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Studies of the use of elemento-organic compounds of the fifteenth and sixteenth groups in organic synthesis

LXXV *. Reduction of some organic compounds by tertiary stibines

Yao-Zeng Huang *, Chen Chen, Fanghua Zhu and Yi Liao

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai (China)

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Abstract

Trialkylstibines can reduce nitroarenes to azoxy compounds, quinone to hydroquinone, and *p*-toluenesulfonyl chloride to *p*-toluenesulfinic acid in good yields under mild conditions. Debromination of α-bromophenylacetonitrile or 1,2-dibromo-1-phenylethane by tri-n-butylstibine gives 2,3-diphenylsuccinonitrile or styrene, respectively.

Introduction

One of the characteristic properties of the tertiary stibines is the ease with facility which they reduce some inorganic compounds such as halogens and metal ions [1,2]; the trialkylstibines are oxidized. Trimethylstibine can reduce hydrogen chloride to form dichloro-trimethylstiborane with evolution of hydrogen [3]. However, little attention has been paid to the reduction of organic compounds by tertiary stibines. Debromination of α-bromoacetophenone and benzyl bromide with tributyl- or triphenylstibine gives acetophenone and toluene, respectively, after protolysis [4]. *p*-Tolyl *p*-toluenethiolsulfinate is reduced to ditolyl disulfide by triphenylstibine [5].

As part of our investigations of the synthetic utility of organoantimony compounds [6–12], our attention has been drawn to the reduction of oxygenated functionalities of nitrogen and sulfur by tertiary stibines. We report here that aromatic nitro compounds undergo reduction with trialkylstibines under neutral conditions, to give exclusively azoxy compounds. Tributylstibine also effects the reduction of quinone and *p*-toluenesulfonyl chloride to hydroquinone and sulfinic

* For part LXXIV see ref. 25.

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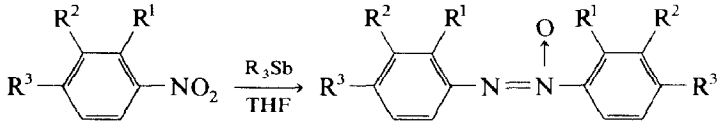
acid, respectively. The debromination of 1,2-dibromo-1-phenylethane gives styrene, and α-bromophenylacetonitrile is coupled to 2,3-diphenylsuccinonitrile with tributylstibine.

Results and discussion

A solution of the nitroarenes (**1**) in THF, when treated with 1.5 equivalent amounts of a trialkylstibine at room temperature, undergoes reduction smoothly. The reaction mixture after chromatography gave the corresponding azoxy compounds (**2**), which can also be obtained by the reduction of nitrobenzene by phosphine [13], in good yields. Further reduction products were not detected. The results are presented in Table 1.



(**1**) (**2**)

Triethylstibine has the same reducing properties as tributylstibine towards nitrobenzene, whereas triphenylstibine is inert even in refluxing tetrahydrofuran. The present reaction proceeds cleanly with nitrobenzene (**1a**) and the halonitroarenes (**1b–1g**) except for *o*-bromonitrobenzene, which gives an intractable mixture. Refluxing enhances the reduction. Nitroarenes bearing an electron-donating group such as (*p*-dimethylamino)nitrobenzene, do not react in refluxing THF, and electron-deficient nitroarenes such as *p*-nitrophthalic anhydride and *p*-nitrobenzoyl chloride, leads to polymerization of the substrates.

The reductions of the aromatic nitro compounds to azoxybenzenes are usually carried out in strongly basic media [13–16]. The outcome of the reduction is not easy to predict owing to competitive side reactions [13]. Recently, the reduction of aromatic nitro compounds with various telluride reagents has been widely investigated [17–21]. Among them, sodium hydrogen telluride and diphenyl detelluride are found to reduce nitroarenes to azoxybenzenes [18,21]. The present method of reduction of nitroarenes with trialkystibines can be used for sensitive compounds

Table 1

Reduction of aromatic nitro compounds with trialkylstibines [a]

