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Aminium Salts-Induced Dimerization of α-Methylstyrene and 1-Aryl-1-Phenylethylenes. Solvent Effect.

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Abstract: The aminium salts-induced dimerization of α-methylstyrene **1b** gives rise, depending on the solvent employed, to high yields of 1,3,3-trimethyl-1-phenylindane **2b**, or 2,4-diphenyl-4-methyl-1-pentene **6b**. Several 1-aryl-1-phenylethylenes **1a,c-e** afford, instead, cyclodimers **2a,c-e**, or 2,5-diaryl-2,5-diphenyltetrahydrofuran derivatives **3a,c-e**.

INTRODUCTION

In the last decade, several leading international groups,[1-5] as well as our own[6a-f] have ascertained that aminium salts, such as *tris*-(2,4-dibromophenyl)aminium hexachloroantimonate (**A**) [E^{red} = 1.66 V. *vs* SCE] and *tris*-(4-bromophenyl)aminium hexachloroantimonate (**B**) [E^{red} = 1.16 V. *vs* SCE], *hole catalysts*, can efficiently promote a great variety of reactions on several classes of electron rich substrates: *e.g.* dienes, hindered olefins, oxiranes, episulphides, and *vic* diols.

In most of the reported reactions, it was stated that the role of aminium salts, especially that of the more powerful **A**, is as one electron oxidant acting either in stoichiometric processes, or as catalysts in cation-radical chain mechanisms, modelled upon Ledwith[7] and Nelsen's[2] classic proposals. For example, the cycloaddition of neutral alkenes to alkene radical cations can be carried out under much milder reaction conditions than the analogous thermal reactions, overcoming, at the same time, the limited success of several cyclobutanations and Diels-Alder reactions.[1]

However, since aminium salts can also behave as an indirect source of protic acid, which might be the true catalytic species,[8-10] possible mechanistic ambiguities can affect these reactions. In other words, reaction products, accountable for by radical cation intermediates, often are also compatible with carbocations forming in protic acid catalyzed processes. In fact, subsequent to the Gassman[8] and Lapouyade's[9] experimental observations, a further illustration of this potential mechanistic complexity was observed by us in the aminium salts-induced reactions of 1,1-diphenylethylene (**1a**), affording high yields of 1,3,3-triphenyl-1-methylindane (95%) (**2a**),[10] the sole reaction product in the protic and/or Lewis acid catalyzed reactions,[11,12] together with trace amounts of 2,2,5,5-tetraphenyltetrahydrofuran (**3a**), 1,1,4-triphenyl-1,2,3,4-tetrahydronaphthalene (**4a**) and 1,1,4-triphenyl-1,2-dihydronaphthalene (**5a**), observed, *instead*, in several photostimulated reactions,[13-18] (see scheme 2 in the results and discussion section).

In this context, in order to gain insights into several still unclear mechanistic details, we report herein the results of a systematic study carried out in methylene chloride and acetonitrile solutions of several other 1,1-disubstituted ethylenes, such as α-methylstyrene [E^{ox}=1.85 V. *vs* SCE] (**1 b**), 1-(4-chlorophenyl)-1-phenylethylene [E^{ox} =1.89 V. *vs* SCE] (**1c**), 1-(4-methylphenyl)-1-phenylethylene [E^{ox} =1.75 V. *vs* SCE] (**1d**), 1-(3-methylphenyl)-1-phenylethylene [E^{ox} =1.75 V. *vs* SCE] (**1e**) and 1-(4-methoxyphenyl)-1-phenylethylene [E^{ox}=1.39 V. *vs* SCE] (**1f**).

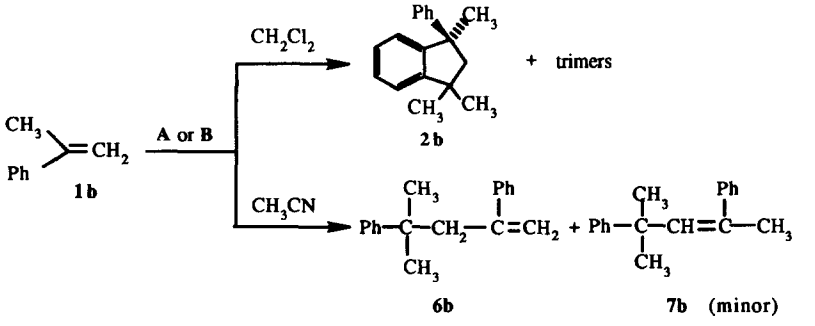
RESULTS AND DISCUSSION

Reactions of α-methylstyrene (1b).

