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Reactions on Aromatic Olefins Induced by Aminium Salts: Protic-Acid or Radical Cation Catalyzed Processes

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Abstract: Aromatic olefins by reaction with aminium salts lead, in strongly acidic reaction media, to different reaction products, arising from the intermediate formation of carbocation or radical-cation species.

INTRODUCTION

Aminium salts have been found to efficiently promote a great variety of reactions on electron rich substrates: *e.g.* Diels-Alder reactions,[1] cycloadditions of molecular oxygen to unsaturated systems,[2] and several other intriguing chemical transformations.[3]

In most of the reported cases, it was ascertained that the role of aminium salts is as one-electron oxidants acting either in stoichiometric processes, or as catalysts in cation-radical chain mechanisms, modeled upon Ledwith[4] and Nelsen's[2] classic proposals. However, possible mechanistic ambiguity has been recognized to affect these reactions, since (a) reaction products, besides being accountable for by radical cation intermediates, often are also compatible with carbocations forming in protic acid catalyzed processes; (b) aminium salts can behave as an indirect source of protic acid, which might be the true catalytic species.[5]

An illustration of this potential mechanistic complexity is provided by the cyclodimerization induced by *tris*-(4-bromophenyl) aminium hexachloroantimonate of 2,4-dimethyl-1,3-pentadiene (**1**) to give 1,3,3,5,5-pentamethyl-4-(1-methylethenyl)cyclohexene (**2**) in good yield. Because **2** was also easily obtainable upon treatment of methylene chloride solutions of **1** with catalytic amounts of various protic acids, including $HSbCl_6$, while a different cyclodimer, 1,3,3,4-tetramethyl-4-(isobutenyl)cyclohexene (**3**), arose under photosensitized electron-transfer conditions, Gassman and Singleton pointed out that the real function of the aminium salt in the formation of **2** was to trigger an acid catalyzed process. Preventing the build up of acid conditions by using a non-nucleophilic base such as 2,6-di-*tert*-butyl-pyridine (**DBP**), in molar excess over the aminium salt initiator, the formation of **2** was, in fact, totally inhibited, but **3** was produced in low yield.[5]

The behaviour of **1**, which might appear rather unusual because no further examples on similar systems of protic acid catalysis under aminium salt conditions emerged, is however quite plausible in view of its peculiar chemical properties, as high stabilization of the allylic carbocation, and large *s-cis* diene conformational population.[1]

In this context, as part of our continuing studies on the aminium salt induced generation and evolution of radical cations from different classes of organic substrates,[3] we report herein the results of a systematic study on several aryl olefins, such as 1,1-diphenylethylene (**4**), tetraphenylethylene (**10**), triphenylethylene (**13**) and bis-fluorenylidene (**16**).

The aminium salts that have been employed as oxidants are *tris*-(2,4-dibromophenyl)aminium hexachloroantimonate (**A**), *tris*-(4-bromophenyl)aminium hexachloroantimonate (**B**) and *tris*-(4-bromophenyl)aminium tetrafluoroborate (**C**).[6-8] Their reactivity has been occasionally compared to that of trityl hexachloroantimonate (**D**) and trityl tetrafluoroborate (**E**).[9] Depending on the substrate, different amounts of specific oxidizing agents were necessary for the complete conversion of the starting material into products of a different kind, which revealed a variety of reaction pathways.

RESULTS AND DISCUSSION

Reactions of 1,1-diphenylethylene (4).

