Aminium Hexachloroantimonate Salts as Latent Sources of Antimony Pentachloride in Pinacolic Rearrangement of Vicinal Diols

Francesco Ciminale, Luigi Lopez,*[a] Angelo Nacci,[a] Lucia D'Accolti,[a] and Floriana Vitale[a]

Dedicated to Professor Giorgio Modena on the occasion of his 80th birthday

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Rearrangements of various vicinal diols (**1a–f**) induced by hexachloroantimonate aminium salts **A** or **B** were found to occur in a similar manner when antimony pentachloride was used instead of aminium salts. Antimony pentachloride is proposed as the active catalytic species, possibly deriving from the oxidation of the hexachloroantimonate anion $SbCl_6^-$ by the aminium counterpart.

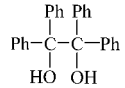
Introduction

Synthetic tris(2,4-dibromophenyl)aminium hexachloroantimonate (**A**) [E^{re} = 1.66 V vs. SCE],[1] and the commercially available "magic blue", or tris(4-bromophenyl)aminium hexachloroantimonate (**B**) [E^{re}> = 1.16 V vs. SCE],[2] have been widely employed, inter alia, to perform stereoselective Diels–Alder [4 + 2] reactions and [2 + 2] cycloadditions of molecular oxygen to particular tetraalkylated olefins and dienes. So far, they appear to be the most distinguished examples of the potential of electron-transfer activation of unsaturated substrates by aminium salt catalysis.[3a,3c] However, chemists still appear reluctant to extend the mechanistic/theoretical aspects of this chemistry to all the other chemical transformations (isomerization, fragmentation, rearrangement, nucleophilic capture and dimerization) induced by aminium salts **A** and **B**.[4a–4e] The most important reasons for this are: (a) difficulties in controlling the various reaction events in processes involving odd-electron species, (b) the observation that factors such as concentration, temperature, solvent polarity and the reaction's atmosphere can directly influence the behaviour of transient cation-radical intermediates, and (c) the possibility for these salts to induce acid-catalysed chemistry.[4a,4b] In this context, Kochi and co-workers,[5] exploring a plausible fast interchange between diamagnetic and paramagnetic intermediates, established that acid-catalysed and electron-transfer processes may not be easily differentiated as formerly thought.[6]

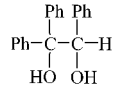
[a] Dipartimento di Chimica, Università di Bari,
Via Orabona 4, 70126 Bari, Italy
Fax: +39-080-5442924
E-mail: lopez@chimica.uniba.it

Proceeding with our interest in the reactivity of aminium salts **A** and **B**, we recently found that these salts may also release antimony pentachloride ($SbCl_5$), which might behave both as a one-electron oxidising agent[7] and as a Lewis acid,[8] in relation to particular reaction conditions and properties of donor substrates.

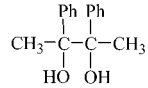
We now report that the involvement of $SbCl_5$ in reactions formally induced by aminium salts **A** and **B** has also been confirmed by study of their reactions with several *vic*-diols, such as benzopinacol (**1a**) [E^{ox} = 1.88 V vs. SCE], 1,1,2-triphenylethane-1,2-diol (**1b**) [E^{ox} = 1.95 V vs. SCE], 2,3-diphenylbutane-2,3-diol (**1c**) [E^{ox} = 2.30 V vs. SCE], 2,3-dimethylbutane-2,3-diol (**1d**) [$E^{ox} > 2.30$ V vs. SCE], 2,2′-biadamantane-2,2′-diol (**1e**) [$E^{ox} > 2.30$ V vs. SCE][9] and (1*S*,2*S*,3*R*,5*S*)-pinane-2,3-diol (**1f**) [$E^{ox} > 2.30$ V vs. SCE]. Although these substrates show increasing oxidation potentials, and thus a decreasing capability to behave as electron-donor substrates,[10a,10c] our original results on aromatic



1a



1b



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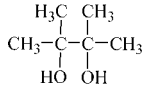
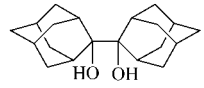
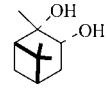


1d



1e



1f

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vic-diols were interpreted in terms of a chain electron-transfer process.[11a,11b]

Results and Discussion

It has been well ascertained that aromatic *vic*-diols are suitable substrates to distinguish an electron-transfer (ET) process from a protic acid-catalysed process, the former leading to mixtures of simple carbonyl compounds from oxidative C–C bond cleavage,[12] the second affording the carbonyl compounds from the well known pinacol rearrangement (Scheme 1).[13a,13b]

