



# Aminium hexachloroantimonate salts: a latent source of antimony pentachloride

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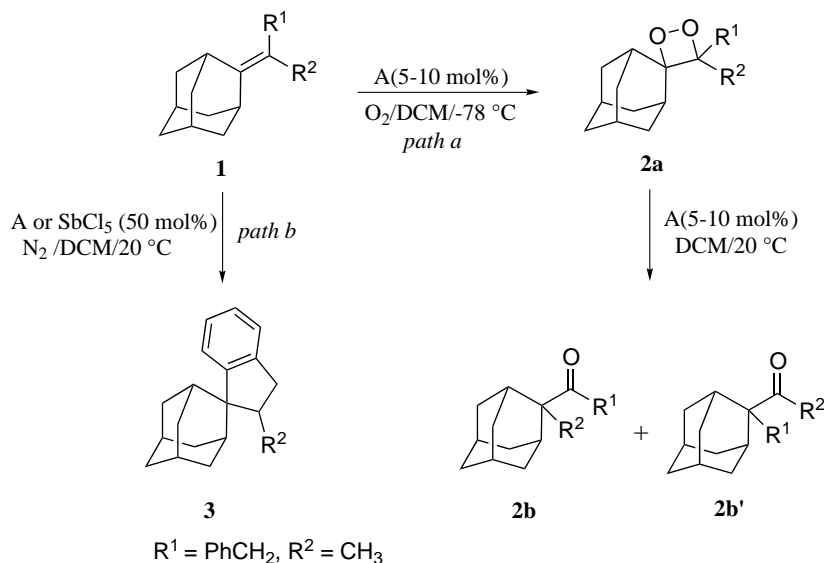
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**Abstract**—Cyclization of an adamantlylidene-based olefin induced by aminium hexachloroantimonate salts under a nitrogen atmosphere revealed that oxidative activation by these salts may be due to  $\text{SbCl}_6^-$ , which in combination with an oxidant counter-ion provides  $\text{SbCl}_5$  as the true reactive species. © 2001 Elsevier Science Ltd. All rights reserved.

The reactivity of triarylamminium salts such as tris(2,4-dibromophenyl)aminium hexachloroantimonate (**A**) and tris(4-bromophenyl)aminium hexachloroantimonate (**B**) in promoting useful chemistry pertains basically to their one-electron oxidant character.<sup>1–3</sup> However, it has been shown that they can also act as promoters of acid-catalyzed processes.<sup>4–6</sup> So far, the oxidative power of these salts has been invariably recognized in the triarylamminium radical cation working as direct acceptor of the electron coming from the electron-rich substrate. On the other hand, the possibil-

ity for these salts to induce acid-catalyzed chemistry has been simply explained on considering them as inevitable sources of protic acid: the radical cations intermediates they generate often being highly acidic species.

We now report that aminium hexachloroantimonates, particularly **A**, may release antimony pentachloride, which can behave as the true active species in both types of above reactions, namely as an oxidant in radical cation chemistry or as a Lewis acid in carbocation-mediated transformations. Clear evidence on the



## Scheme 1.

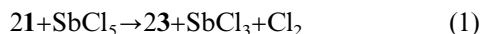
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direct involvement of  $\text{SbCl}_5$  in oxidative behaviour of **A** came from cyclization reaction of an adamantylidene-based olefin induced by this salt in nitrogen saturated dichloromethane (DCM) solutions.

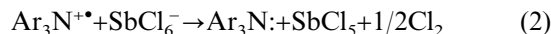
2-(1-Benzylethylidene)adamantane (**1**)<sup>7</sup> [ $E^{\text{ox}} = 1.75$  V versus SCE],<sup>9</sup> upon treatment with catalytic amounts (5–10 mol%) of **A**<sup>10</sup> in oxygen saturated DCM at room temperature, has been found to give carbonyl compounds **2b** (31% isolated yield) and **2b'** (59% isolated yield) (Scheme 1, path a). As previously reported for analogous systems,<sup>11</sup> these compounds result from an aminium salt induced monodeoxygenation process on 1,2-dioxetane intermediate **2a**, whose formation could be revealed by performing reactions at lower temperature ( $-78^\circ\text{C}$ ). Direct implication of the aminium moiety in the generation of radical cations as intermediates of these processes has been reported.

Upon treatment with **A** in nitrogen saturated solutions, **1** still reacted to give a cycloisomer that was obtained in quantitative gaschromatographic yield (86% isolated yield) within 1 h, and identified as 2'-methylspiro[adamantane-2,1'-indane]<sup>12</sup> (**3**) (Scheme 1, path b). Most importantly, we found that: (a) this reaction, far from being catalytic like related oxygenation processes, required *stoichiometric* quantities of **A** amounting to 50 mol%; (b) during the reaction *molecular chlorine* was evolved;<sup>13</sup> (c) *antimony pentachloride*, used instead of the aminium hexachloroantimonate in the same stoichiometric ratio, gave similar reactions, affording quantitative gaschromatographic yield of **3** and  $\text{Cl}_2$  as a by-product, not only under an inert atmosphere but also in oxygenated conditions. All these points can be accommodated in Eq. (1).



