Acid Catalysis in the Aminium Hexachloroantimonate-Induced Cyclodimerization of 1-Aryl-1-phenylethylenes

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The aminium hexachloroantimonate-induced cyclodimerization of various 1-aryl-1-phenylethylenes, affording regioisomeric indane derivatives via a carbocation mechanism, was found to occur in a similar manner when $SbCl_5$ was used instead of the aminium salt, hence antimony pentachloride is proposed as the acid catalyst. Its formation in the reactions with aminium hexachloroantimonates occurs by the oxidation of the $SbCl_6^-$ anion by its aminium counterion. Moreover, this cyclodimerization reaction occurs with much higher efficiency and enhanced regioselectivity in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) than in dichloromethane.

Introduction

Over the last 20 years, persistent and isolable aminium salts, such as the synthetic tris(2,4-dibromophenyl)aminium hexachloroantimonate (**A**) [E_{red} = 1.66 V vs. SCE][1] and the commercially available tris(4-bromophenyl)aminium hexachloroantimonate (**B**) [E_{red} = 1.16 V vs. SCE], have been fruitfully employed as one-electron oxidizing agents for accomplishing novel, selective and highly efficient chemical transformations on a great variety of electron-rich substrates.[2]

However, some reactions induced by aminium hexachloroantimonate salts have unequivocally been classified as acid-catalyzed processes,[3] although the identity of the active acidic species was uncertain. These salts were considered as obvious sources of protic acids, and therefore the radical cation of the substrate, generated by a preliminary electron transfer to the aminium salt, was, in some cases, proposed to be the possible highly acidic species[4] that protonates the parent compound, thus initiating the electrophilic activation.[5] Furthermore, Hart and co-workers showed that the protonation of an aromatic donor, affording its conjugate acid, can also lead to the donor radical cation.[6] Such an interchange between these two different intermediates also means that acid and electron-transfer processes may not be as easily differentiated as formerly thought.[7]

In recent work,[8] we have shown that aminium hexachloroantimonates, particularly **A**, may release antimony pentachloride due to the ability of the aminium radical to oxidize $SbCl_6^-$ according to Equation (1).

$$Ar_3N^{+\cdot} + SbCl_6^- \rightleftharpoons Ar_3N: + SbCl_5 + 1/2\ Cl_2 \qquad (1)$$

This is a non-spontaneous process that takes place when the direct oxidation of the substrate with $Ar_3N^{+\cdot}$ is thermodynamically unfavourable and the substrate can somehow consume $SbCl_5$. Through a slow escape of Cl_2, however, Equation (1) could also account for the decomposition that these hexachloroantimonates undergo over long storage periods in solid state or in solution. In view of a consequent possible $SbCl_5$ contamination of aminium hexachloroantimonates, we used only freshly prepared **A** (max two weeks old; $SbCl_5$-free, as revealed by a pH paper test) for our reactivity experiments. In the **A**-induced cycloisomerization of 2-(1-benzylethylidene)adamantane to give 2′-methylspiro[adamantane-2,1′-indane], we have ascertained that $SbCl_5$ is stoichiometrically involved as a secondary more powerful oxidant, and is responsible for the formation of the intermediate radical cation. Moreover, in view of the Lewis acid nature of $SbCl_5$, we have also anticipated that Equation (1) could serve to explain the acid catalysis brought about by aminium hexachloroantimonate salts.[8]

In support of this hypothesis we now report our results concerning the cyclodimerization of various 1-aryl-1-phenylethylenes **1a**−**i** to indane derivatives **2a**−**f**,**h** and **3c**,**d**,**f**,**h**,**i** (Scheme 1), induced by catalytic amounts of **A** or **B**, along with the equivalent results obtained by using $SbCl_5$ instead of the aminium salt. The reactions were carried out in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) and in the more conventional dichloromethane (DCM).

