JOC The Journal of Organic Chemistry
Article
pubs.acs.org/joc

Probing for a Leaving Group Effect on the Generation and Reactivity of Phenyl Cations

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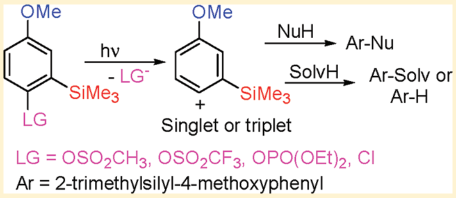
S *Supporting Information*

ABSTRACT: Phenyl cations are smoothly generated by the *photo*heterolytic cleavage of an Ar−LG bond (LG = leaving group). With the aim of evaluating the scope of the method, a series of 4-methoxy-2-(trimethylsilyl)phenyl derivatives (sulfonic, LG = $MeSO_3$ and CF_3SO_3, phosphate, LG = $(EtO)_2(O)PO$ esters and the corresponding chloride) have been compared as probes for evaluating the leaving group ability. The photocleavage was a general reaction, with the somewhat surprising order $(EtO)_2(O)PO \sim Cl > CF_3SO_3 > MeSO_3$ ($\Phi = 0.50$ to 0.16 in CF_3CH_2OH and lower values in $MeCN-H_2O$). The ensuing reactions did not depend on the LGs but only on the structure of the phenyl cation (the silyl group tuned the triplet to singlet intersystem crossing and the electrophilicity) and on the medium (formation of a complex with water slowed the electrophilic reactions).



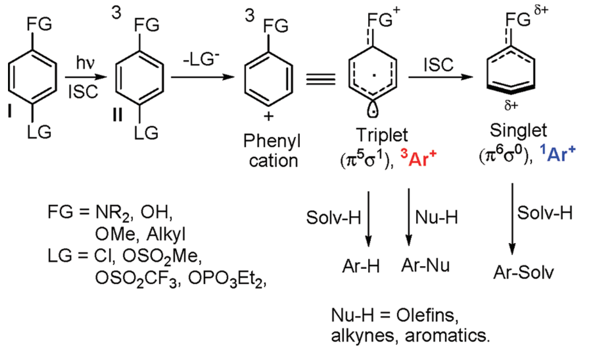
INTRODUCTION

Modern arylation methods are generally based on a metal-mediated activation of an Ar−X bond,[1] most often in aryl iodides, bromides, and sulfonates.[1,2] Esters (sulfonates, phosphates) are convenient intermediates for the conversion of the phenol function into different groups. Actually, the reactivity of aryl triflates toward the oxidative insertion of transition metal complexes rivals that of the widely used halides. Triflates, however, are both base-sensitive and thermally labile, and alternative sulfonate leaving groups such as mesylates, nonaflates,[3] and tosylates[4] have been recently adopted. In particular, mesylates are significantly less expensive and a better choice from the point of view of atom economy. Both Ni-catalyzed[5] and, though less frequently, Pd-catalyzed[6] cross-coupling reactions have been reported. In contrast, the rarely employed aryl phosphates react sluggishly under metal catalysis[7] only with aggressive nucleophiles, such as Grignard or organoaluminum reagents, besides the recently reported reaction with boranes under Suzuki−Miyaura conditions.[8]

Skrydstrup and co-workers proposed a reactivity scale for the Heck reaction, where aryl triflates lay between aryl iodides and bromides, while aryl phosphates lay far below aryl chlorides ($I > OTf \geq Br > Cl > OP(O)(OPh)_2$).[9] In the same way, the leaving ability of sulfonates was found to be OTf > benzenesulfonate > OTs > OMs, with mesylates as the least active leaving group (LG),[10] a result that could be roughly related to the pK_a value of the conjugate acid HX.

In past years, an alternative activation of Ar−Cl and Ar−O bonds has been devised by photochemical means and involves the photoheterolytic cleavage of such bonds.[11] Thus, the irradiation in polar solvents of aryl chlorides, sulfonates (triflates and mesylates), and diethyl phosphates substituted with strong (e.g., NMe_2, OMe,[12] OH[13]) or mild (e.g., *t*-Bu[14] or *n*-alkyl[15]) electron-donating groups caused the heterolytic cleavage of the Ar−LG bond and ultimately gave a triplet phenyl cation. Phenyl cations[11,16] are highly electrophilic species[17,18] that exist in two spin configurations, viz. the singlet ($^1Ar^+$ having a $\pi^6\sigma^0$ structure)[17] or the triplet ($^3Ar^+$ having a $\pi^5\sigma^1$ structure). These two intermediates show a different chemistry, namely, solvolysis for the singlets and addition onto π bond nucleophiles (Nu-H) or homolytic hydrogen abstraction from the solvent for the triplets (Scheme 1).[18]

Scheme 1. Photogeneration and Reactivity of Phenyl Cations



The relative stability of the two spin states depends on the ring substituents FG, with the singlet, in most cases, being the most stable species.[17,18] The multiplicity of the initially photogenerated phenyl cation Ar^+ is that of the excited state (**II**) where the cleavage of the Ar−LG bond takes place. With electron-rich halides and esters, phenyl cations are generated in the triplet state, and chemoselective arylations have been developed.[11] Indeed, phenyl cations have been efficiently generated by detachment of a wide variety of LGs with a marked difference in nucleofugal ability.