However, the rearrangement or oxidation of several aromatic *vic*-diols induced by different one-electron oxidising agents has been the subject of much debate. Arce de Sanabia and Carrion[14] reported that 1,1,2,2-tetrakis(4-methoxyphenyl)ethane-1,2-diol [E^{ox} = 1.39 V vs. SCE] and 1,1,2,2-tetrakis(*p*-tolyl)ethane-1,2-diol [E^{ox} = 1.71 V vs. SCE] gave carbonyl compounds consistent with a pinacol rearrangement on treatment with catalytic amounts of nitrosonium tetrafluoroborate ($NOBF_4$) [E^{red} = 1.28 V vs. SCE].[15] The mechanism they proposed, on the basis of consistent chemical and electrochemical evidence, was a chain electron transfer.[14] In the same paper, the authors also reported that $NOBF_4$ was unable to promote the rearrangement of benzopinacol (**1a**) [E^{ox} = 1.88 V vs. SCE],[10a] underlining that the nitrosonium ion did not act as an acid catalyst or generate protic acid under these conditions.[14]

In contrast, Penn and co-workers reported that molar excesses of iron(III) trisphenanthroline complexes [$Fe^{III}L_3(PF_6)_3$] [E^{red} = 1.09 V vs. SCE][10a–10c] or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [E^{red} = 0.52 V vs. SCE][10a] caused the quantitative oxidation of **1a** to benzophenone (**3**), provided that a molar excess of an organic base, 2,6-di-*tert*-butylpyridine (DBP) [E^{ox} = 1.85 V vs. SCE],[6] was also added to the reaction medium.

In work by Shine and Han,[4c] the presence of a significant molar excess, relative to **1a**, of thianthrene radical cation ($Th^{+\cdot}$ ClO_4^- or BF_4^-) [E^{red} = 1.18 V vs. SCE][16] together with an excess of DBP still, seemingly, led to quantitative amounts of **3**. These results were accounted for by a fast C–C bond cleavage in the intermediate cation-radical (**1a**$^{+\cdot}$) due to its extremely short lifetime.[17] At the same time, Penn and Shine claimed that the only function of the non-nucleophilic base was to prevent the protic acid-catalysed rearrangement of the diols.

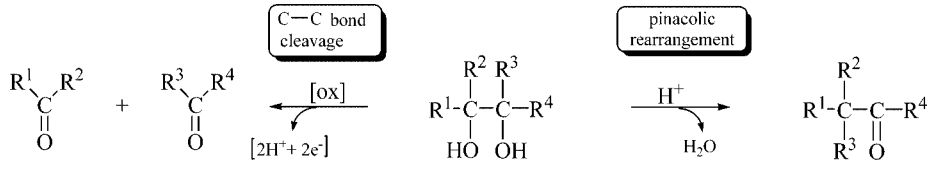
Experimental conditions for the reactions of **1a**–**f** in dichloromethane (DCM) with catalytic amounts (5–10 mol %) of aminium salts **A**, **B** or $SbCl_5$ are reported in the Experimental Section. With the use of aminium salts as catalysts, the intensely green or blue colours of the solutions faded at different rates, depending on the oxidising power of the aminium salt employed. In contrast, the reactions induced by antimony pentachloride took on an initial pale yellow colour, which persisted during the process. Analyses of the reaction mixtures, monitored by TLC until completion (starting materials generally decomposed on GC columns) and then by GC/MS spectrometry and ^1H NMR spectroscopy revealed the formation of new reaction products, fully characterised by comparison of their physical and chemical data with those of authentic commercial or synthesised samples (Table 1).

Table 1. Rearrangements of *vic*-diols to carbonyl compounds induced by aminium salts **A**, **B** and $SbCl_5$.

