

Synthetic Applications of Organoantimony Compounds

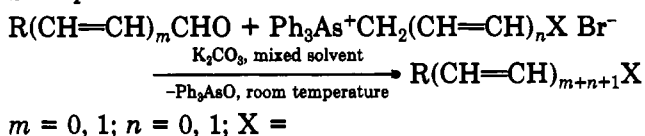
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The birth of the Wittig reaction in 1953 marked the entry of ylides into the arsenal of important synthetic tools.¹ Since then, the Wittig olefination has engendered continuous synthetic and mechanistic interest.² Variants of the Wittig reaction have advantages over the use of phosphoranes.²⁻⁴ The Wittig-type reaction has been extended with elements other than phosphorus. Our interest was to explore the versatility of the reactions carried out with arsenic reagents and antimony reagents.

As for arsenic reagents, especially arsonium ylides, we have written a review article covering the literature up to 1982,^{5a-c} and Lloyd et al. have written a review article covering the literature up to 1986.⁶ A review mainly covering our own work^{7a-1} concerning the facile synthesis of unsaturated aldehydes, ketones, amides, and related natural products via arsonium salts has been published.⁸



CHO, COCH₃, CONR¹R², etc.

Of particular interest is the catalytic Wittig-type reaction: the tri-*n*-butylarsine-catalyzed olefination in the presence of triphenyl phosphite. Its simplicity, moderate reaction conditions, high *E* stereoselectivity, and good yields make it a practical alternative for large-scale synthesis.⁹

Research on the synthetic applications of organoantimony compounds has been done sporadically. As early as 1960, Henry and Wittig claimed that the triphenylstibonium methyllide prepared from Ph₃SbMeI with PhLi reacted with benzophenone to form diphenylacetaldehyde.¹⁰ However, the results could not be confirmed.¹¹ On the other hand, Wittig and Laib claimed that Me₂Sb(CH₂Ph)₂Br reacted with PhLi to yield Me₂SbCH(CH₂Ph)Ph, a product hypothesized to result from the rearrangement of an antimony ylide.¹² Lloyd et al. prepared a number of stable stibonium ylides with strong α -electron-withdrawing groups in the alkylidene moiety by a diazo compound method and found that all of them were inert, even toward 2,4-dinitrobenzaldehyde.¹³ The only successful Wittig-type reaction which occurs with a stibonium ylide is the

interaction between triphenylstibonium tetraphenylcyclopentadienylide and aryl aldehydes to form fulvenes.¹⁴

In contrast to triphenylstibine, which formed stibonium salts with halogeno compounds only with difficulty, trialkylstibine reacted readily with halogeno compounds, especially with α -halogeno carboxylic derivatives, at room temperature to form the substituted halides. A change in the substituent on antimony from phenyl to alkyl causes an acute change in the formation of the stibonium salts and in the reactivities thereof.

Three review articles have been written by Freedman et al.^{15a-c}

Trialkylstibine-Mediated Reactions of Active Bromo Compounds without the Use of Any Added Base (Ion-Pair Pathway)

In a preliminary communication,¹⁶ we reported that tri-*n*-butylstibine can mediate in the olefination of carbonyl compounds with bromoacetic esters. On continuing the study of organoantimony compounds in

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(2) For a recent general review, see: Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* 1989, 89, 863.

(3) For a review on phosphonate carbanions, see: Wadsworth, W. S., Jr. *Organic Reactions*; John Wiley and Sons, Inc.: New York, 1977; Vol. 25, pp 73-253.

(4) For additional general reviews, see: Cadogan, J. I. G., Ed. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: New York, 1979.

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(7) (a) Huang, Y. Z.; Shi, L.; Yang, J. *Tetrahedron Lett.* 1985, 26, 6447. (b) Wang, Y.; Li, J.; Wu, Y.; Huang, Y. Z.; Shi, L.; Yang, J. *Tetrahedron Lett.* 1986, 27, 4583. (c) Shi, L.; Xiao, W.; Ge, Y.; Huang, Y. Z. *Acta Chim. Sin.* 1986, 44, 421. (d) Huang, Y. Z.; Shi, L.; Yang, J. *Tetrahedron Lett.* 1987, 28, 2159. (e) Shi, L.; Xiao, W.; Yang, J.; Wen, X.; Huang, Y. Z. *Tetrahedron Lett.* 1987, 28, 2155. (f) Huang, Y. Z.; Shi, L.; Yang, J.; Cai, Z. *J. Org. Chem.* 1987, 52, 3558. (g) Shi, L.; Yang, J.; Wen, X.; Huang, Y. Z. *Liebigs Ann. Chem.* 1988, 377. (h) Shi, L.; Yang, J.; Wen, X.; Huang, Y. Z. *Tetrahedron Lett.* 1988, 29, 3949. (i) Yang, J.; Shi, L.; Xiao, W.; Wen, X.; Huang, Y. Z. *Heteroatom Chem.* 1990, 1, 75.