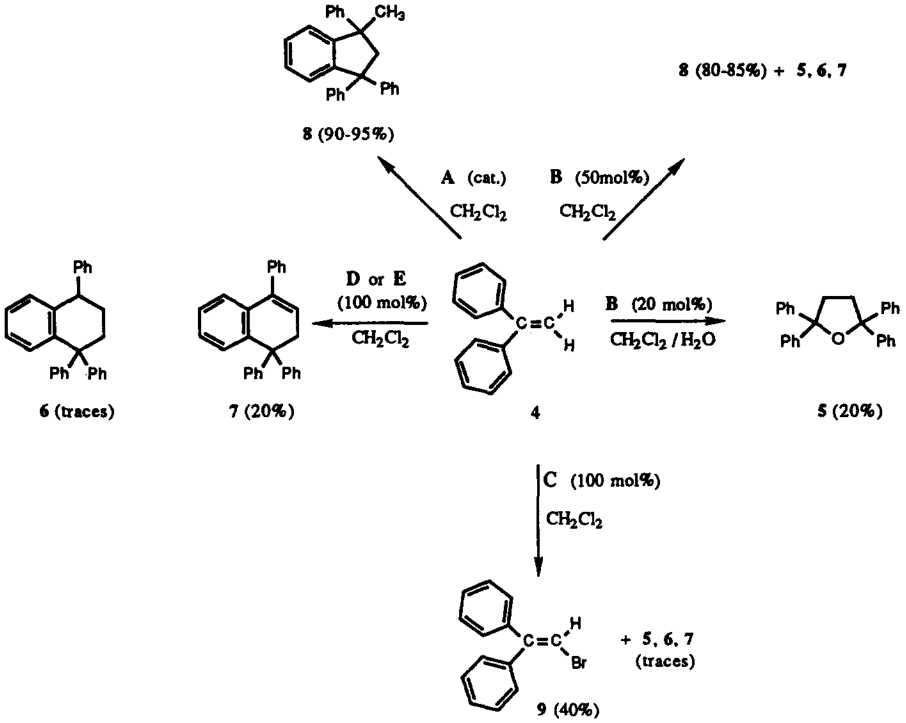
1,1-diphenylethylene **4** was submitted to aminium salt induced reactions, as a substrate that, analogously to **1**, could allow to distinguish between electron-transfer and proton-transfer catalysis. In fact, it is known that **4** undergoes cyclodimerization either under photoinduced electron-transfer conditions or in the presence of an acid as catalyst, leading to well distinct cyclodimers. Different mixtures of 2,2,5,5-tetraphenyl-tetrahydrofuran (**5**), 1,4,4-triphenyl-1,2,3,4-tetrahydronaphthalene (**6**) and 1,1,4-triphenyl-1,2-dihydronaphthalene (**7**) were obtained from photostimulated reactions, depending on the nature of the sensitizer employed,[10] however, when Lewis or protic acids were used, only 1,3,3-triphenyl-1-methyl-indane (**8**) was found as cyclodimer.[11,12]
In our case, **4** [E^{ox}= 1.48 V. vs Ag/Ag$^+$][10] reacted in freshly distilled CH_2Cl_2 with catalytic amounts (5-10 mol %) of **A** [E^{red} = 1.66 V. *vs* SCE][2,6] affording, within one hour, the latter cyclodimer **8** (90-95%), while **5**,**6**,**7** were detected only in trace amounts.

Similar reaction mixtures, **8** (80-85 %) and more appreciable amounts of **5**,**6**,**7** were also obtained upon treatment of methylene chloride solutions of **4** with aminium salt **B**.[E^{red} = 1.16 V. *vs* SCE].[2,6] Due to the weaker oxidizing power of **B** compared with **A**, these latter reactions required greater amounts of the oxidizing agent (50 mol %) and longer reaction time (24 h).

On the contrary, methylene chloride solutions of **4**, upon treatment with equimolecular amounts of *tris*-(4-bromophenyl)aminium tetrafluoroborate $(4\text{-}BrC_6H_4)_3N^{+\cdot}BF_4^-$ [E^{red}= 1.06 V. vs SCE] **C**,[13] or trityl salts $(C_6H_5)_3C^+SbCl_6^-$ or BF_4^- **D**, **E**,[9] afforded, through a slower and partial conversion of the starting material (50-20 %), 2,2-diphenyl ethylene bromide (**9**) (40 %), and the dihydronaphthalene **7** (20 %), as main reaction products, respectively, scheme 1.

All the reaction products have been isolated and fully characterized by physical and spectral data, as reported in the experimental section.

Scheme 1.



On the basis of the fingerprint criterion, the results of the reactions induced by aminium salts **A**,**B**, not withstanding the different reaction rates and the different amounts of the catalyst employed, can be rationalized, more consistently, with a protic acid-catalyzed process, than with a chain radical cation mechanism. This hypothesis has found preliminary evidence by studying the aminium salt **A**-induced reactions on **4** in the presence of different amounts (5-10 mol %) of the non nucleophilic base **DBP**. The base, intercepting the protic acid, totally inhibits the formation of **8**, but not the electron-transfer pathway, leading, in our conditions, to low yields (15-20%) of the tetrahydrofuran **5**. The same reaction product has also been obtained carrying out similar reactions on **4** in wet methylene chloride, also in the presence of 18-oxygen labeled water (20%), see scheme 2.

The slower reactions, the lower conversions of the starting material (20%), and the incorporation of 18-oxygen into the tetrahydrofuran **5*** are straightforward evidence that, under our experimental conditions, radical cation $\mathbf{4}^{+\cdot}$ and then the dimer $\mathbf{4\text{-}4}^{+\cdot}$, trapped by water, are also formed. Furthermore, modified reactions by 1,4-diazabicyclo [2,2,2]-octane (**DABCO**) (E^{ox} = 0.64 V. *vs* SCE)[14] (15 mol %), or 2,3-diphenyl-1,4-dioxene (**DDO**) (E^{ox} 0.96 V. vs SCE)[15] (15 mol%), in the light of their basic properties and much lower oxidation potentials than **4**, appear totally inhibited. On the contrary, a quencher as 1,4-dimetoxybenzene

