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ARTICLE

Deoxygenation of Sulphoxides to Sulphides with Trichlorophosphane

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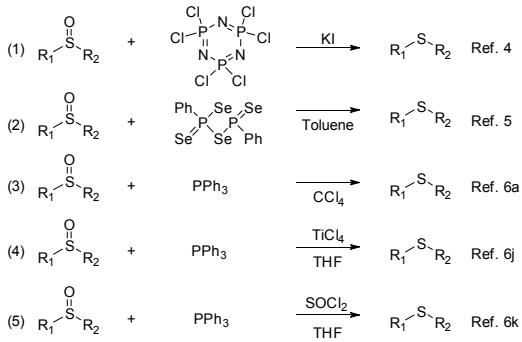
An efficient route to deoxygenation of sulphoxides to sulphides with PCl_3 under mild reaction condition was developed. PCl_3 was used as a reducing agent for the first time to convert sulphoxides to sulphides. The mild conditions, use of cheap and readily available reagent, and broad substrate scope render it a useful strategy for preparing sulphides.

The reduction of sulphoxides to their corresponding sulphides is an important transformation in organic synthesis. Traditional methods to reduce sulphoxides to sulphides involve the use of low-valent metallic species,[1] metal hydride reagents,[2] halide ions,[3] phosphorus compounds,[4] Woollin's reagent,[5] and phosphines[6] (Scheme 1). However, most of the methods have the following disadvantages: 1) the use of expensive reagents, 2) functional group incompatibility, and 3) difficult work-up procedures or harsh reaction conditions. Therefore, development of an efficient and improved atom economy method for the reduction of sulfoxides to the corresponding sulphides is highly desirable.

As we are interested in developing efficient methods to construct C–S bonds,[7] we recently developed a sodium trifluoromethanesulphinate (CF_3SO_2Na)-based transition metal-free trifluoromethylthiolation of electron-rich aromatics in the presence of trichlorophosphane (PCl_3).[8] While studying the mechanism of this transformation, we found that PCl_3 could reduce trifluoromethylsulphoxide to the corresponding trifluoromethylthioether. PCl_3 is an important bulk chemical used in industry to prepare many phosphorus-containing compounds. We investigated the possibility of using PCl_3 as a reductant to convert a normal sulphoxide to its corresponding sulphide. We found that this was indeed the case, and herein report the deoxygenation of sulphoxides to sulphides with PCl_3.



Scheme 1 Representative deoxygenation of sulfoxides to sulphides by phosphorus-containing reagents

First, we treated 1-(butylsulfinyl)-4-methylbenzene **1a** with PCl_3 in 1,4-dioxane at 25 °C, which gave the desired deoxygenation product **3a** in 70% yield (Table 1, Entry 1).To optimize the reaction conditions, various solvents such as ethanol (EtOH), toluene, *N*,*N*-dimethylformamide (DMF), CH_2Cl_2, and acetonitrile (CH_3CN) (Table 1, Entries 2–6) were first examined. It was found that CH_3CN gave the best result (Table 1, Entry 6). Next, the reaction temperature and concentration were optimized. The result showed that increasing the reaction temperature to 40 °C or decreasing it to 10 °C diminished the yield (Entries 7 and 8). However, increasing the concentration of 1a to 0.5 M or decreasing it to 0.17 M did not affect the yield much (Entries 9 and 10). Finally, the equivalent amount of PCl_3 was examined; 1.05 equiv. of PCl_3 was sufficient for the reaction, giving 97% product yield (Table 1, Entries 11-12). Thus, the optimal reaction conditions were as follows: 1.05 equiv. PCl_3 in CH_3CN (0.25 M) at 25 °C.