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(12) Wittig, G.; Laib, H. *Liebigs Ann. Chem.* 1953, 580, 57.

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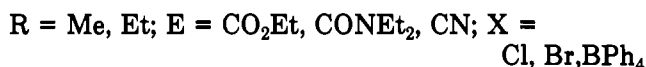
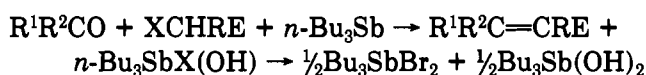
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Yao-Zeng Huang was born in Nantong, Jiangsu, in 1912 and received his B.S. in chemistry from National Central University in 1934. He then spent four years at the Institute of Chemistry, Academia Sinica, under the direction of the late Professor C. K. Chuang, and was appointed associate professor at the same institute in 1947. In 1950, he was appointed professor at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, and became deputy director in 1960. In 1980, he was elected to membership in the Chinese Academy of Sciences and to the deputy directorship of the Division of Chemistry, Chinese Academy of Sciences. His research interests have been primarily in the field of total synthesis of natural products and are presently in the field of organometallic chemistry and methodology.

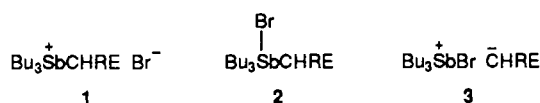
organic synthesis, we have found that trialkylstibines are effective reagents for the formation of a carbon-carbon double bond between α -halogeno carboxylic derivatives, including esters, amides, and nitriles, and carbonyl compounds. α,β -Unsaturated esters, amides, and nitriles were obtained.^{17a,b} In the reactions, quaternary stibonium salts are found to be active intermediates which can be trapped and undergo further reactions.

This is of interest, because the reaction proceeded by nucleophilic attack involving the single antimony-carbon bond in the stibonium salt. No similar example has been found in the literature.



Hoffmann reported that the organic compounds containing a positively polarized halogen atom reacted with tertiary phosphines either by reductive elimination of the halogen or by formation of phosphonium salts or quasiphosphonium salts. The reaction can be accelerated by both electron donors and electron acceptors.¹⁸ Accordingly tertiary stibine may behave similarly.

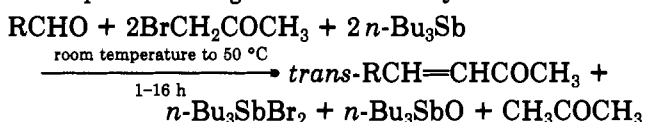
Tributylstibine reacts with an α -halogeno carboxylic derivative to afford the corresponding quaternary stibonium bromide 1. Halophilic attack of antimony can afford pentacovalent stiborane 2, which dissociates to give ion pair 3. The latter adds nucleophilically to a carbonyl substrate R^1R^2CO . The addition intermediate that results fragments to form olefin R^1R^2CO on heating.



When $R^1 = \text{alkyl}$, $R^2 = \text{H}$, $R = \text{H}$, and $E = \text{CO}_2\text{R}$ (or CONEt_2), the products are highly *E* stereoselective. When $R^1 = \text{alkyl}$, $R^2 = \text{H}$, $R = \text{H}$, and $E = \text{CN}$, the *E*:*Z* ratio of products amounts to approximately 3:2.^{17b}

Anion exchange of [(ethoxycarbonyl)methyl]tributylstibonium bromide (1, $R = \text{H}$, $E = \text{COOEt}$) with sodium tetraphenylborate gave the corresponding tetraphenylborate, which reacted with aldehydes on heating to afford olefin products.

α -Enones are important intermediates in organic synthesis. Generally they can be synthesized from aldol condensation, but unsymmetric mixtures are produced. We found a new method for the synthesis of α -enones by the reaction of aldehydes and α -bromo ketones with tri-*n*-butylstibine.¹⁹ Thus, on treatment of aldehydes and bromoacetone with tri-*n*-butylstibine at room temperature, an exothermic reaction takes place, giving the olefin products in good to excellent yields.