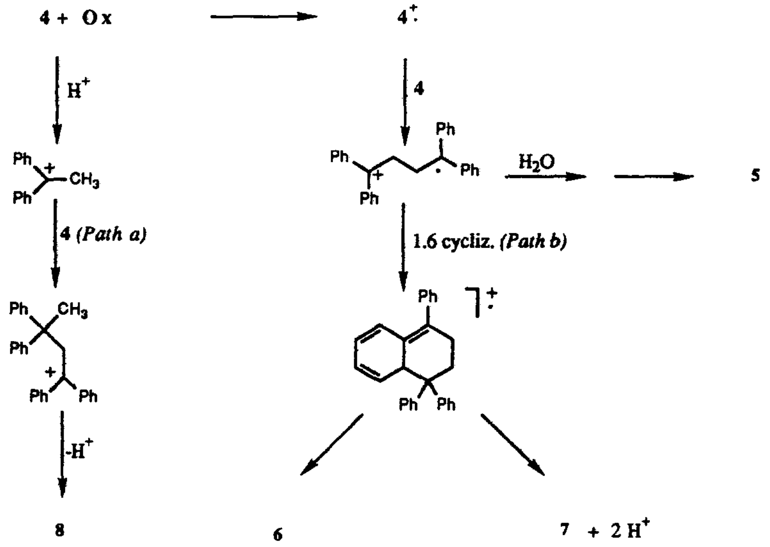
(DMB) [E^{ox}= 1.34 V. vs SCE][16] smoothly influences the reaction rate, but not the conversion of the starting material into **8**.

Such behaviour clearly indicates that an acid catalyzed process, faster than the chain radical cation one, is responsible for the **4** into **8** conversion. Even though scanty, if any, doubt exists regarding the nature of the protic acid ($HSbCl_6$) which catalyzes the cyclodimerization, *path a* , scheme 2, the process in which this is actually formed is not presently known. In any case, it is not merely traces of contaminating acid in the aminium salts that catalyze the cyclodimerization of **4**. In fact, the aminium salts, freshly prepared, have been repeatedly washed with dry diethyl ether until neutral solutions were obtained.[6-8]

In this regard, the Gassman's hypothesis,[5] that head to head dimerization of the primary radical cation with the neutral compound would afford a dimer radical cation, showing strongly acidic hydrogens on β carbons, does not appear plausible. In fact, we actually observe lower yields of products (**5**,**6**,**7**), main reaction products from a pure PET process, in the reactions induced by the stronger oxidizing agent **A**. This latter, with respect to the other aminium or trityl salts, by reaction with **4** would afford the radical cation $4^{+\cdot}$ more efficiently. As a consequence, by dimerization with **4**, we would expect the higher concentration of the dimer radical cation $4\text{-}4^{+\cdot}$, key intermediate in the *path b*, and then an higher yield of **5**,**6**,**7**, scheme 2.

Thus, it is plausible to hypothesize that, although the electron-transfer process between **4** and the aminium salts readily occurs, the inevitable development of protic acid, in the reactions performed with strongly oxidizing species like aminium salts, would promote a fast protonation of the neutral compound. Then the following head to tail dimerization of the intermediate carbocation with neutral olefin must favourably compete with the stepwise cyclodimerization of the radical cation $4^{+\cdot}$.[1]

Scheme 2



Ox = A, B, C, D, E

The results observed with tetrafluoroborate aminium salt **C** appear, at this stage of our investigation, difficult to rationalize. However, we can suggest that the different behaviour is strictly related to the lower thermal stability of the tetrafluoroborate aminium salt with respect to the hexachloroantimonate ones. The decomposition of the former affords low concentration of bromine in the reaction medium,[13] which, as in the N-bromosuccinimide NBS reactions on the same substrate, is responsible for the formation of **9**.

Finally, although the very slow and low conversion of the starting material into **7**, upon treatment of methylene chloride solutions of **4** with equimolecular amounts of both trityl salts, limit the synthetic importance of these reactions, however, the formation of a pure s.e.t. product, notwithstanding the acidic reaction media, appears of interest. In fact, a convincing hypothesis, accounting for our results, could be the existence of a critical protic acid concentration in the medium, which can influence the different mechanistic pathways.

Reactions of tetraphenylethylene (10).

Methylene chloride solutions of tetraphenylethylene **10** [E^{ox}= 1.34 V. vs SCE],[16] a substrate more easily oxidizable than **4**, upon treatment with aminium salts **A**,**B** show a different behaviour. First of all, this substrate is totally inert towards aminium salt **B**, whereas, in order to obtain its total conversion into 9,10-diphenyl phenanthrene (**11**) (90 %) and diphenyl fluorenylidene (**12**) (10%), two equivalents of the stronger aminium salt **A** are required. Furthermore, on the contrary to that observed on **4**, a faster similar reaction also occurs in acetonitrile as solvent. Although, similar experimental results had been observed by treatment of methylene chloride or acetonitrile solutions of **10** with several strong protic or Lewis acids,[17,18] our results can be explained only through a preliminary electron-transfer process between **10** and the aminium salt **A**.