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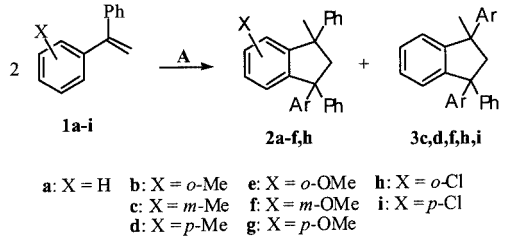
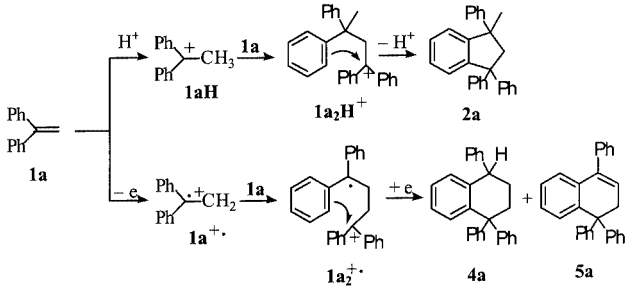


Scheme 1

Results and Discussion

The cyclodimerization of 1-aryl-1-phenylethylenes to indane derivatives was found to be induced by catalytic amounts of aminium hexachloroantimonates **A**,**B**, but not by the tetrafluoroborate analogue of **B**, and was already recognized as being subject to acid activation.[5b] Carbocation intermediates, besides being in agreement with the fact that identical reaction products were also obtained with protic acids instead of the aminium salt, are well able to account for the indanic structure of the observed cyclodimers. As illustrated in Scheme 2 for 1,1-diphenylethylene (**1a**), only a dimer cation, $\mathbf{1a_2H^+}$, that would be generated after protonation of the substrate followed by addition of the ensuing carbocation $\mathbf{1aH^+}$ to a second molecule of **1a**, is appropriate as precursor of the five-membered ring of indane **2a**. The dimer intermediate of a hypothetical radical cation mechanism, $\mathbf{1a_2^{+\cdot}}$, should be the precursor of six-membered ring cyclodimers, such as **4a** and **5a**, which in fact have been found in photostimulated reactions.[9]



Scheme 2

The reaction of 1-aryl-1-phenylethylenes **1a**−**i** with catalytic amounts (10% mol) of aminium salt **A** or **B** were initially carried out in dichloromethane (DCM, 5−10 mL) at room temperature. In this solvent, two of the examined olefins, the *ortho*-substituted **1b**,**h**, were found to be unreactive. To promote the reaction of such inert substrates we used 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) as solvent: the known ability of HFP[10] to promote the formation and reactivity of radical cations and carbocations has been successfully exploited in the radical cation mediated cyclodimerization of stilbene induced by **A**.[11]

The results reported in Table 1 show a general accelerating effect of HFP that can be interpreted in terms of solvent stabilization of the carbocation intermediates. The peculiar stabilizing ability of HFP towards carbocations becomes extremely important for the reactivity of **1b**,**h**, whose carbocations would normally be destabilized due to steric inhibition of resonance caused by the substituent in the *ortho*-position. The reactions of **1b** and **1e** gave the cyclodimers **2b**,**e**, corresponding to cyclization at the aryl ring, with total regioselectivity and high diastereomeric excess (**2b**, *de* = 90; **2e**, *de* = 80). These reactions are mainly controlled by steric effects. The major stereoisomer was isolated in both cases, and **2b** identified as the *cis* isomer by means of an X-ray analysis.[12] Both regioisomers **2h** (40%, *de* = 70) and **3h** (60%, *de* = 55) were obtained with good diastereoselectivity from the *ortho*-chloro derivative **1h**. The formation of the latter regioisomer reflects an electronic effect of the chlorine in the *ortho*-position that, contrary to the steric effect, favours cyclization at the phenyl ring. In the absence of the steric effect of the *ortho*-substituent, the cyclodimerization of **1c**,**d**,**f**,**g**,**i** afforded regioisomers **2c**,**d**,**f** and **3c**,**d**,**f**,**i** in nearly equimolar diastereomeric mixtures. The observed regioselectivity is in agreement with the expected electronic effect of the substituent on the electrophilic cyclization of the intermediate carbocation.

Moreover, the results of Table 1 point to an increased regioselectivity in HFP for the substrate **1c** (entries 8, 11). This could simply reflect the greater stabilization of the dimeric carbocation in HFP than in DCM.

