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A CONVENIENT METHOD FOR THE SYNTHESIS OF DIACYL DISULFIDES

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Abstract: A simple and general method for the synthesis of diacyl disulfides is reported. Sulfur is allowed to react with sodium hydroxide to give sodium disulfide at 65℃ under PTC, which can react with acyl halides to afford diacyl disulfides in good to excellent isolated yields. The effects of solvents and phase transfer catalysts are discussed.

INTRODUCTION

In recent years interest has been shown in the study of organosulfur chemistry[1], and some important reviews have been published[2,3,4]. We also pay attention to the synthesis of diacyl disulfides, which have been synthesized from oxidation of thiocarboxylate[5], treatment of acyl halides with sodium disulfide[6], lithium disulfide [7,8], and hydrogen disulfide[9]. M.Kadomari et al[10]. have reported the synthesis of diacyl disulfides from sodium disulfide and acyl halides under PTC, providing yields superior to the standard method.

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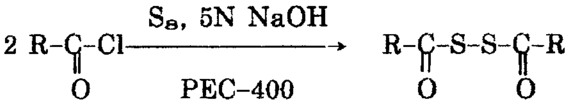
*To Whom Correspondence Should be Addressed.

We wish to report our initial findings on the synthesis of diacyl disulfides by a simple method.



$$2\ \mathrm{R}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{Cl}\xrightarrow[\text{PEC-400}]{\mathrm{S}_8,\ 5\mathrm{N\ NaOH}}\mathrm{R}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{S}-\mathrm{S}-\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R}$$

Scheme 1

We have applied the phase transfer method to the acylation of sulfur. We have found that diacyl disulfides were synthesized in high yields simply from the reaction of an acyl chloride with in a two phase system consisting of benzene, water, and a phase transfer catalyst.

RESULTS AND DISCUSSION

A series of acyl halides were treated with sulfur in the two phase system and good to excellent yields of diacyl disulfides were obtained. The reactions are shown in scheme 1 and the experimental results are summarized in the Table 1.

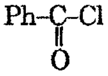
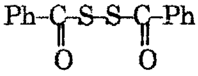
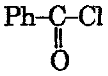
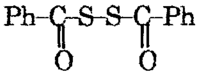
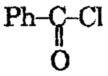
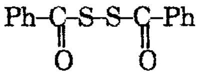
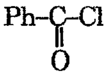
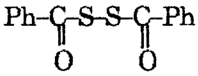
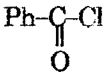
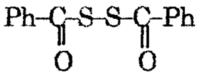
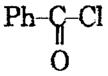
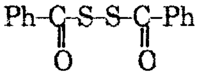
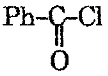
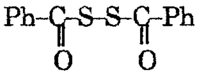
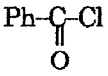
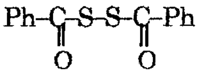
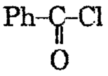
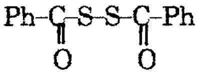
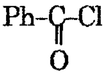
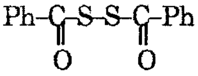
The acyl halides of larger molecular weights and aroyl halides generally gave good yields of diacyl disulfides, with good results. Because of hydrolysis no product could be isolated from acetylchloride. Studies on solvents and catalysts have been undertaken by using benzoyl chloride as starting material. It can be seen from Table 2 that polyether surfactants are excellent phase transfer catalysts, benzene is good solvent, and acetonitrile can also be used.