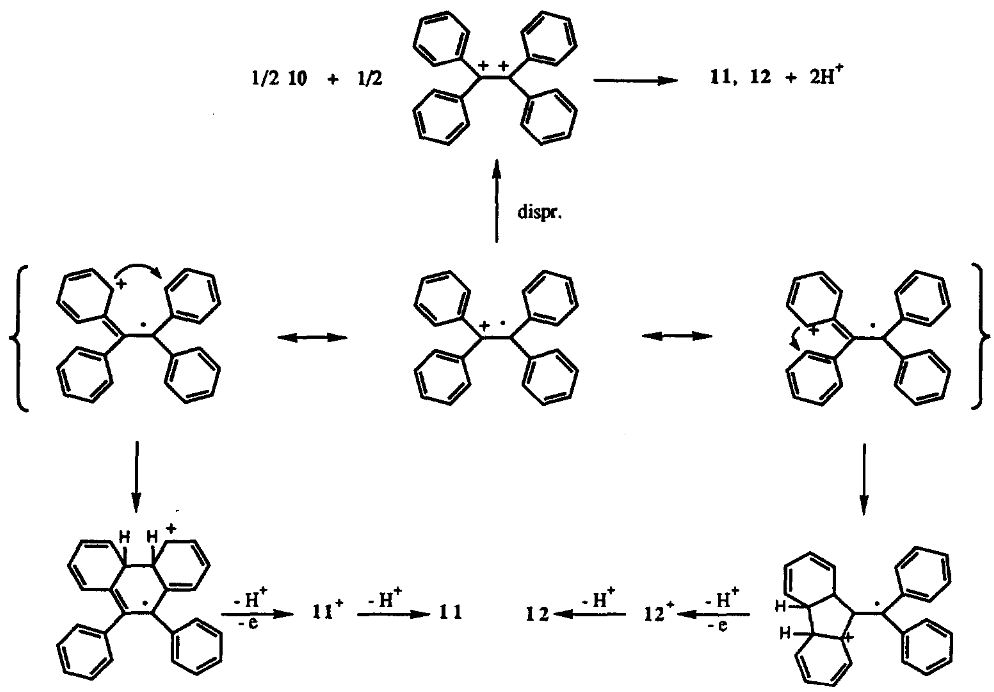
This has been verified as previously reported on **4**. In particular, **DPB**-modified reactions show an expected lower conversion of the starting material, but they are not inhibited at all. In fact, **DBP** does not react significantly with **A**, but it does accelerate the rate of decomposition of the aminium salt.

DABCO and **DDO**-modified reactions, which inhibit the preliminary electron-transfer, are totally quenched. On the contrary, **DMB**-modified reaction, in the light of its similar oxidation potential appear slightly retarded. Furthermore, increasing amounts of aminium salts do not cause further oxidation of the reaction products.[18]

The remarkable solvent effect on the reaction rate, the required stoichiometry, and the cyclic voltammetric experiments, fitting those reported in the literature,[19,20] seem to substantiate that in both solvents, the preliminary esoergonic electron-transfer process is followed by a disproportionation step with the generation of the dicationic species and neutral alkene. The subsequent fast ring closure and deprotonation step would lead to **11** together with minor amounts of **12**, scheme 3.

The electrophilic attack by one of the *ortho* carbons on a vicinal or geminal aromatic ring, directly on the primary cation radical, appears less plausible, see the scheme 3.

Scheme 3



Reactions of triphenylethylene (13).

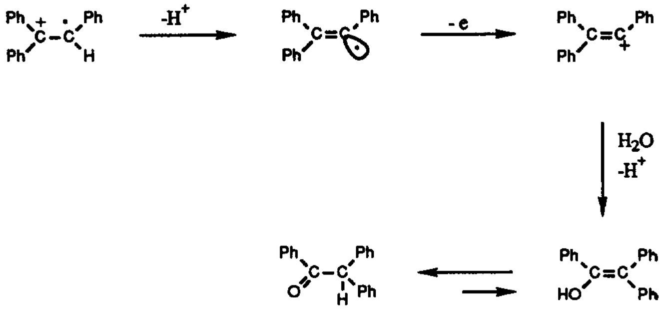
On the contrary to the previous aromatic olefins, methylene chloride solutions of triphenylethylene (**13**) [E^{ox}= 1.54 V. vs SCE][16] by reaction, under oxygen or argon-saturated atmosphere, with two equivalents of **A** slowly afford a mixture of 1,1-diphenyl acetophenone (**14**) and 1,2,2-triphenylethenyl chloride (**15**). No trace of cyclodimer products have been detected.

As previously observed on tetraphenylethylene, **DPB**-modified reactions appear retarded, but not inhibited, whereas, the involvement of water, accounting for **14**, has been tested by performing the same reaction in the presence of 18-oxygen labelled water (20%). Surprisingly, no trace of the isomer 1,1,1-triphenylacetaldehyde, main reaction product in the fast aminium salts-rearrangements on triphenylethylene oxide or 1,1,2-triphenyl-1,2-ethanediol, was observed.[21]

Thus, a mechanism, accounting for our experimental results, would involve the deprotonation of the primary radical cation **13**$^{\dot{+}}$ with formation of the corresponding radical. The subsequent s.e.t. oxidation step would afford the vinyl carbocation, easily trapped by adventitious water. Deprotonation and isomerization of the corresponding enol would lead to the carbonyl compound **14** (scheme 4).