Received: February 9, 2012
Published: March 8, 2012

dx.doi.org/10.1021/jo300290v | *J. Org. Chem.* 2012, 77, 3501−3507

It would be useful to establish how the leaving group affects both the efficiency in phenyl cation generation and the ensuing chemoselectivity of this intermediate and whether the nucleofugal ability of the LGs is related to the pK_a of the conjugate acid liberated, as in thermal reactions. Sparse data support such a relationship also upon irradiation in the case of 7-methoxycoumarin-4-yl-methyl carboxylate, sulfonate, and phosphate esters.[19] Moreover, in the related photogeneration of vinyl cations, it has been reported that leaving group abilities, at least in the halogen series, were related to the acidity of the conjugate acids HX,[20] and in the photogeneration of a naphthylmethyl cation, the photofugacity order for the ionic process showed a preference for the chloride anion with respect to the diethyl phosphate anion.[21]

We reported, however, that the efficiency in the photogeneration of the 4-methoxyphenyl cation depends both on the nature of LG and on the reaction medium used and did not necessarily follow the acidity of the HX. In fact, in 2,2,2-trifluoroethanol (TFE), the Φ_{-1} value was lower for 4-chloroanisole (0.07[22]) than for the corresponding 4-methoxyphenyl diethyl phosphate (0.28[23]), and in a nonprotic solvent such as MeCN, both Φ_{-1} markedly decreased.[22,23] Moreover, sulfonate and phosphate esters of *p*-methoxyphenol were found to be particularly suitable for arylation reactions and exhibited a Φ_{-1} comparable to that of 4-chloroanisole[24] (see below). This may be related to the formation of either an ion couple (Ar^+X^-) or a free Ar^+ cation, a fact that may also affect the course of the ensuing arylation reactions.

Some years ago, we demonstrated that both the efficiency of the Ar−Cl cleavage and the chemoselectivity of the photogenerated phenyl cation can be tuned by inserting one (or two) trimethylsilyl group(s) (TMS) in *ortho*-position with respect to the leaving group LG.[25a] This appeared to be a case of a β-silyl stabilization and made intersystem crossing (ISC) from the triplet to the more stable singlet $^1Ar^+$ viable (Scheme 1).[11a,25]

We now reasoned that such silylated methoxyphenyl cations could be used as probes to give insight on the role of the leaving group in the photogeneration of phenyl cations. In fact, ISC to the singlet competes with the typical reactions of $^3Ar^+$, viz. arylation and reduction, and the product distribution obtained from the aryl cation precursors having different leaving groups could be informative. Toward this aim, the photoreactivity of sulfonate and phosphate esters of 3-methoxy-2-trimethysilylphenol **1a**−**c** and of aryl chloride **1d** has been investigated and the results are illustrated below. The compounds were chosen in order to ensure a marked difference on the pK_a of the conjugate acid liberated (ca. 15 pK_a units from the triflic acid to the diethyl phosphoric acid; see below).

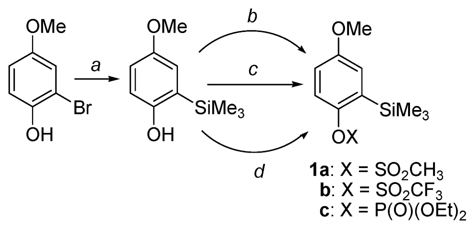
■ RESULTS

Silylated esters **1a**−**c** were easily prepared in a few steps starting from 2-bromo-4-methoxyphenol, as illustrated in Chart 1. For the sake of comparison, the experiments were compared to those with 4-chloro-3-trimethylsilylanisole **1d**.

Photophysical Data of Compounds 1a−d. Esters **1a**−**c** exhibited a weak to moderate fluorescence, with triflate **1b** being less emitting ($\Phi_F < 0.05$) than chloride **1d** and phosphate **1c** much more ($\Phi_F \sim 0.2$), which is rather independent from the alcohol used as the solvent (Table 1).

Preparative Irradiation. Protic solvents (TFE and water/acetonitrile 1:5) were chosen for the irradiation (λ_{irr} centered at 310 nm) of silyl esters **1a**−**c** (0.05 M), as these had be shown to be convenient with the silicon-free analogues.[12]

Chart 1. Preparation of Silylated Methoxyphenyl Esters 1a−c[a]



[a]Reagents and conditions: (a) BuLi, Me_3SiCl, −78 → 25 °C, then H^+, 76%; (b) CH_3SO_2Cl, Et_3N, DCM, 72%; (c) Tf_2O, Py, 0 → 50 °C, 88%; (d) NaH, $(EtO)_2POCl$, THF, 54%.

Table 1. Fluorescence Quantum Yield (Φ_F) and τ_F of Methoxyphenyl Derivatives 1a−d

	CF_3CH_2OH		CH_3OH[a]		
Ar-$SiMe_3$	$\Phi_F \times 10^2$	λ_{max} (nm)	$\Phi_F \times 10^2$	λ_{max} (nm)	τ_F (ns)
1a	3.8	310	4.6 (5.2)	310 (305)	0.28[b]
1b	0.29	313	0.32 (<0.1)	*b*	*b*
1c	19	307	18 (4.2)	312 (311)	0.92 (0.94)
1d	0.7	310	1.3 (1.9)[c]	311	<0.2 (1.6)[c]

[a]In parentheses are the data of the silicon-free analogues. [b]Too weak to be measured. [c]See ref 23.

