## Metal-Free Cross-Coupling Reactions of Aryl Sulfonates and Phosphates through Photoheterolysis of Aryl–Oxygen Bonds**

Marco De Carolis, Stefano Protti, Maurizio Fagnoni,* and Angelo Albini*

Metal-mediated cross-coupling reactions have been extensively developed for the formation of aryl–carbon bonds. In these reactions, an aryl–halogen (mostly Br or I) or an aryl–oxygen bond is activated in the starting compound, for example, an aryl sulfonate[1] can be used in the Suzuki–Miyaura procedure for the synthesis of biphenyls.[2,3] A limitation of these syntheses is the severe experimental conditions that must be employed, such as an inert atmosphere, strictly anhydrous solvents, and the use of a base or a high temperature. Furthermore, although triflates are the most reactive precursors for the aryl sulfonate series they are less easily handled and are relatively expensive. Efforts to extend the reaction to the less reactive mesylates[6] and tosylates have met with some success.[1,6,7] Another class of reagents with a potential O-leaving group is the aryl phosphates, of which to our knowledge only a couple of examples have been reported. These involve coupling the phosphate with Grignard reagents in the presence of phosphane–nickel(II) complexes.[8]

We have recently identified an alternative cross-coupling reaction, in which the aryl-substituted bond in the starting compound is cleaved heterolytically, rather than activated, by a photochemical reaction. For example, the photosensitized decomposition of diazonium salts allowed general access to a triplet phenyl cation[9] (Scheme 1) which in turn reacted with olefins and aromatic compounds[10] to generate aryl–carbon
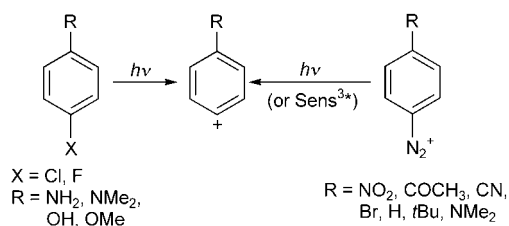
Scheme 1. Photochemical generation of triplet phenyl cations.

[*] M. De Carolis, S. Protti, Dr. M. Fagnoni, Prof. A. Albini
Department of Organic Chemistry
University of Pavia
Via Taramelli 10, 27100 Pavia (Italy)
Fax: (+39) 0382-507-323
E-mail: fagnoni@unipv.it
       angelo.albini@unipv.it

bonds. The electrophilic character of these salts limits the choice of nucleophiles that can be used in the photoarylation reactions, since there will be competing thermal reactions. However, aryl cations could also be photogenerated starting from electron-donating substituted aryl halides, such as chloro- or fluoroanilines,[11] chlorophenols, and chloroanisoles[12] (Scheme 1). Delocalization of the positive charge on the electron-donating substituents in the resulting aryl cation as well as the use of a polar medium resulted in efficient photoheterolysis. Extending the scope of this mild, metal-free cross-coupling reaction would greatly increase its synthetic significance.

We reasoned that the incorporation of O-leaving groups might also be beneficial in the aryl cation precursor, thus enabling the reaction to be applied to the readily available and versatile family of aryl esters. There are no precedents for such processes, and what is known about these compounds points to homolytic cleavage of the ArO—X bond, as exemplified by the (radical) photo-Fries reaction of organic esters.[13] The photochemistry of their inorganic counterparts (aryl sulfonates and phosphates) has also not been extensively studied. Aryl tosylates were reported to undergo the photo-Fries reaction in polar solvents,[14] but aryl triflates eliminated the triflate group both on irradiation in acetone[15a] and under photoelectron transfer conditions (for example, from pentafluorophenyl triflate[15b]), although this is known for a very limited number of cases. Furthermore, the nickel-mediated synthesis of biphenyl starting from phenyl triflate was favored in UV light.[15c] The photolability of the aryl tosylates, like the aryl phosphates, has been known for 50 years and represents one of the first examples of photoinduced nucleophilic substitution.[16] However, this photolability has remained limited to photohydrolysis in water,[17] apart from the intramolecular process reported for alken-1-ylarylmethyl phosphates[18a] and of bi- and triaryl phosphates,[18b] where aryl–vinyl or aryl–aryl bonds are formed. Conversely, photofragmentation of the P—OAr bond occurred through resonant two-photon reactions on irradiation of the 4-methoxyphenyl-diethyl phosphate in cyclohexane.[18c]

