Catalytic Action of Triarylstibanes: Oxidation of Benzoins into Benzyls Using Triarylstibanes Under an Aerobic Condition

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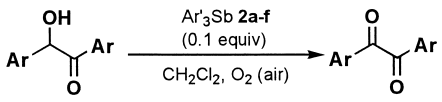
Benzoins are simply oxidized to benzils in excellent yields with a catalytic amount of triarylstibanes under an aerobic condition. This catalytic oxidation is heteroatom-specific in the antimony compound and no reaction take place with other group 15 reagents such as triphenylphosphane, -arsane and -bismuthane. The reaction should involve an oxidation–reduction cycle between stibane Sb(III) and stiborane Sb(V) under air.

Key words triarylstibane; catalyst; aerobic oxidation; benzoin; benzil

The synthetic application of organic and inorganic antimony compounds is an important subject which has been highlighted to both organic and inorganic chemist.[1—5] As for the application of trivalent organoantimony compounds (stibanes), a wide variety of reactions such as self-coupling reactions,[6,7] cross-coupling reactions,[8—13] photoreaction,[14] and asymmetric reactions with optically active organoantimony compounds[15—19] have been reported during the last two decades. On the other hand, the conversion of benzoin into benzil has been accomplished by oxidation with a variety of reagents; *i.e.*, bismuthane oxide,[20] bismuthane imides,[21] alumina-supported copper sulfate under microwave irradiation,[22] and the Burgess reagent,[23] and by transition metal-catalyzed oxidation with bismuth nitrate-copper acetate,[24] aerobic oxygen,[25,26] diacetoxyiodobenzene,[27] and allyl diethyl phosphate.[28] In this respect, pentavalent antimony compounds such as stibane oxide,[20] diacetoxytriphenystiborane,[29] dibromotriphenylstiborane,[30,31] and stibane imides[21] were also known to be effective for this reaction. We now disclose that trivalent triarylstibane (Ar_3Sb) in itself is an effective catalyst for oxidation of diaryl-α-ketoalcohols into the corresponding α-diketones under an aerobic condition, although stibane has been known to oxidize thiols into the corresponding disulfides under air.[32] It should be noted that the reaction did not take place with other group 15 (pnictogen) reagents such as triphenylphosphane, -arsane and -bismuthane.

In the course of our extensive studies on application of organoantimony(III) compounds to organic synthesis, we found that treatment of benzoin **1a** with triphenylstibane **2a** in dichloromethane (CH_2Cl_2) under air afforded benzyl **3a** in excellent yield, although benzyl alcohol, 4-nitrobenzyl alcohol, 1,2,3,4-tetrahydro-1-naphthol, benzhydrol, and hydrobenzoin did not give any oxidized products. Oxidation did not occur when tributylstibane was used instead of **2a**. These unexpected results suggest that **2a** functions as oxidant for certain alcohols. In this regard, we undertook to examine the oxidation of benzoin **1a** as a model substrate under a variety of reaction conditions; *i.e.*, use of various triarylpnictogen reagents (Ph_3P, Ph_3As, Ar_3Sb, and Ph_3Bi), variation of the ratio of **3a** to pnictogen reagent, and absence or presence of air or oxygen. As shown in Table 1, pnictogen reagents except for triphenylstibane were ineffective for the oxidation of **1a**. A remarkable decrease in the yield of the oxidized product **3a** under an argon atmosphere indicates the presence of



1a-g **3a-g**

Ar=a: Phenyl
b: 2-Furyl
c: 2-Thienyl
d: 2-Pyridyl
e: 4-Methylphenyl
f: 4-Methoxyphenyl
g: 4-Bromophenyl

Ar'=a: Phenyl
b: 4-Methylphenyl
c: 4-Fluorophenyl
d: 4-Chlorophenyl
e: 4-Trifluoromethylphenyl
f: 4-Ethoxycarbonylphenyl

Chart 1

oxygen in reaction medium was essential in the present reaction (entry 5). The oxidation of **1a** was also took place smoothly with a catalytic amount (0.1 eq) of **2a**, however progressive addition of oxygen induced remarkable consumption of **2a** and suppressed the formation of **3a** (compare the results in entries 4 and 10 in Table 1). It can be assumed that the excessive exposure of **2a** to oxygen may give rise to inactive Ph_3Sb-oxo species for the oxidation of **1a**; hence the inactive species could not revert to **2a**.[33—38] These results imply that the oxidation of **1a** into **3a** should be induced by a certain oxidant such as triphenylstibane oxide (Ph_3SbO) generated from the antimony reagent and oxygen. In fact, the reaction of **1a** with catalytic amount of Ph_3SbO brought about the same oxidation to afford **3a** in high yield. Similar results were obtained when tri(*p*-tolyl)- **2a**, tri(*p*-fluorophenyl)- **2c**, tri(*p*-chlorophenyl)- **2d**, tris(*p*-trifluoromethylphenyl)- **2e**, or tri(*p*-ethoxycarbonylphenyl)stibane **2f** were used as antimony reagents, or benzene or tetrahydrofuran was employed as solvents in the present reactions. It was also apparent that the reaction rate was dependent on the electronic nature of the aryl group on the antimony, and the stibanes having electron-attracting group on the *p*-position of the phenyl group improve the reaction time with much recovery of the antimony reagents (entries 13—15 and 17). It should be noteworthy that the oxidized product **3a** was obtained in 93% total yield, when the reaction mixture of **1a** and **2e** (0.1 eq) pretreated for 2.5 h under the same reaction conditions was allowed to react with one more equiv. of **1a** for 5 h. Consequently, the best result was obtained when the reaction was performed in the presence of 0.1 eq of antimony reagent in CH_2Cl_2 at room temperature under an aerobic condition.