In the series of methoxy-substituted substrates **1e**−**g**, it is worth mentioning the singular behaviour of the *para*-isomer **1g**: the reaction in HFP gave very low conversion of the substrate even with higher amounts of catalyst **A** (50 mol %), and traces of the cyclodimers **2g** and **3g** were observed in the mass spectrum. The reaction proceeded only up to 20% conversion in DCM, affording open chain dimers that were identified as (*E*/*Z*)-1,3-(4-methoxyphenyl)-1,3-diphenylbut-2-ene (**6g**,**g′**). Assuming that the dimeric carbocation $\mathbf{1g_2H^+}$ is also the precursor for **6g**,**g′**, the formation of these dimerization products instead of cyclodimers might be due to the delocalisation of the positive charge onto the methoxy group. The resulting reduced electrophilicity at the benzylic carbon of $\mathbf{1g_2H^+}$ would then prevent cyclization and allow deprotonation to form an alkene as a viable alternative (Scheme 3).

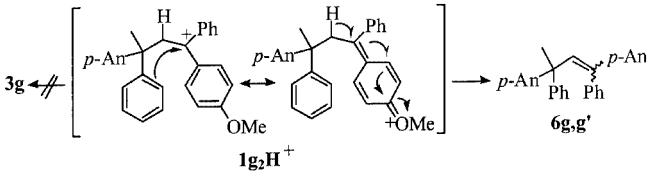
An analogous delocalisation, however, should be inhibited by steric hindrance in the dimeric carbocation of the *ortho* isomer $\mathbf{1e_2H^+}$, which undergoes cyclization like all the other substituted systems.

All the reactions carried out in HFP with catalytic amounts of **A** were repeated with equivalent amounts of $SbCl_5$, under the same conditions. The results revealed a close similarity between the two catalysts, except for a minor difference in regioselectivity for the cyclodimerization of **1c** (entries 8 and 9). As a probe 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 a larger scale cyclodimerization of **1b** (2.5 mmol) with **A** (0.25 mmol) was identified as Cl_2 after trapping with an aqueous NaOH solution (pH = 13); the

Table 1. Cyclodimerization of 1-aryl-1-phenylethylenes **1a**−**i** in HFP and DCM

Entry	Substrate	Solvent	Catalyst[a]	Reaction time [h]	Conv.[b] (%)	Product distribution (%)[c]
1	**1a**	HFP	**A** or $SbCl_5$	0.25	100	**2a**[d] (100)
2		HFP	**B**	5	100	**2a** (85)
3		DCM	**A**	2	100	**2a** (90)
4		DCM	B	10	50	**2a** (85)
5	**1b**	HFP	**A** or $SbCl_5$	6	100	**2b** (100)[e]
6		HFP	B	24	30	**2b** (100)
7		DCM	**A** or $SbCl_5$	24	n.r.	
8	**1c**	HFP	**A**	0.25	100	**2c**,**c′** (90), **3c**,**c′** (10)
9		HFP	$SbCl_5$	0.15	100	**2c**,**c′** (100)
10		HFP	**B**	5	55	**2c**,**c′** (85), **3c**,**c′** (15)
11		DCM	**A**	0.25	100	**2c**,**c′** (55), **3c**,**c′** (45)
12	**1d**	HFP	**A** or $SbCl_5$	0.25	100	**2d**,**d′**[f] (90), **3d**,**d′** (10)
13		DCM	**A**	2	100	**2d**,**d′** (85), **3d**,**d′** (15)
14	**1e**	HFP	**A** or $SbCl_5$	0.25	100	**2e** (100)
15		HFP	**B**	2	100	**2e** (90), **3e** (10)
16		DCM	**B**	24	40	**2e** (100)[g]
17	**1f**	HFP	**A** or $SbCl_5$	0.25	100	**2f**,**f′** (95), **3f**,**f′** (5)
18		DCM	**A**	0.25	100	**2f**,**f′** (90), **3f**,**f′** (10)
19	**1g**	HFP	**A**	24	< 10	**2g**,**3g** (traces)[h]
20		DCM	**A**	24	20	**4g**[f] (75), **4g′** (25)
21	**1h**	HFP	**A** or $SbCl_5$	1	100	**2h** (40),[i] **3h** (60)[i]
22		DCM	**A**	24	n.r.	
23	**1i**	HFP	**A** or $SbCl_5$	1	100	**3i**,**i′**[f] (100)
24		DCM	**A**	24	10	**3i**,**i′** (90)[j]

[a] 10 mol % of catalyst was used. [b] Gas chromatographic conversions were determined by using biphenyl as internal standard; n.r. = no reaction. [c] Area percent calculated over product peaks. Except for **2a**, the percent values refer to diastereomeric mixtures, which, unless otherwise noted, were nearly equimolar. [d] Ref.[3b] [e] A very high diastereoselectivity was observed: > 95:5 for **2b** and > 90:10 for **2e**. [f] Ref.[5b] [g] A complex mixture of products was obtained by performing the reaction with the aminium salt **A**. [h] Tentative identification based on the analogy of their MS fragmentation pattern with that of related indane derivatives. [i] Good diastereoselectivity was observed: > 85:15 for **2h** and > 75:25 for **3h**. [j] Negligible amounts of other unidentified compounds were also detected.