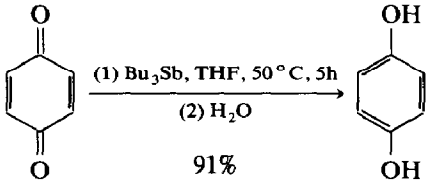
1	Nitroarene			R (in R_3Sb)	Conditions		Yield of **2** (%) [b]
	R^1	R^2	R^3		temp. (°C)	time (h)	
a	H	H	H	Et	r.t.	34	91
b	Cl	H	H	Bu	50	8	95
c	H	H	Cl	Bu	67	0.5	90
d	H	Br	H	Et	r.t.	12	97
e	H	H	Br	Bu	r.t.	16	90
f	H	H	I	Bu	r.t.	14	65
g	Me	H	Cl	Bu	50	1	96

[a] All of the products gave satisfactory ^1H NMR and m.p. as compared with authentic samples. [b] Isolated yields.

that are not compatible with basic media, so it is probably a good alternative to the known procedure for the preparation of azoxybenzenes from aromatic nitro compounds.

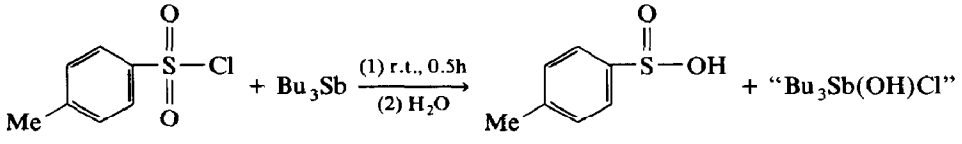
The fate of the stibines was investigated in the case of the reduction of nitrobenzene; the trialkylstibine oxide that was predicted as a common by-product, was, however, isolated as a dihydro-trialkylstiborane because of its hygroscopic nature [22].

Quinone (**3**) when treated with tributylstibine in THF gives the corresponding hydroquinone (**4**) after protolysis. The reduction procedure used was similar to that for triphenylphosphine [23].



(**3**) (**4**)

When *p*-toluenesulfonyl chloride (**5**) and tributylstibine were mixed, an exothermic reaction took place. *p*-Toluenesulfinic acid (**6**) was obtained after the resulting mixture had been protonated with ethanol and chromatographed. The corresponding sulphones are obtained when the mixture of tributylstibine and **5** is treated with appropriate alkyl halides [24].

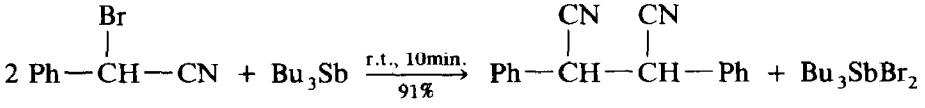


(**5**) (**6**)

In this procedure, an oxidative addition of **5** to tributylstibine probably takes place to form Ts–Sb(Cl)Bu_3.

The reducing ability of the tertiary stibines is weaker than that of the tertiary phosphines, which can reduce arenesulfonyl chlorides to thiophenols and disulfides [23]. It has been reported that the reduction of *p*-tolyl *p*-toluenethiol sulfinate to di-*p*-toluene disulfide was carried out under milder conditions with triphenylphosphine than with triphenylstibine [5].

When tributylstibine was mixed with α-bromophenylacetonitrile (**7**), an exothermic reaction took place immediately. Neither the debromination of **7**, as in case of α-bromoketone [4,24], nor formation of the corresponding stibonium salt, which was given by reaction of bromoacetonitrile with a trialkylstibine [25], was observed, instead 2,3-diphenylsuccinonitrile (**8**) was produced.



(**7**) (**8**)

1,2-Dibromo-1-phenylethane (**9**) is debrominated by tributylstibine at 100°C under nitrogen. Styrene (**10**) was obtained in 70% yield.

$$\underset{\textbf{(9)}}{Ph-\overset{Br}{\overset{|}{C}}H-\overset{Br}{\overset{|}{C}}H_2} + Bu_3Sb \xrightarrow[70\%]{100\,^\circ C,\ 4h} \underset{\textbf{(10)}}{Ph-CH=CH_2} + Bu_3SbBr_2$$

The debromination of 3,4-dibromobutanone is more facile than that of **9**, but 1,2-dibromo-2-methylpropane does not react with tributylstibine even at 150 °C.