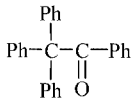
Run[a]	Vicinal diols	Catalysts	*t* [h]	Reaction products (%)
1	**1a**	**A**	0.05	**2a** (100)
2	**1a**	**B**	0.5	**2a** (100)
3	**1a**	**A**/DBP[b]	3	no reaction
4	**1a**	**A**/DBP[c]	3	**2a** (30)
5	**1a**	$SbCl_5$	0.05	**2a** (100)
6	**1a**	$SbCl_5$/DBP[b]	2	no reaction
7	**1b**	**A**	0.15	**2b** (90), **3b** (10)
8	**1b**	$SbCl_5$	0.10	**2b** (94), **3b** (6)
9	**1b**	$SbCl_5$/DBP[b]	2	no reaction
10	**1b**	$HClO_4$	1	**2b** (tr), **3b** (98)
11	**1c**	**A**	1	**2c** (100)
12	**1c**	**B**	24	**2c** (40)
13	**1c**	$SbCl_5$	0.17	**2c** (100)
14	**1c**	$SbCl_5$/DBP[b]	24	no reaction
15	**1d**	**A**	24	**2d** (30), **4d** (15)
16	**1d**	**B**	24	**2d** (tr), **4d** (tr)
17	**1d**	$SbCl_5$	24	**2d** (40), **4d** (10)
18	**1d**	$SbCl_5$/DBP[b]	24	no reaction
19	**1e**	**A**	2	**2e** (100)
20	**1e**	**B**	6	**2e** (60)
21	**1e**	$SbCl_5$	1.3	**2e** (100)
22	**1e**	$SbCl_5$/DBP[b]	24	no reaction
23	**1f**	$SbCl_5$	1.3	**4f** (45), **5f** (45)

[a] All the reactions were performed in DCM solutions, with stirring at room temperature and use of 10 mol % of catalysts relative to starting materials. [b] These results were observed on addition of the diols to equimolar amounts of catalysts and DBP (protocol a). [c] These results were observed on addition of the catalysts to diols in the presence of DBP (protocol b).

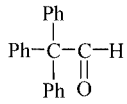
The total conversion of **1a** into 1,1,1-triphenylacetophenone (**2a**) occurred within 3 min with the aminium salt **A** (run 1) and within 30 min with **B** (run 2). Furthermore, the reactions induced by the less powerful aminium salt **B**



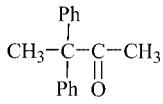
Scheme 1.



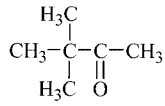
2a



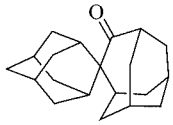
2b



2c



2d



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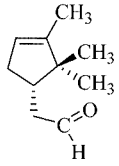
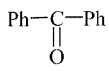
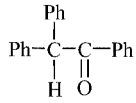


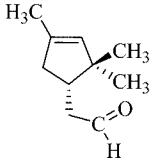
2f



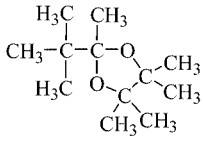
3



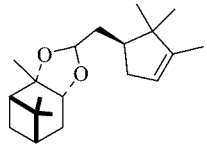
3b



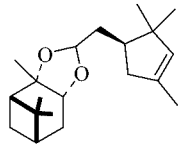
3f



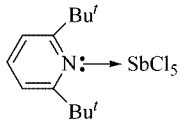
4d



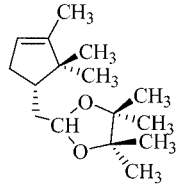
4f



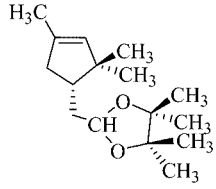
5f



6



7f

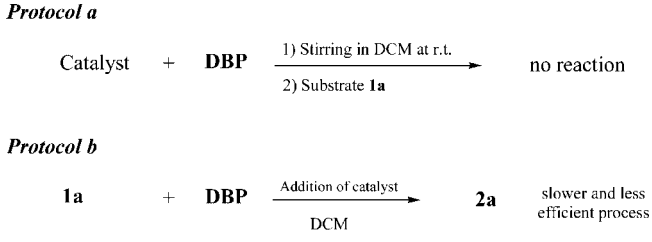


8f

showed the intermediate formation of the corresponding tetraphenylethylene oxide, which underwent an easy rearrangement to **2a** in situ.[18a,18b] Similar reactions, carried out with catalytic amounts of antimony pentachloride, occurred as rapidly as those induced by the powerful aminium salt **A** (3 min, run 5).

The addition of a hindered base, such as 2,6-di-*tert*-butylpyridine (DBP), has previously been used as a diagnostic test to distinguish a protic acid-catalysed reaction from an electron-transfer process in reactions induced by aminium salts.[6] When this test was applied to our reactions conducted with antimony pentachloride, as well as with aminium salts **A** and **B**, as catalysts (runs 3, 4, 6), we found that DBP either could or could not inhibit the rearrangement of starting materials, depending on the protocol applied.