α-Methylstyrene (**1b**) was submitted to aminium salt induced reactions, as a substrate that analogously to **1a** could allow to distinguish between electron-transfer and proton-transfer catalysis. In fact, it has been reported that **1b** undergoes cyclodimerization either under photoinduced electron-transfer conditions,[19,20] or in the presence of protic and Lewis acid as catalysts,[21-24] leading to well distinct cyclodimers. Different mixtures of 1,2-diphenyl cyclobutane and 1-phenyl-1,2-dihydronaphthalene were obtained in the photostimulated radical cation cycloaddition reactions, whereas complex mixtures of 1,3,3-trimethyl-1-phenylindane (**2b**), trimers, and several unsaturated acyclic dimers were obtained in most of the acid-catalyzed reactions.

In our case, **1b** reacted in freshly distilled methylene chloride with catalytic amounts of aminium salts **A** or **B** (5-10 mol %) affording, within 1h, high yields of the cyclodimer **2b** together with minor amounts of three different trimers. The main reaction product, easily isolated by silica gel column chromatography, was fully characterized by physical, spectral data and by comparison with an authentic synthesized sample.[24] On the contrary, if similar reactions were carried out in dry acetonitrile as solvent, by following the same protocol, we observed a slower conversion (1 day) of **1b** into a different main reaction product, fully characterized as 2,4-diphenyl-4-methyl-pent-1-ene (**6b**), together with minor amounts of the double bond isomer 2,4-diphenyl-4-methyl-pent-2-ene (**7b**), scheme 1.

Scheme 1



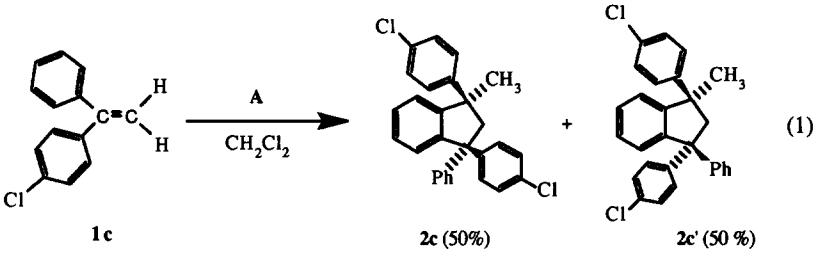
In addition to that, our protic acid-catalyzed reactions on **1b** led to interesting results. In fact, whereas *tri*-fluoromethanesulphonic acid (CF_3SO_3H)-induced reactions gave rise within 30 min to **2b** (90%) and minor amounts of three different trimers, those catalyzed by *tri*-fluoroacetic acid (CF_3COOH) were much slower, affording **2b**, as the main reaction product, but through the clear preliminary formation of **6b**.

Most likely, a common dimer carbocation, *i.e.* 2,4-diphenyl-4-methyl pentyl $(PhC(CH_3)_2CH_2CPhCH_3)^+$, was formed in all studied reactions. This latter would undergo an irreversible electrophilic ring closure to **2b**, or a reversible deprotonation to **6b** and **7b** in relation with the peculiar properties of the solvent and the catalyst employed.

Consistent chemical evidence support this hypothesis: (a) preventing the build up of acid conditions, by using a molar excess of the non nucleophilic base 2,6-di-*tert*-butylpyridine (**DBP**) over the aminium salt initiator, the formation of **2b** and **6b-7b** was totally inhibited; (b) the reactions performed in the presence of equimolecular amounts appeared, *instead*, slower, but not inhibited at all. These latter afforded in methylene chloride and/or acetonitrile solutions lower yields of the same main reaction products observed in the unmodified reactions.

Reactions of 1-aryl-1-phenylethylenes (1c-1e)

