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Abstract: This work deals with reaction of alkyl halides with carbon disulfide in the presence of basic alumina as heterogeneous and reusable reagent. It afforded symmetrical dialkyl trithiocarbonate in moderate to excellent isolated yields. Reaction of 1,2-dichloro ethane with carbon disulfide also proceeded in a similar manner to give a five-membered cyclic trithiocarbonate without formation of any polymeric by-product.

Keywords: Basic alumina, cyclic trithiocarbonate, symmetrical dialkyl trithiocarbonate

Trithiocarbonate compounds constitute an important class of organosulfur compounds that have been used as intermediates for various applications, especially as pesticides, insecticides, and nematocides in agriculture^[1] and as lubricating additives.^[2] In addition to reported insecticidal and fungicidal activities^[3] for several members of the class of organic trithiocrabonates, recently the successful appllication of dibenzyl trithiocarbonate in the living/controlled free-radical polymerization under ⁶⁰Co γ -irradiation was reported.^[4]

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Some procedures for the synthesis of trithiocarbonates have been developed that employ reaction of thiols with thiophosgene,^[5] chlorodithioformates,^[1] or carbon disulfide and alkyl halides under basic conditions.^[6] Another method that appears to be the most widely used involves dialkylation of trithiocarbonate anion with alkyl halides in a two-phase system using an onium salt as a phase-transfer agent.^[3] In 1995, a report by Leung et al.^[7] showed that the reaction of alkyl halides, granulated KOH, and carbon disulfide in anhydrous THF occurs smoothly to give symmetrical trithiocarbonates without requiring the addition of a phase-transfer catalyst (PTC). Very recently a novel procedure for preparation of symmetrical dialkyl trithiocarbonates was reported.^[8] In this method, alkyl halide was reacted with an equivalent of carbon disulfide and cesium carbonate in polar aprotic solvents. Most of these methods have at least one of the following drawbacks: (1) long reaction times, (2) low yields of products, (3) difficulty in separating product from the original reagent and PTC, (4) necessary presence of a PTC, (5) use of aqueous media, (6) use of toxic chemicals such as alkane thiols and thiophosgene, (7) use of an inert atmosphere, and (8) unavailability of the reagents. Therefore the introduction of a new synthetic method for preparation of dialkyl trithiocarbonates is of practical importance.

Alumina (Al₂O₃) is a key industrial material with numerous applications in refining and petrochemistry.^[9] This metal oxide is widely used industrially as filler, adsorbent, drying agent, catalyst, catalyst support, and reagent. γ -Alumina is the transition alumina with a basic property most commonly utilized to carry out surface organic chemistry.^[10,11] In contrast to clays and zeolites, this material does not contain accessible channels or cavities and shows a large surface area and highly porous exteriors available to substrates.

As previously reported, the trithiocarbonate anions $CS_3^{2^-}$ is prepared by treating ammonium sulfide, strong aqueous ammonia, alkali-metal sulfide, or aqueous alkali-metal hydroxide with carbon disulfide.^[12] To increase the yield and reactions rate, a PTC has often been used to promote the reactions in two-phase systems.^[3] Recently, we reported in a short communication the one-pot synthesis of symmetrical dialkyl trithiocarbonates directly from CS_2 and alkyl halides using a commercially available hydroxide form of an anion exchange resin.^[12] The remarkable ability of the basic alumina to promote the various reactions^[13–15] together with reported insecticidal and fungicidal activites of symmetrical dialkyl trithiocarbonate gave us impetus for planning syntheses of various types of symmetrical trithiocarbonates in a one-pot procedure using basic alumina as a cheap, heterogeneous, and



Scheme 1.

Basic Al₂O₃ as Heterogeneous Reagent

reusable reagent. Thus, several symmetrical dialkyl trithiocarbonates were easily prepared by simple mixing of alkyl halides or tosylates with suspension of basic alumina in CS_2 (Scheme 1).

This article shows that this solid base is able to facilitate the generation of the trithiocarbonate anion. It is supported by the fact that benzyl chloride (1 mmol), as a model compound in the presence of basic alumina (2 g) and in CS_2 as solvent and the only sulfur-containing reactant, was easily converted to the corresponding dibenzyl trithiocarbonate under reflux conditions. A set of experiments on the preparation of dibenzyl trithiocarbonate showed that the addition of more than 2 g of basic alumina to the reaction mixture (1 mmol of benzyl chloride in 10 ml of CS_2) does not produce an appreciable increase in the reaction rate, moreover, the conversion of the starting material to the product is not complete even for prolonged reaction times when the alumina proportion is less than 1.5 g. It is worth noting that an increase in reactivity is observed when the required alumina was added to the reaction mixture in two portions.

