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; benzoins; benzil

The synthetic application of organic and inorganic antimony compounds is an important subject which has been highlighted to both organic and inorganic chemists.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 compounds15–19 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 acetae,24 aerobic oxygen,25,26 diacetoxyiodobenzene,27 and allyl diethyl phosphate.28 In this respect, pentavalent antimony compounds such as stibane oxide,20 diacetoxyphenylnystiborane,29 dibromotriphenylstiborane,30,31 and stibane imides32–34 were also known to be effective for this reaction. We now disclose that trivalent triarylstibane (Ar3Sb) 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 (CH2Cl2) 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 (Ph3P, Ph3As, Ar3Sb, and Ph3Bi), 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 oxygen in reaction medium was essential in the present reaction (entry 5). The oxidation of 1a was also take 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 Ph3Sb-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 (Ph3SbO) generated from the antimony reagent and oxygen. In fact, the reaction of 1a with catalytic amount of Ph3SbO brought about the same oxidation to afford 3a in high yield. Similar results were obtained when tri(p-toly1)-2a, tri(p-fluorophenyl)-2c, tri(p-chlorophenyl)-2d, tris(p-trifluoromethylphenyl)-2e, or tri(p-ethoxyphenylphenyl)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 CH2Cl2 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...
could not be isolated by decomposition during chromatographic separation.

were obtained in high yields (88—98%) except in the reaction
substrate specificity and is effective in oxidizing diary-
tion. The results indicate that this aerobic oxidation has high
methanol which have been known to be susceptible to oxida-
tion time. No oxidized products were obtained in the reac-
in 52% yield as a sole isolable product despite prolonged re-

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 elec-
tron-attracting group on antimony reagents may facilitate the
aggregation of Ar3Sb with benzoin and enhance the forma-
tion of the active oxide for the oxidation: the steps
Ar3SbO (0.1 eq) under the same reaction conditions, the re-
action of the active oxide for the oxidation: the steps
and all of the stibane was recovered unchanged. The elec-
tron-attracting group on antimony reagents may facilitate the
aggregation of Ar3Sb with benzoin and enhance the forma-
tion of the active oxide for the oxidation: the steps

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 pyridoxin 1d, in that 1d gave the oxidized product 3d in
52% yield as a sole isolable product despite prolonged re-
tion time. No oxidized products were obtained in the reac-
tion of methyl mandelate, benzoquinol, and 9-anthryln-
methanol 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-keto-
alcohols 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 SbPh3-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 Ph3Sb-benzoin complex
A caused by Sb···O aggregation with non-bonding interac-
tion,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 elec-

Table 1. Oxidation of Benzoin 1a into Benzil 3a with PNictogen Reagentsa)

<table>
<thead>
<tr>
<th>Entry</th>
<th>PNictogen reagent</th>
<th>Reagent/1a (mol eq)</th>
<th>Atmosphere</th>
<th>Time (h)</th>
<th>Yield of 3a%b) (recovery of 1a)</th>
<th>Recovery of PNictogen reagent%/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph3P</td>
<td>1.0</td>
<td>Air</td>
<td>60</td>
<td>0 (98)</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>Ph3As</td>
<td>1.0</td>
<td>Air</td>
<td>48</td>
<td>12 (61)</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>Ph3Sb 2a</td>
<td>1.0</td>
<td>Air</td>
<td>3.5</td>
<td>98 (0)</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>Ph3Sb 2a</td>
<td>1.0</td>
<td>O2</td>
<td>3</td>
<td>82 (0)</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Ph3Sb</td>
<td>1.0</td>
<td>Argon</td>
<td>24</td>
<td>4 (91)</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>Ph3Bi</td>
<td>1.0</td>
<td>Air</td>
<td>60</td>
<td>trace (89)</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td>SbCl3</td>
<td>1.0</td>
<td>Air</td>
<td>24</td>
<td>7 (92)</td>
<td>—d)</td>
</tr>
<tr>
<td>8</td>
<td>Ph3Sb 2a</td>
<td>0.1</td>
<td>Air</td>
<td>5</td>
<td>97 (0)</td>
<td>13</td>
</tr>
<tr>
<td>9</td>
<td>Ph3Sb 2a</td>
<td>0.05</td>
<td>Air</td>
<td>14</td>
<td>88 (0)</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>Ph3Sb 2a</td>
<td>0.1</td>
<td>O2</td>
<td>4</td>
<td>51 (49)</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>Ph3SbO</td>
<td>0.1</td>
<td>Air</td>
<td>5</td>
<td>96 (0)</td>
<td>—e)</td>
</tr>
<tr>
<td>12</td>
<td>(p-Tol)3Sb 2b</td>
<td>0.01</td>
<td>Air</td>
<td>10</td>
<td>88 (0)</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>(p-F-C6H4)3Sb 2c</td>
<td>0.01</td>
<td>Air</td>
<td>3.5</td>
<td>97 (0)</td>
<td>39</td>
</tr>
<tr>
<td>14</td>
<td>(p-Cl-C6H4)3Sb 2d</td>
<td>0.01</td>
<td>Air</td>
<td>3</td>
<td>96 (0)</td>
<td>41</td>
</tr>
<tr>
<td>15</td>
<td>(p-CF3-C6H4)3Sb 2e</td>
<td>0.01</td>
<td>Air</td>
<td>3</td>
<td>96 (0)</td>
<td>61</td>
</tr>
<tr>
<td>16</td>
<td>(p-CF3-C6H4)3Sb 2f</td>
<td>0.05</td>
<td>Air</td>
<td>7</td>
<td>87 (0)</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>(p-CO2Et-C6H4)3Sb</td>
<td>0.1</td>
<td>Air</td>
<td>3</td>
<td>96 (0)</td>
<td>45</td>
</tr>
</tbody>
</table>