The irradiations (up to >80% conversion) were carried out both in neat solvents and in the presence of π bond nucleophiles, viz. either an aromatic compound (benzene) or an alkene (allyltrimethylsilane, ATMS; see Table 2, Schemes 2 and 3). This was done under acetone (0.9 M) sensitization in order to prevent any undesirable homolytic cleavage of the O−S bond known to occur from the singlet state[14] and to ensure an optimized absorption at the wavelength used. An equivalent amount of a base (e.g., Cs_2CO_3) was added in the experiments in TFE in order to buffer the acidity liberated in the reaction[14] (no base required in water−acetonitrile). Irradiations at shorter times (not reported) were also carried out in order to check for the occurrence of secondary processes, but the product distribution was found to change little with the progress of the reaction.

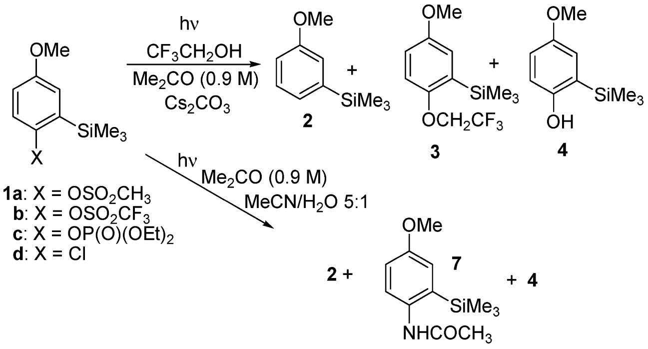
Photochemistry. Irradiation (7−16 h) of a 0.05 M solution of 4-methoxy-2-trimethylsilylphenyl methanesulfonate (**1a**, entries 1−6) in each of the solvents investigated caused extensive conversion (88−100%; see Table 2). In TFE in the presence of Cs_2CO_3, three products were formed, viz. anisole **2** (24%), the trifluoroethyl ether **3** (56%), along with a small amount of methoxy phenol **4** (5%; see Scheme 2). In the presence of benzene (1 M), photosubstitution remained the main path but some biphenyl **5** (19%) was obtained at the expense of both **2** and **3** (Scheme 3). With allyltrimethylsilane (ATMS, 0.5 M), photoallylation to give **6** was efficient (67% yield) though again accompanied by the formation of **2** and **3**. When the solvent was changed to a water−acetonitrile (1:5) mixture, acetanilide **7** (72% yield) became the main product (along with **2** and **4**). The product distribution was marginally affected by 1 M benzene, although traces of **5** have been detected (Scheme 3). The allylation was again efficient with ATMS, even if the yield of allylated **6** was lower than that obtained in TFE. In the last case, however, an excellent mass balance (98%) was reached.

Table 2. Photolysis of 1a−d (0.05 M) in the Presence of Various π Bond Nucleophiles[a]

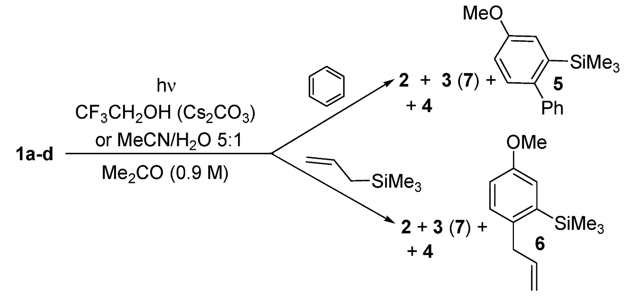
					products (yield %)[b]			
entry	Ar-$SiMe_3$	solvent	nucleophile	t_{irr}, h (conversion, %)	R_D	S_L	A_R	D_P
1	**1a**	TFE[c]	none	12 (100)	**2** (24)	**3** (56)		**4** (5)
2	**1a**	TFE[c]	C_6H_6 1 M	7 (100)	**2** (19)	**3** (42)	**5** (19)	
3	**1a**	TFE[c]	ATMS 0.5 M	7 (95)	**2** (3)	**3** (20)	**6** (67)	
4	**1a**	H_2O/MeCN 1:5	none	16 (92)	**2** (6)	**7** (72)		**4** (13)
5	**1a**	H_2O/MeCN 1:5	C_6H_6 1 M	16 (96)	**2** (4)	**7** (54)	**5** (2)	**4** (16)
6	**1a**	H_2O/MeCN 1:5	ATMS 0.5 M	12 (88)	**2** (4)	**7** (22)	**6** (50)	**4** (22)
7	**1b**	TFE[c]	none	7 (91)	**2** (22)	**3** (44)		
8	**1b**	TFE[c]	C_6H_6 1 M	12 (94)	**2** (4)	**3** (42)	**5** (21)	
9	**1b**	TFE[c]	ATMS 0.5 M	12 (88)	**2** (6)	**3** (26)	**6** (50)	
10	**1b**	H_2O/MeCN 1:5	none	24 (85)	**2** (19)	**7** (47)		
11	**1b**	H_2O/MeCN 1:5	C_6H_6 1 M	24 (91)	**2** (15)	**7** (22)	**5** (3)	
12	**1b**	H_2O/MeCN 1:5	ATMS 0.5 M	24 (92)	**2** (17)	**7** (38)	**6** (8)	
13	**1c**	TFE[c]	none	7 (95)	**2** (8)	**3** (63)		
14	**1c**	TFE[c]	C_6H_6 1 M	7 (93)	**2** (6)	**3** (47)	**5** (27)	
15	**1c**	TFE[c]	ATMS 0.5 M	12 (86)	**2** (3)	**3** (31)	**6** (60)	
16	**1c**	H_2O/MeCN 1:5	none	24 (80)	**2** (9)	**7** (40)		
17	**1c**	H_2O/MeCN 1:5	C_6H_6 1 M	24 (85)	**2** (10)	**7** (56)	**5** (2)	
18	**1c**	H_2O/MeCN 1:5	ATMS 0.5 M	24 (82)	**2** (6)	**7** (52)	**6** (2)	
19	**1d**	TFE[c]	none	6 (100)	**2** (21)	**3** (58)		
20	**1d**	TFE[c]	C_6H_6 1 M	6 (100)	**2** (11)	**3** (46)	**5** (17)	
21	**1d**	TFE[c]	ATMS 0.5 M	6 (100)	**2** (15)	**3** (43)	**6** (18)	
22	**1d**	H_2O/MeCN 1:5	none	25 (92)	**2** (23)	**7** (73)		
23	**1d**	H_2O/MeCN 1:5	C_6H_6 1 M	25 (91)	**2** (16)	**7** (79)	**5** (tr)	
24	**1d**	H_2O/MeCN 1:5	ATMS 0.5 M	25 (87)	**2** (22)	**7** (36)	**6** (31)	