In order to evaluate the further oxidizing property of the stibane in the present reaction, we attempted the reaction of

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Table 1. Oxidation of Benzoin **1a** into Benzil **3a** with Pnictogen Reagents[a)]

Entry	Pnictogen reagent	Reagent/**1a** (mol eq)	Atmosphere	Time (h)	Yield of **3a**/%[b)] (recovery of **1a**)	Recovery of pnictogen reagent/%[c)]
1	Ph_3P	1.0	Air	60	0 (98)	98
2	Ph_3As	1.0	Air	48	12 (61)	69
3	Ph_3Sb **2a**	1.0	Air	3.5	98 (0)	57
4	Ph_3Sb **2a**	1.0	O_2	3	82 (0)	trace
5	Ph_3Sb	1.0	Argon	24	4 (91)	93
6	Ph_3Bi	1.0	Air	60	trace (89)	98
7	$SbCl_3$	1.0	Air	24	7 (92)	—[d)]
8	Ph_3Sb **2a**	0.1	Air	5	97 (0)	13
9	Ph_3Sb **2a**	0.05	Air	14	88 (0)	0
10	Ph_3Sb **2a**	0.1	O_2	4	51 (49)	0
11	Ph_3SbO	0.1	Air	5	96 (0)	—[e)]
12	$(p\text{-Tol})_3Sb$ **2b**	0.1	Air	10	88 (0)	0
13	$(p\text{-F-C}_6H_4)_3Sb$ **2c**	0.1	Air	3.5	97 (0)	39
14	$(p\text{-Cl-C}_6H_4)_3Sb$ **2d**	0.1	Air	3	96 (0)	41
15	$(p\text{-CF}_3\text{-C}_6H_4)_3Sb$ **2e**	0.1	Air	3	96 (0)	61
16	$(p\text{-CF}_3\text{-C}_6H_4)_3Sb$ **2e**	0.05	Air	7	87 (0)	0
17	$(p\text{-CO}_2\text{Et-C}_6H_4)_3Sb$ **2f**	0.1	Air	3	96 (0)	45

a) All reaction was carried out using **1a** (1 mmol) in CH_2Cl_2 (4 ml), see experimental. *b*) Isolated yield. *c*) Calculated from the reagent used. *d*) The reagent ($SbCl_3$) could not be isolated by decomposition during chromatographic separation. *e*) The reagent (Ph_3SbO) could not be isolated by hard adsorption by SiO_2 and 9% of $SbPh_3$ was isolated from the reaction mixture.

Table 2. Catalytic Oxidation of Benzoins **1a**—**g** into Benzils **3a**—**g** with **2a** under Air[a)]

Entry	Substrate	Time (h)	Product **3**	Yield (%)[b)]
1	Benzoin **1a**	12	Benzil **3a**	98
2	2,2′-Furoin **1b**	12	2,2′-Furil **3b**	97
3	2,2′-Thenoin **1c**	8	2,2′-Thenil **3c**	98
4	2,2′-Pyridoin **1d**	24	2,2′-Pyridil **3d**	52
5	4,4′-Dimethylbenzoin **1e**	10	4,4′-Dimethylbenzil **3e**	97
6	4,4′-Dimethoxybenzoin **1f**	12	4,4′-Dimethoxybenzil **3f**	88
7	4,4′-Dibromobenzoin **1g**	10	4,4′-Dibromobenzil **3g**	97

a) All reactions were carried out at room temperature under air using a mixture of **1a**—**g** (1.0 mmol), **2a** (0.1 mmol) and CH_2Cl_2 (4 ml), except for entry 1 (**1a**: 10 mmol, **2a**: 1 mmol). *b*) Isolated yield.

