"One Pot" Two-Step Synthesis of Aryl Sulfur Compounds by Photoinduced Reactions of Thiourea Anion with Aryl Halides

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General methods and materials

Methods: Irradiation was conducted with a 125-W medium pressure Hg lamp emitting maximally at 365 nm (Applied Photophysics Limited). ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50 MHz respectively on a Brucker AC-200 spectrometer, and all spectra are reported in δ (ppm) relative to Me_4Si, with $CDCl_3$ as solvent. Gas chromatographic analyses were performed on a Hewlett Packard 6890 A with a flame-ionization detector, on a HP-5 30 m capillary column of a 0.32 mm x 0.25 μm film thickness, or a HP1 5 m x 0.53 x 2.65 μm film thickness column. GS/MS analyses were carried out on a Shimadzu GC-MS QP 5050 spectrometer, employing a 25 m x 0.2 mm x 0.33 μm HP-5 column.

Materials: *tert*-BuOK, thiourea, the aryl halides, naphthalene, DTBN, thioanisole, diphenyl sulfide, 1-methoxy-4-(methylthio)benzene, 4-(methylthio)nitrobenzene and 4-(methylthio)benzonitrile were all high purity commercial samples which were used without further purification. DMSO, DMF, HMPA, MeCN were purified by standard procedures and stored over molecular sieves (4 Å). EtOH absolute grade was used without further purification. The thiourea anion (**1**) was generated in situ by acid-base deprotonation using *tert*-BuOK. All the products are known and exhibited physical properties identical to those reported in the literature. Also, they were isolated by radial chromatography from the reaction mixture and characterized by ^{1}H and ^{13}C NMR and mass spectrometry.

4-(Mercapto)benzophenone: to a solution of 4-benzoylbenzene thiolate obtained from 10.5 mmol of *ter*-BuOK, 10 mmol of the thiourea and 0.5 mmol of the bromobenzophenone in 10 mL of DMSO (according to the general procedure described), 10 mL of a NH_4NO_3 saturated solution was added and then acidification with 0.3 mL of HCl (37%) until decoloration of the solution (pH≅ 2). The mixture was extracted with ethyl ether (3x20 mL), the organic extract was washed twice with water, dried and the 4-(mercapto)benzophenone was isolated by radial chromatography (85.6mg, 80%) and its physical properties were similar to the reported in literature.[1]

Bis(4-benzoylphenyl) disulfide: to a solution of 4-benzoylbenzene thiolate obtained from 10.5 mmol of *ter*-BuOK, 10 mmol of the thiourea and 0.5 mmol of the bromobenzophenone in 10 mL of DMSO (according to the general procedure described). A mixture of iodine (0.13 gr, 0.51 mmol) and potassium iodide (0.25 gr, 1.5 mmol) was added and then the mixture stirred until the dark brown color disappeared. 30 mL of water was added and the mixture was acidificated with 0.3 mL of HCl (37%) and then extracted with ethyl ether (3x20 mL). The organic extract was washed twice with water, dried and the bis(4-benzoylphenyl) disulfide was isolated by radial chromatography (74.8mg, 70%) and its physical properties were similar to the reported in literature.[1]

4-(Phenylthio)benzophenone: to a solution of 4-benzoylbenzene thiolate obtained from 10.5 mmol of *ter*-BuOK, 10 mmol of the thiourea and 0.5 mmol of the bromobenzophenone in 10 mL of DMSO (according to the general procedure described), 2.5 mmol of *ter*-BuOK and 40 mmol of IPh were added and the reaction mixture irradiated for 3h. The reaction was quenched with addition of methyl iodide (6 equiv) and 30 mL of water, and then the mixture was extracted with methylene chloride (3x20 mL). The organic extract was washed twice with water, dried and the 4-phenylthiobenzophenone (35%) was quantified by GLC with the internal standard method.

Registry No. 1-(methylthio)naphthalene,[2] [10075-72-6]; 2-(methylthio)naphthalene,[3] [7433-79-6]; bis-(1-naphthyl) sulfide,[4a] [607-53-4]; bis(2-naphthyl) sulfide,[4b] [613-81-0]; 2-(methylthio)pyridine,[5] [18438-38-5]; 3-(methylthio)pyridine,[6] [18794-33-7]; 2-(methylthio)quinoline,[6] [40279-26-3]; 2-(methylthio)pyrazine,[7] [21948-70-9]; 2-(methylthio)pyrimidine,[8] [823-09-6]; 2-(methylthio)acetophenone,[9] [1441-97-0]; 4-(methylthio)benzophenone,[10] [23405-48-3]; 4-(phenylthio)benzophenone,[11] [6317-78-8]; 4-(mercapto)benzophenone,[12][1620-94-6]; bis(4-benzoylphenyl) disulfide,[1] 1,4-bis(methylthio)benzene,[13] [699-20-7]; bis[4-(methylthio)phenyl] sulfide,[13] [125877-23-8]; bis(3-pyridyl) sulfide,[14] [57331-00-7]; bis(2-pyridyl) sulfide,[15] [4262-06-0].

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