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In this reaction, 2 equiv of tri-*n*-butylstibine and bromoacetone had to be used to convert the aldehyde completely, and the debrominated ketone was always formed as byproduct. Products with an *E* double bond were formed exclusively.

Aldol condensation is one of the most important methods of carbon-carbon bond formation but usually results in mixtures of products arising from self-condensation, mixed condensations, and retro-aldol reaction. Numerous efforts have been made to improve the procedure, of which the transition-metal-catalyzed reaction of silyl enol ethers with carbonyl compounds²⁰ and the reaction of halogeno ketones with carbonyl compounds promoted by $\text{CeI}_3\text{-NaI}$ ²¹ seem to be the most promising.

In our studies of the synthesis of α -enones by the reaction of aldehydes and bromo ketones with tri-*n*-butylstibine, when 3-bromobutan-2-one was heated with 2-furaldehyde in the presence of tributylstibine at 90 °C for 6 h, 4-(2-furyl)-3-methylbuten-2-one was obtained (47%), accompanied by 4-(2-furyl)-4-hydroxy-2-methylbutan-2-one (39%). At room temperature, no reaction between these compounds took place, suggesting that a catalyst was necessary if the β -hydroxy ketone was to be obtained as the main product.

On the basis of this consideration, a catalytic amount of iodine (2-4 mol %) was added to a mixture of equivalent amounts of 3-bromobutan-2-one, aldehyde, and tributylstibine and the mixture was stirred at room temperature until the aldehyde completely disappeared. After treatment with a protic solvent, the reaction mixture was chromatographed to give β -hydroxy ketone in excellent yield.

A mechanism of our I_2 -catalyzed reaction of α -bromo ketones with aldehydes mediated by trialkylstibine has been proposed. The diastereoisomers of the reactions of 12 aldehydes with 3-bromobutanone were estimated by proton NMR showing that the erythro:threo ratio is approximately 1:1 in each case.²²

Cyclopropane derivatives activated by two electron-withdrawing substituents at a geminal position, the so-called electrophilic cyclopropanes, have been recognized as useful intermediates in organic synthesis. Their inter- and intramolecular ring opening reactions by various nucleophiles have been studied intensively and applied to the synthesis of several natural products.²³ Cyclopropanes with three electron-withdrawing substituents, two on C-1 and one on C-2, have been synthesized by the reaction of α -chloroacrylate and α -chloroacrylonitrile with methylene compounds by means of cuprous oxide-isocyanide complex.²⁴ Alternatively, they can be obtained from the reaction of ethyl dibromomalonate and olefins in DMSO promoted by copper.²⁵

Our approach to the cyclopropanes is by the reaction of dibromomalonate and its analogues with elec-

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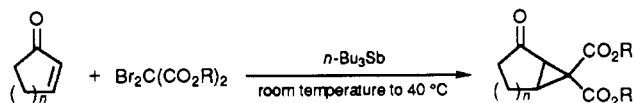
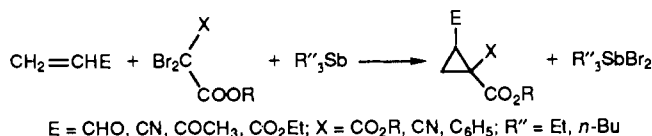
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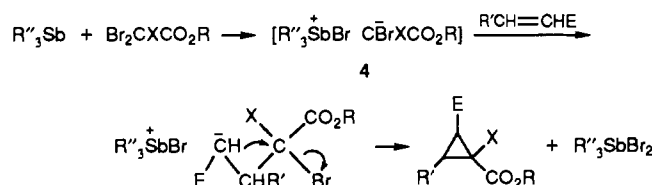
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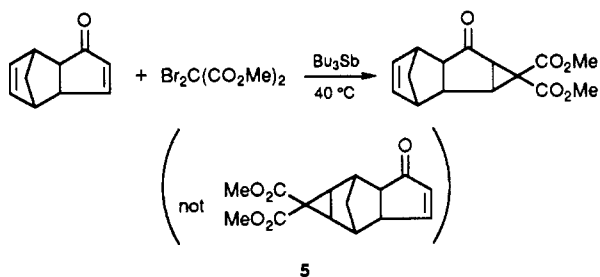
tron-deficient olefins mediated by organoantimony compounds.²⁶ The reaction takes place easily under mild conditions and gives the cyclopropane derivatives in high yields. We found that, besides the terminal olefins such as acrolein, acrylonitrile, methyl vinyl ketone, and acrylic esters, cyclic α,β -unsaturated ketones such as 2-cyclopentenone and 2-cyclohexenone can also react with dibromomalonate to give bicyclic compounds.