Scheme 3

chloride ions (5/3Cl^- per Cl_2) formed were determined chromatographically (1.25 mmol of Cl_2 expected for total conversion of 2.5 mmol of **A** [Equation (1)]; 0.86 mmol found). However, the catalytic engagement of the Lewis acid in the cyclodimerization reaction does not require a total conversion of **A** into $SbCl_5$. Both these findings — the **A**/$SbCl_5$ equivalence and **A** into $SbCl_5$ conversion — strongly support the hypothesis that $SbCl_5$ is the active species responsible for electrophilic catalysis in reactions induced by the aminium hexachloroantimonate **A**. Consequently the lower reactivity of **B** (shown in Table 1) could be ascribed to a reduced efficiency of formation of the Lewis acid catalyst due to the lower oxidation potential of tris(4-bromophenyl)aminium compared to tris(2,4-dibromophenyl)aminium radical cation. On the other hand, hexachloroantimonate salts with a non-oxidising cation, such as tribenzylmethylammonium hexachloroantimonate [$(PhCH_2)_3CH_3N^+SbCl_6^-$], are completely inactive in promoting the cyclodimerization, thus indirectly confirming that, in the case of aminium salts **A** and **B**, the oxidising ability of the aminium radical cation is essential for release of the Lewis acid catalyst from $SbCl_6^-$.

A Brønsted acid such as trifluoroacetic acid (TAA) was also found to induce the cyclodimerization of our substrates, although not very efficiently: an equimolar amount of TAA vs. substrate was necessary for reasonable conversions to be reached at longer reaction times either in DCM or in HFP.

The addition of a hindered base such as 2,6-di-*tert*-butylpyridine (DBP) has previously been used in reactions of aminium salts in order to distinguish an induced acid catalysis — supposedly a Brønsted acid catalysis — from a direct electron-transfer mechanism.[13] When this test was applied to the aminium hexachloroantimonate-induced reactions of **1a**−**i**, we found that DBP, added either in equimolar quantities or in a slight excess vs. the catalyst, inhibited the cyclodimerization giving rise to the formation of a dusty white precipitate and a fading of the solutions. Inhibition and formation of the white precipitate were also observed in the presence of $SbCl_5$. By treatment of a solution of DBP with an equimolar amount of antimony pentachloride we were able to isolate the white precipitate and fully characterize it as the 1:1 complex DBP·$SbCl_5$ (see Exp. Sect.). In

a control experiment, this complex remained inert, thus confirming that inhibition can be considered as a positive outcome of the DBP test also for Lewis acid catalysis induced by aminium hexachloroantimonate salts.

Experimental Section

General Remarks: Dichloromethane was purified by washing with sulfuric acid solution, distilling from over calcium hydride and then storing in the dark under a nitrogen atmosphere over molecular sieves. 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) (Aldrich Co) was used as received. The starting materials **1b**,**i**[14] and the aminium salt **A**[1] were prepared according to known procedures. Antimony pentachloride, 2,6-di-*tert*-butylpyridine and aminium salt **B** were commercial samples from Aldrich Co and were used as received. Melting points were measured on an electrothermal apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-500 MHz instrument, chemical shifts are reported in parts per million (δ), solvent $CDCl_3$. IR spectra (KBr pellets) were recorded with a Perkin−Elmer FT-1710. MS analyses were carried out on a Hewlett−Packard GC/Mass MSD 5970 instrument. Chromatographic analyses were carried out on a Hewlett−Packard gas chromatograph, model 5750 B, equipped with SP 2100 (5%) on Supelcoport 100/120, and on a Dionex 120 (50 × 4 mm ID IONPAC AG14 column, CO_3^{2-} 3.5 mM/HCO_3^- 1.8 mM eluent). TLC was performed on silica gel sheets with fluorescent indicator (Stratocrom SIF-Carlo Erba).