In order to elucidate the action of phase trtnsfer catalysts, we have investigated the reaction of sulfur

Table 1: The synthesis of bi(acyl)disulfides under PEG-400

Entry	Acyl chloride	Time (h)	Product	Yield (%)
1	$PhCH{=}CHCOCl$	3	$(PhCH{=}CHCOS)_2$	70
2	$C_{17}H_{35}COCl$	3	$(C_{17}H_{35}COS)_2$	90
3	$C_{10}H_7CH_2COCl$	3	$(C_{10}H_7CH_2COS)_2$	61
4	$C_{15}H_{31}COCl$	3	$(C_{15}H_{31}COS)_2$	88
5	$C_{11}H_{23}COCl$	3	$(C_{11}H_{23}COS)_2$	95
6	$PhCOCl$	3	$(PhCOS)_2$	96
7	$p\text{-}NO_2PhCOCl$	3	$(p\text{-}NO_2PhCOS)_2$	72
8	p-BrPhCOCl	3	$(p\text{-}BrPhCOS)_2$	89
9	o-BrPhCOCl	3	$(o\text{-}BrPhCOS)_2$	83
10	o-ClPhCOCl	3	$(o\text{-}ClPhCOS)_2$	93
11	p-ClPhCOCl	3	$(p\text{-}ClPhCOS)_2$	90
12	o-IPhCOCl	3	$(o\text{-}IPhCOS)_2$	65
13	$p\text{-}CH_3PhCOCl$	3	$(p\text{-}CH_3PhCOS)_2$	80
14	$m\text{-}NO_2PhCOCl$	3	$(m\text{-}NO_2PhCOS)_2$	80
15	$p\text{-}CH_3OPhCOCl$	3	$(p\text{-}CH_3OPhCOS)_2$	82

Table 2: Effects of Solvents and Catalysts[a,b]

Acyl chloride	Product	Catalyst	Solvent	Yield[c] (%)
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	CTAB	C_6H_6	88
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	PEG-400	C_6H_6	96
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	PEG-600	C_6H_6	96
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	PEG-1500	C_6H_6	90
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	$(CH_3)_4NCl$	C_6H_6	67
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	$(C_2H_5)_4NBr$	C_6H_6	64
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	$(C_2H_5)_4NI$	C_6H_6	70
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	18-C-6	C_6H_6	68
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	PEG-600	CH_2Cl_2	82
 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-Cl}$	 $\mathrm{Ph-\underset{\overset{\Vert}{O}}{C}-S-S-\underset{\overset{\Vert}{O}}{C}-Ph}$	PEG-600	CH_3CN	86

a) The total reaction time was 3 h.

b) The reaction was performed at 0–10℃.

c) Yield of isolated product.