Therefore, we decided to investigate the photochemistry of *N,N*-dimethylamino- and methoxy-substituted phenyl sulfonates **1–3** and **5–7** as well as the phosphates **4** and **8**. These compounds are readily prepared from the corresponding phenols (see the Supporting Information) by irradiation in an argon-flushed polar solution in the presence of either allyltrimethylsilane (ATMS) or benzene (1 M). The *N,N*-dimethylamino derivatives were found to decompose quantitatively (or close to) within 4–5 hours while the methoxy-derivatives needed 20–32 hours (Scheme 2, Table 1). We

1: R = NMe₂, X = SO₂CH₃
2: R = NMe₂, X = SO₂CF₃
3: R = NMe₂, X = SO₂C₆H₄-4-CH₃
4: R = NMe₂, X = PO₃Et₂
5: R = OMe, X = SO₂CH₃
6: R = OMe, X = SO₂CF₃
7: R = OMe, X = SO₂C₆H₄-4-CH₃
8: R = OMe, X = PO₃Et₂

9 **10** **11** **12** R = NMe₂
13 **14** **15** **16** R = OMe
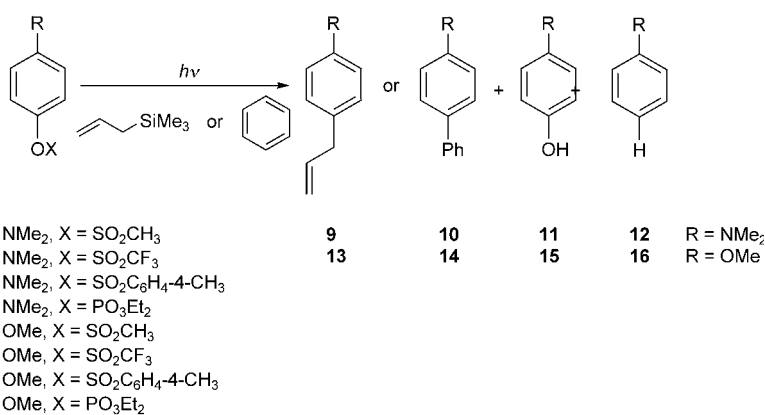
Scheme 2. Arylation reactions by the irradiation of phenyl esters in the presence of allyltrimethylsilane or benzene.

Table 1: Photolysis of 4-*N,N*-dimethylamino esters **1–4** (0.05 M) in the presence of ATMS (1 M) or benzene (1 M).

Entry	Ester	Solvent	Nucleophile	Consumption [%]	t_{IRR} [h]	Yield[a] [%] phenylated	11	12
1	1	MeCN	ATMS	100	4	**9**, 95	–	–
2	1	TFE	ATMS[b]	100	4	**9**, 100	–	–
3	1	H₂O/MeCN	ATMS[c]	100	4	**9**, 100	–	–
4	1	TFE	benzene[b]	100	4	**10**, 100	–	–
5	2	TFE	ATMS	73	5	**9**, 15	81	–
6	2	TFE	benzene	84	5	**10**, 19	56	5
7	3[d]	[d]	ATMS or benzene	29–85	5	[d]	–	
8	4	MeCN	ATMS	100	5	**9**, 82	–	16
9	4	TFE	ATMS	100	5	**9**, 100	–	–
10	4	H₂O/MeCN	ATMS[c]	100	5	**9**, 100	–	–
11	4	TFE	benzene	85	5	**10**, 96	–	4

[a] Yields determined by gas chromatography (GC) analysis based on consumed ester; for preparative results see the Experimental Section. [b] 0.2 M nucleophile. [c] ATMS at 0.5 M for solubility reasons. [d] No photoproducts detected by GC analysis under any of the conditions used for the other esters.

found that cross-coupling reactions had taken place in all cases and gave the corresponding allylated and phenylated derivatives. The product yield depended on the reagent used and on the solvent (MeCN, 2,2,2-trifluoroethanol (TFE), or H₂O/MeCN 1:5). Since acid was liberated in the process, the solutions were buffered by an equimolar amount of triethylamine (except when water was present in solution). Control experiments showed that thermal processes were not involved in the formation of the phenyl–carbon bonds.