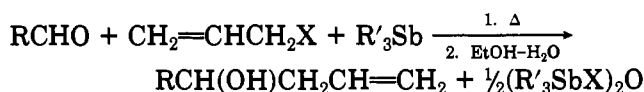
The stereochemistry of all the products has been thoroughly investigated. The proposed reaction mechanism is that the ion pair (4) is the active intermediate.



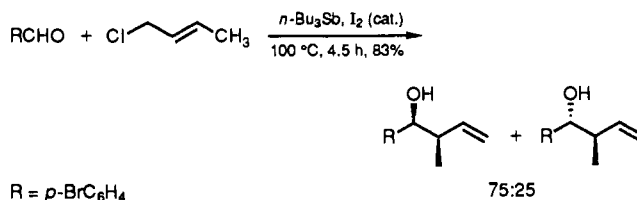
In order to prove that our reaction pathway is not through the carbene intermediate, we ran the following reaction. Dimethyl dibromomalonate reacted with 1-dicyclopentadienone promoted by tributylstibine to give tetracyclo[4.4.0^{3,5}.1^{7,10}]-4,4-bis(methoxycarbonyl)undec-8-en-2-one exclusively. No addition product such as 5 was observed.



Allylation of carbonyl compounds to yield homoallylic alcohols is an important synthetic operation. Many metals have been used to promote this Barbier-type reaction with allyl halides. However, no report appeared in the literature using organometallics. A first example of the Barbier-type reaction by means of organometallics has been achieved.²⁷

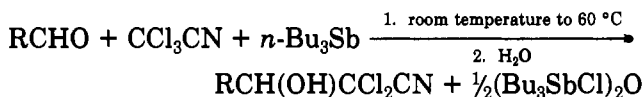


Crotyl chloride reacted with *p*-bromobenzaldehyde mediated by tri-*n*-butylstibine, but a catalytic amount of iodine was needed to promote the reaction. The result is depicted below:



5-(4-Bromophenyl)-2-penten-5-ol, the isomer resulting from the addition of terminal carbon in crotyl to carbonyl compounds, was not found.

α,α -Dichloro- β -hydroxy nitriles are rather inaccessible.²⁸ Burton and co-workers reported that phosphonium ylide from trichloroacetonitrile and triphenylphosphine reacted with benzaldehyde to form 2-chloro-3-phenylacrylonitrile and triphenylphosphine oxide.²⁹ We found that trichloroacetonitrile reacted with aldehydes mediated with tri-*n*-butylstibine to give α,α -dichloro- β -hydroxy nitriles in excellent yields.³⁰



We postulate that the reaction is initiated by halophilic attack of tri-*n*-butylstibine to trichloroacetonitrile resulting in an ion pair, $n\text{-Bu}_3\text{SbCl}^+$ and $^-\text{CCl}_2\text{CN}$.³¹ The ion-pair formation was supported by detection of dichloroacetonitrile from the reaction of tri-*n*-butylstibine with trichloroacetonitrile in protic solvent.

Reaction of Quaternary Stibonium Salts with Carbonyl Compounds by the Aid of Strong Nucleophiles RLi or RMgBr (Pentaorganylstiborane Pathway)

Although pentaorganylstiboranes have long been known,^{32a-d} their applications in organic synthesis have not been exploited. We have noticed that antimony has a greater tendency to form pentaalkyl derivatives than do phosphorus and arsenic. Our aim was thus to explore the scope of the reactivities of pentaorganylstiboranes (λ^5 -stibane³³).