To establish the generality and applicability of this method, various primary, secondary, allylic, and benzylic halides and some tosylates were subjected to the same reaction conditions to furnish the corresponding symmetrical dialkyl trithiocarbonates in moderate to excellent isolated yields (Table 1). As expected, the absolute regioselectivity was observed for the case of 2-chlorobenzyl alcohol, and the only benzylic site was attached by transient CS_3^{2-} species. A notable point of this method is that in case the alkyl halide or tosylate is not soluble in CS_2 , it has been necessary to carry out the reaction in the presence of a few drops of THF.

Contrary to previous reports on the preparation of cyclic trithiocarbonates,^[16] our procedure provides excellent yields of 1,3-dithiolane-2-thione from 1,2-dichloroethane without formation of any polymeric by-product. An attempt to totally convert 1,2-dichloroethane to 1,3-dithiolane-2-thione failed, and yield of the product after evaporation of intact 1,2-dichloroethane and CS₂ was only 48%. It is also worth mentioning that the nature of the leaving group has a considerable effect on the reaction rate. The order of reactivity for different substrates is ROTs > RI > RBr> RCI. The basic alumina can be reused several times without loss of activity. The alumina, recovered by filtration and washed with methanol, has been reused four times to convert benzyl chloride to the dibenzyl trirhiocarbonate, affording the corresponding trithiocarbonate in 85%, 82%, 81%, and 82% yield, respectively.

In summary, this article shows a simple and efficient general access to pure symmetrical trithiocarbonates. Basic alumina, which has been used here for the first time for such conversion, is inexpensive and commercially available. Another interesting behavior of alumina is that it can be reused after simple washing with methanol. The reactions are remarkably clean, and no chromatographic separation is necessary to get the spectrally pure compounds except in a few cases (Table 1, entries 5 and 13) where some starting materials remained because the conversion was less than 100%.

Number	Starting material	Products	Time (h)	Yield (%)
1	CH ₂ Cl		4	85
2	CI CH ₂ CI		6	92
3	O ₂ N-CH ₂ Br	$O_2N - CH_2 - S - CH_2 - S - CH_2 - NO_2$	15	95
4	O2N-CH2CI	O_2N CH_2-S CH_2-S-CH_2 NO_2	30	88
5		CH-S-C-S-CH	5	79
6	CH ₃ I	CH3-S-CH3	2	44

Table 1. Conversion of alkyl halides and tosylates to the corresponding dialkyl trithiocarbonates using basic alumina



Notes. All reactions were carried out in refluxing carbon disulfide. Dialkyl trithiocarbonates were identified by their IR and NMR spectra and also by comparison of their other physical data with those reported.^[12]

Basic Al₂O₃ as Heterogeneous Reagent

EXPERIMENTAL

Alkyl halides and tosylates were from Fluka and Merck or prepared in our laboratory from corresponding alcohols according to known procedures.^[17] All products are known compounds and are identified by comparison of their physical and spectral dat (IR and NMR) with those previously reported.^[12] *Caution*: care should be taken in using CS₂ because of its toxicity and low flash point; therefore, all of the reactions must be carried out under a powerful laboratory fume hood.

General Procedure for the Synthesis of Dialkyl Trithiocarbonates using Basic Alumina

To the suspension of basic Al_2O_3 (1 g) in carbon disulfide (10 ml), alkyl halide or tosylate (1 mml) was added (in cases where alkyl halide or tosylate was not soluble in CS_2 , a few drops of THF were added to the reaction mixture). The reaction mixture was stirred under reflux conditions. In this case, the yellow color often developed immediately and darkened with progress of the reaction. After about 1 h, additional basic alumina (1 g) was added to the reaction mixture and stirred under reflux conditions. The progress of the reaction was followed by thin-layer chromatography (TLC) (CCI₄). On completion of the reaction, the mixture was filtered and washed with carbon disulfide or THF. The filtrate was dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to affored the pure products (TLC, ¹H NMR) in 44–95% isolated yields.

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Basic Al₂O₃ as Heterogeneous Reagent

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