Table 1 shows the results with dimethylaminophenyl esters as the substrates. In particular, photolysis of mesylate **1** in the presence of ATMS (1 M) provided 4-(2-propenyl)-*N,N*-dimethylaniline (**9**) in almost quantitative yield.[19] The formation of 4-phenyl-*N,N*-dimethylaniline (**10**) was quantitative in TFE in the presence of benzene; water/MeCN afforded the next highest yield (48%), although photoreduction to *N,N*-dimethylaniline (**12**) was not negligible. However, triflate **2** gave a low yield of both **9** and **10** (15 and 19%, respectively, in TFE), with deprotection to yield 4-hydroxy-*N,N*-dimethylaniline (**11**) being the main pathway. Tosylate **3** was more resistant to photodecomposition and no products were detected by gas chromatographic analysis (Table 1, entry 7).

The performance of diethylphosphate **4** was very close to that of mesylate **1**. Allylated derivative **9** was produced in a quantitative yield when **4** was irradiated in TFE or MeCN/water while phenylated **10** was produced in a yield of 96% in TFE and about 50% in the other solvents. Phenylation was also examined in MeOH and no significant difference was observed when MeCN was used. The precursor that gave the best results was mesylate **1**, which gave equally good yields when lower amounts of both nucleophiles were employed (see Table 1, entries 2 and 4).

Since the conditions were different from those used in the original study on haloanilines,[11] we tested the cross-coupling reactions of 4-chloro-*N,N*-dimethylaniline under these conditions for comparison. Formation of allylated **9** was quantitative in this case (ATMS could effectively be used at 0.2 M concentration), while phenylation of benzene occurred in a low to moderate yield (24–51%). Again, reduction to *N,N*-dimethylaniline was the main competing process.

Methoxyphenyl esters **5–8** inefficiently absorbed the UV-B light used and reacted only sluggishly.[22] Acetone (0.9 M) sensitization proved efficient even if irradiation times were four to six times longer than those of esters **1–4** ($\approx$20–30 hours).[23,24] Photoreaction of mesylate **5** in the presence of ATMS yielded 4-(2-propenyl)anisole (**13**) and the yield increased from 17% in acetonitrile to 100% in aqueous acetonitrile[25] (Scheme 2, Table 2). Phenylation of benzene

see Table 2, entry 4). Furthermore, the presence of oxygen only slightly affected the yield of **13** from **6** when the reaction was carried out in water/MeCN (Table 2, entry 5).

We then tested 4-(*N,N*-dimethylamino)phenyl (**17**) and 4-methoxyphenyl acetate (**18**) as representative organic esters (Scheme 3). Both compounds underwent photohomolysis of
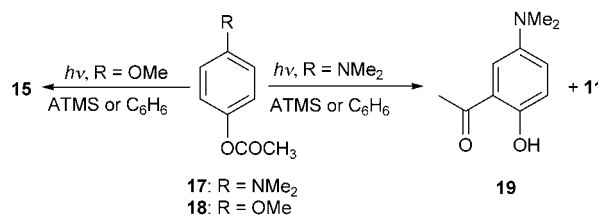
Scheme 3. Photochemical reactions of phenyl acetates.

the acetyl group, and phenols **11** (14–45%) and **15** (close to quantitative) were produced, as well as the photo-Fries product **19** (19–56% yield) in the former case. Carrying out the irradiation in the presence of either ATMS (1 M) or benzene (1 M) did not affect the product distribution and no phenylation products were obtained.

Finally, precursors lacking electron-donating substituents were tested. Thus phenyl mesylate and phenyl triflate were photolyzed both in TFE and water/MeCN (the solvents which gave the best results in the previous cases) in the presence of the above nucleophiles, but neither allylbenzene nor biphenyl were formed.

The above data show that various phenyl sulfonates and phosphates with electron-donating substituents are suitable precursors for the photochemical phenylation of alkenes and arenes. Both mesylate **1** and phosphate **4** could be used for synthesizing *N,N*-dimethylamino derivatives **9** and **10** in quantitative yields, although concurrent paths dramatically lowered the arylation yield in the photodecomposition of triflate **2** and tosylate **3**. Also in the cases of the methoxyphenyl esters, triflate **6** was the best precursor for obtaining both **13** and **14**. The latter compound was also obtained in high yield from mesylate **5** and phosphate **8**,

Table 2: Photolysis of 4-methoxy esters **5–8** in the presence of nucleophiles.