An alternative mechanism, involving the attack of water on the primary radical cation, as in similar photochemical processes, could also account for our experimental results.[22]

Scheme 4

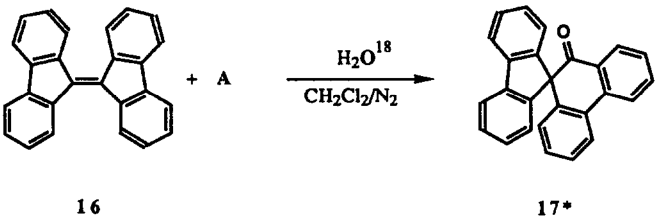


14

The formation of 1,2,2-triphenylethenyl chloride, **15**, provides evidence once again that the reagent **B** may act not only as an one electron-transfer reagent,[3f] but also as a Cl^+ donor,[23] in a manner similar to N-chlorosuccinimide [24] and antimonypentachloride.[25]

Reactions of bis-fluorenylidene (16).

The easy conversion of bis-fluorenylidene **16** into the corresponding spiroketone (**17**) requires only equimolecular amounts of both aminium salts **A** or **B**. In addition to that, similar reactions, carried out under inert atmosphere in the presence of 18-oxygen labelled water (20%), afford high yields of **17*** eq.1. This latter result might be accounted for by the intermediate formation of the elusive epoxide or of the corresponding diol, whose protic-acid, or aminium salt induced pinacol-pinacolone rearrangement readily afford **17**.[21] A similar result had been already reported by us on fluorenylidene-adamantane, whose easy conversion into spiro[2H-adamantyl-2,9'-(10H)-phenanthren]-10'-one still required stoichiometric amounts of both aminium salts.[3f]



eq. 1

16 **17***

However, the observed stoichiometry, makes the previous mechanistic pathway unsuitable, and more detailed investigations are warrented to find some confirmations to a mechanistic hypothesis, which involves nucleophilic attack of water, rate determing step, directly on the primary radical cation **16**$^{\cdot+}$. The following deprotonation would afford the α-hydroxy radical intermediate, whose subsequent electron-transfer oxidation and ring closure might be ensured by antimony pentachloride, in equilibrium with the hexachloroantimonate anion.

CONCLUSIONS

Although the oxidation potentials of our aromatic olefins confirm the suggestion that aminium salts, in particular A, may promote efficient, preliminary electron transfer processes to radical cations, our experimental results show that structure effects, coupled with the protic acid reaction media developed, influence differently their subsequent conversion into the reaction products. Thus, the mechanistic discussions associated with the evolution of these and other radical cations require the systematic use of probes to evaluate if aminium salts lead to a faster protic acid catalyzed process, or promote a chain radical cation process.[1,5,26]

EXPERIMENTAL SECTION

Melting points were taken on an electrothermal apparatus and are uncorrected. ^{1}H-and ^{13}C-NMR spectra were recorded on a Varian XL-200 MHz instrument. 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. The starting materials **1**, **4**, **10**, **13** are pure commercial sample (Aldrich Co). **16** has been synthesized according to the McMurry's procedure.[27] **DABCO** , **DBP**, **DMB** commercial samples from Aldrich Co, have been dried before use. **DDO** has been synthesized as reported in the ref. 15. Aminium salts (**A**, **B**, **C**) have been synthesized following the procedure reported in the refs 6-8. Trityl hexachloroantimonate and tetrafluoroborate **D**, **E**, commercial samples (Aldrich Co), have been used as received.

Reactions of 1,1-diphenylethylene with aminium salts: Synthesis of 1,3,3-triphenyl- 1-methyl-indane (8).

A catalytic amount of *tris*-(2,4-dibromophenyl)ammoniumyl hexachloroantimonate A (0.106 g, 0.10 mmol).is rapidly added to a solution of 1,1-diphenylethylene 4 (0.180 g, 1mmol) in distilled methylene chloride (20 ml) at room temperature under stirring. The intensely green colour of the solution turns to blue within a few minutes. The reaction mixture, monitored by tlc (hexane: ethyl ether 9:1 as eluant) and/or by gc/ms spectrometry, reveals, within 1h, the total disappearance of the starting material and the formation of a new main product with molecular peak m/e 360. Trace amounts of other products with molecular peaks m/e 360, 358, and 376 are also recorded. 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 white crystalline product (0.162 g. 90%) has been fully characterized, as **8**, by physical and spectral data.

M.p. 143-144 °C (lit. 143 °C);[12] ms (m/e %): 360 (53), 345 (100), 283 (24), 269 (56), 268 (38), 267 (62), 254 (26), 205 (24), 165 (15), 91 (22); ^{1}H nmr ($CDCl_3$): δ = 7.42-7.07 (m, 19H), 3.49 (d, J = 13.5 Hz, 1H), 3.19 (d, J = 13.5 Hz, 1H), 1.64 (d, J = 2.5 Hz, 1H) ppm; ^{13}C ($CDCl_3$) δ = 28.88, 51.18, 60.93, 61.38 ppm and aromatic signals; ir (KBr pellet) υ =3061, 3032, 2974, 1598, 1491, 1446, 1032, 769, 754, 703 cm^{-1}. The product shows consistent elemental analysis.