With the optimized conditions in hand, we extended the reaction by using a series of sulphoxides (Table 2). First, aryl-alkyl, aryl-cyclopropyl, aryl-allylic, aryl-propargyl, aryl-alkene, and aryl-benzyl sulphoxides were examined, and the corresponding sulphides (**3b**–**3g**) were obtained in good yields. Notably, ester, carboxylic acid, amide, trifluoromethyl and difluoromethyl groups (**1h**–**1l**) were tolerant during this transformation. Thereafter, sulphinyldibenzene (**1m**), diphenyl sulphoxides with electron-withdrawing (**1n**) and electron-donating group (**1o** and **1p**), diphenyl sulphoxides with phenol and acetate group (**1q** and **1s**) as well as cyclic phenyl-phenyl

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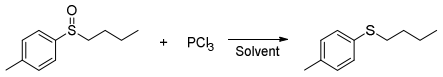
and phenyl-heterocyclic sulphoxides (**1r** and **1t**) were examined, and the corresponding sulphides (**3m–3t**) were obtained in good to excellent yields. Notably, when the tetra *ortho*-methyl phenyl-phenyl sulfoxide (**1p**) was used as a substrate, the steric effect did not affect the yield. Finally, the alkyl-alkyl and benzyl-benzyl sulphoxides were examined, and the corresponding sulphides (**3u** and **3v**) were obtained in good yield.

Table 1 Optimization of conditions for deoxygenation **1a** with PCl_3.[a]

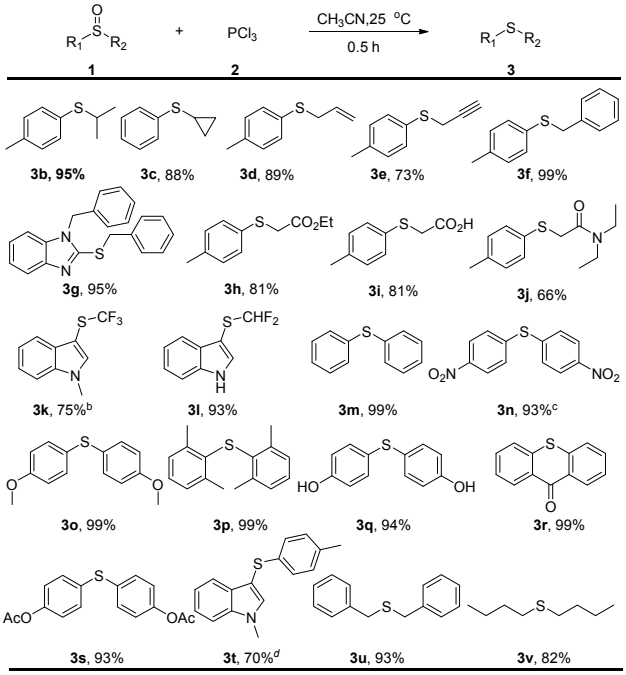


1a 2 3a

Entry	**2** (eq.)	Solvent	Concentration of **1a** (M)	Temperature (°C)	Yield (%)
1	1.0	1,4-Dioxane	0.25	25	70
2	1.0	EtOH	0.25	25	7
3	1.0	Toluene	0.25	25	87
4	1.0	DMF	0.25	25	14
5	1.0	CH_2Cl_2	0.25	25	92
6	1.0	CH_3CN	0.25	25	95
7	1.0	CH_3CN	0.25	10	92
8	1.0	CH_3CN	0.25	40	91
9	1.0	CH_3CN	0.5	25	93
10	1.0	CH_3CN	0.17	25	93
11	1.05	CH_3CN	0.25	25	97
12	1.1	CH_3CN	0.25	25	97

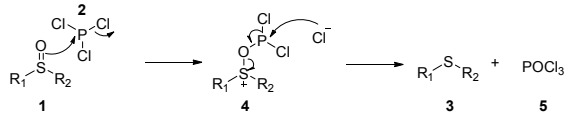
[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equiv), PCl_3 (0.5-0.55 mmol), solvent (1.0-3.0 mL) at indicated temperature.

Table 2 Deoxygenation of sulfoxides to sulfides with trichlorophosphane.[a]



[a] Reaction conditions: **1b-1v** (0.5 mmol), **2** (0.525 mmol), CH_3CN (2.0 mL), 25 °C for 0.5 h [b] The reaction was carried out in 0 °C. [c] The reaction was stirred for 6 h [d] The reaction was carried out in -15 °C

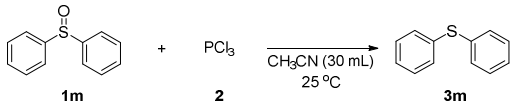
Based on literature,[6k] a possible mechanism of this transformation is proposed in Scheme 2. Initially, PCl_3 (**2**) should be attacked by the oxygen of sulfoxide **1** to generate the salt **4**, which was decomposed to sulphide **3** and phosphoryl trichloride **5**.