Entry	Ester	Solvent	Nucleophile	Consumption [%]	t_{IRR} [h]	Yield[a] [%]		
						phenylated	15	16
1	5	TFE	ATMS	79	30	**13**, 73	–	6
2	5	H₂O/MeCN	ATMS[b]	100	24	**13**, 100	–	–
3	5	H₂O/MeCN	benzene	100	24	**14**, 58	–	8
4	6	TFE	ATMS	100	30	**13**, 100 (48)[c]	–	–
5	6	H₂O/MeCN	ATMS[b,d]	100	24	**13**, 90	–	9
6	6	TFE	benzene	100	28	**14**, 97	–	–
7	6	H₂O/MeCN	benzene	100	24	**14**, 74	–	9
8	7	TFE	ATMS	71	22	**13**, 23	21	–
9	7	TFE	benzene	85	22	**14**, 15	12	–
10	8	TFE	ATMS	100	30	**13**, 44	–	12
11	8	TFE	benzene	100	24	**14**, 96	–	–

[a] Yields determined by gas chromatographic (GC) analysis based on consumed ester; for preparative results see the Experimental Section. [b] ATMS at 0.5 M for solubility reasons. [c] 0.2 M nucleophile. [d] Under nondeaerated conditions.

was less satisfactory, since the maximum yield of 4-phenylanisole (**14**) was 58% both in water/MeCN and TFE. Triflate **6** gave moderate to excellent yields of both **13** and **14**, especially in TFE—a much better performance than both aminophenyl triflate **2** and methoxyphenyl mesylate **5**. Tosylate **7** gave complex mixtures with poor yields of the phenylation products (not exceeding 23%), with deprotection being by far the main pathway. Again, TFE was the best solvent for the arylation reactions starting from phosphate **8**, and photoproducts **13** and **14** were isolated in 44 and 96% yields, respectively.

Of the methoxyphenyl esters examined, triflate **6** gave the best results. The reaction proceeded fairly efficiently in TFE with a 0.2 M concentration of nucleophile (48% with ATMS,

while tosylate **7** gave complex mixtures. Phenyl esters performed better than phenyl halides in the arylation of arenes,[26] where the latter precursors underwent reduction to a considerable extent (see below). The initiating photoheterolysis step liberated mineral acids during the reaction. The use of triethylamine as a buffer prevented the irradiated solutions from darkening and gave a clean reaction. Particularly noteworthy is that a mixed solvent containing water exerted a sufficient buffering effect.[27]

The photoreactions of phenyl halides substituted with electron-donating groups[11,12] and of benzenediazonium salts[10] supports the theory that the arylation of esters results from the triplet state of the precursor. In this case, two

competitive cleavage paths operate (Scheme 4), with photo-homolysis of the O–X bond forming a phenyloxy radical and photoheterolysis of the phenyl–O bond yielding a phenyl cation in the triplet state. The first pathway accounts both for
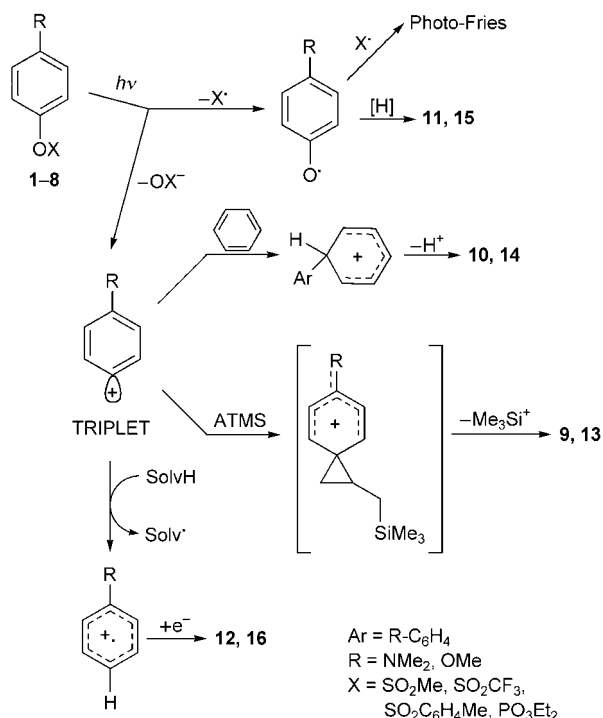
Scheme 4. Mechanistic paths in the photodegradation of esters **1–8**.