In fact, if **1a** was added, over a few minutes, to stirred DCM solutions of equimolar amounts of catalysts and DBP (*protocol a*) the rearrangement was totally inhibited (runs 3, 6). The starting material was recovered unchanged and we concomitantly observed the formation of a white, dusty precipitate. In contrast, on addition of catalysts to stirred solutions of **1a** and DBP (equimolar amounts relative to the catalysts, *protocol b*), the conversion to **2a** was merely retarded and less efficient (run 4) (Scheme 2).



Scheme 2.

The same precipitate was also observed upon treatment of dichloromethane solutions of DBP with equimolar amounts of $SbCl_5$, as well as with aminium salts **A** and **B**. This precipitate, fully characterized as reported in the Experimental Section, shows ^1H and ^{13}C NMR spectra (Figure 1) totally different from those recorded on the pure base.

The two different behaviour patterns might be ascribed to the fast formation of a 1:1 DBP–$SbCl_5$ nonoxidising complex **6** (*protocol a*) and to competitive reactions of the catalyst towards the substrate and DBP, respectively (*protocol b*). In any case, it is not merely traces of contaminating antimony pentachloride in the aminium salts employed that would catalyse the pinacol rearrangement of starting mate-

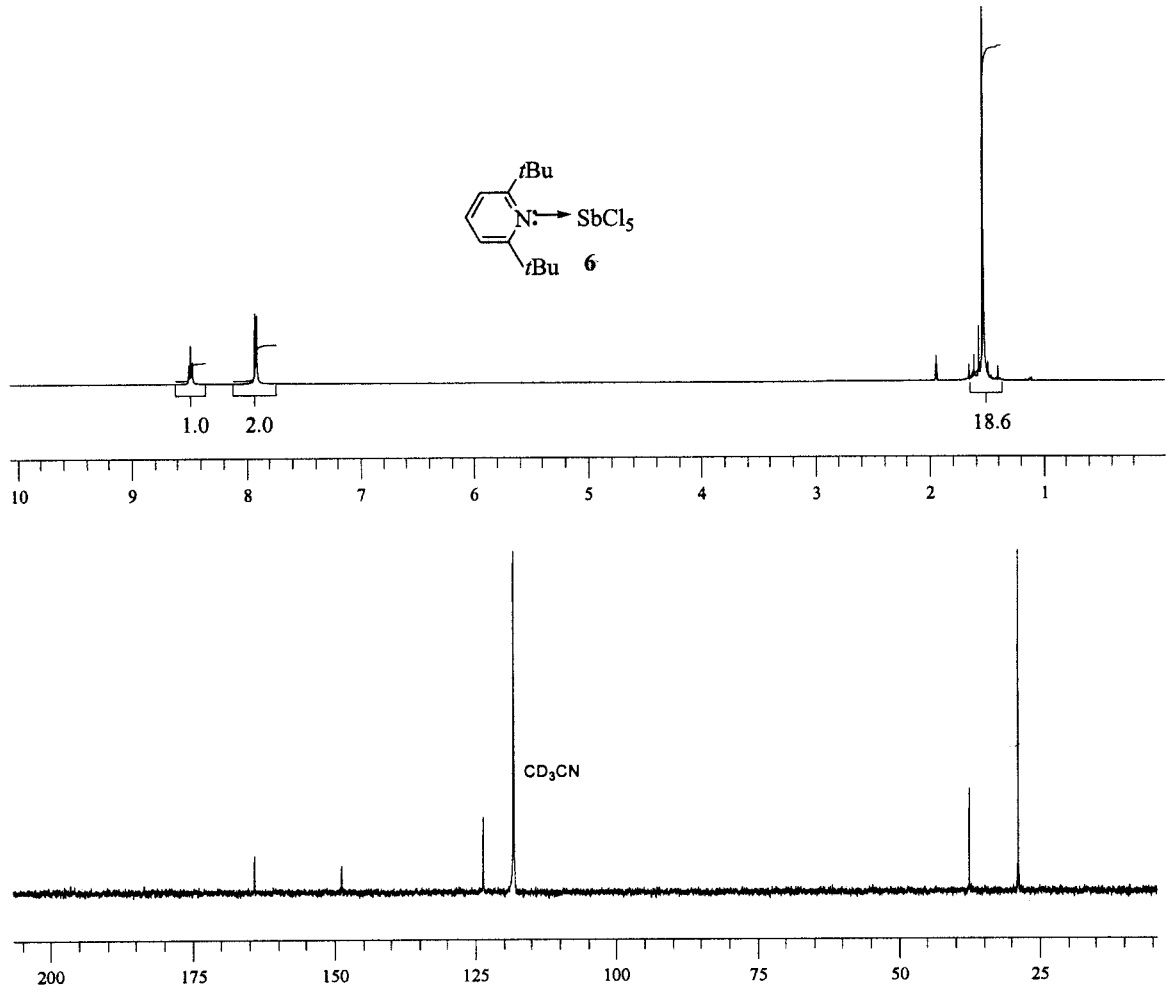


Figure 1. ^{1}H and ^{13}C NMR spectra of the complex **6**.

rials. In fact, the aminium salts **A** and **B**, freshly prepared, were repeatedly washed with dry, cold diethyl ether until neutral solutions were obtained. As a consequence, we claimed that the observed inhibition can be considered a positive outcome of the DBP test for protic and Lewis acid catalysis.[6]

The same protocol was applied to other aromatic derivatives, such as **1b** or **1c**, showing higher oxidation potentials than **1a**. In particular, analyses of reaction mixtures arising from treatment of **1b** with catalytic amounts of aminium salts **A** and $SbCl_5$ (runs 7–9) revealed the total disappearance of starting materials and the concomitant formation of rearranged carbonyl compounds: namely triphenylacetaldehyde (**2b**, 94–90% yield) and benzhydryl phenyl ketone (**3b**, 6–10%).

These experimental results apparently differ from those observed by use of various protic acids as catalysts in different solvents.[13a,13b] For example, **1b** afforded **3b**, as the sole reaction product, upon treatment of its solutions with perchloric acid ($HClO_4$, run 10) or concentrated sulfuric acid,[13a] but the aldehyde **2b** when 40% sulfuric acid solution was used.[13a] Unreacted glycol **1b** was, instead, recovered upon treatment of its DCM solution with catalytic amounts of *p*-toluenesulfonic acid (*p*-**TSA**).