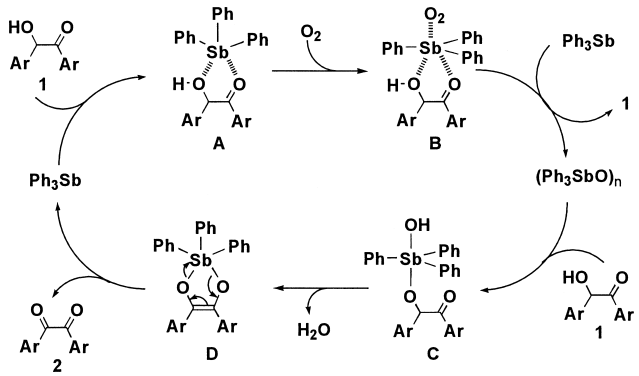

Chart 2

other α-ketoalcohols with **1a**, and the results are summarized in Table 2. The ketoalcohols **1a**—**g** were treated under the standard conditions employed for entry 8 in Table 1 (**1b**—**g**: 1 mmol, **2a**: 0.1 mmol), except for entry 1 (**1a**: 10 mmol, **2a**: 1 mmol). In all cases, the corresponding α-diketones **3a**—**g** were obtained in high yields (88—98%) except in the reaction of pyridoin **1d**, in that **1d** gave the oxidized product **3d** in 52% yield as a sole isolable product despite prolonged reaction time. No oxidized products were obtained in the reaction of methyl mandelate, benzopinacol, and 9-anthranylmethanol which have been known to be susceptible to oxidation. The results indicate that this aerobic oxidation has high substrate specificity and is effective in oxidizing diary-α-ketoalcohols into the corresponding α-diketones.

A plausible mechanism of the oxidation reaction is shown in Chart 2. The initial step of this reaction should involve the oxidation of **2a** into $SbPh_3$-oxo species (oxide) with aerobic oxygen, although the structure of the oxide could not be specified at present.[33—38)] The formation of the oxide may be assisted by the formation of Ph_3Sb-benzoin complex A caused by Sb···O aggregation with non-bonding interaction,[39,40)] because prolonged contact (>48 h) of **2a** with air or oxygen without benzoin did not form any oxides and all of the stibane was recovered unchanged. The electron-attracting group on antimony reagents may facilitate the aggregation of Ar_3Sb with benzoin and enhance the formation of the active oxide for the oxidation: the steps $Ar_3Sb \rightarrow \mathbf{A} \rightarrow \mathbf{B} \rightarrow (Ar_3SbO)_n$ in Chart 2. The oxide thus formed may react with benzoin to form pentavalent antimony intermediates **C** and **D** which undergo reductive antimony(III) elimination to give benzoin and trivalent **2a**. This hypothesis should be supported by the following fact. When benzoin was treated with the commercially available Ph_3SbO (0.1 eq) under the same reaction conditions, the reaction mixture showed the formation of **2a** along with **3a**, accompanying the progress of the reaction. Consequently, this reaction should involve an oxidation–reduction catalytic cycle between stibane Sb(III) and stiborane Sb(V).

In summary, we have disclosed that triarylstibane is a useful catalyst for the oxidation of diary-α-ketoalcohols into the corresponding α-diketones under air. Although a wide variety of the transformation of α-hydroxyketones into α-diketones has been reported, the present finding is attractive from the viewpoint of the catalytic action of trivalent organoantimony compounds.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot

stage apparatus and are uncorrected. Mass spectra (MS) were recorded on a JEOL JMP-DX300 instrument. ^{1}H-NMR spectra were recorded on a JEOL JNM-ECP500 (500 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. Column chromatography was performed on Silica Gel 60N (Kanto Chemical Co., Inc.). Tri(*p*-tolyl)- **2b** (mp 128—131 °C, lit.[41] 127 °C), tri(*p*-fluorophenyl)stibane **2c** (mp 93—95 °C, lit.[42] 91.8 °C), tri(*p*-chlorophenyl)stibane **2d** (mp 102—104 °C, lit.[42] 111.5 °C), tris(*p*-trifluoromethylphenyl)stibane **2e** (mp 130—132 °C), and tri(*p*-ethoxycarbonylphenyl)stibane **2f** (mp 74—76 °C) were prepared by the reaction of $SbCl_3$ or $SbBr_3$ with appropriate Grignard reagents,[43] and Ph_3SbO was obtained from Tokyo Kasei Kogyo Co., Ltd., Catalog No. T 1850.

General Procedure for Oxidation of Benzoins To a stirred solution of benzoin **1a** (1 mmol) in CH_2Cl_2 (4 ml) was added **2a** (0.1 mmol) at room temperature under air. The mixture was stirred for 8—24 h at the same temperature, and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (for **3a**, **c**, **e**), CH_2Cl_2/hexane (for **3b**, **f**, **g**) or CH_2Cl_2/ethyl acetate (for **3d**) as eluents. The products were identified by comparing their melting points, TLC, ^{1}H-NMR and MS spectra with those of the authentic samples. **3a**: Yellow prisms (from hexane–CH_2Cl_2), mp 94—95 °C (lit.[44] 94—95 °C), **3b**: Yellow needles (from hexane–CH_2Cl_2), mp 167—168 °C (lit.[45] 168—169 °C), **3c**: Yellow needles (from hexane–CH_2Cl_2), mp 83—84 °C (lit.[45] 84—85 °C), **3d**: Yellow needles (from $CHCl_3$), mp 155—156 °C (lit.[45] 155—156 °C), **3e**: Yellow prisms (from hexane–CH_2Cl_2), mp 102—104 °C (lit.[44] 102—103 °C), **3f**: Yellow needles (from hexane–CH_2Cl_2), mp 131—133 °C (lit.[44] 131—132 °C), **3g**: Yellow needles (from $CHCl_3$), mp 225—226 °C (lit.[44] 226 °C).

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