It has been found that the quaternary stibonium salts $[n\text{-Bu}_3\text{SbCH}_2\text{E}]^+\text{X}^-$ (E = Ph, CH=CH₂, CH=CHCO₂Et, CO₂Et, CN; X = Br, I, BPh₄) on treatment with RLi (R = *n*-Bu, *t*-Bu, Ph) afford pentaorganylstiboranes, $n\text{-Bu}_3\text{Sb}(\text{R})\text{CH}_2\text{E}$, which react with aromatic aldehydes, to give, after subsequent hydrolysis, homoallylic alcohol, homoallylic alcohols, ethyl 5-aryl-5-hydroxypent-2-enoate, ethyl β -hydroxypropionates, and β -aryl- β -hydroxypropionitriles, respectively, in good to excellent yields. The reaction is chemoselective for aldehydes,³⁴ but not cyclic ketones.^{35a} However, in the presence of AlCl₃, pentaorganylstiborane can react with ketones to give tertiary alcohols in good yields.^{35b}

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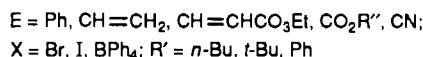
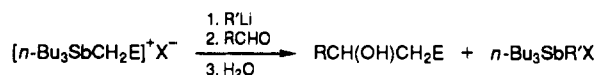
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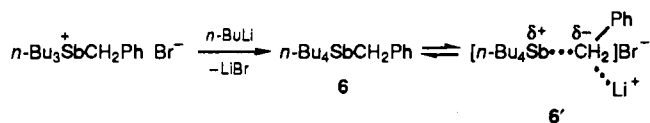
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An alkylolithium is not only a strong base but also a strong nucleophile. The antimony atom of the stibonium salt is an electrophile with a large atom radius, so the alkylolithium can attack the antimony atom preferentially and displace the anion X⁻, instead of abstracting a proton and forming an antimony ylide, as occurs in the case of phosphonium or arsonium analogues. A pentaorganylstiborane (6) thus may be formed as shown below. This species may become polarized in the presence of Li⁺ to form 6', which by nucleophilic addition to the aldehydes can afford, after hydrolysis, homobenzylic alcohols.



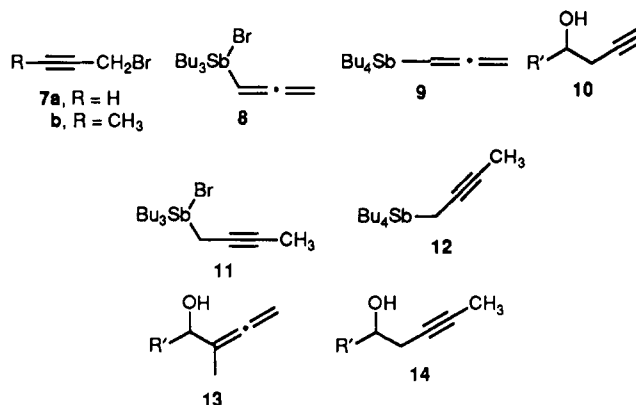
In fact, when benzyltri-*n*-butylstibonium bromide was treated with *n*-BuLi, we did isolate an intermediate *n*-Bu₄SbCH₂Ph (6) which was stable only under nitrogen but which could be characterized by mass spectrometry.³⁶ If the reaction was stopped at this stage (-78 °C) and allowed to reach room temperature, addition of benzaldehyde still gave the product alcohol. Thus, it appears that pentaorganylstiborane 6 is most likely the intermediate.

The pentaorganylstiborane R''₃SbR'₂ or R''₄SbR' reacts with acyl chlorides RCOCl to give ketones RCOR' in good yields. Selective transfer of crotyl, phenyl, benzyl, or methyl takes place, resulting in a single ketone product when R'' is butyl, which serves as an anchoring group and does not transfer. The order of transfer is CH₃CH=CHCH₂ > Ph > PhCH₂ > Me > Et > *n*-Bu.^{35b}

Selective propargylation and allenylation of carbonyl compounds are interesting since the products can readily undergo functional interconversion and are required as intermediates for the synthesis of compounds related to numerous biologically active natural products. Generally, the propargylic anions are employed in the reaction. However, their applicability in organic synthesis has been limited because of difficulty in controlling the regioselectivity of the reaction. It has been pointed out that the propargylic anion is generally in equilibrium with allenic anions, and a troublesome mixture of acetylenic and allenic alcohol is obtained in the condensation with carbonyl compounds.