Close mechanistic examination of these reactions showed that the kinetically controlled ratio of **2b** to **3b** depended to some extent on the solvent and acid employed, and it was further complicated by the conversion of the aldehyde to the ketone under protic acid conditions.[13a,13b] In contrast, under our reaction conditions, the ratio between these latter carbonyl compounds did not change within three days. Given that phenyl is normally a better migrating group than hydrogen, this might be due either to a preferential coordination of the Lewis acid $SbCl_5$ to the hydroxy group linked to the more substituted carbon atom, then directly affording the less thermodynamically stable carbonyl compound **2b**, but also to a reduced efficiency of the Lewis acid in promoting the internal conversion between carbonyl compounds.

As reported above for **1a**, we still found that DBP, added either in equimolar amounts or in slight excess with regard to the catalysts (**A**, $SbCl_5$), either could or could not inhibit its rearrangement, depending on the protocol (*a* or *b*) applied.

Analogous results were achieved with 2,3-diphenylbutane-2,3-diol (**1c**), which afforded 3,3-diphenylbutan-2-one (**2c**, run 11) as the sole rearranged ketone within 1 h with catalysis by aminium salt **A**. In contrast, the reaction induced by the less powerful aminium salt **B** was apparently slower and less efficient (24 h, 40% conv, run 12). In contrast, the reaction afforded **2c** within 10 min when carried out with antimony pentachloride as catalyst (run 13). On addition of DBP this reaction was also found to be inhibited (run 14).

The different reaction rates observed in runs 11–12 and, in part, for the substrate **1a** in runs 1–3 might be accounted for by the hypothesis that aminium salts, due to the capability of the aminium cation-radical to oxidize the hexachloroantimonate anion ($SbCl_6^-$),[7,8] may effectively behave as latent sources of antimony pentachloride, as in Equation (1).

$$Ar_3N^{+\bullet} + SbCl_6^- \longrightarrow Ar_3N: + SbCl_5 + 1/2\ Cl_2 \quad (1)$$

The oxidation of chloride ion to molecular chlorine would occur more quickly with aminium salt **A** (ΔG = –12.2 kcal mol^{-1}) than with **B** (ΔG = –0.7 kcal mol^{-1}) and take place when: (a) the direct oxidation of electron-rich substrates with cation-radical Ar_3N+. was thermodynamically disfavoured (endoergonic processes), (b) cation-radical intermediates could not be withdrawn from the preliminary electron-transfer equilibria, the back electron-transfer process then prevailing, or (c) the substrate could somehow consume $SbCl_5$.