3,4-Dimethyl-*cis*-1,3-diphenyl-1-(*o*-tolyl)indane (2b): A catalytic amount of tris(2,4-dibromophenyl)aminium hexachloroantimonate **A** (0.105 g, 0.10 mmol) was rapidly added to a stirred solution of **1b** (0.194 g, 1.00 mmol) in HFP (10 mL) at room temperature. The reaction mixture, whose intensely green color faded slowly, was monitored by TLC (petroleum ether/ethyl acetate, 20:1) and by GC-MS spectrometry, revealing the total disappearance of starting material within 6 h, and the simultaneous formation of a main reaction product with molecular peak m/z = 388. The excess of aminium salt was destroyed by addition of diethyl ether (2 mL). The reaction mixture was then poured into water (10 mL) and extracted with diethyl ether (2 × 10 mL). The organic phase was separated, dried with sodium sulfate, and the solvent was removed in vacuo. After column chromatography (silica gel; petroleum ether/ethyl acetate, 20:1) of the residue, pure **2b** was obtained as a pale yellow crystalline product (0.175 g, 90%). Recrystallization from methanol furnished colorless crystals for X-ray analysis.[12] M.p. 175−176 °C. IR (KBr): $\tilde{\nu}$ = 3055, 3020, 2967, 1492, 1444, 770, 758, 744, 731, 697, 637 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 (s, 3 H), 1.53 (s, 3 H), 1.91 (s, 3 H), 2.78 (d, J = 13.8 Hz, 1 H), 3.53 (d, J = 13.8 Hz, 1 H), 7.36−6.63 (m, 17 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.9, 22.2, 24.4, 51.7, 60.8, 60.9, 125.0, 125.5, 125.6, 125.9, 126.3, 127.15, 127.10, 128.1, 128.4, 128.9, 129.9, 132.2, 134.5, 136.6, 147.6, 147.9, 148.3, 149.6, 150.7 ppm. MS: m/z (%) = 388 (20) [M$^+$], 373 (11), 297 (100), 295 (7), 283 (14), 282 (19), 281 (11), 265 (13), 219 (22), 105 (16), 91 (26). $C_{30}H_{28}$ (388.22): calcd. C 92.73, H 7.26; found C 92.87, H 7.16.

Reaction of 1-(Phenyl)-1-(*m*-tolyl)ethylene (1c) with Aminium Salt A or $SbCl_5$: The above procedure was followed for the aminium salt **A** or antimony pentachloride induced cyclodimerization of 1-phenyl-1-(*m*-tolyl)ethylene (**1c**). GC-MS analysis of the reaction mixture revealed the formation of diastereomeric pairs of the two regioisomeric indane derivatives **2c**,**c′** and **3c**,**c′**. The stereoisomers formed in nearly equal amounts, while the regioselectivity was dependent on the solvent and the catalyst employed. Reaction times and product compositions, determined by gas chromatography, are reported in Table 1. The *cis-trans* pair **2c**,**c′** was observed from the reaction with $SbCl_5$ in HFP, whose final GC-MS spectrogram showed basically only two equally intense peaks at 16.30 and 16.56 min (capillary column MDN-1, 30m, 0.25 mm ID, 0.25um film thickness), with very similar fragmentation patterns represented by the following fragments: m/z (%) = 388 (38) [M$^+$], 373 (54) [M$^+$ − CH_3], 311 (58) [M$^+$ − C_6H_5], 297 (100) [M$^+$ − $CH_3C_6H_4$], 283 (13), 282 (34), 281 (32), 219 (30), 105 (15), 91 (22). Accordingly, with the presence of diastereotopic protons at C-2, the ^{1}H NMR spectrum of this mixture showed four doublets, centered at δ = 3.38 (J = 13.4 Hz, 1 H), 3.34 (J = 13.5 Hz, 1 H), 3.13 (J = 13.5 Hz, 1 H) and 3.06 (J = 13.4 Hz, 1 H) ppm.

Two minor peaks (retention times: 16.10 and 16.41 min), alternating with those corresponding to **2c**,**c′**, were observed in the GC-MS spectrogram of the product mixture obtained from the reaction with **A** in HFP. These showed a common fragmentation pattern that was assigned to **3c**,**c′**: m/z (%) = 388 (42) [M$^+$], 373 (56) [M$^+$ − CH_3], 311 (10) [M$^+$ − C_6H_5], 297 (100) [M$^+$ − $CH_3C_6H_4$], 295 (15), 283 (20), 282 (38), 281 (42), 105 (14), 91 (22). Correcting our previous attribution,[5b] we based the identification of these regioisomers on a comparison between the relative abundances of the m/z = 311 peak corresponding to the [M$^+$ − C_6H_5] fragment: the loss of a phenyl group from the molecular ion would be slightly more probable from 1,3-diphenyl-substituted 4-methylindanes **2c**,**c′** than from 1-phenyl-substituted indanes **3c**,**c′**, thus giving rise to a peak of higher relative abundance (58 as opposed to 10).

