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Looking for a Paradigm for the Reactivity of Phenonium Ions

Stefano Protti,[a] Daniele Dondi,[a] Mariella Mella,[a] Maurizio Fagnoni,[a] and Angelo Albini*[a]

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The addition of a photogenerated phenyl cation to an alkene offers an entry, under mild conditions, to the phenethyl cation/phenonium ion system in organic solvents. Taking advantage of this, a product study has been carried out in parallel with a computational characterization of the intermediates. Thus, 4-methoxy- and 4-dimethyaminophenyl cations have been photogenerated from the corresponding chlorobenzenes in the presence of mono- to tetrasubstituted olefins in polar or protic media. The chemistry that occurs has been correlated with the degree of anchimeric assistance offered by the phenyl group, as predicted by calculations. Two limiting situations arise, the first one when starting from mono- or 1,2-disubstituted alkenes. In these cases, calculations evidence a large stabilization of the intermediate (phenonium character), particularly with electron-donating substituents on the aromatic ring, and the main products in acetonitrile are phenethyl chlorides. Variation of the ion-stabilizing solvent such as trifluoroethanol (TFE) leads to alkyl and hydride migration before chloride addition. In contrast, with less electron-rich aromatics and highly substituted alkenes the stabilization of the intermediate is modest and the typical reaction is deprotonation to yield an allylbenzene or, in TFE, the formation of a phenethyl ether. In between these two extremes, there are intermediate cases, more easily directed by a change in the conditions. These generalizations and the mildness of the method help to assess the synthetic potential of this reaction.

Introduction

The β-stabilization effect of the aryl group in phenethyl cations and the attending formation of a σ-bridged intermediate, the phenonium ion, was first evidenced by Cram[1] through pioneering studies on the stereochemical course of the solvolysis of optically active phenethyl sulfonates. The role of such an intermediate has since been explored from both the experimental[2] and computational points of view.[3] Recent work favours a continuum of situations in between the phenethyl cation **I** and the σ-bridged structure **III**, and the possible role of a weak π complex **II** (see Scheme 1).[4] Substituents on the ring and on the phenethyl moiety clearly affect the structure and reactivity of the intermediate, as do the medium characteristics. Apart from the initial experiments, most mechanistic studies have been carried out under conditions quite different to those suitable for preparative purposes, for example, in the gas phase[5] or in superacids,[2] a fact that has contributed to the slow development of synthetic processes via this intermediate. Application of this intermediate in organic synthesis for carbon–carbon or carbon–heteroatom bond formation was reported in the 90s by Olah and co-workers.[6,7,10] More recently, the synthetic potential of these carbocations has been pointed out by Nagumo and Akita and coworkers, with the suggested synthesis of oxygen heterocycles (lactones and tetrahydrofurans)[11] upon solvolysis of the corresponding phenethyl sulfonates. This approach (Scheme 1, a) is appealing for synthetic applications,[12] whereas other methods, such as the ring-opening of benzocyclobutene in superacids, are of spectroscopic interest.[13] Some years ago we demonstrated a novel, mild access to phenonium ions by the addition of triplet phenyl cation **IV**, photogenerated from phenyl halides or esters,[14] to olefins (Scheme 1, b).[15–17] The first-formed triplet adduct cation with alkenes has a diradical character (**V**), just like the starting phenyl cation, but then intersystem crossing occurs to the more stable singlet phenethyl cation/phenonium ion system (**I**/**III**), which, contrary to what happens in the triplet manifold, undergoes addition of nucleophiles. The multiplicity-dependent selectivity has been exploited in some three-component photoarylations[15,17a–17c,18a] (Scheme 1, c) and in the intramolecular version when the trap bears two nucleophilic sites, as is the case with ω-alkenols[19] and ω-alkenoic acids.[20] Whatever the mode of generation, the phenonium may be involved competitively in various processes (nucleophile addition, deprotonation and rearrangement). This often leads to an unsatisfactory selectivity, but no systematic examination of such competition and on the dependence on structure and conditions has been carried out, also because of the limited choice allowed for the generation of the key intermediate. The mild conditions of the

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[a] Department of Chemistry, University of Pavia,
V. Le Taramelli 12, 27100 Pavia, Italy
Fax: +39-0382-987323
E-mail: angelo.albini@unipv.it

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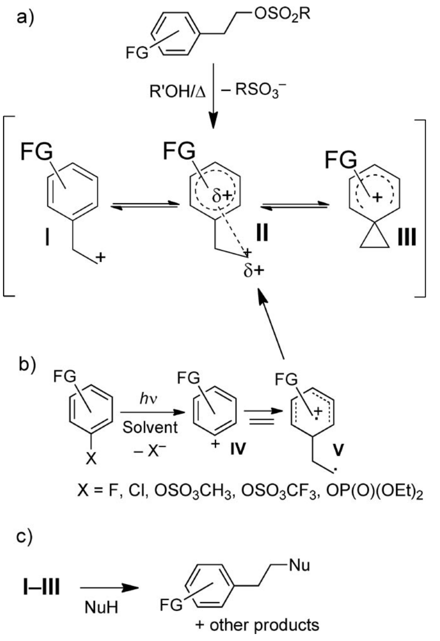
phenyl cation path offers a convenient way to explore this point. Accordingly, an experimental and computational study was performed and is reported below.



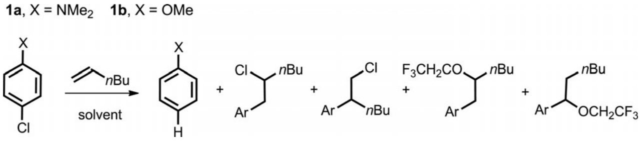
Scheme 1.

Results and Discussion

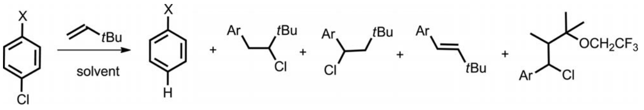
As indicated in part b of Scheme 1, the adduct cations were generated from the trapping by alkenes of aryl cations arising from the photoheterolysis of electron-donating-substituted phenyl chlorides, namely 4-chloro-*N*,*N*-dimethylaniline (**1a**)[21] and 4-chloroanisole (**1b**).[18] Alkenes with increasing degrees of substitution (1-hexene, 3,3-dimethyl-1-butene, cyclohexene, 2-methyl-2-butene and 2,3-dimethyl-2-butene) were used as traps in two solvents, acetonitrile and 2,2,2-trifluoroethanol (TFE). Irradiation was performed until complete consumption of the aryl chloride, except where indicated, and the adducts formed were separated by chromatography, identified and quantified. In addition to adducts, reduced products, *N*,*N*-dimethylaniline (**2a**) and anisole (**2b**), respectively, were consistently formed as minor products and their amounts were determined by GC analysis.