The reducing properties of tertiary stibines towards some organic compounds indicate that they could be useful as mild reducing reagents in organic chemistry.

Experimental

1,2-Dibromo-1-phenylethane [26], triethylstibine [27], tributylstibine [28] and triphenylstibine [29] were prepared by standard procedures. α-Bromophenylacetonitrile, prepared by bromination of phenylacetonitrile with bromine by a published procedure [30], is a colorless oil (b.p. 110 °C/5Torr, ^{1}H NMR: 5.40(s, 1H), 7.37(s, 5H)) which decomposes on standing. Reactions were performed under nitrogen to protect trialkylstibines from oxidation. All the products are known and were identified by direct comparison with authentic samples.

Reduction of aromatic nitro compounds: To a stirred solution of nitroarene (1 mmol) in THF (2 ml), was injected a trialkylstibine (1.8 mmol) under nitrogen. The mixture was stirred at room temperature, or refluxed for certain hours. The progress of the reaction was monitored by TLC on silica gel. Shortly before **1** had almost completely disappeared, the reaction was quenched by adding ethanol and the mixture was left open to the air. The resulting mixture was then poured into an alumina-silica gel (1 : 1) column. Chromatography with ethyl acetate as eluent gave a crude azoxy compound **2**, which was recrystallized from an appropriate solvent. The melting points of the products were compared with those of authentic samples.

Identification of antimony product: In a typical procedure, 1 mmole of nitrobenzene and 1.5 mmoles of tributylstibine were allowed to react to give the azoxybenzene, which was isolated as above. The residue on the alumina-silica gel column was chromatographed with methanol as eluent. Evaporation of the solvent gave a colorless oil, its ^{1}H NMR and IR spectra were the same as dihydro-tributylstiborane obtained before [31]. The isolated yield was 43% (210 mg).

Reduction of quinone: Quinone (210 mg, 1.9 mmol) and tributylstibine (600 mg, 2.0 mmol) were dissolved in THF (1 ml) and stirred at 50 °C for 5 h. After treatment with ethanol (2 ml), the mixture was chromatographed as above, to give 200 mg of white solid (91%) of hydroquinone; m.p. 170 °C. (lit. 169 °C [32]).

Reduction of p-*toluenesulfonyl chloride:* A mixture of *p*-toluenesulfonyl chloride, (380 mg, 2.0 mmol), and tributylstibine (645 mg, 2.2 mmol) in a capped vessel reacts exothermically. After stirring at room temperature for 0.5 h and work-up as above, 305 mg of *p*-toluenesulfinic acid was obtained; m.p. 84 °C. (lit. 86 °C [33]). Yield; 98%. ^{1}H NMR(TMS/CCl_4): 2.42(s, 3H), 7.30(d, *J* 8.0 Hz, 2H), 7.71 (d, *J* 8.0 Hz, 2H), 11.3(s, 1H).

Coupling of α-bromophenylacetonitrile: To α-bromophenylacetonitrile (400 mg, 2.0 mmol) in a capped vessel, was added tributylstibine (675 mg, 2.3 mmol) by injection and under vigorous stirring. The reaction is exothermic. The mixture was cooled to room temperature, and a white solid separated. Work-up as above gave

210 mg of the crystalline 2,3-diphenylsuccinonitrile, which was recrystallized from ethyl acetate; m.p. 118–121° C. It is probably a mixture of *dl* and *meso* isomers. (lit. 160° C, meso isomer [34]). Yield 91%. ^{1}H NMR (TMS/$CDCl_3$): 4.21(s, 2H), 7.34(m, 10H); IR(KCl): 2220cm^{-1}, MS: *m/z* (rel. intensity): 232(M^+, 4), 116(100%).

Debromination of α,β-dibromostyrene: A mixture of 1,2-dibromo-1-phenylethane (130 mg, 0.5 mmol) and tributylstibine (170 mg, 0.6 mmol) was stirred and heated at 100° C in a capped vessel for 4 h. The ^{1}H NMR spectrum of the reaction product showed that styrene had formed in 70% yield.

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