We found that the reaction of tri-*n*-butylstibine and propargyl bromide (7a, R = H) gave, instead of propargyltributylstibonium bromide, allenyltributylstibonium bromide (8), which is stable and cannot react with aldehydes even under heating to 120 °C, but can be readily converted into allenyltetra-butylstiborane (9) by reaction with *n*-butylmagnesium bromide in THF at low temperature. The pentaorganylstiborane 9 reacted smoothly with various aldehydes R'CHO to give homopropargylic alcohols 10 exclusively in excellent yields.³⁷

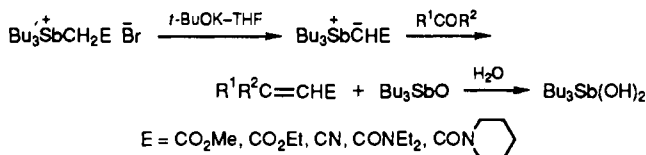
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The reaction of tributylstibine and bromo-2-butyne (7b, R = CH₃) gave butynylstibonium bromide 11, which reacted with *n*-butylmagnesium bromide to afford pentaorganylstiborane 12. The latter reacted with aromatic aldehydes to give almost exclusively the allenic alcohols 13, and with aliphatic aldehydes to give preferentially allenic derivatives 13 accompanied by butynylic derivatives 14 (13:14 = 2:1 to 4:1).

Reactions of Quaternary Stibonium Salts with Carbonyl Compounds by the Aid of LDA or *t*-BuOK (Stibonium Ylide Pathway)

We mentioned above that, by the aid of strong nucleophiles RLi or PhLi, the reactions of quaternary stibonium salts with carbonyl compounds gave, after hydrolysis, the secondary alcohols. The intermediates were found to be pentaorganylstiborane. On the contrary, by the aid of less nucleophilic strong base, LDA or *t*-BuOK, from the butyl ligand-stibonium salts we obtained stibonium ylides, which reacted with carbonyl compounds to give olefins as shown below.³⁸



The ylide intermediate has been evidenced by tandem reaction.

Lloyd et al.³⁹ prepared a number of stable stibonium ylides with strong electron-withdrawing groups in the alkylidene moiety by a diazo compound method, but found that all of them were inert, even toward 2,4-dinitrobenzaldehyde. The only successful Wittig reaction which occurs with a stibonium ylide is the interaction between triphenylstibonium tetraphenylcyclopentadienylidene and aryl aldehydes to form fulvenes.¹⁴ Some stibonium ylides have been suggested as possible intermediates in some reactions.^{40,41}

We found a novel olefination of diazo compounds including dimethyl diazomalonnate, ethyl diazoacetate, and diazoacetylacetone with carbonyl compounds mediated by tributylstibine and a catalytic amount of Cu^IX (X = I, Br, Cl).⁴²

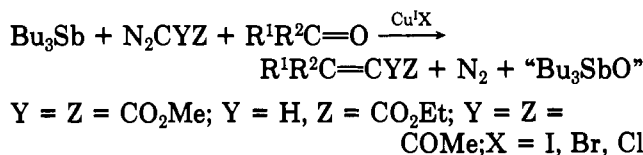
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(39) Ferguson, G.; Glidewell, C.; Gosney, I.; Lloyd, D.; Metcalfe, S.; Lumbroso, H. *J. Chem. Soc., Perkin Trans. 2* 1988, 1829.

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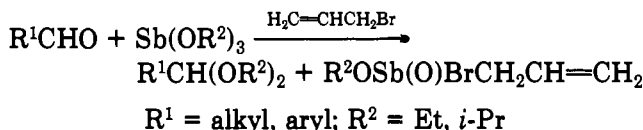
(41) Chen, C.; Huang, Y. Z.; Shen, Y. C.; Liao, Y. *Heteroat. Chem.* 1990, 1, 49.



The reaction is proposed to occur through a tributylstibonium methylyde bearing strong electron-withdrawing groups. In the absence of tributylstibine or CuX catalyst, olefination did not occur at all.

Selective Acetalization of Aldehyde with Trialkoxystibine Using Allyl Bromides

Usually, acetalization is accomplished with alcohols or orthoformic esters in an acidic medium.⁴³ We have found a new aldehyde-selective acetalization method by means of trialkoxystibine with the aid of allyl bromides. This method should be applicable to acid-sensitive or protic-solvent-sensitive aldehydes.⁴⁴

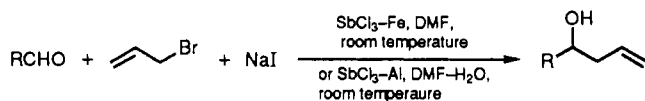


The reaction proceeded conveniently in high yields. This procedure constitutes a new method for selective protection of aldehyde groups, especially suitable to acid-sensitive or protic-solvent-sensitive compounds.