Because the reactions considered involved the release of acidity,[17d] it was checked in every case that this did not induce acid-catalysed secondary processes and in some cases a base (Cs_2CO_3) was added to buffer the solution. The results are presented in Tables 1–3. Thus, irradiation of 4-chloro-*N*,*N*-dimethylaniline (**1a**) in the presence of 1-hexene afforded the regioisomeric phenethyl chlorides **3a** and **3′a** in acetonitrile, but only the **3a** in TFE (Table 1). 4-Chloroanisole (**1b**) gave the analogous adduct (isomer **3b** only) in acetonitrile, but in TFE **3b** was accompanied by phenethyl ether **4b** as well as by benzyl ether **5b**, indeed, the most abundant product.

Table 1. Products from the photoreaction of 4-chloro-*N*,*N*-dimethylaniline (**1a**) and 4-chloroanisole (**1b**) with monosubstituted alkenes.[a]



1a	MeCN	**2a**, 5	**3a**, 35	**3′a**, 18		
1a	TFE[b]	**2a**, 3	**3a**, 45			
1b	MeCN	**2b**, 5	**3b**, 54			
1b	TFE[c]	**2b**, 5	**3b**, 36		**4b**, 10	**5b**, 40



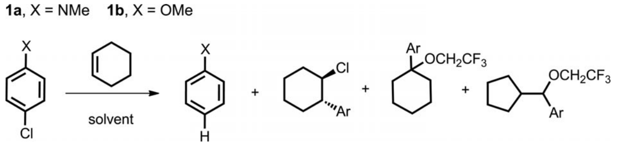
1a	MeCN	**2a**, 10	**6a**, 40			
1a	TFE			[d]		
1b[e]	AcOEt	**2b**, 6	**6b**, 25	**7b**, 16	**8b**, 19	
1b	TFE[c]	**2b**, 13			**8b**, 22	**9b**, 55

[a] Ar = $p\mathrm{NMe_2C_6H_4}$ or $p\mathrm{OMeC_6H_4}$. Experimental conditions: ArCl (0.05 M) and the alkene (0.5 M) were irradiated in a degassed solution of the chosen solvent until the complete consumption of the aromatic. Isolated yields based on consumed **1**, except in the case of compounds **2a**,**b**, were determined by GC analysis. Data presented as product, yield [%]. [b] 90% conversion of **1a**. [c] Caesium carbonate (0.025 M) was added. [d] Sluggish reaction forming a complex mixture. [e] The same distribution products were obtained in MeCN, but the conversion of **1b** was lower (<50%).

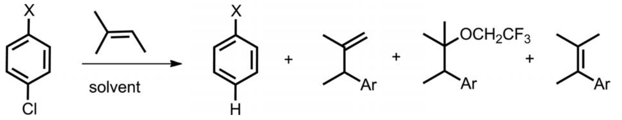
As for the other primary alkenes tested, with 3,3-dimethyl-1-butene, **1a** gave the phenethyl chloride **6a** in 40% yield in MeCN, whereas irradiation in TFE gave a complex mixture, a result not improved by adding Cs_2CO_3. Anisole **1b** gave analogous chlorides **6b** and **7b** along with styrene **8b** in MeCN. In this solvent the photoreaction occurred with limited conversion, but in ethyl acetate the reaction proceeded to completion with the formation of the same compounds. In TFE, ether **9b** was by far the most abundant product (55% yield) along with **8b**.

In the presence of cyclohexene, the corresponding *trans*-1-aryl-2-chlorocyclohexane **10a** was the only adduct formed in both solvents from **1a** and correspondingly **10b** was formed from **1b** in MeCN, whereas in TFE, **10b** was accompanied by rearranged benzyl ethers **11b** and **12b**, as previously established (Table 2).[18,22] Irradiation with 2-methyl-2-butene gave the allyl derivatives **13** as the major products from both halides in acetonitrile, along with a small amount of methoxystyrene **15b** in the case of **1b**. Irradiation in TFE gave phenethyl ethers **14a**,**b** as the main products. Finally, chlorides **1a**,**b** gave the corresponding allylbenzenes **16a**,**b** in the presence of 2,3-dimethylbutene in acetonitrile and TFE, although comparable yields of alkylbenzene **17b** and ethers **18b** and **19b** were likewise formed from **1b** in TFE (Table 3).

Table 2. Products from the photoreaction of **1a** and **1b** with cyclohexene and 2-methyl-2-butene.[a]



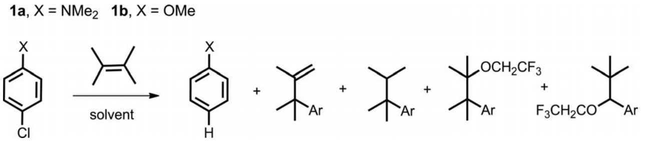
1a	MeCN	**2a**, 30	**10a**, 55		
1a	TFE	**2a**, 11	**10a**, 59		
1b	MeCN	**2b**, 3	**10b**, 30		
1b	TFE[b]	**2a**, 10	**10b**, 9	**11b**, 20	**12b**, 21



1a	MeCN	**2a**, 15	**13a**, 54		
1a	TFE	**2a**, 15	**13a**, 5	**14a**, 43	
1b	MeCN	**2b**, 5	**13b**, 55		**15b**, 12
1b	TFE[b]	**2b**, 5	**13a**, 54	**14b**, 50	**15b**, 18

[a] See Table 1 for experimental details. Data presented as product, yield [%]. [b] Caesium carbonate (0.025 M) added.