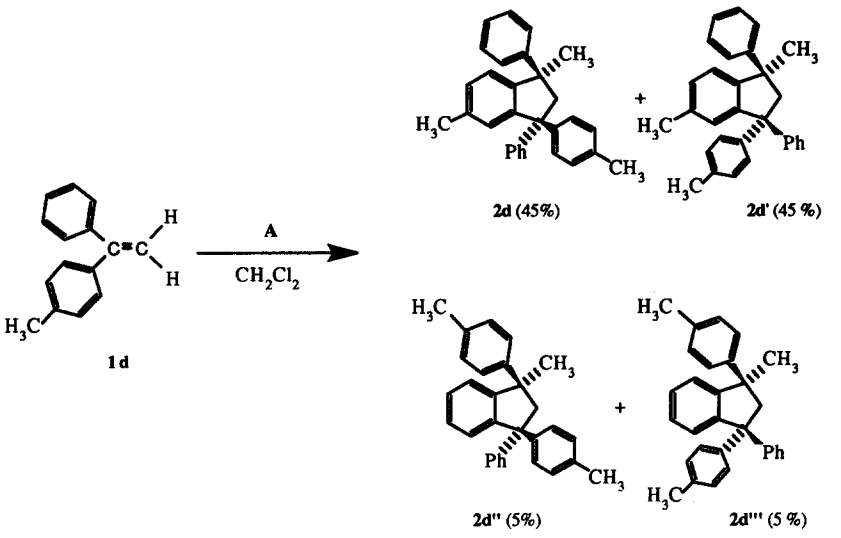
By following the same protocol, methylene chloride solutions of **1c**, the substrate with the higher oxidation potential, upon treatment with aminium salts **A** or **B** (10-50 mol %) showed a different behaviour. First of all, this substrate was practically inert towards aminium salt **B**, whereas, its total conversion into an equimolecular mixture of diasteroisomeric 1,3-bis(4-chlorophenyl)-3-phenyl-1-methylindanes **2c,c'** was achieved, within 16 h, when 50 mol % of the stronger aminium salt **A** was added to the reaction solution, eq. (1).



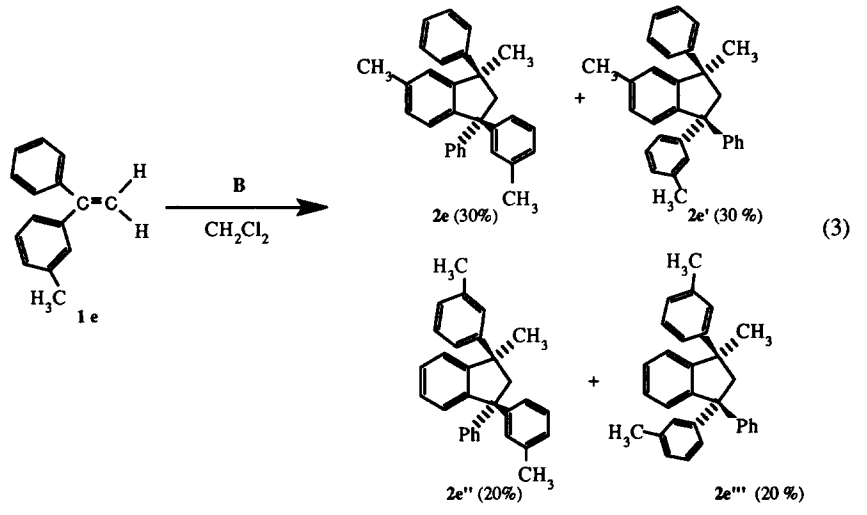
1c **2c** (50%) **2c'** (50 %) (1)

Reactions modified by 1,4-dimethoxybenzene (**DMB**) [E^{ox}= 1.34 V. *vs* SCE], and those performed with protic acids such as CF_3SO_3H, CF_3COOH, led to similar mixtures of isomers **2c,c'**. On the contrary, the aminium salt-induced reactions, performed in the presence of equivalent amounts of **DBP**, led slowly (18 h) to low yields (15%) of the 2,5-di(4-chlorophenyl)-2,5-diphenyltetrahydrofuran (**3c**.). Low yields of **3c**, or the labeled product **3c***, were also obtained when the reaction of **1c** with **A** was carried out: (i) in wet methylene chloride; (ii) by adding 18-oxygen labeled water (20 %) to the reaction mixture; (iii) in acetonitrile as solvent.

Substrates **1d-e**, with oxidation potentials lower than those of **1a-c**, upon treatment of their methylene chloride solutions with catalytic amounts (10-20 mol %) of **A** or **B** led to pairs of diasteroisomeric indane derivatives **2d,d'** (90%) and **2d'',d'''** (10%), or **2e,e'** (60 %) and **2e'',e'''** (40 %), respectively, eq. (2), (3).



(2)