a) All reaction was carried out using 1a (1 mmol) in CH2Cl2 (4 ml), see experimental.  b) Isolated yield.  c) Calculated from the reagent used  d) The reagent (SbCl3) could not be isolated by decomposition during chromatographic separation.  e) The reagent (Ph3SbO) could not be isolated by hard adsorption by SiO2 and 9% of SbPh3 was recovered from the reaction mixture.

Table 2. Catalytic Oxidation of Benzoins 1a—g into Benzils 3a—g with 2a under Aira)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time (h)</th>
<th>Product Yield (%)b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzoin 1a</td>
<td>12</td>
<td>Benzil 3a 98</td>
</tr>
<tr>
<td>2</td>
<td>2,2'-Furil 1b</td>
<td>12</td>
<td>2,2'-Furil 3b 97</td>
</tr>
<tr>
<td>3</td>
<td>2,2'-Thenil 1c</td>
<td>8</td>
<td>2,2'-Thenil 3c 98</td>
</tr>
<tr>
<td>4</td>
<td>2,2'-Pyridoxin 1d</td>
<td>24</td>
<td>2,2'-Pyridoxin 3d 52</td>
</tr>
<tr>
<td>5</td>
<td>4,4'-Dimethylenbenzoin 1e</td>
<td>10</td>
<td>4,4'-Dimethylenbenzoin 3e 97</td>
</tr>
<tr>
<td>6</td>
<td>4,4'-Dimethoxybenzoin 1f</td>
<td>12</td>
<td>4,4'-Dimethoxybenzoin 3f 88</td>
</tr>
<tr>
<td>7</td>
<td>4,4'-Dibromobenzoin 1g</td>
<td>10</td>
<td>4,4'-Dibromobenzoin 3g 97</td>
</tr>
</tbody>
</table>

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 CH2Cl2 (4 ml), except for entry 1 (1a: 10 mmol, 2a: 1 mmol).  b) Isolated yield.

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 JAMP-DX300 instrument. 1H-NMR spectra were recorded on a JEOL JNM-ECP500 (500 MHz) spectrometer in CDCl3 as an internal standard. Column chromatography was performed on Silica Gel 60N (Kanto Chemical Co., Inc.).

**General Procedure for Oxidation of Benzoins**

To a stirred solution of benzoin 1a (1 mmol) in CH2Cl2 (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. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (for 3a, c, e) or CH2Cl2/hexane (for 3b, f, g) or CH2Cl2/ethyl acetate (for 3d) as eluents. The products were identified by comparing their melting points, TLC, 1H-NMR and MS spectra with those of the authentic samples.

**References and Notes**


33) It is well known that triarylstibane oxides (Ar3SbO) including Ar3Sb-p-tolyl, Ar3Sb-fluorophenyl, Ar3Sb-p-toluyl and Ar3Sb-p-chlorophenyl exist in various forms (dimeric, oligomeric or polymeric form) depend on the preparation methods, and chemical properties of them vary markedly with their structure.