Analogous protocol has been followed carrying out similar reactions in wet methylene chloride. However, monitoring the reaction as usual, we observe by gc/ms spectrometry, after 10h, the partial conversion of **4** (20%) into a new main product, whose fragmentation pattern fits that observed for the product identified as **5**.[10]

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 %) 376 (1), 299 (100), 281 (21), 222 (32), 180 (55), 165 (21), 105 (74), 77 (43); ^{1}H nmr ($CDCl_3$): δ= 7.60-7.13 (m, 20H), 2.64 (s, 4H) ppm, consistent with those reported for 2,2,5,5-tetraphenyl-tetrahydrofurane.[10] 18-oxygen labeled **5*** shows by gs/ms spectroscopy the following fragmentation pattern: ms (m/e %) 301 (11), 300 (25), 299 (100), 224 (4), 222 (43), 107 (9), 105 (86).

Similar reaction conditions have been followed by using *tris*-(4-bromophenyl)ammoniumyl hexachloroantimonate **B**, as catalyst. The reaction products have been identified by gc/ms spectrometry. Analogous protocol has been applied in the several **DABCO, DDO, DPB** and **DMB**-mediated aminium salt reactions.

Reactions of 1,1-diphenylethylene with trityl hexachloroantimonate D: Synthesis of 1,1,4-triphenyl-1,2-dihydronaphthalene (7).

An equimolecular amount of trityl hexachloroantimonate **D** (0.577 g, 1mmol) is rapidly added to a solution of **4** (0.180 g, 1mmol) in distilled methylene chloride (20 ml), at room temperature under stirring. The initial yellow solution rapidly turns into an intensily green colour, persisting for several days. The reaction, strongly acidic, has been monitored by tlc (hexane as eluant) and gc/ms spectrometry. After 72 h, nonetheless the partial conversion of the starting material into reaction products (20-30 %), the solvent is 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 starting material, the crude reaction product, (yield not optimized), shows the following spectral data ms: (m/e %) 358 (50), 268 (22), 267 (100), 167 (27); ^{1}H nmr ($CDCl_3$): δ= 7.32- 7.12 (m, 19 H), 5.96 (t, J = 4.7 Hz, 1H), 3.27 (d, J = 4.7 Hz, 2H) ppm, consistent with those reported in the literature.[10]

Reactions of tetraphenylethylene with aminium salts. Synthesis of 9,10-diphenylphenanthrene (11).

An equimolecular amount of *tris*-(2,4-dibromophenyl)ammoniumyl hexachloroantimonate **A** (1.02 g, 1 mmol) is rapidly added to a solution of **10** (0.332 g, 0.1 mmol) in distilled methylene chloride (30 ml) at room temperature under stirring. The intensily green colour of the solution fades within 1h. The reaction, monitored as usual, reveals by tlc the starting material, the corresponding amine, and two new spots with R_{fs} 0.56 and 0.48 (petroleum ether 40/70: ethyl ether 25:1 as eluant). The total conversion of the starting material requires an additional equimolecular amount of A.

Two equivalents of aminium salt are also required for a similar reaction carried out in acetonitrile as solvent. The faster reaction occurs with the precipitation of the corresponding *tris*-(2,4-dibromophenyl)amine. The solvent is then removed in vacuo and the residual, adsorbed on silica gel, is chromatographed with the previous mixture of solvents. After the elution of the amine, the collected white crystalline product shows the following physical and spectral data: m.p. 238 °C from n-hexane (lit. 238-239 °C); [18,19] ms (m/e %) 330 (100), 329 (22), 313 (10), 254 (8), 253 (42), 252 (40), 165 (11), 163 (15), 162 (15), 157 (21), 156 (45), 150 (18), 143 (8); ^{1}H nmr (CDCl$_3$) δ= 8.82 (ddd, J = 0.6 Hz, J = 1.2 Hz, J = 8.2 Hz, 2H), 7.67 (ddd, J = 1.8 Hz, J = 6.5 Hz, J = 8.2 Hz, 2H), 7.57 (ddd, J = 0.6 Hz, J = 1.8 Hz, J = 8.2 Hz, 2H), 7.49 (ddd, J = 1.2 Hz, J = 6.5 Hz, J = 8.2 Hz, 2H), 7.33-7.13 (m, 10H) ppm; ^{13}C nmr (CDCl$_3$): δ= 139.54, 137.18, 131.86, 131.03, 129.97, 127.83, 127.57, 126.61, 126.46, 126.39, 122.47 ppm; ir (KBr pellet) υ =3055, 3030, 1488, 1444, 1420, 1074, 1028, 759, 728, 703, 628 cm^{-1}. The consistent elemental analysis confirms the structure proposed for this reaction product. The subsequent elution leads to a mixture of the previous 9,10-diphenylphenanthrene with the isomer 9H-fluorene, 9-(diphenylmethylene), whose structure has been fully characterized by spectral data and comparison with those of an authentic sample, prepared by following the well known Mc Murry's procedure.[27]