Table 3. Products from the photoreaction of **1a** and **1b** with 2,3-dimethyl-2-butene.[a]

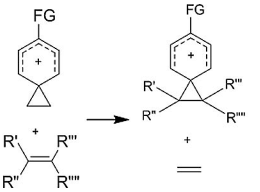


1a	MeCN	**2a**, 15	**16a**, 64			
1a	TFE	**2a**, 5	**16a**, 60			
1b	MeCN	**2b**, 2	**16b**, 49			
1b	TFE[b]	**2b**, 2	**16b**, 21	**17b**, 14	**18b**, 17	**19b**, 7

[a] Ar = $p\mathrm{NMe_2C_6H_4}$ or $p\mathrm{OMeC_6H_4}$. See Table 1 for experimental details. Data presented as product, yield [%]. [b] Caesium carbonate (0.025 M) added.

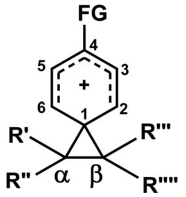
In parallel to the experimental study, DFT calculations were carried out on the key intermediates, singlet adduct cations **I/III**, formally resulting from the reaction with increasingly methyl-substituted alkenes, from ethylene to 2,3-dimethyl-2-butene.[23] The structures were optimized in vacuo and checked to have no imaginary frequencies. Solvent effects were evaluated by single-point calculations of the optimized geometries by using the CPCM method (see the Supporting Information).

In all cases, the minima corresponded to structures in which the Cα–Cβ bond (see Table 4) lies in the plane perpendicular to that of the six-membered ring. Substituents at Cα and Cβ made such cations less stable, with an almost monotonic increase in energy of 3.5–4 kcal mol^{-1} per methyl group, with the energy of the tetramethyl system twice as much as that with the *tert*-butyl group, as shown in Figure 1 in which the energy involved in the isodesmic reaction [Equation (1)] is reported.[25] The effect (resulting from the algebraic sum of two contributions by the methyl groups, the stabilization of the alkene and the destabilization of the phenonium ion) was slightly stronger (by ca. 1 kcal mol^{-1}) for the 4-methoxy-substituted derivatives than for the 4-dimethylamino derivatives. As for the geometry, the six-membered ring had the expected cyclohexadienyl structure already evidenced in previous studies of phenonium ions.[13,26] As for the spirocyclopropane ring, the introduction of substituents caused a lengthening of the C1–Cα(β) bonds, with a stepwise increase of about 0.03 Å for each methyl group added in the $\mathrm{NMe_2}$ series and of 0.04 Å in the OMe series (see Table 4, some examples of the geometries are shown in Figure 2). Thus, the most stable configuration varied from a "fully formed" phenonium ion, as in the case of **20** (FG = $\mathrm{NMe_2}$, C1–Cα 1.577 Å), to what appears to be a complex rather than a covalently bonded structure (see **24b**, FG = OMe, C1–Cα 1.674 Å) or to a strongly asymmetric structure (see **23b**). A parallel effect is the diminishing of the fraction of positive charge calculated on the cyclopropane with increasing substitution (see the total charge on the cyclopropane moiety, which varies from 0.26 to 0.18 and from 0.31 to 0.18 in the two series in Table 5; correspondingly, more charge remains at C^4).



(1)

Table 4. Calculated geometries for selected substituted phenonium intermediates.



Cation	FG	R′	R′′	R′′′	R′′′′	C^1–C$_α$ [Å]	C^1–C$_β$ [Å]
20	$\mathrm{NMe_2}$	H	H	H	H	1.577	1.577
21	$\mathrm{NMe_2}$	H	H	H	Me	1.574	1.611
21′	$\mathrm{NMe_2}$	H	H	H	*t*Bu	1.570	1.630
22-*trans*-22	$\mathrm{NMe_2}$	H	Me	H	Me	1.608	1.608
***cis*-22**	$\mathrm{NMe_2}$	H	Me	Me	H	1.606	1.607
23	$\mathrm{NMe_2}$	H	Me	Me	Me	1.596	1.661
24	$\mathrm{NMe_2}$	Me	Me	Me	Me	1.641	1.642
20	MeO	H	H	H	H	1.594	1.594
21	MeO	H	H	H	Me	1.583	1.648
21′	MeO	H	H	H	*t*Bu	1.571	1.697
***trans*-22**	MeO	H	Me	H	Me	1.632	1.632
***cis*-22**	MeO	H	Me	Me	H	1.628	1.633
23	MeO	H	Me	Me	Me	1.591	1.759
24	MeO	Me	Me	Me	Me	1.674	1.674

Furthermore, the cyclopropane-localized charge increased somewhat (by 1 to 10%) on passing from an aprotic to a protic solvent, although the effect was smaller for tri-

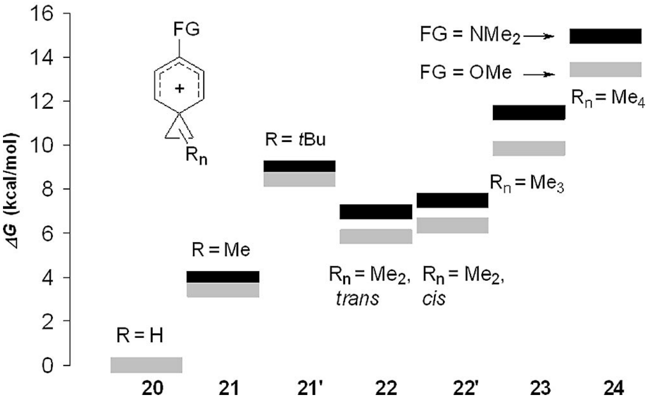
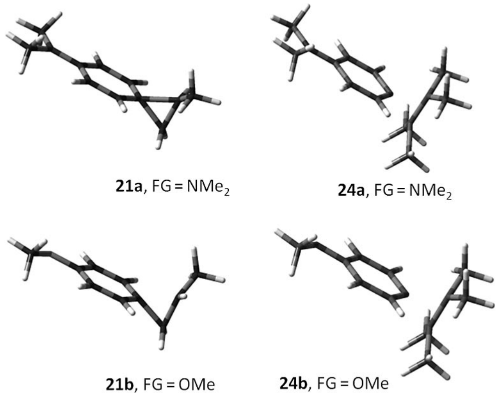


Figure 1. Calculated ΔG for the isodesmic reaction in Equation (1) for methoxy- (grey bars) and dimethylamino-substituted (black bars) cations. For the numbering, see Table 4.


