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DIRECT CONVERSION OF CARBOXYLIC ACIDS AND CARBOXYLIC ESTERS INTO S,S'-DIPHENYL ACETALS AND PHENYL SULFIDES WITH THEXYLPHENYLTHIOBORANE

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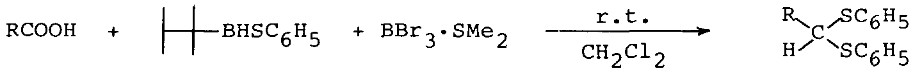
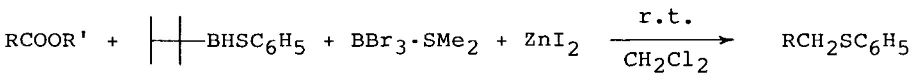
Summary: Reaction of carboxylic acids with thexylphenylthioborane in methylene chloride at room temperature gives S,S'-diphenyl acetals in high yields and carboxylic esters are converted into phenyl sulfides in the presence of zinc iodide under similar conditions.

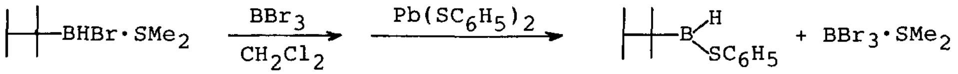
The growing importance of organic sulfur compounds in organic synthesis has recently stimulated the development of numerous useful synthetic methods of the preparation of thioacetals and sulfides.[1] In general, thioacetals are prepared by the acid catalyzed or Lewis acids promoted reaction of aldehydes and ketones with thiols, whereas sulfides are obtained by the alkylation of thiolate anions with alkyl halides. However, there has been no practical method for one-step synthesis of thioacetals and sulfides from carboxylic acids and esters, respectively.

In connection with our research program toward the development of new hydride reducing agents, we have had occasion to study the reducing properties of aryl- and alkylthioboranes. Although it was reported that aryl- and alkylthioboranes hydroborated olefins and readily reduced acids, aldehydes, and ketones to the corresponding alcohols, their synthetic usefulness has been limited due to the facile cleavage of etheral solvents like tetrahydrofuran.[2] We wish to report that thexylphenylthioborane, capable of simultaneously transferring a hydride and phenylmercapto moiety, is exceedingly effective for direct conversion of carboxylic acids and esters into S,S'-diphenyl acetals and phenyl sulfides, respectively.





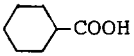
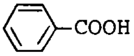
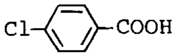
Thexylphenylthioborane was prepared as follows. To a methylene chloride solution (80 ml) of thexylbromoborane-dimethyl sulfide complex (4.40 g, 25 mmol)[3] under nitrogen at room temperature was added boron tribromide (6.25 g, 25 mmol).[4] The reaction mixture was stirred for 1 h and followed by the addition of bis-(phenylthio) lead (5.30 g, 12.5 mmol).[5] After 30 min of being stirred at room temperature, precipitated lead bromide was removed and the resulting solution was transferred to the 100 ml volumetric flask. The concentration of the reagent was adjusted to 0.25M solution by the addition of methylene chloride. The ^{11}B-NMR spectrum of the reagent exhibited a doublet (J_{B-H}=160 Hz) at -8.1 ppm relative to boron trifluoride etherate. The reagent in methylene chloride could be stored in a refrigerator under nitrogen for several weeks without little decomposition.



Direct conversion of carboxylic acids into S,S'-diphenyl acetals has been achieved with 2,2 equiv of thexylphenylthioborane in methylene chloride at room temperature[6] and Table 1 summarizes some typical experimental results. Simple aliphatic acids are generally converted into S,S'-diphenyl acetals in high yields and alicyclic acids, cyclohexanecarboxylic acid and sterically hindered 1-admantanecarboxylic acid, work equally well. Furthermore, carboxylic acids containing bromo and ester group are also converted into S,S'-diphenyl acetals without attacking such reducible functional groups by the reagent. However, reaction of benzoic acid with 2.2 equiv of the reagent gives 71% of phenyl S,S'-diphenyl acetal along with 14% of benzyl phenyl sulfide. The similar result is obtained with p-chlorobenzoic acid. It has been previously noted that a small amount of benzyl phenyl sulfide is formed in the reduction of benzoic acid with phenylthioborane.[2b]