[a] Reaction sensitized by acetone (0.9 M). [b] Yields were based on consumed aryl silane and determined by GC. According to the discussion section, the observed pathways have been classified as follows: R_D = Reduction, S_L = Solvolysis, A_R = Arylation, D_P = Deprotection [c] Cesium carbonate (0.025 M) added.

Scheme 2. Product Distribution in the Irradiation of Aromatics 1a−d in Neat Solvents



Scheme 3. Product Distribution in the Irradiation of Aromatics 1a−d in the Presence of π Bond Nucleophiles



4-Methoxy-2-trimethylsilylphenyl trifluoromethanesulfonate (**1b**, 0.05 M, entries 7−12) was almost completely consumed after 7 h irradiation in neat TFE, showing a product distribution quite similar to **1a**. Thus, silylated anisole **2** (22%) and trifluoroethyl ether **3** (44%) were exclusively formed (Table 2). Differently from **1a**, no photodeprotection was observed in all of the photolysis experiments of triflate **1b**. Arylation products have been likewise formed in variable amounts when either benzene or ATMS were added to the reaction mixture (21 and 50% yields, respectively) though solvolysis remained the main process. When using aqueous acetonitrile as the solvent, the Ar−C bond formation was significantly diminished (**5** and **6** formed in less than 10% amount) and compound **7** was again by far the main product. Notice that no desilylation took place in all of the experiments performed.

Photolysis of 4-methoxy-2-trimethylsilylphenyl diethyl phosphate (**1c**, entries 13−18) in TFE (Table 2) caused an efficient consumption of the substrate (<12 h irradiation time), and photosubstitution and photoreduction were the preferred processes. The mass balance (>80%) was high in the experiments in the presence of the nucleophiles, where the yield of biphenyl **5** (27%) was much lower than that of allylated **6** (60%). The arylation strongly decreased in MeCN/water mixture, where formation of solvolytic amide **7** was favored.

4-Chloro-3-trimethylsilylanisole (**1d**, entries 19−24) was completely consumed after 6 h irradiation in TFE and almost completely (>85%) in 25 h in aqueous acetonitrile (Table 2). In neat solvents, photosubstitution was by far the main process observed. Arylation yields were modest, particularly when using benzene as the nucleophile, and contrary to the previous cases, the yield of allylated **6** was larger in MeCN/water mixture (31%) than in TFE (18%). Photosubstitution products were consistently the main compounds in each experiment, and reduction was also present in a 10−20% yield.

Quantum Yield Measurements. The decomposition quantum yield (Φ_{-1}) of esters **1a**−**c** (5×10^{-3} M) was measured by irradiation in TFE and H_2O/MeCN (1:5) at 254 nm. The results are shown in Table 3 in comparison with silicon-free analogues and with **1d**. The Φ_{-1} values ranged from 0.16 to 0.5 in TFE but did not exceed 0.24 in 1:5 H_2O/MeCN. The values in aqueous acetonitrile were consistently lower than those in TFE. The order of photoreactivity in TFE is **1c** > **1b** > **1a**, which is the same as that observed with silicon-free aryl esters. The introduction of a silyl group made the photoheterolysis of the Ar−O bond more efficient and strongly enhanced (up to a factor of 4 with **1b**) the values of Φ_{-1}. The aqueous medium levels the photoreactivity of **1a** and **1b**.