21a, FG = NMe$_2$ **24a**, FG = NMe$_2$

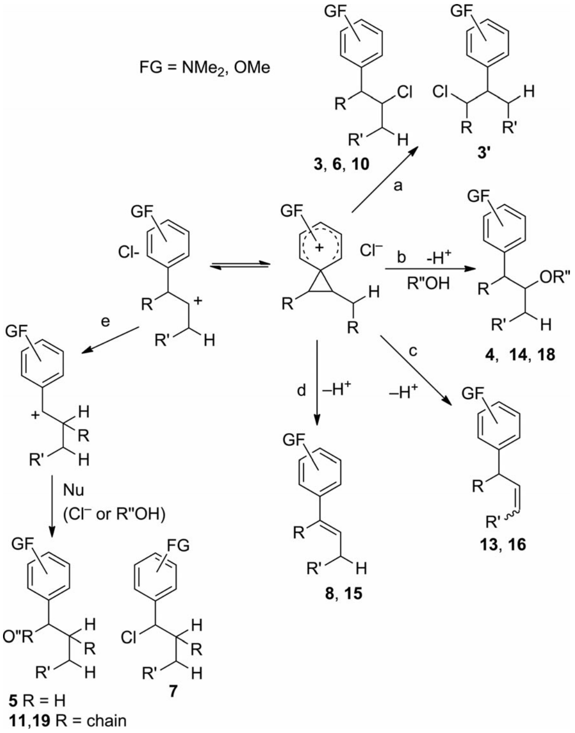
21b, FG = OMe **24b**, FG = OMe

Figure 2. Geometries of the cations **21** and **24**.

Table 5. Computed Mulliken charges of the cation adducts and paths followed in the photoarylation (lettering, see Scheme 2 and Table 4).

Cation-FG	Solvent	Fractional charge[a]			Reaction path[b]	
		Cα	Cβ	cyclopropane	main	minor
21-NMe$_2$	MeCN	0.115	0.118	0.248	a	
21-NMe$_2$	ROH[a,b]	0.122	0.12	0.259	a	
21′-NMe$_2$	MeCN	0.096	0.113	0.223	a	
22-NMe$_2$	MeCN	0.104	0.104	0.215	a	
22-NMe$_2$	ROH	0.111	0.111	0.227	a	
23-NMe$_2$	MeCN	0.117	0.078	0.197	c	
23-NMe$_2$	ROH	0.119	0.089	0.210	b	c
24-NMe$_2$	MeCN	0.095	0.095	0.185	c	
24-NMe$_2$	ROH	0.096	0.096	0.184	c	
21-OMe	MeCN	0.145	0.16	0.298	a	
21-OMe	ROH	0.155	0.164	0.312	e, a	b
21′-OMe	MeCN	0.13	0.155	0.265	a	e, d
21′-OMe	ROH	0.141	0.157	0.238	e	d
cis-**22**-OMe	MeCN	0.131	0.131	0.250	a	
cis-**22**-OMe	ROH	0.141	0.141	0.266	e	a
23-OMe	MeCN	0.135	0.092	0.217	c	d
23-OMe	ROH	0.137	0.106	0.231	b	c
24-OMe	MeCN	0.101	0.101	0.181	c	
24-OMe	ROH	0.104	0.104	0.187	c	e, b

[a] Calculated fractional charges in either acetonitrile or methanol. [b] Experimentally observed path in either acetonitrile or trifluoroethanol.



Scheme 2.

and tetramethyl derivatives. The addition of phenyl cations to alkenes (see Scheme 1, b) is a convenient approach to phenonium ions that are thus generated at room temperature in solution in the presence of weak nucleophiles such as the chloride anion or TFE. This is an important advantage because the limited choice of precursors and/or the harsh conditions required in the other methods of generation have previously hampered the rationalization of the chemistry that occurs and the comparison with computational data.[13,24,26]

The experimentally observed processes are presented in Scheme 2 and lead to a) phenethyl halides, b) phenethyl ethers, c) allylbenzenes, d) styrenes and e) benzyl halides or ethers as a result of a hydrogen or carbon shift. Correlations with the calculated properties of the ions were established, as discussed below (see Scheme 2 and Table 5).

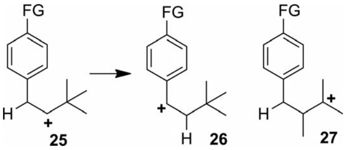
a) Formation of phenethyl chlorides: The reaction is characteristic of mono- and 1,2-disubstituted olefins. The intermediate cation can have both large (with FG = OMe) and small (with Me$_2$N) differences in length between the C1–Cα and C1–Cβ bonds. Characteristically, these species showed a large amount of charge on the cyclopropane ring (> 0.21), but a small difference between the charges at Cα and Cβ (< 0.025). Reasonably, a tight ion pair, Ar$^+$ Cl$^-$, was formed and addition across the alkene termini occurred almost simultaneously. The small charge difference between Cα and Cβ is reflected in the formation of both regioisomers in the reaction of chloroaniline with 1-hexene in MeCN, although in the more charge-stabilizing TFE the arylation was regioselective.

b) Formation of phenethyl ethers (solvent addition): This differed from the previous group by there being a larger difference between the charges at Cα and Cβ (> 0.03). This increased the "hard" character of the cation and facilitated attack by alcohols versus in-cage recombination with the chloride anion.

c) Deprotonation of the allylic position: This process occurred with cations with a small amount of charge at the cyclopropane ring (< 0.22). This is characteristic of tri- and tetrasubstituted olefins, in which steric reasons reduced donation to the phenyl cations and weakened the bonding. With these intermediates, weak nucleophiles such as the solvents used acted as bases.

d) Benzylic deprotonation: Some of the above intermediates also yielded a styrene as a byproduct. The requisites for such a minor path are not clear, but apparently this has something to do with steric reasons, because it is limited to the *tert*-butyl and trimethyl derivatives.

e) Rearrangement (observed in TFE): This reaction occurred with weakly bonded (Cα–Cβ > 1.63 Å) asymmetric cations (bond lengths differing by > 0.006 Å) bearing a large amount of charge at the cyclopropane moiety (> 0.23). As such, it was mainly observed with the 4-methoxy-substituted derivatives, not with the strongly donating 4-amino-substituted derivatives. Note that in this case, Wagner–Meerwein chemistry, well known under strongly acidic conditions,[27,28] occurred here in neutral media. Interestingly, in the case of the adduct with 3-methyl-1-butene (**25**), both hydride migration from the benzylic position (**26**) and an alkyl shift from the tertiary position (**27**) took place (and in MeCN the only case of rearrangement coupled with chloride addition was observed, see Scheme 3). This is clearly due to the high asymmetry of the intermediate involved.