The close similarity of behaviour between the aminium hexachloroantimonate **A** and  $\text{SbCl}_5$  would be easily understood considering  $\text{SbCl}_6^-$  as a possible precursor of the latter, which thus should also be responsible for the transformations formally induced by **A**. Tests on reactivity of various hexachloroantimonates and aminium salts pointed out that the active role of  $\text{SbCl}_6^-$ , though indirect, is essential for these reactions and strictly dependent on the oxidative power of its counter ion. In fact, with tris(4-bromophenyl)aminium hexachloroantimonate [ $E^{\text{red}} = 1.16$  V versus SCE] or trityl hexachloroantimonate [ $E^{\text{red}} = 0.64$  V versus SCE] cycloisomerization of **1** was still observed, but was apparently slower and less efficient ( $\sim 40\%$  after 1 week) than those with **A** [ $E^{\text{red}} = 1.66$  V versus SCE]. On

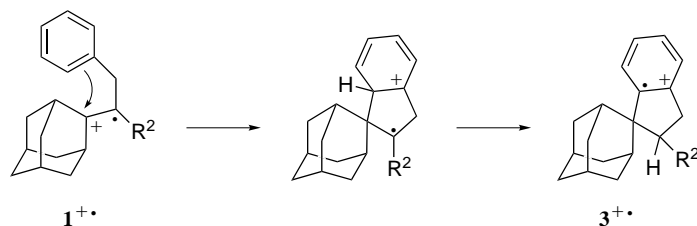
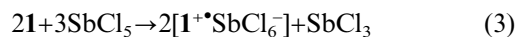
the other hand, in similar reactions carried out either with tris(4-bromophenyl)aminium tetrafluoroborate [ $E^{\text{red}} = 1.06$  V versus SCE] and trityl tetrafluoroborate [ $E^{\text{red}} = 0.46$  V versus SCE] or with the non-oxidant triphenylbenzylammonium hexachloroantimonate, no traces of **3** were detected. The mechanistic relationship between the aminium salt **A** and  $\text{SbCl}_5$  would rely on the capability of the aminium radical to oxidize  $\text{SbCl}_6^-$ , as shown in Eq. (2).<sup>14</sup>



The chloride ion to molecular chlorine oxidation by tris(2,4-dibromophenyl)aminium radical cation is an exergonic process ( $\Delta G = -12.2$  kcal/mol), which would contribute to loose  $\text{SbCl}_5$  from the strong coordination to chloride in  $\text{SbCl}_6^-$ . Even so, this is not a spontaneous process since it occurs only in the presence of the substrate which should consume  $\text{SbCl}_5$ . Clear evidence that the tris(2,4-dibromophenyl)aminium radical cation is capable of easily oxidizing a chloride ion was provided by reactions performed in the presence of equimolar quantities of tetrabutylammonium chloride: a more vigorous evolution of  $\text{Cl}_2$  was observed, and as a consequence of the consumption of the primitive oxidizing agent (the aminium radical), the **1** to **3** cycloisomerization was completely inhibited.

The chemistry described in Eq. (2) is reminiscent of the explanation given by Kochi<sup>15</sup> to account for the efficacy of triethyloxonium hexachloroantimonate in the one-electron oxidation of several aromatic hydrocarbons: in that case was the alkylating power of the oxonium ion toward  $\text{SbCl}_6^-$  to free  $\text{SbCl}_5$  as the effective oxidant. Furthermore, the role of  $\text{SbCl}_5$  as one-electron oxidant in our reactions under a nitrogen atmosphere is strongly suggested by the observed 2:1 stoichiometry. This corresponds exactly to the redox stoichiometry that has been established by Kochi<sup>15</sup> for reactions of preparation of crystalline aromatic radical cation hexachloroantimonates using  $\text{SbCl}_5$ .

A plausible mechanism that would also account for  $\text{Cl}_2$  development is illustrated in the sequence of Eqs. (3)–(5): the initial formation of the substrate radical cation **1**<sup>•+</sup> is followed by rearrangement (see Scheme 2) into the product radical cation **3**<sup>•+</sup>, which in turn would oxidize the hexachloroantimonate ion to give the neutral product and molecular chlorine. Summation of the stoichiometries of Eqs. (3)–(5) does result in the 2:1 stoichiometry of Eq. (1).



Scheme 2.



Stoichiometric requirement of  $\text{SbCl}_5$  by itself would militate against the hypothesis that this reagent may act as a Lewis acid, in which case a catalytic process seems to be most likely. However, the weak consistency of an acid mechanism found confirmation in results of reactions carried out with  $\text{BF}_3$  or  $\text{CF}_3\text{CO}_2\text{H}$  also used in more than stoichiometric amount: with both, Lewis and protic acid, no reaction was observed.

