J. Chem. Research (S),
1998, 454–455†

Synthesis of Symmetrical Dialkyl Trithiocarbonates Using a Polymer Supported System†

Bahman Tamami* and A. R. Kiasat

Department of Chemistry, Shiraz University, Shiraz, Iran

Symmetrical dialkyl trithiocarbonates were readily snythesized in excellent yields from alkyl halides and carbon disulfide under mild reaction condition in the presence of a regenerable hydroxide form of an anion exchange resin.

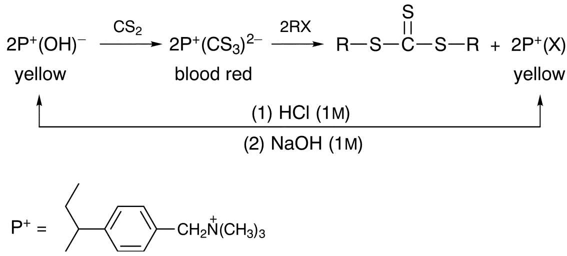
Dialkyl trithiocarbonates constitute an important class of compounds that are very useful intermediates for preparation of pesticides in agriculture[1–3] and lubricating additives.[3,4] Their synthesis has received considerable attention and several methods have been utilized, *e.g.* reactions of thiols with thiophosgene,[5] chlorodithioformates,[2] or with 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.[7] In this case carbon disulfide is first converted into a trithiocarbonate anion under strong basic conditions.[8] The anion is then transferred by a phase-transfer agent from the aqueous to the organic phase to complete a nucleophilic substitution reaction with the alkyl halide. Recently Leung *et al.*.[9] discovered that the reaction between alkyl halides, granulated KOH and carbon disulfide in anhydrous THF occurs smoothly to give symmetrical trithiocarbonates without requiring the addition of PTC. Each of the above methods has at least one of the following drawbacks: (1) long reaction time, (2) low yields of products, (3) difficulty in separating product from the original reagent and PTC, (4) necessary presence of a phase transfer catalyst (PTC), (5) use of aqueous media, (6) use of toxic chemicals with unpleasant odours such as alkane thiols and thiophosgene, (7) use of an inert atmosphere and (8) unavailability of the reagents. Therefore the introduction of a new method for preparation of dialkyl trithiocarbonates is of practical importance.

The immobilization of reagents on polymeric supports has been investigated extensively.[10] 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 enable the recovery and regeneration of the supported reagents.

In continuation of our efforts to utilize polymer-supported systems in chemical reactions,[11,12] we describe a new approach to easy and efficient one-step synthesis of symmetrical dialkyl trithiocarbonates directly from carbon disulfide and alkyl halides using a commercially available hydroxide form of an anion-exchange resin.

Results and Discussion

The blood red trithiocarbonate anion CS_3^{2-} is prepared by treating ammonium sulfide, strong aqueous ammonia, alkali-metal sulfide or aqueous alkali-metal hydroxide with carbon disulfide.[8] To increase the yield and reaction rate, a PTC has often been used to promote the reactions in two-phase systems.[7] However, we discovered that polymer-supported thrithiocarbonate can easily be formed from carbon disulfide in the presence of the hydroxide form of anion-exchange resin Amberlyst A-26. Thus, several symmetrical dialkyl trithiocarbonates were prepared by the reaction of this polymer-supported trithiocarbonate, formed *in situ*, with alkyl halides (Scheme 1).



Scheme 1

Formation of polymer-supported trithiocarbonate is indicated by a distinct change of the resin from light yellow to blood red when it is added to carbon disulfide. It is supported by the fact that, on completion of the reaction between this reagent and alkyl halides, dialkyl trithiocarbonates with high yields are obtained as the only products. With progress of the reaction the resin changes from blood red to yellow.

Primary, secondary, allylic and benzylic halides are converted into corresponding dialkyl trithiocarbonates as exclusive and virtually pure products according to TLC and ^1H NMR in considerably short times and in excellent yields (Table 1). Contrary to previous reports on the preparation of cyclic trithiocarbonates,[7d,14] our procedure provides excellent yields of 1,3-dithiolane-2-thione from 1,2-dibromoethane in a comparatively very short time (entry 5), without formation of any polymeric by-product. It is worth also mentioning that the nature of the halide ion has a considerable effect on the reaction rate. The order of reactivity for different alkyl halides is RI > RBr > RCl.