Scheme 3.

In view of this satisfying correlation, a paradigm for the reactions via phenonium ions could be proposed. Although a detailed picture presumably requires consideration of more parameters, a rough classification is already apparent by using only two, as indicated in Figure 3, in which the total charge on the cyclopropane moiety is plotted versus the length of the bond to the most substituted carbon (C1–Cβ). In other terms, the strength of the stabilizing donation from the phenyl ring (clearly always stronger with the NMe_2 group) is compared with the asymmetry of the cyclopropane moiety. Moving towards the upper left corner involves an increase in "phenonium" character (symmetric cyclopropane, strong, short C1–Cα, C1–Cβ bonds, large amount of charge on the cyclopropane ring). A strong electron-donating substituent (NMe_2) and an unhindered olefin favour such structural characteristics (represented by points above the diagonal). The preferred path is a, arising from in-cage nucleophilic addition, as indeed expected from a strong charge on the cyclopropane moiety. At the left border of this region, when the cation is more asymmetric because an OMe is substituted for a NMe_2 group or a more charge-stabilizing solvent such as TFE is adopted, a cationic rearrangement (path e) participates. Below the diagonal, less-stabilized ions are present, that is, those that contain either a less-donating substituent (OMe) or a more substituted cyclopropane. Here, the six-membered ring contributes to a lesser extent so that the charge remains higher at Cα,β. Therefore the solvent acts as a base rather than as nucleophile (path c). At the upper limit of this region, and with less substituted cations, solvolysis (path b, but not chloride addition) is observed.

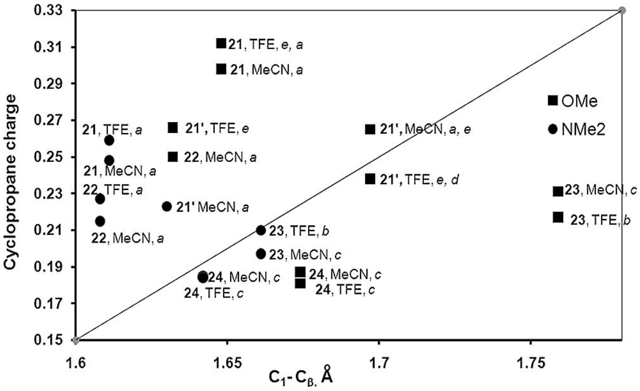


Figure 3. Correlation between the calculated charge at the cyclopropane moiety and the C1–Cβ bond length for phenonium ions. For numbering, see Table 4. At each point the main process occurring (paths a–e in Scheme 2) and the solvent in which the reaction was carried out are indicated.

Summing up, reagents that undergo process a exclusively are grouped close to the *y* axis and those undergoing process c are exclusively close to the *x* axis. Here, the process occurring is determined by the reagent structure, with little alternative. Points close to the diagonal on the other hand are more subject to cationic rearrangement (path e) and more sensitive to conditions, for example, the main path for intermediate **23a** is c in MeCN and b in TFE. These characteristics make the last group of cations better suited to attack by external nucleophiles, which is the most useful reaction from a synthetic point of view, and more easily directed.

Conclusions

The chemistry of phenonium ions has been revisited on the basis of a systematic comparison of the reaction pathways via this intermediate, generated in organic solvents under neutral conditions. This has allowed a rationalization of structure and medium effects. Nucleophilic addition, deprotonation and rearrangement compete in a way that is correlated with the calculated charge distribution and bond lengths in the ions. The diagram in Figure 3 offers a practical way to predict the preferred path(s) and support the recently growing interest for syntheses via phenonium ions. The study further evidences the versatility of photochemical reactions that often arrive at a highly reactive intermediate under mild conditions that can be varied at choice with minimal effect on the photochemical activation step and thus offers a way to direct the ensuing reactions of such an intermediate. In particular, these results rationalize the course of the second addition (phenonium + alkene) step in the three-component syntheses based on the scheme in Equation (2).

$$\text{Ph–X} + h\nu \rightarrow \text{phenyl cation} + \text{alkene} \rightarrow \text{phenonium} + \text{nucleophile} \rightarrow \text{three-component adduct} \quad (2)$$

Considering that the initial phenyl cation addition step had been previously rationalized, the present conclusions help the development of the synthetic applications of this sequence.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded with a 300 MHz spectrometer. The structural assignments were made on the basis of the ^{1}H and ^{13}C NMR spectra as well as by DEPT-135 experiments. Chemical shifts are reported in ppm downfield from TMS. 4-Chloroanisole (**1b**), anisole (**2b**) and all the olefins used were commercial samples and were freshly distilled before use. 4-Chloro-*N*,*N*-dimethylaniline (**1a**) and *N*,*N*-dimethylaniline (**2a**) were prepared from the corresponding anilines.[29] The presence of photoproducts **2a** and **2b** was determined by comparison with authentic samples and the amount determined from calibration curves.

General Procedure for the Photolysis of Chlorides 1a and 1b: A solution (30 mL) containing the chosen chloride (0.05 M) and olefin (0.5 M) in degassed acetonitrile or 2,2,2-trifluoroethanol (TFE) was irradiated in a multilamp reactor fitted with six 15 W phosphor-coated lamps until complete consumption of the aromatic substrate (except where indicated). In the case of the irradiation of **1b** in TFE, caesium carbonate (0.025 M) was added to the solution before irradiation to avoid acid-catalysed secondary processes. The photolysed solution was then evaporated and the resulting residue purified by column chromatography (eluent: cyclohexane/ethyl acetate). Irradiation of **1a** in acetonitrile in the presence of 1-hexene, cyclohexene and 2,3-dimethyl-2-butene have previously been reported by our research group.[22] In the latter case, a 1 M concentration of the chosen olefin was used and anhydrous potassium carbonate (K_2CO_3) was added in some cases to the irradiating solution. To have a set of comparable data we repeated the experiments under the above conditions.