Table 3. Quantum Yield of Photodecomposition (Φ_{-1}) of Phenyl Trimethylsilyl Esters 1a−c and Chloride 1d in Protic Media Measured at 254 nm

	quantum yields (Φ_{-1})[a]	
Ar-$SiMe_3$	CF_3CH_2OH	H_2O/MeCN (1:5)
1a	0.16 (0.055)	0.11
1b	0.3 (0.07)	0.11
1c	0.50 (0.28)[c]	0.24
1d	0.43[b] (0.07)[d]	0.068[b] (0.01)[d]

[a] In parentheses is the quantum yield of the silicon-free analogue. [b] From ref 25a. [c] From ref 23. [d] From ref 22.

To summarize, the effect caused by introducing an ester group in the place of a chloro atom is not uniform since this made the aromatic more reactive in 1:5 H_2O/MeCN, whereas in TFE, only phosphate **1c** has a Φ_{-1} comparable with **1d**. The Φ_{-1} values have been likewise measured in TFE at 310 nm under acetone-sensitized conditions (not shown), and comparable values to that measured at 254 nm were observed except for the case of **1c** where Φ_{-1} was halved.

■ DISCUSSION

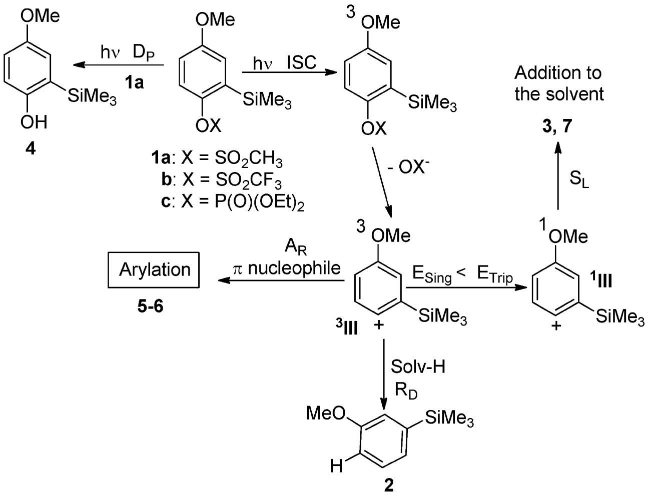
As previously demonstrated for the case of compound **1d**,[25] the introduction of a trimethylsilyl group onto an aromatic (whether chloroanisole or a sulfonate or phosphate ester of 4-methoxyphenol) did not significantly affect either the fluorescence efficiency or the singlet lifetime (see Table 1). Thus, one can assume that ISC in silylated compounds **1a**−**c** is comparable to that of the parent phenyl esters ($\Phi_{ISC} \geq 0.7$)[12] and the Ar−O bond cleavage in esters **1a**−**c** has to arise from the triplet state. The formation of triplet phenyl cations from these esters was feasible as it was for the desilylated analogues.[12] Photoheterolysis of the Ar−O bond took place as the exclusive path, except for the case of mesylate **1a**, where a partial deprotection, probably arising from the singlet, induced the cleavage of the ArO−S bond.[14] Notice further that no Photo-Fries products from the sulfonyl radical liberated in the process have been detected. In analogy with **1d**, the photodecomposition quantum yield (Φ_{-1}) in TFE was consistently higher for trimethylsilyl-substituted esters **1a**−**c** in comparison with the silicon-free analogues, confirming that the presence of a R_3Si group favors the photocleavage of substituted anisoles (Table 3).

If the photolability of the Ar−X bond follows the order of the HX pK_a values, the reactivity order would be Tf (pK_a = −14.9)[10] > Cl (pK_a = −7) > Ms (pK_a = −1.9)[10] > phosphate (pK_a = 0.71).[26] Table 3 shows that this is not the case and that the order depends on the reaction medium. The phosphate is the most efficient leaving group in the series, and noteworthy, there is no competing cleavage of the ArO−P bond. The reactivity order is little affected in passing from silicon-free (phosphate > Cl = Tf > Ms) to silicon-containing anisole derivatives (phosphate ∼ Cl > Tf > Ms). The effectiveness of the LGs level in mixed aqueous medium, where at any rate the phosphate group is again the best one and the sulfonic esters perform better than the chloride (phosphate > Ms = Tf ∼ Cl). The mesylate group appeared to be the LG less affected by the solvent since the Φ_{-1} value of **1a** is the same in the two protic media considered.

As a matter of fact, TFE was confirmed as the elective solvent for the phenyl cation generation and thus the best medium for carrying out arylation reactions. The processes occurring were reduction (R_D, to give the dechlorinated analogue **2**), substitution (S_L, yielding **3** or **7**), and photodeprotection of the ester group (D_P; see compound **4**). Arylation (A_R) took place in the presence of π nucleophiles, leading to functionalized benzenes **5** and **6** (Scheme 3 and Table 2). Under the present conditions (irradiation in protic solvents under acetone sensitization), no secondary desilylation took place as previously observed in related compounds.[25a]

The product distribution observed is consistent with a triplet phenyl cation intermediate (^{3}**III**; see Scheme 4). Hydrogen abstraction from the solvent (to afford **2**) or addition onto π nucleophiles is a diagnostic reaction of these species. Computational investigations have previously demonstrated that, because of the β-stabilizing effect of the $SiMe_3$ group in these cations, the singlet (^{1}**III**) lies lower in energy and it is accessible via ISC.[25] This unselective intermediate undergoes photosolvolysis reactions and adds to the reaction medium (Scheme 4).