The chemistry described in Equation (1) was reminiscent of the explanation given by Kochi to account for the efficacy of triethyloxonium hexachloroantimonate [$(Et)_3O^+$ $SbCl_6^-$] in the one-electron oxidation of several aromatic hydrocarbons:[19] in that case the alkylating power of the oxonium ion toward $SbCl_6^-$ to give $SbCl_5$.

Tests on the reactivities of various hexachloroantimonate salts with nonoxidizing cations, such as tribenzylmethylammonium [$(PhCH_2)_3CH_3N^+SbCl_6^-$] and triphenylbenzylammonium [$(Ph)_3PhCH_2N^+SbCl_6^-$], indirectly confirmed that the oxidizing ability of the counterion Ar_3N+. was of pivotal importance for the release of antimony pentachloride in solution. In fact, they appeared completely inert in promoting the pinacolic rearrangement of *vic*-diols.

As further evidence for $SbCl_5$ formation from **A**, according to Equation (1), we looked for chlorine evolution during the aminium salt-induced reactions. The gas evolved during the process, notwithstanding the small scale of our reactions and the limited amount of chlorine evolved from the catalyst (10 mol %), was identified by bubbling the gas into a double-phase trap containing potassium iodide in water and dichloromethane. The iodine was confirmed by UV/Vis spectrophotometry. Through a slow escape of Cl_2 we can also account for the slow decomposition that these hexachloroantimonate aminium salts undergo over long storage periods in solid state or in solution.

The pivotal importance of the reaction in Equation (1) was also confirmed by the experimental results achieved on aliphatic and cycloaliphatic substrates such as 2,3-dimethylbutane-2,3-diol (**1d**), 2,2′-biadamantane-2,2′-diol (**1e**) and (1*S*,2*S*,3*R*,5*S*)-pinane-2,3-diol (**1f**), which would be more and more inert to oxidation by an electron-transfer pathway. In fact, it has been reported by Penn that the reactions of 0.01 M acetonitrile solutions of **1d** with 50 mol % of different [Fe^{III} phenanthroline] complexes were apparently inefficient, as the starting material was recovered unchanged after 24 h.[10b,10c] The lack of reactivity of **1d**, coupled with the facile cleavage of **1a** and **1c**, upon treatment of their acetonitrile solutions with the same catalyst, was reported to be clear evidence of correlation of the reaction rates with oxidation potentials of the glycols, in agreement with the Marcus theory of a preliminary outer sphere electron-transfer process.[20]

In contrast, we observed that stirred DCM solutions of **1d** (10^{-2} M), upon treatment with catalytic amounts of **A** (10 mol%) or antimony pentachloride as catalysts, gave slow conversions (runs 15, 17), of the starting material into mixtures of 3,3-dimethylbutan-2-one (**2d**) and the corresponding acetal **4d**.[21] As expected, similar reactions carried out with the less powerful aminium salt **B** were apparently much slower and less efficient (run 16). The same protocol was also applied to 2,2′-biadamantane-2,2′-diol (**1e**) (runs 19–22) and (1*S*,2*S*,3*R*,5*S*)-pinane-2,3-diol (**1f**), which afforded high yields of spiro[adamantane-2,4′-homoadamantan-5′-one] (**2e**) and a 1:1 mixture of [(*S*)-2,2,3-trimethyl-3-cyclopentenyl]acetaldehyde (1*S*,2*S*,3*R*,5*S*)-pinane acetal (**4f**) and [(*S*)-2,2,4-trimethyl-3-cyclopentenyl]acetaldehyde (1*S*,2*S*,3*R*,5*S*)-pinane acetal (**5f**), respectively (run 23).[11c] These reaction products were accounted for by the intermediate formation of equimolar amounts of [(*S*)-2,2,3-trimethyl-3-cyclopentenyl]acetaldehyde (**2f**) and [(*S*)-(2,2,4-trimethyl-3-cyclopentenyl]acetaldehyde (**3f**), the fast subsequent reactions of which with the diols would lead to the corresponding acetals.[11c] In order to account for this mechanistic hypothesis, we performed similar reactions by adding the aminium salt **A** or antimony pentachloride to DCM solutions of **1f** and pinacol **1d** in equimolar amounts. These reactions led to the concomitant formation of pinane acetals **4f** and **5f**, together with a new pair of acetals in the form of [(*S*)-2,2,3-trimethyl-3-cyclopentenyl]acetaldehydepinacol acetal (**7f**) (M^+ = 252 by MS) and [(*S*)-2,2,4-trimethyl-3-cyclopentenyl]acetaldehyde pinacol acetal **8f** (M^+ = 252).