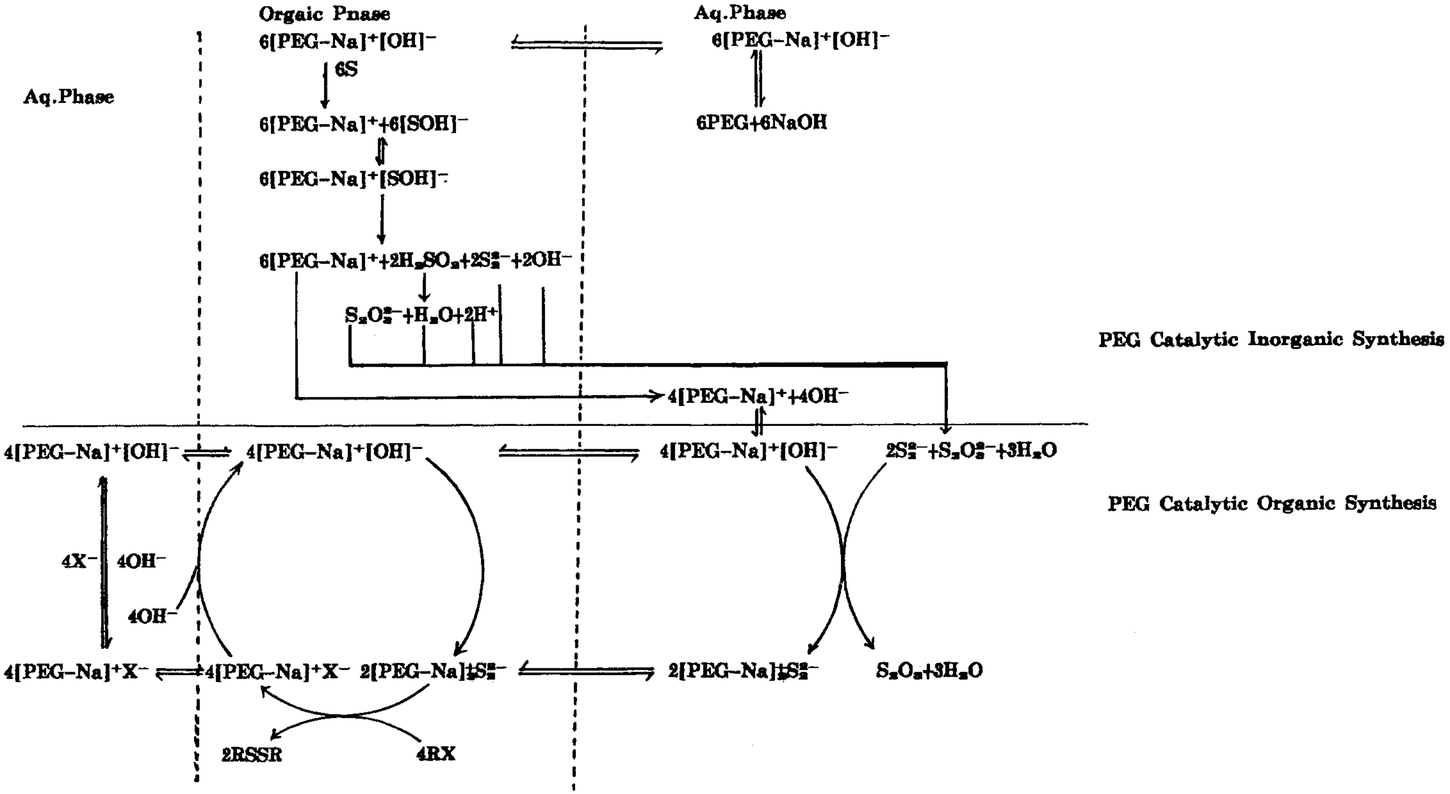
without them. The reaction of sulfur with sodium hydroxide was continued for 8 h at 70–80℃, but with no yellow(S_2^{2-}) in the aqueous layer. Only a few drops of PEC- 400 was added into the system, the aqueous layer becomes yellow after 5 minutes. When the same reaction is carried out without the phase transfer catalyst the yield of diacyl disulfide is only 15%. It seems that phase transfer catalysts not only effect the inorganic reaction but also catalyze the synthasis of diacyl disulfides.

An original attempt was made to introduce phase transfer catalysis into inorganic reaction system by Deng and Chen.[11] Deng et al.,[12] have also reported the mechanism of a sulphur disproporionation reaction at dilute alkali under phase transfer conditions, which is the same as the one which occurs at high temperature.

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

Under concentrated alkali,the mechanism is different, because the reaction appcarance and yields of diacyl disulfides can not be explained using the mechanism given by Deng and Chen.[11,12] On the basis of our experimental results, we tentatively propose the mechanism shown in Scheme 2.

We consider that the mechanism include two part, inorganic synthesis and organic synthesis under phase transfer catalysis. 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$[PEG\text{–}Na]^+OH^-$ which,



R=Acyl; X=Cl,Br

Scheme 2

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 reduction 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. ^{1}HNMR spectra(80 MHz) were recorded in $CDCl_3$ using a FT-80 spectrometer. Microanalyses were measured using Carlo Elba 1106 microelemental analyser.

General Procedure.-Sulfur powder (12.5 mmol) was dissolved in benzene(30 ml) then reacts with sodium hydroxide (5N 20 ml) at 65-70℃ under PEG-400 (0.005 mmol) to give the yellow solution of sodium disulfide. Then the reactor was cooled to 0-10℃ with ice and acyl chloride (10 mmol) was added dropwise into the mixture. When the yellow color disappeared in the aqueous layer, the reaction was completed. The organic layer was separated, washed with water (3 × 10 ml), and dried ($MgSO_4$). The solvent was removed by evaporation under reduced pressure to afford the pure diacyl disulfide.