Scheme 4. Photochemistry of Arylsilanes 1a−c



The addition of the triplet cations onto π nucleophiles is slowed by the silyl group both by electronic (β-stabilization)[25] and steric effects. This made the addition more selective, with consistently better results with ATMS than with benzene, in agreement with the nucleophilicity order.[27] Indeed, the arylation of benzene was always dwarfed by solvolysis. Notice further that the arylation of ATMS was more efficient with silylated esters than with the corresponding chloride, exactly as observed for the nonsilylated compounds.[12,28] At any rate, complexation of phenyl cations by a nucleophilic solvent such as water[18] suppressed arylation reactions (Table 2) in all but a couple of cases (including the allylation of **1d**).

Finally, we attempted to recognize whether the leaving anion affected the chemistry of the photogenerated phenyl cations. To this aim, we compared the product selectivity with different LGs, as shown in Table 4. Perhaps surprisingly, no marked difference appeared from these comparisons, and in neat solvents, the reduction/substitution ratio did not change significantly for Ar−Cl and Ar−O cleavage, despite the fact that the quantum yields changed by a factor >5. Likewise, the arylation proportion in the presence of π traps depended little on the LG. Thus, the chemistry observed depended on the nature of the phenyl cation involved rather than from the structure of the aromatic used as precursor, or in other words, the reaction is satisfactorily described as a S_N1 process.

Table 4. Comparison of the Product Distribution between 1d and Esters 1a−c upon Irradiation in Protic Media

	reduction/ substitution		arylation/reduction + substitution			
$Ar\text{-}SiMe_3$	TFE (neat)	H_2O/ MeCN 1:5 (neat)	TFE C_6H_6 1 M	TFE ATMS 0.5 M	H_2O/ MeCN 1:5; C_6H_6 1 M	H_2O/ MeCN 1:5; ATMS 0.5 M
1d	27:73	24:76	23:77	24:76	0:100	35:65
1a	30:70	24:76	31:69	74:26	3:97	2:98
1b	33:67	29:71	31:69	61:39	8:92	13:87
1c	11:89	18:82	34:66	64:36	3:97	3:97

This work demonstrates the large scope of the photoactivation of Ar−X bonds, which applies uniformly, though with varied efficiency, to bonds of different strengths under similar, mild conditions, contrary to metal catalysis that usually depends dramatically on the bond energy. The order of reactivity in the photocleavage of compounds **1a**−**d** is related neither to the strength of the acid liberated nor to what is generally observed in metal-mediated cross-coupling reactions. It would appear that photoheterolysis is effective also with leaving groups not necessarily pertaining to the family of the "good leaving group in organic synthesis" (phosphates here are an example) and possibly may be further extended.

The stabilizing effect of phenyl cations by a silicon atom in the β position plays the same role with (methoxy)phenyl esters as in the corresponding chloride. The end products maintain the $SiMe_3$ function, thus offering an entry to highly functionalized aromatics, for example, via oxidative coupling reactions.[29] As an alternative, due to the easy removal,[30] the $SiMe_3$ group can be considered as a directing, removable group. Moreover, the introduction of the TMS group, optionally coupled with the further stabilization by aqueous media, allows tuning the triplet versus singlet cation chemistry, shifting to the formation of the Ar−heteroatom bond in place of Ar−C bonds.

The efficient photoheterolysis of the Ar−O bond in aryl phosphates and sulfonates could have useful implications. As an example, the release of stable phosphate-based biologically interesting molecules from suitable "caged" precursors has been intensively investigated.[31] Compound **1c** could be a candidate for this aim, where aryl phosphates have not yet been used.[7] On the other hand, the photochemical generation of strong sulfonic acid via photoinduced Ar−O or O−S cleavage[14,32] in aryl sulfonates found application in photolithography and biology.[31,32]

■ EXPERIMENTAL SECTION

NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of ^1H and ^{13}C NMR, as well as DEPT-135 experiments; chemical shifts are reported in parts per million downfield from Me_4Si. The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes and a multilamp reactor fitted with six 15 W phosphor-coated lamps (maximum of emission 310 nm) for the irradiation. The progress of the reaction was followed by GC analyses. Photolyzed solutions have been concentrated in vacuo and purified by chromatographic separation (Millipore (60 Å, 35−70 μm) silica gel, eluant: cyclohexane/ethyl acetate mixtures). Quantum yields were measured at 254 nm (4 Hg lamps, 15 W). Benzene and allyltrimethylsilane (ATMS) were commercially available and freshly distilled before use. 4-Chloro-3-trimethylsilylanisole (**1d**) was prepared starting from 3-bromoanisole.[25a]

Emission measures have been carried out by means of a spectrofluorimeter. Fluorescence lifetime measurements have been carried out by using a single photon counter.