Scheme 2 Proposed reaction pathway

To support our mechanism, **1a** was treated with PCl_3 under the optimized condition and the reaction was quenched with excess of pyrrolidine. GC-MS showed that tri(pyrrolidin-1-yl)phosphine oxide was one of the major components of the residue.[9]

Finally, to illustrate the potential practical application of this deoxygenation protocol, the reaction was scaled-up using 2 g of the substrate **1m**. As shown in Scheme 3, the desired product **3m** was obtained in 97% yield.



Scheme 3 Scale-up of the trifluoromethylthiolation reaction

Experimental

1) General methods and material

All solvents were distilled prior to use. The solvents for reaction were refluxed over and distilled from Na (for toluene and 1,4-dioxane) or CaH_2 (for DCE，DMF and MeCN) or Mg (for EtOH) under a nitrogen atmosphere. Unless otherwise noted, chemicals were used as received without further purification. For chromatography, 200–300 mesh silica gel was employed. ^1H, $^{19}F\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 400 MHz, 376 MHz and 100 MHz respectively. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. HRMS was performed on an FTMS mass instrument. Melting points are reported as uncorrected.

General Procedure for Deoxygenation of Sulfoxides (Table 2).

Add a sulphoxide (0.5 mmol) to dry CH_3CN (2 mL) in a flame-dried Schlenk tube. Then the trichlorophosphane (0.525 mmol) was added into the solvent by syringe at indicated temperature. The mixture was stirred at indicated temperature for 0.5 hour or 6 hours. Then, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to afford the pure product.

Butyl(p-tolyl)sulfane (3a):[10] After purification by silica gel column chromatography (PE), compound ***3a*** was isolated as a colorless oil (87 mg, 97%); R_f (PE) = 0.37. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24-7.21 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 2.86 (t, *J* = 7.4 Hz, 2H), 2.28 (s, 3H), 1.62-1.53 (m, 2H), 1.47-1.37 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7, 133.3, 129.7, 129.6, 34.0, 31.4, 22.0, 21.0, 13.7.

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Isopropyl(p-tolyl)sulfane (3b):[11] After purification by silica gel column chromatography (N-Pentane), compound ***3b*** was isolated as a colorless oil (78 mg, 95%); R_f (PE) = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.11-7.09 (m, 2H), 3.34-3.24 (m, 1H), 2.32 (s, 3H), 1.26 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 132.9, 131.8, 129.7, 38.8, 23.3, 21.2.

Cyclopropyl(phenyl)sulfane (3c):[12] After purification by silica gel column chromatography (PE), compound ***3c*** was isolated as a colorless oil (66 mg, 88%); R_f (PE) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.34 (m, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.13-7.09 (m, 1H), 2.20-2.14 (m, 1H), 1.06-1.01 (m, 2H), 0.70-0.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 128.8, 126.8, 125.1, 12.3, 8.6.

Allyl(p-tolyl)sulfane (3d):[13] After purification by silica gel column chromatography (PE), compound ***3d*** was isolated as a yellow solid (72.8 mg, 89%); R_f (PE) = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.26 (m, 1 H), 7.26-7.24 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.92-5.81 (m, 1H), 5.11-5.06 (m, 1H), 5.06-5.02 (m, 1H), 3.52-3.49 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 134.0, 132.3, 130.9, 129.7, 117.5, 38.1, 21.2.

Prop-2-yn-1-yl(p-tolyl)sulfane (3e):[14] After purification by silica gel column chromatography (PE), compound ***3e*** was isolated as a yellow oil (59 mg, 73%); R_f (PE) = 0.45. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.36 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.55 (d, *J* = 2.8 Hz, 2H), 2.34 (s, 3H), 2.22 (t, *J* =1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 131.4, 131.3, 129.9, 80.2, 71.6, 23.5, 21.2.

Benzyl(p-tolyl)sulfane (3f):[5] After purification by silica gel column chromatography (PE : EA = 100 : 1), compound ***3f*** was isolated as a white solid (105 mg, 99%); R_f (PE) = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.18 (m, 7H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.04 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 136.7, 132.7, 130.9, 129.7, 129.0, 128.6, 127.2, 40.0, 21.2.