Bis(3-phenylacryloyl) Disulfide 1. m.p 140-141℃ (lit.,[10,15] 135-135.5℃; 139℃); IR ν max KBr /cm^{-1} 3120w, 1704s, 1684s, 686w, 622w; 450w; ^{1}H NMR(80 MHz, $CDCl_3$) δ 6.79 (s, 2H, –CH=C), 6.98 (s, 2H, CH-CO-), 7.37-7.42 (m, 10H, ArH); Anal. Calcd. for $C_{18}H_{14}O_2S_2$: C, 66.21; H, 4.25. Found: C, 66.26; H, 4.29.

Bis(octadecanoyl) Disulfide 2. m.p 72-73℃ IR ν max KBr/cm^{-1} 2950s, 2850s, 1724s, 1700s, 514m, 425w; ^{1}H NMR(80 MHz, CDCl$_3$) δ 0.85–1.29 (q, 66H, (CH$_2$)$_{15}$CH$_3$), 1.50–1.59 (t, 4H, -CH2-CO-); Anal. Calcd. for $C_{36}H_{70}O_2S_2$: C, 72.06; H, 11. 67. Found: C, 72.24; H, 11.71.

Bis(1-naphthylacetyl) Disulfide 3. m.p 111–112℃; IR υmax KBr/cm^{-1} 3044w, 2890m, 1735s, 1718v.s, 653m; 462m; 'H NMR (80 MHz, CDCl$_3$) δ 7.40–7.89 (m, 14H, ArH), 4.40 (s, 4H, –CH$_2$CO–); Anal. Calcd. for $C_{24}H_{18}O_2S_2$: C, 72.11; H, 4.50. Found: C, 71.64; H, 4.48.

Bis(hexadecanoyl) Disulfide 4. m.p 78– 79 ℃ ; IR υ max KBr/cm^{-1} 2953s, 2849s, 1723s, 1699s, 516m, 450w; 'H NMR (80 MHz, CDCl$_3$) δ 0.87–1.30 (q, 58H, ($^{-}$CH$_2$)$_{13}$CH$_3$), 1.55–1.60 (t, 4H,–CH$_2$–CO–), Anal. Calcd. for $C_{32}H_{62}O_2S_2$: C,70.99; H, 11.42. Found: C, 70.85; H, 11.44.

Bis(dodecanoyl) Disulfide 5. m.p 62– 63℃; IR υmax KBr/cm^{-1} 2954s, 2917s, 2848s, 1701s, 1698s, 584m; 464m; 'H NMR (80 MHz, CDCl$_3$) δ 0.89–1.31 (q, 42H, ($^{-}$CH$_2$)$_9$CH$_3$), 1.57–1.61 (t, 4H, -CH$_2$CO–), Anal. Calcd. for $C_{24}H_{46}O_2S_2$: C, 66.66 H, 9.32. Found: C, 66.97; H, 9.23.

Bis(benzoyl) Disulfide 6. m.p 129–130℃; (lit.,[10] 129–130℃); IR υmax KBr/cm^{-1} 3047w, 1700s, 1681s, 674m, 648w, 440w; 'H NMR (80 MHz, CDCl$_3$) δ 7.35–7.70(m, 10H, ArH); Anal. Calcd. for $C_{14}H_{10}O_2S_2$: C, 61.32, H, 3.68. Found: C,61.31; H, 3.65.

Bis(p–nitrobenzoyl) Disulfide 7. m.p 179–180℃; (lit.,[10] 180–180.5℃); IR υmax KBr/cm^{-1} 3105m, 1735s, 1695v.s, 614m, 474m; 'H NMR (80 MHz, CDCl$_3$) δ 7.80–8.20 (q, 8H, ArH, J=8.80); Anal. Calcd. for $C_{14}H_8N_2O_6S_2$: C,46.49, H, 2.30. N, 7.54. Found: C, 46.15; H, 2.20; N, 7.69.

