DIRECT CONVERSION OF SATURATED AND UNSATURATED CARBOXYLIC ACIDS INTO ALDEHYDES BY THEXYLBROMOBORANE-DIMETHYL SULFIDE

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Summary: Thexylbromoborane-dimethyl sulfide readily reduces aliphatic carboxylic acids, including α, β -unsaturated ones, to aldehydes in excellent yields. However, the yields of aromatic aldehydes vary with the substituents.

The development of an apparently ideal reagent, thexylchloroborane-dimethyl sulfide, for the direct partial transformation of acyclic and alicyclic carboxylic acids into aldehydes solved an important long-standing problem in organic synthesis.^{1,2} In the course of a systematic study of the reducing characteristics of thexylbromoborane-dimethyl sulfide,³ we have found that this reagent, as well, selectively converts carboxylic acids to the corresponding aldehydes in the presence of several functionalities, including double bonds. We now describe this facile reduction of such carboxylic acids, including d, β -unsaturated ones, to the corresponding aldehydes by thexylbromoborane-dimethyl sulfide.

The reagent, thexylbromoborane-dimethyl sulfide, is readily prepared by hydroborating 2,3-dimethyl-2-butene with monobromoborane-dimethyl sulfide in methylene chloride.⁴ Monobromoborane-dimethyl sulfide is easily prepared by treating borane-dimethyl sulfide with a half equiv of bromine in carbon disulfide.⁵

Thexylbromoborane-dimethyl sulfide reduces aliphatic carboxylic acids to aldehydes in yields of 92-99%. Regardless of the structural types of the aliphatic acids, the yields of aldehydes are almost quantitative within 1 h at room temperature. Even aliphatic diacids such as succinic, adipic, 1,10-decanedicarboxylic, α -camphoric and maleic acids are converted into the dialdehydes in yields of 93-99%. Alicyclic carboxylic acids such as cyclopropane- and cyclohexanecarboxylic acids work equally well.

The reagent tolerates many organic functionalities, viz., esters, epoxides, acid chloride, halides and nitro compounds. For example, haloaliphatic acids provide the corresponding haloaldehydes in good yields(85-95%). However, the most interesting feature of this reagent is its reluctance to hydroborate double bonds.

Thexylbromoborane-dimethyl sulfide is a much milder and hence more selective reducing agent than thexylchloroborane-dimethyl sulfide, ⁶ and simple olefins are resistant to hydroboration with this reagent even at room temperature. whereas the chloro-derivative readily hydroborates double bonds. Thus, d,β -unsaturated carboxylic acids such as methacrylic, crotonic and cinnamic acids are readily converted into the corresponding olefinic aldehydes in yields of 94-99%

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without attack on the double bond.



Table 1. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids with Thexylbromoborane-Dimethyl Sulfide in Carbon Disulfide^a-Methylene Chloride at Room Temperature^{ℓ}

Acid	Yield of aldehyde(%) ^c	Acid	Yield of aldehyde(%) ^C
Acetic	87	Cyclohexanecarboxylic	99(89) ^e
Butyric	92	Chloroacetic	95
Hexanoic	94	Bromoacetic	85
Decanoic	94	6-Bromohexanoic	95
Stearic	98(92) ^d	Methacrylic	94
Isobutyric	99	Crotonic	94
Isopentanoic	98	Cinnamic	99(87) ^e
Pivalic	89	Benzoic	49
Phenylacetic	90	x- Naphthoic	45
Diphenylacetic	89	Terephthalic	95
Triphenylacetic	95	m-Nitrobenzoic	75
Succinic	93	o-Chlorobenzoic	93
Adipic	99	m-Chlorobenzoic	81
1,10-Decanedicarboxylic	99	p-Aminobenzoic	90
Cyclopropanecarboxylic	99	p-Cyanobenzoic [£]	90(81) ^d

^{a)}Essential solvent for the hydrogen evolution step: less than 50 volume % in total reaction mixture. ^{d)}Aliphatic carboxylic acids were reacted with 5% excess reagent(2.1 equiv for monocarboxylic and 4.2 equiv for dicarboxylic acids) for 1 h, and aromatic carboxylic acids with 50% excess reagent(3 equiv for monocarboxylic and 6 equiv for dicarboxylic acids) for 9 h, both at room temperature, after the hydrogen evolution at -20°C. ^{c)}Analysis with 2,4-di-nitrophenylhydrazine. ^{d)}Yields are based on the analytically pure aldehydes isolated after evaporation of solvent, following treatment of the adduct with formaldehydes.^{1,7} ^{e)}Yields of distilled product. ^{f)}Reacted with 3.1 equiv of reagent; only terephthalaldehyde formed.

The reduction of aromatic carboxylic acids by this reagent is sluggish, requiring 3 equiv of the reagent and 9 h at room temperature. The yields are significantly lower than those in the aliphatic series and it appears that they may be influenced by substituents on the aromatic ring. For example, the yields of both benzoic and \measuredangle -naphthoic acids were ca. 50%, whereas the yields of m-nitro-, o-chloro-, m-chloro- and p-aminobenzoic acids were much better(75-93%). On the other hand, the reduction of terephthalic acid with 6 equiv of the reagent gave the corresponding dialdehyde in very good yield(95%).

The nitrile function of p-cyanobenzoic acid was also partially reduced; the reaction with 3.1 equiv of the reagent gave terephthalaldehyde in a yield of 90%. The possibility for transformation of nitriles into aldehydes is under study.

The bisulfite procedure for the isolation of aldehyde products, adopted for reactions with thexylbromoborane-dimethyl sulfide, ¹appeared also to be applicable to this case. The isolated yields using this procedure are quite reasonable.

The following procedure for reduction of cyclohexanecarboxylic acid is illustrative. An oven-dried, 100 mL flask, fitted with a side-arm and a bent adapter connected to a mercury bubbler, was charged with 53 mmol of cyclohexanecarboxylic acid and 35 mL of carbon disulfide.⁸ The flask was immersed in a cold bath and maintained at -20° C. One equiv of precooled(0° C) thexylbromoborane-dimethyl sulfide solution in methylene chloride was added dropwise with stirring. After complete evolution of the hydrogen, the cold bath was removed and the reaction mixture was warmed to room temperature. The other 1.1 equiv of the reagent was added and the reaction mixture was stirred for 1 h at room temperature. Analysis of an aliquot with 2,4-dinitrophenylhydrazine indicated a yield of 99%.

The rest of the reaction mixture(50 mmol) was transferred via a double-ended needle to a flask containing 50 mL of cold water in an ice-water bath and then hydrolyzed with vigorous stirring for 1 h at room temperature. The mixture was saturated with sodium chloride and the separated organic layer was subjected to the sodium bisulfite isolation procedure.^{1,7} The yield of pure cyclohexane-carboxaldehyde was 89%.

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References and Notes

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- 8. We have observed that carbon disulfide seems to be essential in the solvent for the step of hydrogen evolution. Carbon disulfide readily dissolves hydrogen bromide (<u>3</u>), which is formed competitively from the reaction of carboxylic acid and reagent. The dissolved hydrogen bromide then reacts with thexylacyloxyborane (<u>2</u>), the undesired intermediate, and thus converts it into the desired intermediate, thexylacyloxybromoborane (<u>1</u>).



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