1-benzyl-2-(benzylthio)-1H-benzo[d]imidazole (3g):[15] After purification by silica gel column chromatography (PE : EA = 10 : 1), compound ***3g*** was isolated as a white solid (156 mg, 95%); R_f (PE : EA = 10 : 1) = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.41-7.37 (m, 2H), 7.31-7.26 (m, 3H), 7.26-7.20 (m, 4H), 7.17-7.15 (m, 2H), 7.10-7.08 (m, 2H), 5.23 (s, 2H), 4.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8, 143.8, 136.9, 136.3, 135.8, 129.2, 128.9, 128.8, 128.0, 127.8, 127.0, 122.3, 122.2, 118.6, 109.4, 47.7, 37.7.

Ethyl 2-(p-tolylthio)acetate (3h):[16] After purification by silica gel column chromatography (PE : EA = 10 : 1), compound ***3h*** was isolated as a white oil (85mg, 81%); R_f (PE : EA = 10 : 1) = 0.44; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.31 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.15 (q, *J* =7.2 Hz, 2H), 3.57 (s, 2H), 2.31 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 137.4, 131.4, 131.1, 129.9, 61.5, 37.6, 21.1, 14.2.

2-(p-tolylthio)acetic acid (3i):[17] after purification by silica gel column chromatography (EA), compound ***3i*** was isolated as a yellow solid (74 mg, 81%); R_f (EA) = 0.26; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.17 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.60 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 137.6, 131.1, 131.0, 130.1, 37.5, 21.2.

N,N-diethyl-2-(p-tolylthio)acetamide (3j):[18] after purification by silica gel column chromatography (PE : EA = 3 : 1), compound ***3j*** was isolated as a colorless oil (78 mg, 66 %); R_f (PE : EA = 5 : 1) = 0.24; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.68 (s, 2H). 3.36 (q, *J* = 7.2 Hz, 2H), 3.31 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 3H), 1.18 (t, *J* = 7.2 Hz 3H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7, 137.3, 131.5, 131.4, 129.8, 42.6, 40.4, 37.8, 21.1, 14.5, 13.0.

1-methyl-3-((trifluoromethyl)thio)-1H-indole (3k):[8] After purification by silica gel column chromatography (PE : EA = 20 : 1), compound ***3k*** was isolated as a yellow solid (86.5mg, 75%); R_f (PE : EA = 10 : 1) = 0.50; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.38-7.25 (m, 4H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 137.1, 130.4, 129.6 (q, *J* = 308.0 Hz, 1C), 123.1, 121.4, 119.6, 110.0, 93.3 (q, *J* = 2.0 Hz, 1C), 33.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -44.96 (s, 3F).

3-((difluoromethyl)thio)-1H-indole (3l):[7f] After purification by silica gel column chromatography (PE : EA = 8 : 1), compound ***3l*** was isolated as a brown solid (90 mg, 91%); R_f (PE : EA = 8 : 1) = 0.34; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.80-7.78 (m, 1H), 7.46 (d, *J* = 2.8 Hz, 1H), 7.42-7.40 (m, 1H), 7.30-7.23 (m, 2H), 6.68 (t, *J* = 57.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 132.0,129.8, 123.4, 121.4, 121.2 (t, *J* =274.0 Hz, 1C), 119.4, 111.8, 96.7 (t, *J* = 3.7 Hz, 1C); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -91.96 (d, *J* = 60.1 Hz, 2F).

Diphenylsulfane (3m):[4d] After purification by silica gel column chromatography (PE), compound ***3m*** was isolated as a colorless oil (92mg, 99 %); R_f (PE) = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.31 (m, 5H), 7.29-7.25 (m, 3H), 7.23-7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 131.2, 129.3, 127.1.

Bis(4-nitrophenyl)sulfane (3n):[4d] After purification by silica gel column chromatography (PE : DCM = 2 : 1), compound ***3n*** was isolated as a yellow solid (128 mg, 93 %); R_f (PE : DCM = 3 : 1) = 0.33**;** ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.25 (dd, *J* = 8.4, 1.6 Hz, 4H), 7.64 (dd, *J* = 8.4, 2.0 Hz, 4H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 146.7, 142.2, 131.3, 124.8.

