian VXR-400 instrument. Mass spectra were recorded on a Finnigan MAT-113 instrument.

Bis(2,3,5,6-tetrafluoro-4-pyridyl) sulfide (2f). Yield 95%, m.p. 54—56 °C. Found (%): C, 36.00; F, 45.67; N, 8.42; S, 9.55. $C_{10}F_8N_2S$. Calculated (%): C, 36.10; F, 45.76; N, 8.40; S, 9.65. ^{19}F NMR ($CDCl_3$), δ: −90.5 (m, 4 F, F(2), F(6)); −135.2 (m, 4 F, F(3), F(5)). ^{13}C NMR ($CDCl_3$), δ: 125.2 (m, C(4)); 143.2 (dm, C(3), C(5), $J_{C,F}$ = 259.8 Hz); 144.3 (dm, C(2), C(6), $J_{C,F}$ = 243.3 Hz). MS (EI, 70 eV), *m/z*: 332 $[M]^+$.

Bis(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl) sulfide (2g). Yield 90%, m.p. 62—64 °C. Found (%): C, 35.94; F, 56.92; S, 6.75. $C_{14}F_{14}S$. Calculated (%): C, 36.07; F, 57.05; S, 6.88. ^{19}F NMR ($CDCl_3$), δ: −59.0 (s, 6 F, CF_3); −133.3 (m, 4 F, F(3), F(5)); −140.8 (m, 4 F, F(2), F(6)). ^{13}C NMR ($CDCl_3$), δ: 111.2 (m, C(4)); 115.2 (t, C(1), $J_{C,F}$ = 21.1 Hz); 120.4 (q, CF_3); 144.2 (dm, C(3), C(5), $J_{C,F}$ = 261.0 Hz); 146.7 (dm, C(2), C(6), $J_{C,F}$ = 250.4 Hz). MS (EI, 70 eV), *m/z*: 466 $[M]^+$.

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