In conclusion, the present procedure has the following advantages:(1) reaction work-up is very easy and product

Table 1 Conversion of alkyl halides into dialkyl trithiocarbonates using the polymer-supported system[a]

RS—CS—SR[b]	RX	Reaction time/h	Isolated yield (%)
1	$PhCH_2Br$	1.5	96
2	$PhCH{=}CHCH_2Br$	1.5	91
3	p-$O_2NC_6H_4CH_2Br$	2	93
4	$CH_2{=}CHCH_2Br$	0.5	94
5	$BrCH_2CH_2Br$	1.5	91
6	CH_3I	1	90
7	$CH_3CHBrCH_2CH_3$	7	90
8	C_4H_9Cl	7	91
9	C_4H_9Br	4	95
10	C_4H_9I	2.5	93

[a] All reactions carried out in refluxing carbon disulfide. [b] Dialkyl trithiocarbonates were identified by their IR and NMR spectra and also by comparison of their other physical data with those reported.[2,3,7d,9,13]

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

isolation consists of simple filtration of spent polymeric reagent and evaporation of the solvent, (2) reactions occur in an organic solvent, CS_2, which acts also as the only sulfur-containing reactant, (3) high yields of products are obtained in considerably short reaction times, and (4) the polymeric support can be regenerated and reused repeatedly. This one-pot procedure can be used as an easy, mild, efficient, versatile and safe alternative to already available methods, and is suitable for macroscale laboratory preparation. Its extension to the synthesis of unsymmetrical dialkyl trithiocarbonates is in progress.

Experimental

IR spectra were recorded on a Perkin-Elmer IR-157-G spectrophotometer, ^1H NMR spectra in $CDCl_3$ on a Bruker Avance DPX instrument (250 MHz). Chemical shifts are reported in ppm (δ) downfield from TMS. Amberlyst A-26 (OH^-) and carbon disulfide were from Fluka. Alkyl halides were from Fluka and Merck or prepared in our laboratory from corresponding alcohols according to known procedures. **CAUTION**: care should be taken in using CS_2 due to its toxicity and low flash point.

General Procedure for the Synthesis of Dialkyl Trithiocarbonates using the Polymer-supported System.—Amberlyst A-26 (OH^-) (2 g, 1 mmol OH^- g^{-1}, 20–50 mesh) was added to carbon disulfide (10 ml), and stirred at room temperature for about 3 min. The resin changed from light yellow to blood red. To this suspension was added alkyl halide (1 mmol) and the reaction mixture stirred under reflux. The progress of the reaction was followed by TLC (CCl_4). On completion of reaction the mixture was filtered and washed with carbon disulfide or THF. The filtrate was dried over anhydrous sodium sulfate and solvent evaporated under reduced pressure to afford the pure products (TLC, ^1H NMR) in 90–96% isolated yields. The spent polymeric reagent was regenerated by repeated washings with HCl solution, treatment with sodium hydroxide (1 M) solution, and finally with distilled water. The regenerated resin can be used repeatedly as the polymeric support. One hundredfold scale-up reactions could be performed.