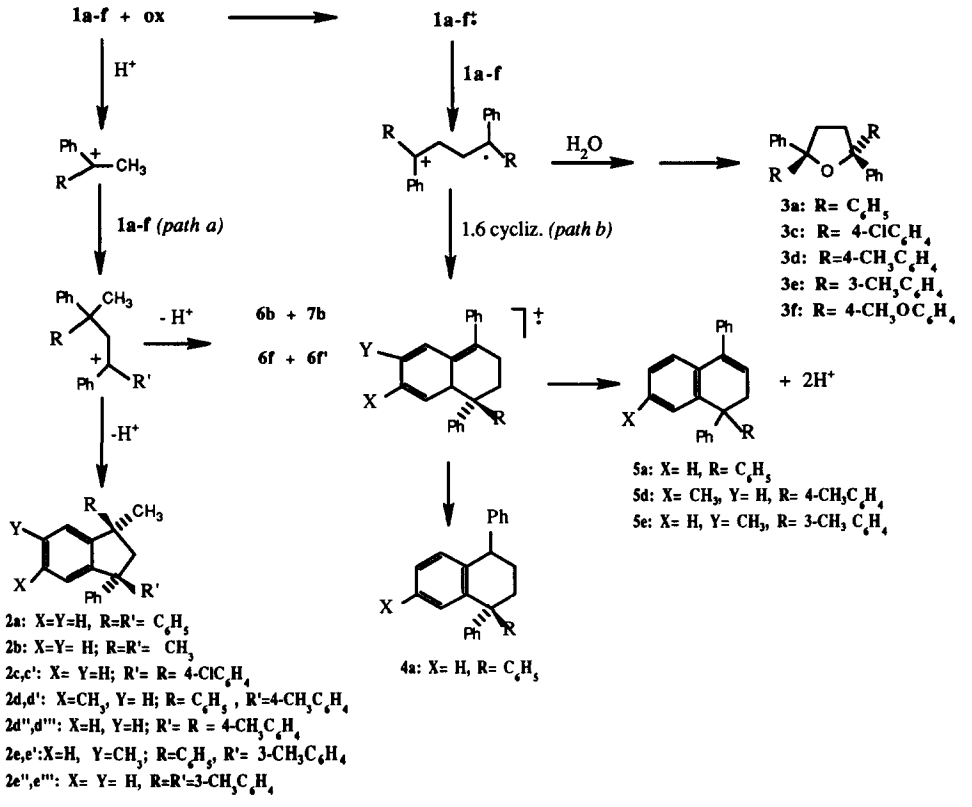
(3)

The reactions modified by **DBP**, as well as those performed in acetonitrile as solvent, afforded low yields (15-20 %) of the corresponding tetrahydrofuran derivatives **3d,e**, together with minor amounts of 1-phenyl-1-aryl-1,2-dihydro-7-, or 6-methyl-naphthalene **5d,e**, detected by gc/ms spectrometry. In addition to that, the protic acid induced-processes led to reaction mixtures, similar to those observed in the aminium salts-catalyzed reactions.

On the basis of the fingerprint criterion, these results (scheme 1 and eqs. 1-3), as those obtained on the unsubstituted derivative **1a**,[10] can be better accounted for by protic acid-catalyzed process, than with a chain radical cation mechanism. In this regard, no doubt exists on the nature of the protic acid ($HSbCl_6$) which catalyzes the cyclodimerization of **1a-e**, but the step in which this is actually formed is not presently known.[10] Thus, it is plausible to hypothesize that, although the s.e.t. processes between **1a-e** and the powerful

aminium salt A might readily occur in methylene chloride, as well as in acetonitrile solutions, the inevitable development of the protic acid would promote, *mainly in methylene chloride*, a fast protonation of neutral compounds. Then, the following head to tail addition of the intermediate carbocations (**1a-f**$^{+}$) to the parent neutral olefins (*path a*) must favourably compete with the stepwise cyclization of the dimer radical cations (**1a-f**$^{+\cdot}$, *path b*), scheme 2.

Scheme 2



On the other hand, the slow and less efficient formation of tetrahydrofuran derivatives **3a**,**c-f** (15-20 %), together with minor amounts of 1,2-dihydronaphthalene derivatives **5a**,**d**,**e**, basically arising from photosensitized electron-transfer reactions, [13-18] as well as in our **D B P**-modified reactions, and in acetonitrile solutions, appear the more convincing proofs that, preventing the build up of acidic conditions, the head to head addition of the primary radical cations to the corresponding neutral olefins would readily afford the dimer radical cations. These latter would react with adventitious and/or added water, or subside a stepwise 1,6-cyclization process, affording tetrahydrofuran and/or 1,2-dihydronaphthalene derivatives, respectively. No trace of the cyclobutane derivatives, arising from 1,4-cyclization of the acyclic dimer radical cations, was observed.