Reaction of 1-(Phenyl)-1-(*p*-tolyl)ethylene (1d) with Aminium Salt A or $SbCl_5$: Appreciable differences between the reaction of 1-phenyl-1-(*p*-tolyl)ethylene (**1d**) with **A** or $SbCl_5$, carried out following the above procedure, were not detected. A mixtures of indane derivatives **2d**,**d′** and **3d**,**d′** with high regioselectivity in favour of the former pair was obtained in both the solvents (see Table 1). The product identification has been reported previously.[5b]

1-(*o*-Anisyl)-4-methoxy-3-methyl-*cis*-1,3-diphenylindane (2e): This compound was obtained from 1-(*o*-anisyl)-1-phenylethylene (**1e**, 0.210 g, 1 mmol) following the usual protocol. The end of the reaction (15 min) was revealed by TLC and GC-MS spectrometry analyses. Crystallization from methanol of the crude reaction product (0.193 g, 92%) gave colorless crystals of **2e**. M.p. 122−123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.81 (s, 3 H), 3.09 (d, J = 13.9 Hz, 1 H), 3.43 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 3.84 (d, J = 13.9 Hz, 1 H), 7.38−6.43 (m, 17 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 28.4, 50.2, 53.9, 54.8, 54.9, 59.1, 111.0, 111.5, 119.4, 119.5, 125.1, 125.8, 126.5, 126.6, 126.7, 127.20, 127.22, 127.5, 128.0, 129.0, 130.3, 134.8, 135.9, 148.7, 149.6, 150.3, 157.2, 157.3 ppm (28 different carbons are consistent with the hindered rotation of one of the phenyl groups, most likely the one in the α-position with respect to the *o*-anisyl group). MS: m/z (%) = 420 (92) [M$^+$], 405 (41), 299 (59), 297 (100), 235 (23), 203 (23), 105 (20), 91 (61). $C_{30}H_{28}O_2$ (420.21): calcd. C 85.68, H 6.71; found C 85.49, H 6.56.

Reactions of 1-(*m*-Anisyl)-1-phenylethylene (1f) with Aminium Salt A or $SbCl_5$: As reported for **1c**, the aminium salt **A** or antimony pentachloride induced cyclodimerization of 1-(*m*-anisyl)-1-phenylethylene (**1f**) afforded a mixture of four different indane isomers **2f**,**f′** and **3f**,**f′**. The regioselectivity found was practically independent of the solvent (**2f**,**f′**/**3f**,**f′**: 95:5 in HFP, 90:10 in DCM). Identification of regioisomers as nearly equimolar pairs of stereoisomers was based on GC-MS analysis of the product mixtures. According to the criterion of the [M$^+$ − C_6H_5] fragment, described above for **1c**,

assignments were as follows: **2f**,**f′**: two major peaks of nearly equal intensity with retention times of 26.30 and 27.15 min (capillary column MDN-1, 30m, 0.25 mm ID, 0.25 um film thickness) and very similar fragmentation patterns: *m*/*z* (%) = 420 (88) [M^+], 405 (24) [$M^+ - CH_3$], 343 (89) [$M^+ - C_6H_5$], 313 (100) [$M^+ - CH_3OC_6H_4$], 297 (14), 235 (31), 91 (15); **3f**,**f′**: two minor peaks at 23.10 and 23.71 min retention times with the following representative fragmentation pattern: *m*/*z* (%) = 420 (100) [M^+], 405 (24) [$M^+ - CH_3$], 343 (20) [$M^+ - C_6H_5$], 313 (27) [$M^+ - CH_3OC_6H_4$], 297 (33), 235 (25), 207 (23), 91 (26). The ^{1}H NMR spectrum of the product mixture showed four doublets (minor component was not detected) centered at δ = 3.36 (*J* = 13.5 Hz, 1 H), 3.33 (*J* = 13.5 Hz, 1 H), 3.07 (*J* = 13.5 Hz, 1 H), 3.05 (*J* = 13.5 Hz, 1 H) ppm.