Bis(phenylmethyl) trithiocarbonate **1**:[3,9] IR, 1065 cm^{-1} ($C{=}S$); ^1H NMR, δ 7.36–7.41 (5 H, m), 4.71 (2 H, s). Bis(3-phenylprop-2-enyl) trithiocarbonate **2**:[9] IR, 1065 cm^{-1} ($C{=}S$); ^1H NMR, δ 7.28–7.45 (5 H, m), 6.71 (1 H, d), 6.3 (1 H, m) and 4.25 (2 H, d). Bis(*p*-nitrophenylmethyl) trithiocarbonate **3**: IR, 1060 cm^{-1} ($C{=}S$); ^1H NMR, δ 7.4 (2 H, d), 7.98 (2 H, d) and 4.7 (2 H, s). Di(prop-2-enyl) trithiocarbonate **4**:[2,3,9] IR, 1060 cm^{-1} ($C{=}S$); ^1H NMR, δ 5.94 (1 H, m), 5.27 (1 H, d), 5.21 (1 H, d) and 4.1 (2 H, d). 1,3-Dithiolane-2-thione **5**:[3,9,13] IR, 1065 cm^{-1} ($C{=}S$); ^1H NMR, δ 4 (2 H, s). Dimethyl trithiocarbonate **6**:[7d,13] IR, 1070 cm^{-1} ($C{=}S$); ^1H NMR, δ 2.8 (3 H, s). Di-*sec*-butyl trithiocarbonate **7**:[7d] IR, 1065 cm^{-1} ($C{=}S$); ^1H NMR, δ 4.2 (1 H, m), 1.71 (2 H, m), 1.41 (3 H, d) and 1.1 (3 H, t). Dibutyl trithiocarbonate **8**,**9**,**10**:[2,3,9] IR, 1050 cm^{-1} ($C{=}S$); ^1H NMR, δ 3.4 (2 H, t), 1.73–1.67 (2 H, m), 1.5–1.39 (2 H, m) and 0.98 (3 H, t).

We are grateful to Shiraz University Research Council for partial support of this work.

Received, 5th January 1998; Accepted, 27th April 1998
Paper E/8/00161H

References

1 W. D. Habicher and R. Mayer, *DDR Pat.*, 67416, 1969 (*Chem. Abstr.*, 1970, **72** 12149).

2 H. C. Godt and A. E. Wanns, *J. Org. Chem.*, 1961, **26**, 4047 and refs therein.

3 L. Degani, R. Fochi, A. Gatti and V. Regondi, *Synthesis*, 1986, 894 and refs therein.

4 N. N. Kozhemyakina, Vinogradova and I. E. Neftepererab, *Neft Khim.* (*Moscow*), 1973, **1**, 19 (*Chem. Abstr.*, 1973, **79**, 21264).

5 F. Duus, in *Comprehensive Organic Chemistry*, ed. D. Barton and W. D. Ollis, Pergamon, New York, 1979, vol. 3, p. 342; M. Bogemann, S. Peterson, O. E. Schultz and H. Soll, in *Methoden der organischen chemie*, ed. E. Muller, Houben-Weyl, Berlin, 1955, vol. 9, p. 804.

6 A. Sugawara, M. Shirahata, S. Sato and R. Sato, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 3353; P. J. Wepplo and P. P. Wright, Jr., *Ger. Pat.*, 2937334, 1980 (*Chem. Abstr.*, 1980, **93**, 149828d).

7 (*a*) F. Runge, Z. El-Hewchi, H. J. Renner and E. Taeger, *J. Prakt. Chem.*, 1960, **11**, 284; (*b*) Y. Hori, Y. Nagano, S. Miyake, S. Teramoto and H. Taniguchi, *Chem. Express*, 1986, **1**, 311; (*c*) A. Sugawara, K. Huscgawa, K. I. Suzuki, Y. Takahashi and R. Sato, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 435; (*d*) A. W. M. Lee, W. H. Chan and W. C. Wong, *Synth. Commun.*, 1988, **18**, 1531; (*e*) R. Herges and C. Hoock, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1611.

8 E. Wertheim, *J. Am. Chem. Soc.*, 1926, **348**, 836.

9 M. K. Leung, D. T. Hsich, K. H. Lee and J. C. Liov, *J. Chem. Res.* (*S*), 1995, 478.

10 D. C. Sherrington and P. Hodge, *Synthesis and Separation Using Functional Polymers*, Wiley, Chichester, 1988; K. Takamato, Y. Inaki and R. M. Ottennbrite, *Functional Monomers and Polymers, Procedures, Synthesis and Applications*, Marcel Dekker, New York, 1987.

11 B. Tamami and A. R. Kiasat, *Synth. Commun.*, 1996, **21**, 3953.

12 B. Tamami and A. R. Kiasat, *Synth. Commun.*, 1998, **28**, 1275.

13 H. Hagiwana, M. Numata, K. Konishi and Y. Oka, *Chem. Pharm. Bull.*, 1965, **13**, 253.

14 L. M. Leung, W. H. Chan and S. K. Leung, *J. Polym. Sci. Part A: Polym Chem.*, 1993, **31**, 1799.