Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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To cite this article: Jin-Xian Wang , Chin-Hsien Wang , Wenfeng Cui & Yulai Hu (1995) A Facile Method for the Syntheses of Dialkyl Disulfides from Sulfur Under Phase Transfer Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:22, 3573-3581, DOI: 10.1080/00397919508015492

To link to this article: http://dx.doi.org/10.1080/00397919508015492

SYNTHETIC COMMUNICATIONS, 25(22), 3573-3581 (1995)

A FACILE METHOD FOR THE SYNTHESES OF DIALKYL DISULFIDES FROM SULFUR UNDER PHASE TRANSFER CONDITIONS

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Abstract: A convenient reaction of alkyl halides with sulfur in alkaline medium has been found to afford disulfides in good to excellent isolated yield under phase transfer conditions.

Phase transfer catalysis is one of the most attractive techniques in organic synthesis.[1] The process is versatile, fast, inexpensive, involves smoth workup, gives good yields and needs less drastic conditions compared to conventional methods of synthesis. The technique has a very broad scope of application.[2] Surprisingly, however, few practical applications have been devised for inorganic synthesis.[3]

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The chemistry of organic sulfides, which are of interest from the viewpoint of organic synthesis, biochemistry, catalysis, organic ligand complexes, and polymer chemistry, has been well studied.[4]

Several methods for the preparation of organic disulfides have been described.[4–8] One of them consists of oxidizing the corresponding thiols, a reaction which has been extensively studied with a variety of reagents. Several reagents such as, bromodimethylsulfonium bromide,[9] bromine/aqueous potassium hydrogen carbonate[10], bis[trinitratocerium(IV)]chromate,[11] sulfonyl chlorides,[12] SeO_2,[13] cluster $(n\text{-}Bu_4N)_2[Fe_4S_4(SR)_4]/O_2$,[14] barium permanganate,[15] $Bu_3SnOMe/FeCl_3$,[16] benzyltrimethylammonium tribromide,[17] 2,2′-dithiopyridine-1,1′-dioxide,[18] $(BrCH_2CH_2)_2SeBr_2$,[19] $M_2B_4O_8/O_2$,[20] 5,5-dibromomeldrum's acid,[21] corresponding chloroselenane,[22] Co(II) salcen/O_2/air,[23] Na_2TeO_3,[24] p- toluenesulphonyl chloride [25] etc., have been used in the field. Disulfides can be easily prepared by electrochemical oxidation of the corresponding thiols in methanol/sodium methoxide solution under conditions of constant current,[26] thiol acetate with clayfen in the absence of solvent [27] and oxidative cleavage of aryl or alkyl tert-butyl sulfides.[28] Although there are a number of methods available in the literature for the synthesis of disulfides, the most commonly employed method for the direct conversion of benzyl halides to disulfides has been using Na_2S_2 or Na_2S/S.[29] Usually, dialkyl polysulfides are obtained from alkyl halides and sulfur in an alkaline medium.[30]

$$\underset{1_{a-k}}{2RX}+\underset{2}{2S}\xrightarrow[C_6H_6,\ 65^\circ C]{NaOH,\ PEG-400}\underset{3_{a-k}}{RSSR}$$

	R	X		R	X
a	$CH_2=CH-CH_2$	Cl	g	$p-ClC_6H_4CH_2$	Cl
b	$n-C_4H_9$	Cl	h	$o-BrC_6H_4CH_2$	Br
c	$i-C_4H_9$	Cl	i	$p-O_2NC_6H_4CH_2$	Br
d	$t-C_4H_9$	Cl	j	$o-O_2NC_6H_4CH_2$	Br
e	$n-C_5H_{11}$	Cl	k	$\beta-C_{10}H_7CH_2$	Br
f	$C_6H_5CH_2$	Cl			

Scheme 1

Recently, we have reported the synthesis of di(acyl) disulfides and di(acyl)diselenides from sulfur or selenium with halides in alkalin medium under phase transfer conditions.[31], [32]In this paper, we have now used a phase-transfer method for the reaction of sulfur with alkyl halides. Dialkyl disulfides (3) can be synthesizedin high yield simply from the reaction of an alkyl halides (1) with sulfur (2)in a two phase system consisting of benzene, water, and a phase -transfer catalyst. The reactions are shown in Scheme 1 and the results are summarized in the Table 1.