Irradiation of 4-Chloro-*N*,*N*-dimethylaniline (1a) in the Presence of 1-Hexene in Acetonitrile: A solution containing **1a** (233 mg, 1.5 mmol, 0.05 M) and 1-hexene (1.90 mL, 15 mmol, 0.5 M) in acetonitrile (30 mL) was irradiated for 5 h. Column chromatography (eluent: cyclohexane/ethyl acetate, 99:1) gave 191 mg of a mixture of *N*,*N*-dimethyl-4-(2-chlorohexyl)aniline (**3a**; 126 mg 35% yield) and *N*,*N*-dimethyl-4-[1-(chloromethyl)pentyl]aniline (**3′a**; 65 mg, 18% yield). The spectroscopic data of the photoproducts are in agreement with the literature.[22]

In 2,2,2-Trifluoroethanol (TFE): A solution containing **1a** (233 mg, 1.5 mmol, 0.05 M) and 1-hexene (1.90 mL, 15 mmol, 0.5 M) in TFE (30 mL) was irradiated for 8 h (90% of **1a** consumed). Column chromatography (eluent: neat cyclohexane) afforded **3a**[22] (162 mg, 45% yield, based on the consumption of **1a**, oil).

3a: ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 0.90–1.00 [t, J(H,H) = 7 Hz, 3 H], 1.25–1.65 (m, 6 H), 2.90–3.00 (m, 2 H), 2.95 (s, 6 H), 4.10–4.15 (m, 1 H), 6.70–7.15 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6 (CH_3), 23.2 (CH_2), 30.5 (CH_2), 38.2 (CH_2), 41.0 (CH_3), 45.2 (CH_2), 66.1 (CH), 113.7 (CH), 127.0, 131.2 (CH), 150.9 ppm. IR (neat): $\tilde{\nu}$ = 2930, 1614, 1521, 1347, 1163, 807 cm^{-1}. $C_{14}H_{22}ClN$ (239.78): calcd. C 70.13, H 9.25, N 5.84; found C 68.8, H 9.3, N 5.7.

Irradiation of 4-Chloroanisole (1b) in the Presence of 1-Hexene: The photolysis of **1b** in both acetonitrile and TFE in the presence of 1-hexene has been described previously by our research group.[16]

Irradiation of 1a in the Presence of 3,3-Dimethyl-1-butene in Acetonitrile: A solution of **1a** (233 mg, 1.5 mmol, 0.05 M) and 3,3-dimethyl-1-butene (1.95 mL, 15 mmol, 0.5 M) in TFE (30 mL) was irradiated for 4 h. Purification by column chromatography (eluent: neat cyclohexane) afforded 144 mg of *N*,*N*-dimethyl-4-(2-chloro-3,3-dimethylbutyl)aniline (**6a**; 40% yield, oil). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (s, 9 H), 2.70–2.75 [dd, J(H,H) = 12 and 3.5 Hz, 1 H], 2.95 (s, 6 H), 3.85–3.90 [t, J(H,H) = 12 Hz, 1 H], 4.05–4.10 [dd, J(H,H) = 10 and 3.5 Hz, 1 H], 6.80–7.20 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.2 (CH_3), 34.6, 40.5 (CH_3), 45.9 (CH_2), 58.1 (CH), 111.8 (CH), 127.6, 129.7 (CH), 149.2 ppm. IR (neat): $\tilde{\nu}$ = 2949, 1609, 1519, 1347, 1164, 817 cm^{-1}. $C_{14}H_{22}ClN$ (239.78): calcd. C 70.13, H 9.25, N 5.84; found C 70.1, H 9.3, N 5.7.

In TFE: Compound **1a** (233 mg, 1.5 mmol, 0.05 M) and 3,3-dimethyl-1-butene (1.95 mL, 15 mmol, 0.5 M) in TFE (30 mL) were irradiated for 4 h. The photolysed solution was evaporated, but purification by column chromatography afforded a complex mixture of photoproducts that were not fully characterized.

Irradiation of 1b in the Presence of 3,3-Dimethyl-1-butene in Ethyl Acetate: Compound **1b** (200 µL, 1.5 mmol, 0.05 M) and 3,3-dimethyl-1-butene (1.95 mL) in ethyl acetate (30 mL) were irradiated for 24 h. The photolysed reaction was evaporated and the resulting residue purified by column chromatography to afford 139 mg of a mixture of 2-chloro-1-(4-methoxyphenyl)-3,3-dimethylbutane (**6b**; 85 mg, 25% yield), 1-chloro-1-(4-methoxyphenyl)-3,3-dimethylbutane (**7b**; 54 mg, 16% yield) and 54 mg of (*E*)-1-(4-methoxyphenyl)-3,3-dimethyl-1-butene (**8b**; 19% yield, oil).

6b: ^{1}H NMR (300 MHz, $CDCl_3$, from the mixture): δ = 1.15 (s, 9 H), 3.20–3.25 [dd, J(H,H) = 14 and 2 Hz, 2 H], 3.80 (s, 3 H) 3.80–3.90 (m, 1 H), 6.85–7.15 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, from the mixture): δ = 26.7 (CH_3), 36.1, 45.6 (CH_2), 55.1 (CH_3), 58.2 (CH), 113.6 (CH), 130.0 (CH), 131.4, 158.1 ppm. **7b**: ^{1}H NMR (300 MHz, $CDCl_3$, from the mixture): δ = 0.95 (s, 9 H), 2.70–2.80 (m, 2 H), 3.80 (s, 3 H), 4.05–4.15 [dd, J(H,H) = 13 and 3.5 Hz, 1 H], 6.80–7.15 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, from the mixture): δ = 28.2 (CH_3), 34.4, 38.7 (CH_2), 55.0 (CH_3), 75.9 (CH), 113.1 (CH), 130.0 (CH), 130.0 (CH), 131.8, 158.2 ppm. IR of the mixture (neat): $\tilde{\nu}$ = 2957, 1509, 1246, 1038 cm^{-1}. **8b**: ^{1}H NMR (300 MHz, $CDCl_3$):[30] δ = 1.00 (s, 9 H), 3.80 (s, 3 H), 5.55–5.60 [d, J(H,H) = 13 Hz, 1 H], 6.35–6.40 [d, J(H,H) = 13 Hz, 1 H], 6.80–7.15 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$):[30] δ = 31.1 (CH_3), 33.9, 55.1 (CH_3), 112.8 (CH), 126.6 (CH), 130.0 (CH), 131.5, 142.4 (CH), 157.9 ppm. IR (neat): $\tilde{\nu}$ = 2957, 1509, 1246, 1038 cm^{-1}. $C_{13}H_{18}O$ (190.28): calcd. C 82.06, H 9.53; found C 81.8, H 9.6.