M.p. 235° C from ethylacetate (lit 235-236);[28] ms (m/e %) 330 (100), 329 (36), 313 (11), 254 (16), 253 (90), 252 (78), 250 (25), 165 (12), 163 (18), 162 (11), 157 (20),150 (16), 143 (6); ^{1}H nmr (CDCl$_3$): δ = 7.54 (ddd, J = 0.5 Hz, J = 1.2 Hz, J = 7.5 Hz, 2H), 7.28-720 (m, 10H), 7.08 (ddd, J = 1.0 Hz, J = 7.5 Hz, J = 8.0 Hz, 2H), 6.77 (td-like due to ddd, J_d = 1.2 Hz, J_t = 8.0 Hz, 2H), 6.47 (ddd, J = 0.5 Hz, J = 1.0 Hz, J = 8.0 Hz, 2H) ppm; ^{13}C nmr (CDCl$_3$) δ = 145.53, 142.96, 140.49, 138.69, 134.17, 129.69, 128.84, 128.22, 127.65, 126.43, 124.90, 119.27 ppm; ir (KBr pellet) υ = 3055, 3025, 1487, 1442, 1346, 1309, 1276, 1030, 736, 701 cm^{-1}.

1,1-diphenylacetophenone (14).

A similar procedure has been followed for the synthesis of **14** (60 % yield), whose physical and spectral data are consistent with those of an authentic sample, prepared as reported in the literature.[29]
m.p. 134-135; ms (m/e %) 272 (2), 167 (40), 105 (100), 77 (19); ^{1}H nmr (CDCl$_3$): δ = 8.03-7.95 (m, 2H), 7.58-7.18 (m, 13 H), 6.03 (s, 1H) ppm; ^{13}C nmr (CDCl$_3$): δ = 199.82, 139.35, 137.15, 133.21, 129.3, 129.11, 128.97, 127.83, 59.43 ppm; ir (KBr) υ = 3065, 2978, 1683 cm^{-1}.

The 1,2,2-triphenylethenyl chloride, **15**, has been identified by comparison with the gc/ms fragmentation pattern of an authentic sample, prepared by reaction of **13** with an excess of N-chlorosuccinimide: ms (m/e %) 292 (34), 291 (21), 290 (100), 256 (15), 255 (61), 254 (29), 253 (45), 252 (40), 240 (26), 239 (34), 176 (11), 126 (13), 77 (4).

[9H-fluorene-9,9'(10'H)-phenanthren]-10'-one (17).

An eqimolecular amount of *tris*-(2,4-dibromophenyl)ammoniumyl hexachloroantimonate A (0.106 g. 0.1mmol) is rapidly added to a solution of 9H-fluorene, 9-(9'H-fluoren-9-ylidene) **16** (0.328g 0.1mmol) in distilled methylene chloride (30 ml) under stirring at room temperature. The green colour of the solution fades slowly. The reaction, monitored by gc chromatography, shows, after 3 h, the peaks corresponding to *tris*-(o,p-dibromophenyl)amine, unreacted starting material (trace amounts), and to a new product in high yield. The solvent is removed in vacuum, and the residual, adsorbed on silica gel is purified by silica gel column chromatography with hexane/diethylether 10:1 as eluant. After the elution of the corresponding amine, the crude reaction product , 0.250g (76% yield), white crystals from benzene/ethanol, shows physical and spectral data consistent with those of **17**: m.p. 262-263 °C (lit.^{30} 262-263 °C); ms (m/e %) 344 (100), 316 (75), 315 (81), 289 (13), 172 (12), 157 (39), 156 (22), 143 (16); ^{1}H-nmr (CDCl$_3$): δ = 8.51-7.94 (m, 3H), 7.89-7.65 (m, 3H) 7.59-6.87 (m, 9H), 6.57 (d, 1H) ppm; ^{13}C-nmr (CDCl$_3$): δ = 197.25, 147.07, 141.62, 139.32, 134.91, 129.24, 128.57,128.34, 128.11, 128.06, 127.95, 124.75, 123.24, 120.59, 68.71 ppm; ir (KBr): υ = 3071, 3015, 1683, 1600, 1450, 1266, 1242, 1131, 857, 752, 730, 655, 618 cm^{-1}.