4-Chloro-1-(*o*-chlorophenyl)-3-methyl-*cis*-1,3-diphenylindane (2h) and 1,3-Bis(*o*-chlorophenyl)-3-methyl-1-phenylindane (3h): The same protocol has been followed for the aminium salt **A** (0.11 g, 0.1 mmol) induced cyclodimerization of 1-(*o*-chlorophenyl)-1-phenylethylene (**1h**, 0.214 g, 1 mmol) in HFP (10 mL). The reaction, monitored as usual, required 10 h for the total conversion of the starting material and formation of the two main reaction products. The crude reaction product was purified by chromatography on a silica gel column using petroleum ether as eluent. After elution of tris(2,4-dibromophenyl)amine, due to the very similar R_f values of the main reaction products, we collected the first crude solid (0.068 g, R_f = 0.39, petroleum ether), as a mixture of **2h** (90%) and **3h** (10%), The major component was characterized as **2h** on the basis of the following data: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.70 (s, 3 H), 3.20 (d, *J* = 14.5 Hz, 1 H), 4.05 (d, *J* = 14.5 Hz, 1 H), 6.90−7.38 (m, 17 H) ppm. MS: *m*/*z* (%) = 432 (6) [$M^+ + 2$], 430 (35) [$M^+ + 2$], 428 (51) [M^+], 417 (11), 415 (61), 413 (100) [$M^+ - CH_3$], 351 (8) [$M^+ - C_6H_5$], 319 (7), 317 (21) [$M^+ - ClC_6H_5$], 305 (8), 303 (30) [317 − CH_2]. A second, pure reaction product (R_f = 0.37) was characterized as **3h** after crystallization from methanol. Yield: 0.090 g, m.p. 240−241 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.90 (s, 3 H), 3.41 (d, *J* = 14.3 Hz, 1 H), 4.18 (d, *J* = 14.3 Hz, 1 H), 6.45−6.80 (m, 7 H) 6.90−7.60 (m, 10 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.8, 52.6, 52.9, 61.1, 125.3, 125.6, 125.7, 126.2, 127.0, 127.1, 127.3, 127.4, 128.1, 128.2, 131.1, 131.4, 131.6, 132.8, 133.9, 143.3, 144.0, 146.0, 146.5, 149.0, 149.2 ppm. MS: *m*/*z* (%) = 432 (4) [$M^+ + 4$], 430 (26) [$M^+ + 2$], 428 (34) [M^+], 417 (13), 415 (69), 413 (100) [$M^+ - CH_3$], 351 (8) [$M^+ - C_6H_5$], 319 (11), 317 (27) [$M^+ - ClC_6H_5$], 305 (23), 303 (77) [317 − CH_2]. Identification of the regioisomers was based on the relative abundance of the *m*/*z* = 303 peak, which is significantly different in the two mass spectra. The higher relative abundance (77 compared to 30) displayed in the latter fragmentation was reasonably assigned to **3h** in agreement with the previously reported[5b] mass fragmentation for the analogous chlorocyclodimer **3i**, in which the *m*/*z* = 303 peak is present with 100 relative abundance. $C_{28}H_{22}Cl_2$ (428.11): calcd. C 78.32, H 5.16; found C 78.75, H 5.14. Very similar results were obtained when using antimony pentachloride as catalyst.

2,6-Di-*tert*-butylpyridine·Antimony Pentachloride Complex:[15] This precipitated as a white solid upon mixing equimolar amounts of 2,6-di-*tert* butylpyridine and antimony pentachloride in DCM or HFP. M.p. 128−130 °C. IR (KBr): $\tilde{\nu}$ = 3374, 3014, 2877, 2861, 2747, 1620, 1529, 1376, 1250, 1190, 888, 819,738 cm^{-1}. ^{1}H NMR (500 MHz, CD_3CN): δ = 1.5 (s, 18 H), 7.92 (d, 2 H), 8.48 (t, 1 H) ppm. ^{13}C NMR (CD_3CN): δ = 28.8, 37.5, 123.6, 148.7, 164.1 ppm. $C_{13}H_{21}Cl_5NSb$ (486.92): calcd. C 31.84, H 4.32, N 2.86; found C 31.35, H 4.10, N 2.78.

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