The structures of these latter compounds were ascertained by comparison of their GC/MS fragmentation patterns with that of an unisolated sample **7f**, synthesised by treatment of the aldehyde **2f** with equimolar amounts of **1d** in the presence of catalytic amounts of *p*-toluenesulfonic acid (*p*-TSA).

In conclusion, we believe that the involvement of antimony pentachloride in pinacolic rearrangements of *vic*-diols, formally induced by hexachloroantimonate aminium salts **A** and **B**, finds confirmation in the following facts: (a) the close similarity in behaviour between reactions in-

duced by antimony pentachloride and by aminium salt **A**, (b) the observed inhibition of reactions modified by addition of equimolar amounts (vs. the catalysts) of the non-nucleophilic base DBP, (c) the characterization of the 1:1 DBP/$SbCl_5$ complex, and (d) the reactivity of aliphatic *vic*-diols,[21] which, contrary to aromatic *vic*-diols,[10a,10c] show high oxidation potentials not affected by aryl–aryl interactions, to make their preliminary electron-transfer oxidation totally unsuitable.

Experimental Section

Melting points were taken on an electrothermal apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Varian XL 200 and Bruker AM 500 MHz instruments. IR and MS spectra were performed on a Perkin–Elmer FT-1710 (KBr pellets) and on a Shimadzu QP5000 instrument, respectively. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter. GC analyses were carried out on a HP 5890A gas chromatograph with a capillary column (ZB-1, 30 m, 0.25 mm i. d.). Dichloromethane was purified by washing with sulfuric acid solution and distillation over calcium hydride and was then stored in the dark under nitrogen and over molecular sieves. Acetonitrile (HPLC grade from Carlo Erba Co.) was used as received. Starting materials **1a**–**d**, **1f** and 2,6-di-*tert*-butylpyridine (DBP) were commercial samples from Aldrich Co. Aminium salts **A**[1] and **B**[2] and substrate **1e**[9] were synthesized by the procedures reported in the literature.

Pinacol–Pinacolone Rearrangement of Diols 1a–f by Antimony Pentachloride. General Procedure: Catalytic amounts of DCM solutions of antimony pentachloride (10 mol %) were rapidly added, under air at room temperature, to stirred solutions of **1a**–**f** (100 mol %) in dry CH_2Cl_2 (10 mL). The solutions adopted a pale yellow colour, which persisted through the process. The progress of the reactions was monitored by TLC until completion, and then by GC and GC/MS spectroscopy. The reaction mixtures were quenched with sodium hydrogencarbonate solution ($NaHCO_3$ 10%, 5 mL), then dichloromethane (10 mL) was added. The organic layer was separated and dried over sodium sulfate (Na_2SO_4). The solvent was removed in vacuo, and the reaction products, isolated by column chromatography (silica gel, petroleum ether/ethyl ether 10:1 as eluent), were fully characterized by physical, spectroscopic data, and comparison with authentic synthesized samples, already reported in the literature.

Triphenylacetophenone (2a): M.p. 179–180 °C (lit.[4c] 179–180 °C). IR (KBr): $\tilde{\nu}$ = 3087, 1674, 701 cm^{-1}. MS (*m*/*z* %): 243 (M^+ – PhCO, 100), 165 (54), 105 (9), 77 (6).

Triphenylacetaldehyde (2b): M.p. 104–105 °C (lit.[13b] 104–105 °C). ^1H NMR ($CDCl_3$): δ = 10.28 (s, 1 H) 7.25–7.06 (m, 15 H) ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2724, 1685 cm^{-1}. MS (*m*/*z* %): 243 (M^+ – CHO, 100), 165 (56).

Benzhydryl Phenyl Ketone (3b): M.p. 134–135 °C (lit.[13b] 133–135 °C). ^1H NMR ($CDCl_3$): δ = 8.03–7.95 (m, 2 H), 7.58–7.18 (m, 13 H), 6.06 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 199.82, 139.35, 137.05, 133.21, 129.30, 129.11, 128.97, 127.83, 59.43 ppm. IR (KBr): $\tilde{\nu}$ = 3065, 2978, 1683 cm^{-1}. MS (*m*/*z* %): 272 [M^+, 2], 167 (40), 105 (100), 77 (19).