Table I shows results of reaction of sulfur with sodium hydroxide and alkyl chloride under phase transfer catalysis.

The results show that the phase transfer catalyst is not only involved in production of the disulfide ion in solution, but also catalyses the substitution reaction on the alkyl chlorides. For example, in order to elucidate the

Table 1 Dialkyl disulfides 3a–k prepared

Product	Yield (%)^a	M.p. or B.p. (Lit. value)	Spectral and analytical data
3a	80	88–90/22mmHg (78–80/16mmHg)^b	δ 5.8(2H, q, =CH–), 5.01(4H, q, CH_2=C–), 2.82(4H, d, –CH_2S); ν max 3082m, 2987m, 2905w, 579m, 429w
3b	78	98–100/5mmHg (94/3mmHg)^b	δ 1.29(6H, t, CH_3), 1.25–1.65(8H, m, $[CH_2]_2$–), 2.63(4H, t, CH_2S); ν max 2957vs, 2870s, 676m, 618w, 424w
3c	79	124–126/20mmHg (120/12mmHg)^b	δ 1.32(12H, d, CH_3), 1.82(2H, m, CH), 2.70(4H, d, CH_2S); ν max 2957vs, 2910m, 674m, 614w, 429w
3d	45	66–68/5mmHg (88/12mmHg)^b	δ 1.32(18H, s, CH_3); ν max 2959vs, 2862m, 697m, 615w, 466w
3e	76	118–119/7mmHg (119/7 mmHg)^b	δ 1.20(6H, t, CH_3), 1.21–1.62(12H, m, $[CH_2]_3$), 2.64(4H, t, CH_2S); ν max 2957vs, 2870m, 507w, 419w,
3f	95	71–72 (71–72)^b	δ 7.20–7.79(10H, m, ArH), 3.80(4H, s, CH_2S); ν max 3051w, 2964w, 2909ws, 708m, 564m, 465m; $C_{14}H_{14}S_2$: requires C, 68.29; H, 5.73. Found: C, 68.58; H, 5.82.

3g	97	60–61	δ 7.36–7.60(8H, q, ArH), 3.81(4H, s, CH_2S); ν max 3080w, 2980w, 2879w, 697m, 519w, 464w; $C_{14}H_{12}Cl_2S_2$: requires C, 53.23; H, 3.81; Found: C, 52.98; H, 3.74.
3h	70	87–88	δ 7.37–7.98(8H, m, ArH), 3.94(4H, s, CH_2S); ν max 3079w, 2879w, 699s, 666m, 528m, 486m; $C_{14}H_{12}Br_2S_2$: requires C, 41.60; H, 2.97; Found: C, 41.50; H, 2.99.
3i	80	111–113	δ 7.34–8.01(8H, m, ArH), 4.06(4H, s, CH_2S); ν max 3080w, 2872w, 622s, 539m, 473m; $C_{14}H_{12}N_2O_4S_2$: requires C, 50.00; H, 3.57; N, 8.33. Found: C, 50.25; H, 3.50; N, 8.21.
3j	75	106–107	δ 7.28–7.59(8H, m, ArH), 3.94(4H, s, CH_2S); ν max 3075m, 2940w, 2872w, 657w, 572w, 439w; $C_{14}H_{12}N_2O_4S_2$: requires C, 50.00; H, 3.57; N, 8.33. Found: C, 50.09; H, 3.56; N, 8.31.
3k	90	116–117	δ 7.22–7.81(14H, m, $C_{10}H_7$), 3.92(4H, s, CH_2S); ν max 3080w, 2980w, 2879w, 645w, 579w, 479w; $C_{22}H_{18}S_2$: requires C, 76.30; H, 5.20; Found: C, 76.04; H, 5.20.