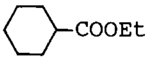
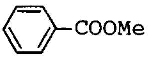
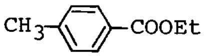
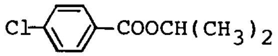
Since carboxylic esters are generally inert to the reagent, we considered the possibility of activating the carbonyl group of esters by the addition of Lewis acids. Among several Lewis acids tested with methyl phenylacetate as a model compound, zinc iodide gives the best results for clean conversion of methyl phenylacetate into benzyl phenyl sulfide. The use of other Lewis acids such as titanium tetrachloride, stannic chloride, and boron trifluoride etherate gives benzyl phenyl sulfide as a major product along with benzyl S,S'-diphenyl acetal and S-phenyl phenylethanethioate in variable ratios. The best condition found for clean reaction is to employ 1.0 equiv of zinc iodide and 2.5 equiv of the reagent for each mole of esters in methylene chloride. Under the present condition, methyl phenylacetate is cleanly converted into benzyl phenyl sulfide in 91% yield in 10 h.[7] Table 2 shows the efficiency, applicability, and scope of the present method. Several esters such as methyl, benzyl, and isopropyl ester are cleanly converted into the corresponding phenyl sulfides in high yields. The present method can be successfully applied to the preparation of

Table 1. Preparation of S,S'-Diphenyl Acetals from Carboxylic Acids[a]

RCOOH	Time,h	Yield, %[b] $RCH(SC_6H_5)_2$	RCOOH	Time,h	Yield, %[b] $RCH(SC_6H_5)_2$
$CH_3(CH_2)_6COOH$	4	87	$Br(CH_2)_{10}COOH$	5	87
$C_6H_5CH_2COOH$	2	81		3	84
$(CH_3)_2CHCOOH$	4	87	1-adamantane-carboxylic acid	5	87
$(CH_3)_3CCOOH$	4	81		7	71(14)[c]
$MeOOC(CH_2)_4COOH$	3	82		6	75(15)[c]

[a] The reaction was carried out with 2.2 equiv of the reagent in methylene chloride at room temperature. [b] The yields refer to isolated products. [c] The numbers in parentheses indicate the isolated yields of benzyl phenyl sulfide and p-chlorobenzyl phenyl sulfide.

Table 2. Preparation of Phenyl Sulfides from Carboxylic Esters.[a]

RCOOR'	Time,h	Yield, %[b] $RCH_2SC_6H_5$	RCOOR'	Time,h	Yield, %[b] $RCH_2SC_6H_5$
$CH_3(CH_2)_6COOCH_2C_6H_5$	10	91	$MeOOC(CH_2)_4COOMe$	15	64[c]
$C_6H_5CH_2COOMe$	10	91	1-admantanecarboxylic methyl ester	15	81
$C_6H_5CH_2COOCH(CH_3)_2$	10	93		8	82
$Br(CH_2)_5COOMe$	11	83		15	78
	20	73		20	72

[a] The reaction was carried out with 2.5 equiv of the reagent and 1.0 equiv of zinc iodide in methylene chloride at room temperaure. [b] The yields refer to isolated products. [c] 5.0 Equiv of the reagent and 2.0 equiv of zinc iodide were used.

various phenyl sulfides from esters of structurally different carboxylic acids including sterically hindered acids and aromatic acids.

Further studies on the synthetic utility of thexylphenylthioborane and related reagents and mechanistic insights of the present reactions are in progress.

Acknowledgment. We gratefully acknowledge the financial support from Korea Science and Engineering Foundation.

References and Notes

1. (a) A. I. Meyer, " Heterocycles in Organic Synthesis ", Wiley Insterscience, New York, 1974. (b) B. T. Grobel and D. Seebach, *Synthesis*, 357 (1977). (c) E. Block, " Reaction of Organo Sulfur Compounds ", Academic Press, New York, 1978.
2. (a) D. J. Pasto, *J. Am. Chem. Soc.*, *84*, 3777 (1962). (b) D. J. Pasto, C. C. Cumbo, and P. Bulasubamaniyan, *J. Am. Chem. Soc.*, *88*, 2187 (1966).
3. Thexylbromoborane-dimethyl sulfide complex was prepared by the hydroboration of 2,3-dimethyl-2-butene with monobromoborane-dimethyl sulfide complex in methylene chloride.
4. Thexylbromoborane-dimethyl sulfide complex did not react with bis(phenylthio) lead to give thexylphenylthioborane. Thus, boron tribromide was added to liberate thexylbromoborane.
5. R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.* (A), 947 (1967).
6. In a typical experiment, to a solution of phenylacetic acid (186 mg, 1.35 mmol) in methylene chloride (5 ml) at room temperature was added a solution of thexylphenylthioborane and boron tribromide-dimethyl sulfide complex in methylene chloride (0.25M, 12 ml, 3.0 mmol). The reaction mixture was stirred at room temperature for 2 h and evaporated to dryness under reduced pressure. The residue was passed through a short column of silica gel using ethyl acetate and hexane (1:10) as an eluant to yield benzyl S,S'-diphenyl acetal (356 mg, 81%). It is noteworthy that 1-phenyl-2-phenylthioethene and phenyl acetaldehyde were also formed in 15-20% yield, respectively, when the reaction mixture was quenched with 3N NaOH or 10% HCl.
7. In addition to benzyl phenyl sulfide, methyl phenyl sulfide was also isolated in 70% yield.

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