In TFE: A solution of **1b** (200 µL, 1.5 mmol, 0.05 M), 3,3-dimethyl-1-butene (1.95 mL, 15 mmol, 0.5 M) and Cs_2CO_3 (222 mg, 0.75 mmol, 0.025 M) in TFE (30 mL) was irradiated for 12 h and then evaporated. Purification by column chromatography (eluent: neat cyclohexane) afforded 63 mg of **8b** (22% yield) and 239 mg of 1-chloro-1-(4-methoxyphenyl)-2,3-dimethyl-3-(2,2,2-trifluoroethoxy)butane (**9b**; 55% yield, oil).

9b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80–0.85 [d, J(H,H) = 7 Hz, 3 H], 1.25 (s, 6 H), 1.80–1.85 (m, 1 H), 2.05–2.15 (m, 1 H), 3.00–3.05 [dd, J(H,H) = 13 and 2 Hz, 1 H], 3.75–3.85 [q, J(H,F) = 12 Hz, 2 H], 3.80 (s, 3 H), 6.85–7.10 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 21.5 (CH_3), 22.7 (CH_3), 31.1, 36.6 (CH_2), 43.9 (CH), 55.1 (CH_3), 59.8 [q, J(C,C) = 75 Hz, CH_2], 79.1, 113.4 (CH), 126.0 [q, J(C,F) = 275 Hz, CF_3], 129.2 (CH), 133.6, 157.7 ppm. IR (neat): $\tilde{\nu}$ = 2968, 1614, 1521, 1136, 948, 817 cm^{-1}. $C_{15}H_{21}F_3O_2$ (290.32): calcd. C 62.06, H 7.29; found C 62.3, H 7.3.

Irradiation of 1a in the Presence of Cyclohexene in Acetonitrile: A solution containing **1a** (233 mg, 1.5 mmol, 0.05 M) and cyclohexene (1.50 mL, 15 mmol, 0.5 M) in acetonitrile was irradiated for 6 h. The photolysed solution was then evaporated and the resulting residue purified by column chromatography (eluent: cyclohexane/ethyl acetate, 95:5) to afford 197 mg of *trans*-1-chloro-2-[4-(dimethylamino)phenyl]cyclohexane (**10a**; 55%, oil). The spectroscopic data are in agreement with the literature.[22] $C_{14}H_{20}ClN$ (237.77): calcd. C 70.72, H 8.48, N 5.89; found C 70.4, H 8.6, N 5.7.

In TFE: A solution of **1a** (233 mg, 1.5 mmol, 0.05 M) and cyclohexene (1.50 mL, 15 mmol, 0.5 M) in TFE (30 mL) was irradiated for 6 h. Purification by column chromatography (eluent: neat cyclohexane) led to 210 mg of **10a** (59% yield).

Irradiation of 1b in the Presence of Cyclohexene: The photolysis of **1b** in both acetonitrile and TFE has been described previously by our group.[18]

Irradiation of 1a in the Presence of 2-Methyl-2-butene in Acetonitrile: A solution of **1a** (233 mg, 1.5 mmol, 0.05 M) and 2-methyl-2-butene (1.60 mL, 15 mmol, 0.5 M) in TFE (30 mL) was irradiated for 4 h. The photolysed solution was evaporated and the resulting residue purified by column chromatography (eluent: neat cyclohexane) to afford 180 mg of a mixture of **2a** (27 mg, 15% yield) and 4-(1,2-dimethyl-2-propenyl)-*N*,*N*-dimethylaniline (**13a**; 153 mg, 54% yield).

13a: ^{1}H NMR (300 MHz, $CDCl_3$, from the mixture): δ = 1.40–1.45 [d, J(H,H) = 7 Hz, 3 H], 1.70 (s, 3 H), 3.00 (s, 6 H), 3.35–3.45 [q, J(H,H) = 7 Hz, 1 H], 4.85–4.95 [d, J(H,H) = 14 Hz, 2 H], 6.75–7.30 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7 (CH_3), 20.2 (CH_3), 40.7 (CH_3), 45.5 (CH), 109.1 (CH_2), 112.6, 112.7 (CH), 127.9 (CH), 130.0, 149.9 ppm. IR of the mixture (neat): $\tilde{\nu}$ = 2929, 1616, 1552, 1281, 1161, 970, 819 cm^{-1}.

In TFE: A solution of **1a** (233 mg, 1.5 mmol, 0.05 M) and 2-methyl-2-butene (1.60 mL, 15 mmol, 0.5 M) in TFE (30 mL) was irradiated for 6 h and then evaporated. Purification by column chromatography (eluent: neat cyclohexane) afforded 187 mg of 3-[4-(dimethylamino)phenyl]-2-methyl-3-(2,2,2-trifluoroethoxy)butane (**14a**; 43% yield, oil). GC analysis also showed the presence in the photolysed solution of a small amount of **13a** (14 mg, 5% yield based on GC calibration curve).

14a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 6 H), 1.45–1.50 [d, J(H,H) = 7 Hz, 3 H], 2.75–2.85 [q, J(H,H) = 7 Hz, 1 H], 2.95 (s, 6 H), 3.70–3.85 [q, J(H,F) = 8 Hz, 2 H], 6.75–7.20 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3 (CH_3), 21.9 (CH_3), 23.6 (CH_3), 40.6 (CH_3), 47.7 (CH), 60.0 [q, J(C,C) = 34 Hz, CH_2], 79.0, 112.0 (CH), 125.0 [q, J(C,F) = 262 Hz, CF_3], 129.6 (CH), 131.2, 149.1 ppm. IR (neat): $\tilde{\nu}$ = 2929, 1616, 1552, 1281, 1161, 970, 819 cm^{-1}. $C_{15}H_{22}F_3NO$ (289.34): calcd. C 62.27, H 7.66, N 4.84; found C 62.4, H 7.7, N 4.9.