The main reaction products **2a-d'''** have been fully characterized through the mass fragmentation patterns of indane derivatives. In fact, the first step in the fragmentation of the molecular ions is the loss of the methyl group in the position 1, leaving a positive stabilized charge at the benzylic position. This step is followed by

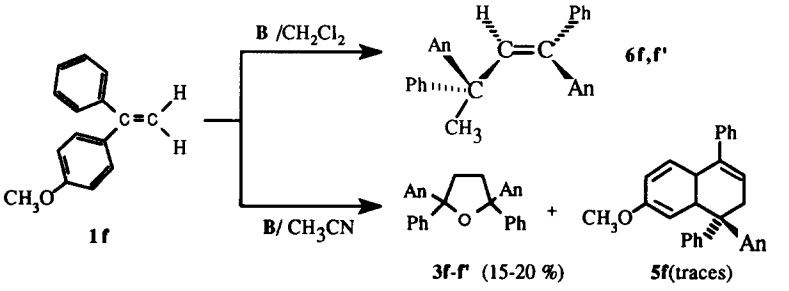
loss of a neutral arene, *i.e.*phenyl or aryl from position 3, and hydrogen from 2, to give indane carbonium ions, stabilized by two benzylic positions. In addition to that, molecular ions of **2c,c'**, and the corresponding fragments with both chlorine atoms show, as expected, three isotopic peaks in the ratios 9:6:1. The products have also been characterized by ^1H nmr, showing AB pattern quartets, as described in the experimental section.

Reactions of 1-aryl-1-(4-methoxyphenyl) ethylenes (1f)

Surprisingly, methylene chloride solutions of 1-(4-methoxyphenyl)-1-phenylethylene **1f**, upon treatment with aminium salt **A** (10-50 mol %) showed a different behaviour. Basically, notwithstanding the electron-transfer process between **1f** and the aminium salt **A** should be exoergonic, the observed reaction products can only be accounted for by a protic-acid catalysed dimerization process. In fact, these latter showed fragmentation patterns, by gc/ms spectrometry, consistent with those of the geometrical isomers (Z) and (E)-1,3-diphenyl-1,3-di(4-methoxyphenyl)-but-1-ene **6f,f'**, whereas, no trace of the corresponding 1,2-dihydronaphthalene **5f**, or the indane derivate **2f**, were detected. ^1H and ^{13}C nmr spectra confirmed the assigned structures. Low conversions into similar mixtures of reaction products were also observed in the protic-acid (CF_3COOH) induced reactions.

Similar reactions, carried out in acetonitrile as solvent, gave rise to low yields of the 3,4-tetrahydrofuran derivatives **3f,f'** (15-20 %) together with minor amounts of 1,2-dihydronaphthalene **5f**, detected only by gc/ms spectrometry, scheme 3. Apparently, the low and slow conversion of **1f** could be ascribed to a faster complexation reaction of Lewis acid on the methoxy group. This would reduce the exoergonicity of the initial electron-transfer process , and then the yield of the corresponding reaction products.[25,26]

Scheme 3



Thus, our results are consistent with a mechanism in which the carbocation intermediates add to neutral olefins to give dimer carbocations, which in turn can cyclize through an electrophilic attack of thecarbocation moiety on the more activated aromatic ring, or deprotonate to acyclic olefins. However, the single electron-transfer pathway cannot be discharged at all, as confirmed by the results obtained in the base-modified reactions, as well as in the more polar and basic solvent, *i.e.* acetonitrile. More detailed investigations on these and several other substrates are in progress.

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Experimental Section

Melting points were taken on an electrothermal apparatus and are uncorrected. ^{1}H-and ^{13}C-NMR spectra were recorded on a Brucker-500 MHz instrument, chemical shifts are reported in parts per million (δ), solvent $CDCl_3$. IR, MS spectra were performed, respectively, on a Perkin-Elmer FT-1710 (KBr pellets), and on a Hewlett-Packard GC/Mass MSD 5970 instruments. GC analyses were carried out on a Hewlett-Packard gas chromatograph, model 5750 B, on columns (1/4"x15 feet) packed with SP 2100 (5% on Supelcoport 100/120. TLC were performed on silica gel sheets with fluorescent indicator (Stratocrom SIF-Carlo Erba). Dichloromethane was purified by washing with sulphuric acid solution, distillation over calcium hydride and then stored in the dark under nitrogen atmosphere and over molecular sieves. Acetonitrile (Carlo Erba HPLC grade) was used as received. The starting materials **1a,b** are pure commercial samples (Aldrich Co), whereas substrates **1c-f** were synthesized, accordingly with known procedures.[26] **DBP, DMB** commercial samples from Aldrich Co, have been used as received. Aminium salts (**A, B**) have been synthesized by following the procedure reported in the references 27,28

Reactions of α-methylstyrene (1b) with aminium salts: Synthesis of 1,3,3-trimethyl-1-phenyl indane (2b).