Bis(4-methoxyphenyl)sulfane (3o):[4d] After purification by silica gel column chromatography (PE : EA = 10 : 1), compound ***3o*** was isolated as a white solid (121 mg, 99 %); R_f (PE : EA = 10 : 1) = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.25 (m, 4H), 6.85-6.81 (m, 4H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 132.9, 127.6, 114.9, 55.5.

Bis(2,6-dimethylphenyl)sulfane (3p):[19] After purification by silica gel column chromatography (PE), compound ***3p*** was isolated as a white solid (119 mg, 99 %); R_f (PE) = 0.61; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06-6.99 (m, 6H), 2.22 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 134.5, 128.6, 127.0, 21.8.

4,4'-thiodiphenol (3q)[20] after purification by silica gel column chromatography (PE : EA = 1 : 1), compound ***3q*** was isolated as a white solid (102 mg, 94%); R_f (PE : EA = 1 : 1) = 0.52; ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.62 (s, 2H), 7.14 (d, *J* = 8.4 Hz, 4H), 6.73 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, d_6-DMSO): δ 157.0, 132.7, 124.7, 116.3.

9H-thioxanthen-9-one (3r):[4d] After purification by silica gel column chromatography (PE : EA = 10 : 1), compound ***3r*** was isolated as a yellow solid (104 mg, 99 %); R_f (PE : EA = 10 : 1) = 0.37; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64-8.61 (m, 2H), 7.65-7.57 (m, 4H), 7.51-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.1, 137.4, 132.4, 130.0, 129.5, 126.4, 126.1.

Thiobis(4,1-phenylene) diacetate(3s): after purification by silica gel column chromatography (PE : EA = 5 : 1), compound ***3s*** was isolated

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as a white solid (141 mg, 93 %); R_f (PE：EA = 5 : 1) = 0.41; Mp = 71-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.8 Hz, 4H), 7.04 (d, *J* = 8.8 Hz, 4H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 150.1, 133.0, 132.3, 122.6, 21.2; HRMS (MS) *e*/z calcd for $C_{16}H_{14}O_4S$ $(M+H)^+$ 303.0686, found 303.0674.

1-methyl-3-(p-tolylthio)-1H-indole(3t)*:**[21] After purification by silica gel column chromatography (PE : EA = 100 : 1), compound ***3t was isolated as a white solid (86 mg, 70 %); R_f (PE : EA = 100 : 1) = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.38-7.35 (m, 1H), 7.31 (s, 1H), 7.30-7.26 (m, 1H), 7.17-7.13 (m, 1H), 7.03-7.00 (m, 2H), 6.97-6.95 (m, 2H), 3.82 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 136.1, 134.9, 134.6, 130.0, 129.5, 126.3, 122.6, 120.5, 119.9, 109.8, 101.4, 33.1, 20.9.

Dibenzylsulfane (3u)*:**[5] After purification by silica gel column chromatography (PE : EA = 50 : 1), compound ***3u was isolated as a white solid (99 mg, 93 %); R_f (PE : EA = 100 : 1) = 0.27; ^{1}H NMR (400 MHz, $CDCl_3$): δ7.33-7.22 (m, 10H), 3.60 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 129.1, 128.6, 127.1, 35.8.

Dibutylsulfane (3v)*:**[4d] After purification by silica gel column chromatography (N-Pentane), compound ***3v was isolated as a colorless oil (60 mg, 82%); R_f (PE) = 0.8; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53-2.49(m, 4H), 1.61-1.53 (m, 4H), 1.46-1.36 (m, 4H), 0.92 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.0, 22.2, 13.8.

Conclusions

In conclusion, we developed an efficient route for the deoxygenation of sulphoxides to sulphides with PCl_3 under mild reaction conditions for the first time. Both aliphatic and aromatic sulphoxides could be reduced to the corresponding sulphides in moderate to excellent yields. Thus, the mild conditions and the use of cheap and readily available reagent in addition to the broad substrate scope render it a useful strategy for preparing sulphides.

Conflicts of interest

There are no conflicts of interest to declare.

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