Irradiation of 1b in the Presence of 2-Methyl-2-butene in Acetonitrile: A solution of **1b** (200 µL, 1.5 mmol, 0.05 M) and 2-methyl-2-butene (1.60 mL, 15 mmol, 0.5 M) in acetonitrile (30 mL) was irradiated for 14 h. The photolysed solution was evaporated and the resulting residue purified by column chromatography (eluent: neat cyclohexane) to afford 177 mg of a mixture of 4-(1,2-dimethyl-2-propenyl)anisole (**13b**; 145 mg, 55% yield, oil) and 4-(1,2-dimethyl-1-propenyl)anisole (**15b**; 32 mg, 12% yield, oil).

13b: ^{1}H NMR[31] (300 MHz, $CDCl_3$, from the mixture): δ = 1.30–1.35 [d, J(H,H) = 7 Hz, 3 H], 1.60 (s, 6 H), 3.35–3.40 [q, J(H,H) = 7 Hz, 1 H], 3.80 (s, 3 H), 4.85–4.95 [dd, J(H,H) = 13 and 2 Hz, 2 H], 6.85–7.15 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, from the mixture): δ = 20.0 (CH_3), 45.6 (CH_3), 55.1 (CH_3), 109.5 (CH_2), 113.5 (CH), 128.1 (CH), 137.1, 149.4, 157.8 ppm. IR of the mixture (neat): $\tilde{\nu}$ = 2966, 1511, 1246, 1177, 1035, 833 cm^{-1}.

15b: ^{1}H NMR[32] (300 MHz, $CDCl_3$, from the mixture): δ = 1.60 (s, 3 H), 1.80 (s, 3 H), 1.95 (s, 3 H), 3.80 (s, 3 H), 6.85–7.10 (AA′BB′, 4 H) ppm. ^{13}C NMR[33] (75 MHz, $CDCl_3$, from the mixture): δ = 20.5 (CH_3), 21.1 (CH_3), 22.0 (CH_3), 55.1 (CH_3), 113.1 (CH), 113.2, 128.3, 129.3 (CH), 137.7, 157.4 ppm.

In TFE: A solution of **1b** (200 µL, 1.5 mmol, 0.05 M) and 2-methyl-2-butene (1.60 mL, 15 mmol, 0.5 M) in TFE (30 mL) was irradiated for 14 h and then evaporated. Purification by column chromatography afforded 253 mg of a mixture of **15b** (48 mg, 18% yield) and 2-(4-methoxyphenyl)-3-methyl-3-(2,2,2-trifluoroethoxy)butane (**14b**; 205 mg, 50% yield). A small amount of **14b** was obtained by further purification of the mixture by column chromatography (eluent: neat cyclohexane).

14b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 3 H), 1.15 (s, 3 H), 1.30–1.35 [d, J(H,H) = 7 Hz, 3 H], 2.80–2.85 [q, J(H,H) = 7 Hz, 1 H], 3.70–3.80 [q, J(H,F) = 8.5 Hz, 2 H], 3.85 (s, 3 H), 6.80–7.20 (AA′BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (CH_3), 22.2 (CH_3), 23.4 (CH_3), 48.2 (CH), 55.1 (CH_3), 59.6–60.9 [q, J(C,C) = 34 Hz, CH_2], 78.7, 113.0 (CH), 122.5–129.3 [q, J(C,F) = 276 Hz, CF_3], 129.9 (CH), 135.4, 158.0 ppm. IR (neat): $\tilde{\nu}$ = 2973, 1611, 1513, 1281, 1160, 1036, 970, 832 cm^{-1}. $C_{14}H_{19}F_3O_2$ (276.29): calcd. C 60.86, H 6.93; found C 60.6, H 6.9.

Irradiation of 1a in the Presence of 2,3-Dimethyl-2-butene in Acetonitrile: A solution containing 233 mg of **1a** (233 mg, 1.5 mmol, 0.05 M) and 2,3-dimethyl-2-butene (1.80 mL, 15 mmol, 0.5 M) in acetonitrile (30 mL) was irradiated for 4 h and then evaporated. Purification by column chromatography (eluent: neat cyclohexane) afforded 195 mg of *N*,*N*-dimethyl-4-(1,1,2-trimethyl-2-propenyl)aniline (**16a**; 64% yield, oil). The spectroscopic data are in agreement with the literature.[22] $C_{14}H_{21}N$ (203.32): calcd. C 82.70, H 10.41, N 6.89; found C 82.5, H 10.3, N 6.7.

In TFE: A solution containing 233 mg of **1a** (1.5 mmol, 0.05 M) and 2,3-dimethyl-2-butene (1.80 mL, 15 mmol, 0.5 M) in TFE (30 mL) was irradiated for 6 h. The photolysed solution was evaporated and the resulting residue purified by column chromatography (eluent: neat cyclohexane) to afford 183 mg of **16a** (60% yield, oil).

Irradiation of 1b in the Presence of 2,3-Dimethyl-2-butene: The photolysis of **1b** in the presence of 2,3-dimethyl-2-butene in both acetonitrile and TFE has been described previously by our research group.[18]

DFT Calculations: Optimizations were carried out at the UB3LYP/6-31G(d) level of theory by using the Gaussian 03 package.[34] Frequency calculations were evaluated at the same level of theory and in this way the structures reported were certified as minima. The energies and charges of the solvated cation were evaluated by the CPCM method[35] using the (in vacuo) optimized geometries with acetonitrile as solvent and methanol as a model for trifluoroethanol. The solvent cavity was calculated by applying the united atom topological model to the radii optimized at the HF/6-31G(d) level of theory. The calculated energies and atomic coordinates are reported in the Supporting Information.

Supporting Information (see footnote on the first page of this article)**:** Computational data for phenonium intermediates **20**–**24** and ^{1}H and ^{13}C NMR spectra of compounds **3**–**19**.

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