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REFERENCES AND NOTES

1. Bauld, N. L *Tetrahedron* **1989**, *45*, 5397 and refs therein.
2. Nelsen, S. F. *Acc. Chem. Res.* **1987**, *20*, 269 and refs therein.
3. (a) Lopez, L.; Troisi, L. *Tetrahedron* **1992**, *35*, 7321 and refs therein.
   (b) Bauld, N.L.; Mirafzal, G.A. *J. Am. Chem. Soc.* **1991**, *113*, 3613.
   (c) Marra, A.; Malle, J.M.; Amatore C.; Sinay, P. *Synlett* **1990**, 572.
   (d) Akasaka, T.; Fukuoka, K.; Ando, W. *Tetrahedron Lett.* **1991**, *32*, 7695.
   (e) Lopez, L.; Troisi, L. *Tetrahedron Lett.* **1989**, *30*, 3097.
   (f) Lopez, L.; Troisi, L.; Mele, G. *Tetrahedron Lett.* **1991**, *32*, 117.
4. Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.
5. Gassman, P.G.; Singleton, D.A. *J. Am. Chem. Soc.* **1984**, *106*, 6085 and 7993.
6. Baker, T. N.; Doherty, W.P.; Kelly, W.S.; Newmeyer, W.; Rogers, J.E.; Spaulding, R.E.; Walters, R.I. *J. Org. Chem.* **1965**, *30*, 3714.
7. Bell, F.A.; Ledwith, A.; Sherrington D.C. *J. Chem. Soc. (C)* **1969**, 2719.
8. Barton D.H.R.; Haynes, R.K.; Leclerc, G.; Magnus, P.D.; Menzies, I.D. *J.Chem. Soc. Perkin I* **1975**, 2055.
9. Okada, K.; Hisamitsu, K.; Mukai, T. *Tetrahedron Lett.* **1981**, *22*, 1251.
10. (a) Maroulis, J.; Shigemitsu, Y.; Arnold, D.R. *J. Am. Chem. Soc.* **1978**, *100*, 535.
    (b) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356 and refs therein.
    (c) Mattay, J.; Vondenhof, M.; Denig, R. *Chem. Ber.* **1989**, *122*, 951 and refs therein.
    (d) Gollnick, K.; Schanatterer, A. *Tetrahedron Lett.* **1984**, *25*, 2735.
    (e) Moutet, J.C.; Reverdy, G. *Tetrahedron Lett.* **1979**, 2389.
    (f) Majima, T.; Pac, C.; Nakaspne, A.; Sakurai, H. *J. Am. Chem. Soc.* **1981**, *103*, 4499.
11. Evans, A.G.; Price, D. *J. Chem. Soc.* **1959**, 2982.

12. Wolovsky, R.; Maoz, N. *J. Org. Chem.* **1973**, *38*, 4040.

13. Eberson, L.; Larsson, B. *Acta Chem. Scand.* **1986**, *40*, 210.

14. Haselbach, E.; Vautey, E.; Suppan, P. *Tetrahedron* **1988**, *44*, 7344 and refs.therein.

15. Schaap, A.P.; Zaklika, K.A.; Kashar, B.; Fung, L.W.M. *J. Am. Chem. Soc.* **1980**, *102*, 389.

16. (a) Mattes, S.L.; Farid, S. *Organic Photochemistry,* Padwa, A (ed) Dekker , M. New York Vol. 6, *chpt 4*, **1983** and refs therein.
(b) Santamaria, J. "*Photoinduced Electron Transfer*", ed. by Fox, M.A.; Chanon, M. Elsevier, Amsterdam **1988**, Part B, 483.
(c) Lopez, L. *Topics in Curr. Chem.*, ed. by Mattay, J., Springer & Verlag Berlin, Heidelberg **1990**, *156*, 117.

17. (a) Gatzke, A.L.; Stairs, R.A.; Diaper, D.G.M. *Can. J. of Chem.* **1968**, *46*,3695.
(b) Ohwada, T.; Shudo K. *J. Am. Chem. Soc.* **1988**, *110*, 1862 and refs therein.

18. Olah, G. A.; Grant, J.L.; Spear, R.J.; Bollinger, J.M.; Serianz, A.; Sipos, G. *Ibid.* **1976**, *98*, 2501 and refs therein.

19. Stuart, J. D; Ohnesorge, W. E. *J. Am. Chem. Soc.* **1971**, *93*, 4531.

20. (a) Svanholm, U.; Ronlan, A., Parker V.D *ibid.* **1974**, *96*, 5108.
(b) Kozhevnikov, I.V.; Eberson, L. *New. J. Chem* . **1992**, *16*, 351.

21. Lopez, L.; Mele, G.; Mazzeo, C. *J. Chem. Soc. Perkin I Comm.* **1994**, 779.

22. Akaba, R.; Aihara, S.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn* **1991**, *64*, 1419.

23. Bracke, W.; Cheng, W.J.; Pearson, J.M.; Szwarc, M. *J. Am. Chem. Soc.* **1969**, 91, 203.

24. Meijer, E.W.; Kellog R.M.; Wynberg, H. *J. Org. Chem.* **1982**, 47, 2005.

25. Wieringa, J.H.; Strating, J.; Wynberg, H. *Tetrahedron Lett.* **1970**, 4579.

26. Reynolds, D.W.; Lorenz, K.T.; Chiou, H.S.; Belville, D.; Paboa, R.A.; Bauld, N.L. *J. Am. Chem. Soc.* **1987**, *109*, 4960.
Lopez, L.; Mele, G.; Fiandanese, V.; Cardellicchio, C.; Nacci, A. *Tetrahedron* **1994**, *50*, 000

27. McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708.

28. Luisa, M.; Franco, T.M. B.; Herold, B.J.; Evans, J.C.; Rowlands, C.C. *J. Chem. Soc. Perkin Trans II* **1988**, 443.

29. Gebhart,Jr., H.J.; Adams, K.H. *J. Am. Chem. Soc.* **1954**, *76*, 3925.

30. Poshkus, A.C.; Herweth, J.E. *J. Org. Chem.* **1964**, 2567.

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