An Efficient SbCl₃-Metal System Allylation, Reduction, and Acetalization of Aldehydes

The allylation of aldehydes to homoallylic alcohols is of synthetic importance, and a number of metals have been used to promote Barbier-type allylation of aldehydes with allyl halides. Recently, metallic antimony⁴⁵ and trialkylstibine-mediated²⁷ Barbier-type reaction at 60–80 °C has appeared in the literature. We found that the active zero-valent antimony generated from SbCl₃-Fe or -Al could induce allylation of aldehydes with allylic halides at room temperature to give high yields of the corresponding homoallylic alcohols with high regio- and chemoselectivity.⁴⁶

The less reactive allyl bromide reacted with the same aldehydes to give homoallylic alcohols (80–90%) at 60 °C (4.5–7 h). However, addition of sodium iodide allowed the reaction temperature to be reduced to ambient. Metallic aluminum, when it replaced metallic iron, was also effective in a DMF-H₂O (3:1) medium.



A variety of aldehydes reacted smoothly to give the homoallylic alcohols in good yields. α,β -Unsaturated aldehydes afforded only 1,2-addition products. Aldehydes containing a hydroxy group such as *p*-hydroxy- or *o*-hydroxybenzaldehyde gave the corresponding products leaving the OH group intact. Since acetophenone present in benzaldehyde was recovered, the reaction is chemoselective.

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(43) For a review, see: Menskens, F. A. J. *Synthesis* 1981, 501.

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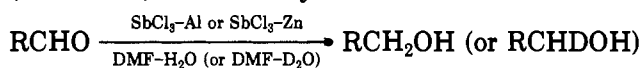
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(46) Wang, W. B.; Shi, L. L.; Xu, R. H.; Huang, Y. Z. *J. Chem. Soc., Perkin Trans. 1* 1990, 424.

Reaction of crotyl bromide with *p*-chlorobenzaldehyde under similar reaction conditions provided the homoallylic alcohol with the erythro isomer predominately.

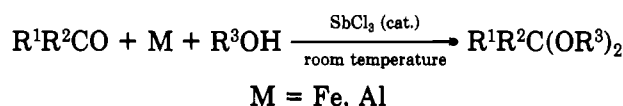
The reaction mechanism suggested is that an allyl-antimony reagent is formed through the oxidative addition of an allyl halide to zero-valent antimony generated in situ by reduction of antimony(III) chloride with metallic iron or aluminum. Because of the erythro selectivity, the reaction with an aldehyde seems to proceed via a noncyclic transition state.⁴⁷

Concerning the reduction of aldehydes to alcohols, we have reported that, in the presence of Lewis acids, diphenylstibine reacted with carbonyl compounds to afford, after hydrolysis, alcohols in excellent yields.⁴⁸ Recently, an indirect electroreduction of acetophenone to 1-phenylethanol in the presence of SbCl₃ was reported by Ikeda.⁴⁹ We found that SbCl₃-Al/DMF-H₂O (system A) and SbCl₃-Zn/DMF-H₂O (system B) were effective reducing systems for conversion of aldehydes to alcohols in excellent yields. When the reduction was carried out in DMF-D₂O, the aldehydes were converted to deuterium-labeled alcohols (RCHDOH) conveniently.⁵⁰

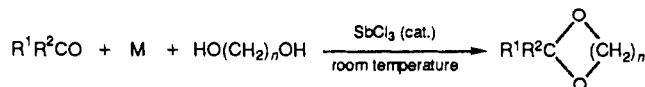


A variety of aldehydes were reduced smoothly with either reduction system. In system A (SbCl₃-Al/DMF-H₂O), the reaction proceeded faster than in system B (SbCl₃-Zn/DMF-H₂O). With α,β -unsaturated aldehydes, reduction occurred only at the C=O position, leaving the carbon-carbon double bonds intact. Neither unconjugated double bonds nor cyclic ketones were attacked. When a mixture of benzaldehyde and acetophenone was allowed to react with system A or B, the former was reduced preferentially.

In the above SbCl₃-Al/DMF-H₂O or SbCl₃-Zn/DMF-H₂O system, when methyl or ethyl alcohol was used as solvent instead of DMF-H₂O, the acetalization product was obtained in almost quantitative yield. A catalytic amount of SbCl₃ was effective for this purpose;⁵¹ in the absence of Fe or Al, the reaction did not occur.



This method could also be applied to diols (ethylene glycol and propylene glycol). The operation is the same as that for monoalcohols. This acetalization method could be applied to ketones.



