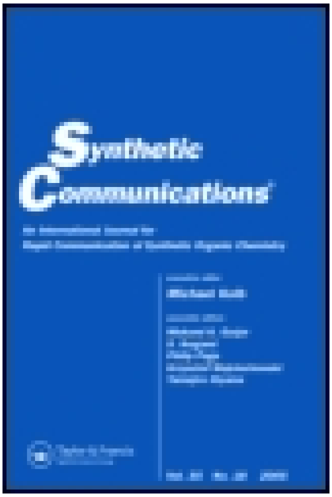

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Synthesis of Diacyl Bisulfides Using a Polymer Supported Reagent

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SYNTHESIS OF DIACYL DISULFIDES USING A POLYMER SUPPORTED REAGENT

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ABSTRACT: Various diacyl disulfides are prepared easily in high yields from the corresponding acid chlorides under mild and non-aqueous conditions using a polymer supported reagent obtained from elemental sulfur and Amberlyst $(OH)^-$. The polymeric reagent is regenerable.

Several methods have been reported in the literature for synthesis of diacyl disulfides. These are, for example, oxidation of thiocarboxylate ions[1], treatment of acyl halides with sodium disulfide[2], lithium disulfide[3], or hydrogen disulfide[4]. As a modified method Kadomari, et al[5] reported synthesis of

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diacyl disulfides from sodium disulfide and acyl halides in a two phase system using an onium salt as a phase transfer agent. Most recently Wang, et al[6] introduced a conveniet method of preparation of the title compound from acyl chlorides using sulfur, benzene/NaOH(aq) system with the help of polyethylene glycol as a PTC. However, each of the above methods suffer from at least one of the following drawbacks: 1) low yields, 2)difficulty in separation of product from the original reagent, 3)use of aqueous medium, 4) reactions to be carried out under PTC conditions, 5)formation of by products, 6)hydrolysis of some acid chlorides under reaction conditions, 7)use of inert atmosphere, and 8)environmental hazard due to toxic nature of sulfur containing starting material.

The immobilization of reagents on polymeric supports has been investigated extensively[7]. This is primarily because insoluble polymeric reagents, among other features, expand the range of applicable solvents, increase the ease of work-up and product purification, lower the environmental hazards, and in most cases provide for recovery and regeneration of the supported reagents.

Having the above facts in mind, we wish to report an improved, efficient and easy synthesis of diacyldisulfides, under mild and nonaqueous conditions, in high yields using a polymer supported reagent.

Polymeric reagent was easily prepared by the reaction of the hydroxide form of Amberlyst A-26 with elemental sulfur in benzene. Presumably, in the presence of OH^- form of the resin and elemental sulfur, $S_2^=$ species are formed[6,8]. This is supported by the fact that on completion of the reactions between this reagent and acyl chlorides high yields of diacyl disulfides were

Table : Conversion of acid chlorides to acyl disulfides using polymer supported reagent[a].

Entry	Acyl chloride	Product[b]	Time(min)	isolated yield (%)
1	$PhCOCl$	$(PhCOS)_2$	20	98
2	p-$MePhCOCl$	$(p$-$MePhCOS)_2$	30	94
3	p-$NO_2PhCOCl$	$(p$-$NO_2PhCOS)_2$	50	90
4	o-$ClPhCOCl$	$(o$-$ClPhCOS)_2$	50	94
5	$PhCH{=}CHCOCl$	$(PhCH{=}CH$-$COS)_2$	20	92
6	$PhCH_2COCl$	$(PhCH_2COS)_2$	20	96
7	CH_3COCl	$(CH_3COS)_2$	15	83

a) Reaction performerd in benzene at room temperature.

b) Products were identified by comparison of their melting points, IR, and ^{1}HNMR spectra with those of the authentic samples.

obtained as the only products. The amount of $S_2^=$ on the polymer was estimated, by the amount of an acid chloride consumed in a reaction, as 1.2 mmol $S_2^=$ per gram of the reagent. Table I shows the conversion of several acyl chlorides to their corresponding diacyl disulfides using this polymer supported reagent. Benzene proved to be the best reaction medium.

The advatages of this method of diacyl disulfide synthesis are, 1)the reaction can be performed in non-aqueous medium that is suitable for water sensetive substrates or those that undergo hydrolysis, for example, acetyl chloride is reported to undergo hydrolysis when a two-phase system is used[6],

2) low reaction times and high yields 3) excess of the reagent can be used, 4) pure products can be obtained by simple filtration and subsequent evaporation of the solvent, and 5) the polymeric reagent is easily regenerable.

In conclusion simple work up procedure and the advantages mentioned above make this method useful in the synthesis of a variety of diacyl disulfides.

EXPERIMENTAL

Amberlyst A-26(OH)$^-$ and benzene were purchased from Fulka company. Required acyl chlorides either were purchased from Fluka or were prepared in our laboratory from corresponding carboxylic acids according to the known procedures. Reaction products were identified by comparison of the IR, melting point, and ^{1}HNMR with those of the authentic samples.

Preparation of the Polymeric Reagent and General Procedure for Converison of Acyl Chlorides to Diacyl Disulfides.

Amberlyst A-26 (OH)$^-$ was dried under vacuum in the presence of P_2O_5 at 40°C for 6 hrs. Dried resin (1 g) was added to a solution of sulfur (3 g) in dry benzene (40 ml), and the mixture was stirred at 45°C for 40 minutes. Color of the resin changed from light yellow to red-brown. Solvent was decanted and now the supported resin washed several times with dry benzene until no sulfur remained. To the suspension of the resin in benzene (15 ml)[9], acid chloride (1.5 mmol) was added and the mixture was stirred at room temperature while the color changed from red-brown to original yellow. Progress of the reaction was followed by TLC (eluent: CCl_4/ether, 4/1). On completion of reaction the mixture was filtered and washed with dry benzene. Evaporation of the combined filtrates afforded the pure products in 83-98% yields.

The spent polymeric reagent was regenerated by repeated washings with NaCl solution and subsequent treatment with sodium hydroxide solution (2N) and finally with distilled water. This resin was then supported according to the above procedure, and shows the same efficiency in reactions as the original.

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9. Polymer supported reagent has to be used in the wet form. It will slowly lose its activity if dried.

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