A catalytic amount of *tris*-(2,4-dibromophenyl)ammoniumyl hexachloroantimonate **A** (0.083 g, 0.10 mmol) is rapidly added to a methylene chloride (10 ml) solution of α-methylstyrene **1b** (0.236 g, 2 mmol) at 0° C, or room temperature, under stirring. The intensely green colour of the solution fades within 10 min. The reaction mixture, monitored by tlc (hexane:ethyl ether 9:1 as eluant) and/or by gc/ms spectrometry, reveals the total disappearance of the starting material and the formation of a new main product with molecular peak m/e 236. Minor amounts of three different trimers with molecular peaks m/e 354 are also observed. The excess of aminium salt is destroyed by addition of ethyl ether, then the solvent is removed in vacuo. The residual, adsorbed on silica gel, is purified by silica gel column chromatography with the previous eluant. After the elution of the amine, the crude white crystalline product (0.158 g, 68%) has been fully characterized as **2b**, by physical and spectral data: m.p.= 52 °C (lit. 52 °C);[24] ms m/e (%): 236 (M^+, 15), 221 (100), 143 (64), 128 (15), 114 (14), 105 (15), 71 (41), 77 (12); ^{1}H nmr ($CDCl_3$): δ = 1.06 (s, 3H), 1.37 (s, 3H), 1.71 (s, 3H), 2.22 (d, 1H, J = 13Hz), 2.44 (d, 1H, J = 13 Hz), 7.14-7.33 (m, 9H) ppm; ^{13}C nmr ($CDCl_3$): δ = 30.28, 30. 58, 30. 79, 42.76, 50.70, 59.14, 122.44, 124.89, 125.37, 126. 58, 127.09, 127.83, 148.61, 150.91, 152.10 ppm. The product shows consistent elemental analysis. Similar reactions, induced by the weaker aminium salt lead to the same reaction mixtures.

An analogous protocol has been followed in dry acetonitrile as solvent. However, monitoring the reaction as usual, we observe by gc/ms spectrometry, within 1 day, the total disappearance of the starting material and the contemporary formation of two different isomers in the ratio 9:1. Their fragmentation patterns and ^{1}H-nmr spectra (reactions directly performed in the nmr test-tube with CD_3CN as solvent) fit those observed for the product identified as **6b** and **7b.** The solvent is removed in vacuo and the residual has been purified by silica gel column chromatography (petroleum ether: ethyl ether 9:1 as eluant). From several pure fractions has been isolated a liquid (0.112 g) of pure 2,4-diphenyl-4-methyl-pent-1-ene **6b**, fully characterized by spectral data: ms (m/e %): 236 (M^+, 5), 119 (100), 91 (53), 77 (12); ^{1}H nmr ($CDCl_3$): δ = 1.21 (s, 6H), 2.81, (s, 2H), 4.61 (d, 1H, J = 1.29 Hz), 5.16 (d, 1H, J = 1.29 Hz), 7.09-7.43 (m, 10H) ppm. Only few fractions containing the isomer 2,4-diphenyl-4-methyl-pent-2-ene **7b** have been isolated. This latter has been characterized as above: ms (m/e %): 236 (M+ 44), 221 (46), 143 (100), 128 (38), 115 (26), 105 (33), 91 (68), 77 (28); ^{1}H nmr ($CDCl_3$): δ = 1.58 (s, 6H), 1.61 (s, 3H), 6.16 (dd, 1H J = 1.30 Hz), 7.09-7.43 (m, 10H) ppm. The reactions induced by protic acid as CF_3SO_3H and CF_3COOH have been followed by gc/ms spectrometry.

Reactions of 1-(4-chlorophenyl)-1-phenylethylene (1c) with aminium salts: Synthesis of 1,3-bis(4-chlorophenyl)-3-phenyl-1-methyl-indanes (2c,c').

Freshly prepared *tris*-(2,4-dibromophenyl)ammoniumyl hexachloroantimonate **A** (0.204 g, 0.2 mmol) is rapidly added to a solution of 1-(4-chlorophenyl)-1-phenylethylene **1c** (0.085 g, 0.4 mmol) in distilled methylene chloride (20 ml) at room temperature, under stirring. The intensely green colour of the solution lasts for several hours before to turn blue. The reaction mixture, monitored by tlc (hexane: ethyl ether 9:1 as eluant) and/or by gc/ms spectrometry, reveals, within 15h, the total disappearance of the starting material and the formation of a pair of isomeric products with close, but different retention times. The excess of aminium salt is destroyed by addition of ethyl ether until the colour fades. The solvent is then removed in vacuo and the residual, adsorbed on silica gel, is purified by silica gel column chromatography with the previous eluant. After the elution of the amine, the crude mixture (0.079 g. 93%) has been fully characterized, by spectral data. The first isomer **2c** (retention time 23.77 min) shows the following mass fragmentation pattern: m/e (%): 432 (M^{+4}, 4), 430 (M^{+2}, 27), 428 (M^{+}, 37), 417 (7), 415 (41), 413 (62), 355 (2), 353 (11), 351 (17), 303 (100), 302 (35), (301 (35), 268 (33), 267 (15), 266 (31), 265 (61), 239 (30), 204 (23), 189 (22), 165 (27), 125 (35), 91 (23), 77 (13) A very similar pattern has been recorded for the isomer **2c'** (retention time 24.32 min.). The unsolved mixture has been analyzed by ^1H nmr, showing in $CDCl_3$ the following spectrum: δ = 7.52-7.07 (m, 34H), 3.50 (d, J = 13.5 Hz, 1H), 3.42 (d, J = 13.52 Hz, 1H), 3.248 (d, J= 13.50 Hz, 1H), 3.165 (d, J= 13.52 Hz, 1H), 1.73 (s, CH_3, 6H) ppm.