3,3-Diphenylbutan-2-one (2c): M.p. 41 °C (lit.[10a] 41 °C). ^1H NMR ($CDCl_3$): δ = 7.38–7.21 (m, 10 H), 2.14, (s, 3 H), 1.90 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 209.04, 143.52, 128.30, 126.85, 62.25, 27.55, 26.36 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 1709, 701 cm^{-1}. MS (*m*/*z* %): 224 [M^+, 3], 181 (100), 165 (29), 103 (34), 77 (22), 43 (17).

Spiro[adamantane-2,4′-homoadamantan-5′-one] (2e): M.p. 177 °C (lit.[18a,23,24] 176–178 °C). ^1H NMR ($CDCl_3$): δ = 2.75–2.65 (m, 1 H), 2.55–2.45 (m, 1 H), 2.15–0.77 (m, 26 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 219.3, 129.8, 127. 8, 49.8, 38.5, 37.7, 36.1, 34.2, 33.4, 32.7, 31.1, 30.6, 29.9, 28.9, 27.9, 27.3, 26.3, 26.2, 25.9, 21.7 ppm. IR (KBr): $\tilde{\nu}$ = 2955, 2931, 2926, 2915, 1681 cm^{-1}. MS (*m*/*z* %): 284 (100) [M^+].

2,6-Di-*tert*-butylpyridine/Antimony Pentachloride Complex: On addition, with stirring at room temperature, of equimolar amounts of 2,6-di-*tert*-butylpyridine to a dichloromethane solution of antimony pentachloride a dusty, white precipitate was observed. This, collected by filtration and dried under vacuum, showed the following physical and chemical properties: m.p. 128–130 °C. ^1H NMR (500 MHz, CD_3CN): δ = 8.48 (t, 1 H), 7.92 (d, 2 H), 1.5 (s, 18 H) ppm. ^{13}C NMR (CD_3CN): δ = 164.1, 148.7, 123.6, 37.5, 28.8 ppm. IR (KBr): $\tilde{\nu}$ = 3374, 3014, 2877, 2861, 2747, 1620, 1529, 1376, 1250, 1190, 888, 819, 738 cm^{-1}. $C_{13}H_{21}Cl_5NSb$ (486.92): calcd. C 31.84, H 4.32, N 2.86; found C 31.35, H 4.10, N 2.78.

[(*S*)-2,2,3-Trimethyl-3-cyclopentenyl]acetaldehyde (1*S*,2*S*,3*R*,5*S*)-Pinane Acetal (4f) and [(*S*)-2,2,4-Trimethyl-3-cyclopentenyl]acetaldehyde (1S,2S,3R,5S)-Pinane Acetal (5f): Equimolar amounts of these acetals were obtained upon treatment of dichloromethane solutions of **1f** with catalytic amounts of antimony pentachloride. By GC/MS spectrometry, this unsolved pair of reaction products showed the same fragmentation patterns as authentic samples prepared individually by acid-catalysed (*p*-toluenesulfonic acid) reactions of pinane diol **1f** (85 mg, 0.5 mmol) with equimolar amounts of (2,2,3-trimethyl-3-cyclopentenyl)acetaldehyde (**2f**) and (2,2,4-trimethyl-3-cyclopentenyl)acetaldehyde (**3f**) (76 mg, 0.5 mmol), respectively.[11c] The involvement of the aldehydes **2f** and **3f** as intermediates in the reactions of diol **1f** with catalysts **A**, **B** and $SbCl_5$ was accounted for by carrying out similar reactions on DCM solutions of **1f** in the presence of an equimolar amount of pinacol **1d**. This reaction led to the simultaneous formation of two different acetals, namely **4f** and **5f**, together with (2,2,3-trimethyl-3-cyclopentenyl)acetaldehyde pinacol acetal (**7f**) and (2,2,4-trimethyl-3-cyclopentenyl)acetaldehyde pinacol acetal (**8f**). The structure of **7f** was confirmed by an acid-catalysed reaction between the aldehyde **2f** and an excess of **1d**, with subsequent comparison of its fragmentation pattern with that observed in the reaction of the diol **1f** carried out in the presence of pinacol **1d**.

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