Synthesis of 4-Methoxy-2-trimethylsilylphenol (4). For the preparation of the title compound, we modified the procedure reported for the synthesis of 2-(trimethylsilyl)phenol.[33] To an anhydrous THF solution of 2-bromo-4-methoxyphenol[34] (4 g, 19.5 mmol) kept under nitrogen was added slowly *n*-BuLi (1.6 M solution in hexane, 27 mL, 43 mmol) at −78 °C. After 40 min stirring, freshly distilled trimethylsilyl chloride (6.4 mL, 50 mmol) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 4 h, then quenched with 1 N HCl (20 mL). After being stirred overnight, extraction with ethyl acetate and purification of the raw material by column chromatography afforded phenol **4** as a colorless solid (2.9 g, 76% yield, mp 46−48 °C). **4**: Spectroscopic data are in accord with the literature.[35] Anal. Calcd for $C_{10}H_{16}O_2Si$: C, 61.18; H, 8.21. Found: C, 61.1; H, 8.1.

Synthesis of 4-Methoxy-2-trimethylsilylphenyl Methanesulfonate (1a). Following a literature procedure for the synthesis of 4-methoxyphenyl methanesulfonate,[12] 4-methoxy-2-trimethylsilylphenol (**4**, 300 mg, 1.5 mmol) was treated with methanesulfonyl chloride (0.14 mL, 1.8 mmol) and triethylamine (0.32 mL, 2.3 mmol) in dichloromethane (7 mL) at 0 °C. After distillation at reduced pressure, mesylate **1a** was obtained as a colorless oil (302 mg, 72% yield). **1a**: ^1H NMR ($CDCl_3$) δ 7.45 (d, 1 H, J = 9 Hz), 7.00 (d, 1 H, J = 3 Hz), 6.90 (dd, 1 H, J = 3 and 9 Hz), 3.80 (s, 3 H), 3.20 (s, 3 H), 0.4 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 157.3, 147.7, 133.6, 121.3 (CH), 120.6 (CH), 114.7 (CH), 55.5 (CH_3), 38.1 (CH_3), −0.1 (CH_3); IR (neat) ν/cm^{-1} 2956, 1366, 840. Anal. Calcd for $C_{11}H_{18}O_4SSi$: C, 48.15; H, 6.61. Found: C, 48.0; H, 6.6.

Synthesis of 4-Methoxy-2-(trimethylsilyl)phenyl Trifluoromethanesulfonate (1b). According to the procedure for the synthesis of 2,5-[bis(trimethylsilyl)]phenyl-1,4-trifluoromethanesulfonate,[36] phenol **4** (800 mg, 4 mmol) was dissolved in anhydrous pyridine, the resulting solution was cooled to 0 °C under nitrogen, and trifluoromethanesulfonic anhydride was added dropwise. After heating at 50 °C for 1 h and removing the solvent in vacuo, the residue was purified by column chromatography to give **1b** as a colorless oil (1.14 g, 88% yield). **1b**: ^1H NMR[37] (CD_3COCD_3) δ 7.35−7.30 (m, 1 H), 7.10−7.05 (m, 2 H), 3.96 (s, 3 H), 0.30 (s, 9 H); ^{13}C NMR (CD_3COCD_3) δ 159.9, 149.4, 135.2, 122.7 (CH), 122.4 (CH), 119 (q, CF_3, J = 317 Hz) 117.0 (CH), 56.4 (CH_3), 0.4 (CH_3); IR (neat) ν/cm^{-1} 2952, 1504, 1121, 1140, 889. Anal. Calcd for $C_{11}H_{15}F_3O_4SSi$: C. 40.23; H. 4.60. Found: C, 40.2; H, 4.5.

Synthesis of 4-Methoxy-2-trimethylsilylphenyl Diethylphosphate (1c). Following the method previously described by Hatano for the synthesis of (R)-1,1′-binaphthalene-2,2′-bis-(diethoxyphosphinate),[38] phenol **4** (400 mg, 2 mmol) was dissolved in anhydrous THF and treated with NaH at 0 °C. Diethyl chlorophosphate (0.64 mL, 4.4 mmol) was carefully added, then the mixture was stirred at room temperature for 3 h. After usual workup, bulb-to-bulb distillation afforded **1c** as a colorless oil (360 mg, 54% yield). **1c**: ^{1}H NMR ($CDCl_3$) δ 7.40−7.35 (d, 1 H, J = 9 Hz), 6.95−6.90 (d, 1 H, J = 3 Hz), 6.85−6.80 (dd, 1 H, J = 3 and 9 Hz), 4.25−4.05 (m, 4 H), 3.80 (s, 3 H), 1.40−1.30 (m, 6 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 155.7, 149.5, 131.4, 120.7 (CH), 118.5 (CH), 114.6 (CH), 64.3 (CH_2), 55.4 (CH_3), 16.0 (CH_3), 15.9 (CH_3), −1.05 (CH_3); IR (neat) ν/cm^{-1} 2985, 1248, 1038, 974, 840. Anal. Calcd for $C_{14}H_{25}O_5PSi$: C, 50.59; H, 7.58. Found: C, 50.6; H, 7.6.