Analogous protocol has been followed carrying out similar reactions in wet methylene chloride and/or acetonitrile solutions. However, monitoring the reactions as usual, we observe by gc/ms spectrometry, after 16h, the partial conversion of **1c** (20%) into a new main product **3c**, whose fragmentation pattern fits that of the product, identified as **3a**.[10,13-18] The solvent is removed in vacuo and the residual has been purified by silica gel column chromatography (petroleum ether 40/70: ethyl 9:1 as eluant). After the elution of the starting material, the crude reaction product, (yield not optimized) shows the following spectral data: ms m/e (%) 444 (1), 367 (42), 333 (25), 256 (33), 216 (34), 214 (100), 193 (42), 111 (18), (105 (54), (77 (32). ^1H nmr ($CDCl_3$): δ= 7.40-7.13 (m, 18H), 2.58 (m, 4H) ppm. 18-oxygen labeled **3b*** shows by gc/ms spectroscopy the following fragmentation pattern: m/e (%) 446 (1), 216 (100).

Reactions of 1-(4-methylphenyl)-1-phenylethylene (1d) with aminium salts: Synthesis of indane derivatives (2d,d') and (2d",2d"').

The same protocol has been followed for the substrate **1d**, affording, in methylene chloride solutions with both aminium salts **A**, **B** as catalysts (10-20 mol %), the unsolved mixtures of indane derivatives depicted in the equations 2, see test. In particular, monitoring the reactions by gc/ms spectrometry, we observe the formation of four different isomers (two pairs 9:1 ratio) with retention times in the range 16.9-18.2 min. The prevailing isomers **2d** (45 %) and **2d'** (45%) show the characteristic mass fragmentation patterns of indane derivatives; **2d** (16.9 min): m/e (%) 388 (M^{+}, 48), 373 (100), 311(30), 297 (47), 219 (18), 105 (14), 91 (13); **2d'** (17.2 min): 388 (M^{+} 48), 373 (100), 311(23), 297 (47), 219 (17), 105 (13), 91 (11); **2d"** (17.8 min): 388 (M^{+}, 46), 373 (59), 311(14), 283 (100), 219 (18), 105 (14), 91 (13); **2d"'** (18.2 min): 388 (M^{+}, 46), 373 (56), 311(13), 283 (100), 219 (16), 105 (14), 91 (13). The ^1H nmr spectrum, recorded as

usual, shows the expected doublets, centered at δ=3.352 (2H, J = 13.50 Hz, 3.067, (1H, J = 13.47 Hz), 3.048 (1H, J = 13.52 Hz), and those corresponding to the couple **2d"**, **2d"'**; δ = 3.34 (1H, J = 13.56 Hz), 3.33 (1H, J = 13.34 Hz), 3.047 (2H, J = 13.34 Hz) ppm. The same reaction, carried out in the presence of equimolecular amounts of 2,6-di-*tert*-butyl pyridine **DBP** affords low yields (15 %) of 2,5-di-*p*-tolyl-2,5-diphenyltetrahydrofuran **3d**, showing a different retention time (19.207 min), and the characteristic fragmentation pattern of similar compounds; ms (m/e %): 404 (M^+ 2), 327 (96), 236 (49), 194 (100), 119 (69), 105 (48), 91 (33), 77, 22). Low yields of **3d** have also been observed by gc/ms spectrometry in the reactions carried out in wet methylene chloride, as well as in acetonitrile as solvent.
Protic acid (CF_3COOH) catalyzed reactions of methylene chloride solutions of **1d** lead to the same mixture of indane derivatives **2d-2d"'** with the same ratio observed in the aminium salt-induced rections.