Bis(p–bromobenzoyl) Disulfide 8. m.p 143–144 ℃; IR υmax KBr/cm^{-1} 3070w, 1720s, 1687v.s, 642m, 561m, 449w; 'H NMR (80 MHz, CDCl$_3$) δ 7.60–7.99 (q, 8H, ArH, J=8.76); Anal. Calcd. for $C_{14}H_8Br_2O_2S_2$: C,39.18, H, 1.82. Found: C, 38.89; H, 1.86.

Bis(o-bromobenzoyl) Disulfide 9. m.p 95- 96 ℃ ; IR νmax KBr/cm^{-1} 3100w, 1702s, 1697s, 637w, 476w; 'H NMR (80 MHz, $CDCl_3$) δ 7.21-7.65 (m, 8H, ArH,); Anal. Calcd. for $C_{14}H_8Br_2O_2S_2$: C, 38.65, H, 1.68. Found: C, 38.89; H, 1.86.

Bis(o-chliribenzoyl) Disulfide 10. m.p 86-87℃; IR ν max KBr/cm^{-1} 3109w, 1715s, 1700s, 642w, 448w; 'H NMR (80 MHz, $CDCl_3$) δ 7.19-7.64 (m, 8H, ArH,); Anal. Calcd. for $C_{14}H_8Cl_2O_2S_2$: C,48.93, H, 2.32. Found: C, 48.98; H, 2.35.

Bis(p-chlorobenzoyl) Disulfide 11. m.p 120-121℃; (lit.,[10] 121-122℃); IR νmax KBr/cm^{-1} 3118w, 2875w, 2960w, 1718s, 1685, 634s, 487m; 'H NMR (80 MHz, $CDCl_3$) δ 7.44-8.07(q, 8H, ArH J=8.63); Anal. Calcd. for $C_{14}H_8Cl_2O_2S_2$: C, 48.80, H, 2.30. Found: C, 48.98; H, 2.35.

Bis(o-iodobenzoyl) Disulfide 12. m.p 139-140 ℃; IR νmax KBr/cm^{-1} 3120w, 1770s, 1687s, 642m, 462w; 'H NMR (80 MHz, $CDCl_3$) δ 7.79-8.12 (m, 8H, ArH); Anal. Calcd. for $C_{14}H_8I_2O_2S_2$: C, 36.75, H, 1.70. Found: C, 36.68; H, 1.75.

Bis(p-methylbenzoyl) Disulfide 13. m.p 118-119℃; (lit.,[10,16,17] 118-119℃); IR νmax KBr/cm^{-1} 3100m, 1704s, 1691v.s, 648m, 466w; 'H NMR (80 MHz, $CDCl_3$) δ 7.25-8.02(q, 8H, ArH, J=8.28), 2.44(S, 6H, $-CH_3$); Anal. Calcd. for $C_{16}H_{14}O_2S_2$: C, 63.26; H, 4.61. Found: C, 63.50; H, 4.64.

Bis(m-nitrobenzoyl) Disulfide 14. m.p 138-139℃; IR νmax KBr/cm^{-1} 3120w, 1770s, 1687s, 642m, 462w; 'H NMR (80 MHz, $CDCl_3$) δ 7.79-8.12 (m, 8H, ArH); Anal. Calcd. for $C_{14}H_8N_2O_6S_2$: C, 46.43; H, 2.16.N, 7.38. Found: C, 46.15; H, 2.20; N, 7.69.

Bis(p-methoxybenzoyl) Disulfide 15. m.p 120-121℃; (lit.,[10] 120-121.5℃); IR νmax KBr/cm^{-1} 3118w, 2875-2960w, 1718s, 1685s, 634s, 487m; 'H NMR (80 MHz, $CDCl_3$) δ 7.20-7.69(q, 8H,ArH, J=8.20), 2.38 (S, 6H, $-OCH_3$) Anal. Calcd. for $C_{16}H_{14}O_4S_2$: C, 57.80, H, 4.10. Found: C, 57.49; H, 4.19.

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