Irradiation of 1a in Neat 2,2,2-Trifluoroethanol (TFE). A solution of mesylate **1a** (412 mg, 1.5 mmol, 0.05 M), cesium carbonate (244 mg, 0.75 mmol, 0.025 M), and acetone (3 mL, 0.9 M) in TFE (30 mL) was irradiated for 8 h. After the solvent was removed in vacuo, column chromatography afforded 64 mg of 3-methoxyphenyl trimethylsilane **2** (colorless oil, 24% yield) and 234 mg of 2-(2,2,2-trifluoroethoxy)-5-methoxytrimethylsilylbenzene **3** (colorless oil, 56% yield). GC analysis also showed the presence of 4-methoxy-2-trimethylsilylphenol (**4**, 4% yield). **2**: Spectroscopic data are in accord with the literature.[25] Anal. Calcd for $C_{10}H_{16}OSi$: C, 66.61; H, 8.94. Found: C, 66.6; H, 8.9. **3**: ^{1}H NMR ($CDCl_3$) δ 7.00−6.95 (d, 1H, J = 3 Hz), 6.85−6.80 (dd, 1H, J = 3 and 8 Hz), 6.75−6.70 (d, 1H, J = 8 Hz), 4.30−4.20 (q, 2H, J = 8 Hz), 3.80 (s, 3 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 155.5, 154.3, 130.1, 130.0 (q, CF_3, J = 275 Hz), 121.6 (CH), 114.2 (CH), 110.5 (CH), 65.5 (q, CH_2, J = 35 Hz), 55.6 (CH_3), −1.3 (CH_3); IR (neat) ν/cm^{-1} 2955, 1482, 1269, 1216, 1165, 839. Anal. Calcd for $C_{12}H_{17}F_3O_2Si$: C, 51.78; H, 6.16. Found: C, 51.8; H, 6.1.

Irradiation of 1b in 5:1 MeCN/H_2O Mixture. Triflate **1b** (493 mg, 1.5 mmol, 0.05 M) and acetone (3 mL, 0.9M) were dissolved in 30 mL of 5:1 MeCN/H_2O mixture and irradiated for 24 h (85% consumption of **1b**). The solvent was removed in vacuo and the residue purified by silica gel chromatography giving 44 mg of **2** (19% yield based on the consumption of **1b**) and 142 mg of 2-trimethylsilyl-4-methoxyacetanilide (**7**, 47% yield based on the consumption of **1b**). **7**: Spectroscopic data are in accord with the literature.[25] Anal. Calcd for $C_{12}H_{19}NO_2Si$: C, 60.72; H, 8.07; N, 5.90. Found: C, 60.7; H, 8.1; N, 5.9.

Irradiation of 1a in TFE in the Presence of Benzene. Mesylate **1a** (412 mg, 1.5 mmol, 0.05 M), cesium carbonate (244 mg, 0.75 mmol, 0.025 M), acetone (3 mL, 0.9 M), and benzene (27.5 mL, 30 mmol, 1 M) were dissolved in 30 mL of TFE and irradiated for 7 h. Purification of the raw product by silica gel chromatography afforded a mixture of **2** (51 mg, 19% yield), **3** (175 mg, 42% yield), and 4-methoxy-2-trimethylsilylbiphenyl (**5**, 73 mg, 19% yield). **5**: ^{1}H NMR ($CDCl_3$, from the mixture) δ 7.45−7.25 (m, 5H), 7.25−7.15 (m, 1H), 6.95−6.85 (m, 2H), 3.90 (s, 3H), 0.10 (s, 9H); IR (of the mixture) ν/cm^{-1} 2954, 1587, 1478, 1216, 1057, 1040, 838.

Irradiation of 1b in TFE in the Presence of Allyltrimethylsilane (ATMS). Triflate **1b** (493 mg, 1.5 mmol, 0.05 M), cesium carbonate (244 mg, 0.75 mmol, 0.025 M), acetone (3 mL, 0.9 M), and ATMS (2.4 mL, 15 mmol, 0.5 M) were dissolved in TFE (30 mL) and irradiated for 12 h (88% consumption of **1b**). Purification by column chromatography yielded **3** (95 mg, 26% yield based on the consumption of **1b**) and 2-allyl-5-methoxyphenyltrimethylsilane **6** (colorless oil, 145 mg, 50% yield based on the consumption of **1b**). **6**: ^{1}H NMR ($CDCl_3$), δ: 7.15−7.10 (d, 1 H, J = 8.5 Hz), 7.05−7.00 (d, 1 H, J = 2.7 Hz), 6.90−6.85 (dd, 1 H, J = 2.7 and 8.5 Hz), 6.05−5.90 (m, 1 H), 5.15−4.95 (m, 2 H), 3.80 (s, 3 H), 3.50 (d, 2 H, J = 5.56 Hz), 0.35 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 157.0, 139.8, 138.2 (CH), 137.3, 130.2 (CH), 120.3 (CH), 115.5 (CH_2), 113.8 (CH), 55.0 (CH_3), 39.1 (CH_2), 0.1 (CH_3); IR (neat) ν/cm^{-1} 2953, 1478, 1247, 837. Anal. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.9; H, 9.1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and ^{13}C NMR spectra for compounds **1a−d** and **2−7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.P. acknowledges MIUR, Rome (FIRB-Futuro in Ricerca 2008 project RBFR08J78Q), for financial support. We thank Dr. V. Dichiarante for her help.

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