Reactions of 1-(3-methylphenyl)-1-phenylethylene (1e) with aminium salts: Synthesis of indane derivatives (2e,e') and (2e",2e"').

Seemingly, substrate **1e**, affords, in methylene chloride solutions with both aminium salts **A**, **B** as catalysts (10-20 mol %), the unsolved mixtures of indane derivatives depicted in the equation 3, see test. In particular, monitoring the reactions by gc/ms spectrometry, we observed the formation of four different isomers (two pairs 6:4 ratio) with retention times of each isomers in the range 16.9-18.2 min. The prevailing isomers **2e** (30 %) and **2e'** (30%) show the characteristic mass fragmentation patterns of indane derivatives; **2e** m/e (%): 388 (M^+, 38), 373 (54), 311 (15), 297 (100), 219 (27), 105 (18), 91 (23); **2e'**: 388 (M^+ 42), 373 (56),311 (41), 297 (100), 219 (36), 105 (19), 91 (23). The isomers **2e"**, **2e"'** show different retention times, but similar fragmentation patterns by gc/ms spectometry. The ^1H nmr spectrum, recorded as usual, shows the expected doublets, centered at δ=3.35 (1H, J = 13.52 Hz, 3.32, (1H, J = 13.55 Hz), 3.30 (1H, J = 13.54 Hz), 3.29 (1H, J = 13.40 Hz), 3.09 (1H, J = 13.11 Hz), 3.07 (1H, J = 13.43 Hz) 3.05 (1H, 13.52 Hz).

The same reaction, carried out in acetonitrile as solvent leads to low yields of 2,5-di-*m*-tolyl-2,5-diphenyltetrahydrofuran **3e**, showing a different retention time (19.250 min), and the characteristic mass fragmentation pattern of similar compounds: m/e (%): 404 (M^+, 2), 327 (100), 312 (86) 236 (69), 194 (96), 119 (69), 105 (78), 91 (33), 77, 22). Minor amounts of 1,4-diphenyl-1-(*m*-tolyl)-6-methyl-1, 2-dihydronaphthalene **5e** have been observed by gc/ms spectrometry: m/e (%); 386 (M^+, 58), 295 (97), 281 (100), 181 (56). Low yields of **3e** have also been observed by gs/ms spectrometry in the reactions carried out in wet methylene chloride.
Protic acid (CF_3COOH) catalyzed reactions of methylene chloride solutions of **1e** lead to the same mixture of indane derivatives **2e-2e"'** with the same ratio observed in the aminium salt-induced reactions.

Reactions of 1-(4-methoxyphenyl)-1-phenylethylene (1f) with aminium salts: Synthesis of (Z) and (E)-1,4-diphenyl-1,4-di(4-methoxyphenyl)-but-1-ene (6f,f').

Methylene chloride solutions of **1f** treated with catalytic amounts of **A** or **B** as catalysts (10-20 mol %), afforded low yields (20 %) of a pair of isomers. These latter, isolated as usual, have been identified as (Z) and (E)-1,4-diphenyl-1,4-di(4-methoxyphenyl)-but-1-ene **6f,f'**, through the following spectroscopic data: ms m/e (%): **6f** (ret. time 25. 33): 420 (M^+, 42), 223 (80), 197 (100), 165 (58), 135 (62), 115 (36), 91 (26), 77 (26);

6f' (ret. time 27. 6 min): 420 (M^+, 45), 223 (78), 197 (100), 165 (54), 135 (61), 115 (34), 91 (26), 77 (26). The unsolved mixture has also been analyzed by ^{1}H-nmr ($CDCl_3$): δ = 7.24-7.03 (m, 12 H), 6.79-6.75 (m, 6H), 6.69 (s, 1H), 3.78 (s, 3H), 3.76 and 3.75 (s, 3H), 1.44 and 1.40 (s, 3H) ppm; and ^{13}C nmr ($CDCl_3$): δ = 29.34, 49.19, 55.13, 55.29, 113.02, 113.26, 113.39 and aromatic resonances ppm. DEPT experiments confirmed the suggested structure.

Similar reactions, carried out in acetonitrile as solvent afford low yield of tetrahydrofuran derivatives **3f,f'**. These latter have been identified through the characteristic fragmentation patterns by gc/ms spectrometry: **3f** (ret. time 27.18 min) 436 (M^+, 12), 359 (46), 210 (43), 184 (28), 135 (100), 77 (56); **3f'** (ret. time 27.49 min) 436 (M^+, 6), 359 (47), 210 (46), 184 (25), 135 (100), 77 (53). A similar couple of isomers has been detected in the reactions carried out in wet methylene chloride.

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