Me = Fe, Al; *n* = 2, 3

Because of the ready access to reagents, mild reaction conditions, easy workup, and good yields, the SbCl₃-

(47) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* 1980, 102, 7107.

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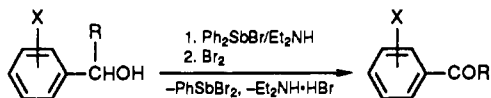
(50) Wang, W. B.; Shi, L. L.; Huang, Y. Z. *Tetrahedron Lett.* 1990, 31, 1185.

(51) Wang, W. B.; Shi, L. L.; Yang, Y. Z. *Tetrahedron* 1990, 46, 3315.

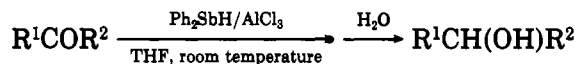
metal system was a facile system for allylation, reduction, and acetalization of aldehydes.

Oxidation and Reduction

The low-valent organometallic reagent bromodiphenylstibine has been found to mediate the oxidation of benzyl alcohols by bromine to give benzaldehydes or ketones in moderate to good yields.⁵²



Numerous metal hydrides and organometallic hydrides are able to reduce carbonyl compounds. Every hydride has its own characteristic feature. However, no report is given in the literature concerning the reactivity of organoantimony hydrides toward carbonyl compounds. We found that, in the absence of Lewis acid, diphenylstibine did not react with carbonyl compounds, but in the presence of Lewis acid, it did react at room temperature to afford, after hydrolysis, alcohols in excellent yields.⁴⁸



Concluding Remarks

Research on the synthetic application of organoantimony compounds has been done only sporadically. As early as 1960, Wittig et al. claimed that the triphenylstibonium methylide prepared from Ph_3SbMeI with PhLi reacted with benzophenone to form diphenylacetaldehyde. However, this result could not be confirmed. For many years, there was some confusion as well as contradictions. We found that, in contrast to triphenylstibine, trialkylstibines react with α -halogeno carboxylic derivatives or α -halogeno ketones readily to form quaternary stibonium salts, the reactions of which can be classified into three categories: (1) Reactions of quaternary stibonium salts with substrates without the use of added base. Thus, the trialkylstibine

promotes reactions of halogeno carboxylic derivatives and carbonyl compounds to give α,β -unsaturated esters, amides, and nitriles; aldehydes and α -bromo ketones to give α -enones; aldehydes and α -bromo ketones in the presence of catalytic amounts of iodine to give β -hydroxy ketones; and aldehydes and trichloroacetonitriles to give α,α -dichloro- β -hydroxy nitriles. In these reactions, quaternary stibonium salts are the active intermediates, which in some cases can be trapped and then undergo further reaction with substrates. The trialkylstibine-promoted cyclopropanation of dibromomalonate and its analogues with electron-deficient olefins occurs readily at 40–50 °C. All the above-mentioned reactions are most likely to be through the ion-pair pathway. (2) Reactions of the quaternary stibonium salts on treatment with strong nucleophiles such as RLi or Grignard reagents afford pentaorganylstiboranes (λ^5 -stibanes), which react with aldehydes to give, after hydrolysis, secondary alcohols. (3) Reactions of the quaternary stibonium salts with less nucleophilic strong bases such as LDA or potassium *tert*-butoxide afford stibonium ylides, which react with carbonyl compounds to produce olefins or epoxides. The ylide pathway is evidenced by tandem reaction and by a one-pot reaction of tributylstibine, diazo compounds, carbonyl compounds, and a catalytic amount of Cu^{I} .

In this Account, a novel selective acetalization of aldehydes with trialkoxystibine using allyl bromide, an efficient SbCl_3 -metal system for allylation, reduction, and acetalization of aldehydes, bromodiphenylstibine-mediated oxidation of benzyl alcohols by bromine, and reduction of some organic compounds by organoantimony hydride are also reported.

This work would not have been possible without the contributions of many delicate graduate students and colleagues. We list them in rough chronological order: Professor Y. C. Shen, Dr. C. Chen, Dr. Y. Liao, Professor L. L. Shi, Dr. W. B. Wang, Ms. F. H. Zhu, and Dr. L. J. Zhang. The funding for this research has come from the National Natural Science Foundation of China and Chinese Academy of Sciences. Thanks are also due to Miss H. X. Jiang for her typing and drawing for the preparation of this manuscript.

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