The fact that radical cation intermediates seem to be involved in cyclization as well as in oxygenation reactions raises mechanistic questions of why the aminium radical cation behaves as an effective oxidant only in the latter type of reactions, and why reactions with  $\text{SbCl}_5$  under an oxygen atmosphere do not afford oxygenation products. To answer these questions one can speculate that the endergonic ( $\Delta G = 2.07$  kcal/mol) one-electron transfer from **1** to the aminium radical cation of **A** would still result effective in generating the active species  $\mathbf{1}^{+\bullet}$  only if this latter can be consumed in a fast reaction with oxygen. According to this, to account for the absence of oxygenation products in reactions with antimony pentachloride, a distinction between radical cation intermediates generated by aminium radical cation and those by  $\text{SbCl}_5$  is in order. A reasonable hypothesis is that the first are formed as free species by an outer-sphere mechanism, while the latter, probably generated by an inner-sphere mechanism, have an ion-pair structure that might preclude reaction with oxygen.

In conclusion, we have found a novel reaction mode for aminium hexachloroantimonate salts, which would apply towards substrates that are difficult to oxidize directly by aminium radical cation. In these cases the aminium salt, especially the more powerful tris(2,4-dibromophenyl)aminium hexachloroantimonate, can behave as a source of  $\text{SbCl}_5$  which in turn works as the active oxidant. However, preliminary results seem to indicate that  $\text{SbCl}_5$  is equivalent to the aminium salt also in reactions proceeding by acid catalysis, e.g. cyclodimerization of 1-aryl-1-phenylethylene.<sup>6</sup>

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- Compound **1** was prepared according to the Adam's procedure in Ref. 8, and was obtained as white solid: mp 43–44°C from pentane. *m/z* (rel abund) 252 ( $\text{M}^+$ , 100), 237 (98), 223 (8), 141 (21), 117 (26), 105 (34), 91 (93), 79 (38), 41 (58);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.63 (s, 1H), 1.74–2.05 (m, 12H), 2.97 (s, 1H) 3.05 (s, 1H), 3.43 (s, 2H), 7.15–7.40 (m, 5H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  17.38, 28.18, 33.06, 33.10, 37.23, 38.93, 119.03, 125.55, 128.20, 128.51, 141.32, 141.82 ppm; IR (KBr) 3028, 2961, 2896, 2843, 1602, 1494, 1454, 1447, 1378, 1351, 1100, 1078, 1053, 1029, 745, 720, 697, 631  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{19}\text{H}_{24}$ : C, 90.41; H, 9.59. Found: C, 90.31; H, 9.60.
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- By cyclic voltammetry in DCM (*n*- $\text{Bu}_4\text{NClO}_4$ , 0.1 M) in the absence of oxygen at 0.05 V/s.
- A** was prepared as described in Baker, T. N.; Doherty, W. P.; Kelly, W. S.; Newmeyer, W.; Rogers, J. E.; Spaulding, R. J.; Walters, R. *J. Org. Chem.* **1965**, *30*, 3714.
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- Compound **3** was obtained as white solid: mp 45–46°C from ethanol. *m/z* (rel abund) 252 ( $\text{M}^+$ , 100), 237 (5), 223 (54), 141 (31), 131 (58), 129 (32), 91 (22), 81 (28), 67 (28), 41 (26);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.79 (d, 3H,  $\text{CH}_3$ ,  $J = 6.7$  Hz), 1.25–2.40 (13, adamantane ring) 2.28 (d, 1H,  $J = 15.2$  Hz), 2.78–2.86 (m, 1H), 2.89 (quintet, 1H,  $J = 6.7$  Hz), 3.14 (dd, 1H,  $J = 15.2$ , 6.25 Hz), 7.11–7.24 (m, 3H), 7.72–7.79 ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  15.43, 27.41, 27.63, 31.87, 32.76, 33.60, 34.72, 35.19, 35.21, 37.24, 39.38, 39.64, 56.41, 125.13, 125.38, 125.74, 127.64, 143.50, 149.66 ppm. IR (KBr) 2902, 2853, 1470, 1455, 1098, 1080, 752, 725, 704  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{19}\text{H}_{24}$ : C, 90.41; H, 9.59. Found: C, 90.18; H, 9.65.
- The identity of  $\text{Cl}_2$  was confirmed by chromatographic analysis of chloride ions obtained according to the reaction  $3\text{Cl}_2 + 6\text{OH}^- \rightarrow 5\text{Cl}^- + \text{ClO}_3^- + 3\text{H}_2\text{O}$  from the evolved gas allowed to bubble into an aqueous NaOH solution: calcd for 1 mmol of **A** (equivalent to 1.5 mmol of  $\text{Cl}_2$  according to Eqs. (1) and (2)): 2.5, found: 1.7 (inevitable leaks in the chlorine trapping system make this value fairly satisfactory).
- In this regard, it is important to note that no ageing effect was observed on the reactivity pattern of **A** within 1 month.
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