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a Yield of isolated product.

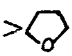
b J. Buckingham et al., Dictionary of Organic Compounds, 5th ed., P1524, P1688, P2294, New York, Loronto, Chapman and Hall, 1982.

action of phase transfer catalysts, we have investigated the reaction of sulfur without them. The reaction of sulfur with sodium hydroxide was continued for 8h at 70–80℃, but with no yellow(S_2^{2-}) in aqueous layer. After only a few drops of PEG–400 was added into the system, the aqueous layer becomes yellow after 5 minutes. The Table 1 shows that the yield of dibenzyl disulfide(3f) is 95%. Under the same conditions but without the phase transfer catalyst for 15 h, the yield of 3f is only 13%.

We also investigated the effects of different phase transfer catalysts on the reactions of S with OH^- and S_2^{2-} with a hydrocarbyl halides. It is found that the activities of the catalysts are in the following order.

PEG–400∼PEG–600>PEG1500>CTMAB∼$(C_2H_5)_4NI$∼18–C–6>$(C_2H_5)_4NCl$∼$(C_2H_5)_4NBr$

The efficiency of various solvents on the formation of dibenzyl disulfides was studied using phase transfer catalysts. The benzene were found to be effective solvents for the reaction,. For various solvents, the effect for the synthesis of dihydrocarbyl disulfides is in the following order:

 >  >CH_3CN>CH_2Cl_2>$CH_3(CH_2)_4CH_3$

An original attempt was made to introduce phase transfer catalysis into inorganic reaction system by Deng and Chen.[3a] Deng et al.,[3b] have also reported the mechanism of a sulphur disproportionation reaction at dilute alkali under phase transfer conditions, which is the same as the one which occurs at high temperature.

$$4S+6OH^- \longrightarrow 2S^{2-}+S_2O_3^{2-}+3H_2O$$

We consider that the mechanism includes two parts, inorganic synthesis and organic synthesis under phase transfer catalysis[33]. The PEG was chosen as the catalyst for the reaction between hydroxide ions in aqueous phase and elemental sulfur in organic phase and the generates S_2^{2-}. Reaction of PEG with NaOH forms $[PEG-Na]^+OH^-$ which, in the presence of S_2^{2-}, generates $[PEG-Na]_2^+S_2^{2-}$ and transfer to organic phase from aqueous phase. $[PEG-Na]_2^+S_2^{2-}$ reacts with the RX rapidly to afford the desired RSSR, and $[PEG-Na]^+OH^-$ is regenerated by ion exchange of $[PEG-Na]^+X^-$ with NaOH. The PEG is used circularly in the reaction.

EXPERIMENTAL SECTION

IR spectra were measured for KBr discs using an Alpha Centauri FT-IR spectrophotometer. H^1NMR spectra(80MHz) were recorded in $CDCl_3$ using a FT-80 spectrometer. Microanalyses were measured using Carlo Elba 1106 microelemental analyser.

General Procedure.-Sulfur powder(12.5mmol) was added to a mixture of PEG-400(0.005 mmol), sodium hydroxide(5M 20ml), and benzene(30ml) at 65-70°C for 3h with stirring. The alkyl halides (10 mmol) was added and the reaction mixture was stirred at 65°C for 1 h. The aqueous layer changed from yellow to colourless immediately. The organic layer was separated, washed with water(3×10ml), and dried ($MgSO_4$). The solvent was removed by evaporation under reduced pressure to afford a crystaline dialkyl disulfide. Recrystallization from ethanol or ethanol/benzene gave the analytically pure products.

We are grateful to the Gansu Natural Science Foundation of China and the Educational Committee of Gansu province for financial support of this project.

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(Received in The Netherlands 24 April 1995)