the formation of deprotected phenols **11** and **15** (important in the photolysis of triflate **2**) and for the photo-Fries reaction that occurs predominantly with acetate **17**. This route also probably has a role in the reactions with tosylates. The triplet phenyl cation formed in the second pathway adds selectively to π nucleophiles. Benzene rearomatization leads to biphenyls **10** and **14**, while elimination of a trimethylsilyl group by ATMS leads to allylbenzenes **9** and **13**.[28] A competing reaction for the triplet cation is reduction by the solvent.[31] The importance of this pathway depends on the starting material (and thus on the nature of the counterion XO⁻) and of the π trap, as well as the solvent chosen. Among the aminophenyl esters reduction is significant particularly with the phosphate, while among the methoxyphenyl esters reduction is particularly significant with the mesylate and the triflate. However, in almost all cases it is possible to choose a solvent where reduction is minimized and arylation occurs in high or quantitatively yield, with TFE and MeCN/water (5:1) often being a good choice.

In summary, the photolysis of phenyl sulfonates and phosphates substituted with electron-donating groups is an appealing method for the phenylation of alkenes and arenes. The method is general and, when all the previous findings with phenyl halides and benzenediazonium salts are considered, compares favorably with metal catalysis[32] in that mild conditions are employed. These reactions are also insensitive to oxygen and moisture (indeed, water can be used as a mixed

solvent) and avoids the use of bases or other aggressive reagents. In addition, a relatively low concentration of the π nucleophile is efficient (often 0.2 M, a 4:1 excess with respect to the ester), and expensive and often unstable catalysts are not required. The success of the reaction is based on the smooth photogeneration of the triplet phenyl cations and their selective reaction with π nucleophiles. Mechanistic studies on this previously unreported efficient photoheterolysis of the phenyl–oxygen bond of these esters are now underway.

Experimental Section

Typical procedure of the phenylation reactions through photoheterolysis of phenyl esters: A solution (18–30 mL) of ester **1–8** (0.05 M), triethylamine (TEA, 0.05 M), and benzene or ATMS (0.2 to 1 M) in the chosen solvent was poured in a quartz tube[33] and purged for 10 min with argon, septum capped, and irradiated with six 15 W phosphor-coated lamps (range of emission 295–335 nm, maximum at 310 nm). The solution was concentrated in vacuo and purified by column chromatography (cyclohexane/ethyl acetate as eluants). In the reactions involving esters **5–8**, acetone (100 μL per mL of solvent, 0.9 M) was added to the reaction mixture. When water/MeCN was used as the solvent, no TEA was added. The yields of isolated products consistently approached those determined by gas chromatographic analysis (Table 1 and Table 2); for example, compound **6→13**, 80%; **6→14**, 85%.

[1] Z.-Y. Tang, Q.-S. Hu, *J. Am. Chem. Soc.* **2004**, *126*, 3058–3059, and references therein.

[2] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483; N. Miyaura, *Top. Curr. Chem.* **2002**, *219*, 11–59.

[3] Very recently, biphenyls were obtained from aromatic ethers either by nickel-catalyzed cross-couplings with aryl Grignard reagents[4] or ruthenium-mediated reactions with aryl boronates.[5]

[4] J. W. Dankwardt, *Angew. Chem.* **2004**, *116*, 2482–2486; *Angew. Chem. Int. Ed.* **2004**, *43*, 2428–2432.

[5] F. Kakiuchi, M. Usui, S. Ueno, N. Chatani, S. Murai, *J. Am. Chem. Soc.* **2004**, *126*, 2706–2707, and references therein.

[6] V. Percec, J.-Y. Bae, D. H. Hill, *J. Org. Chem.* **1995**, *60*, 1060–1065; V. Percec, G. M. Golding, J. Smidrkal, O. Weichold, *J. Org. Chem.* **2004**, *69*, 3447–3452.

[7] A. H. Roy, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 8704–8705; H. N. Nguyen, X. Huang, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 11818–11819; A. Fürstner, A. Leitner, M. Mendez, H. Krause, *J. Am. Chem. Soc.* **2002**, *124*, 13856–13863; D. Badone, R. Cecchi, U. Guzzi, *J. Org. Chem.* **1992**, *57*, 6321–6323.

[8] M. Tanaka, K. Chiba, M. Okita, T. Kaneko, K. Tagami, S. Hibi, Y. Okamoto, H. Shirota, M. Goto, H. Obaishi, H. Sakurai, Y. Machida, I. Yamatsu, *J. Med. Chem.* **1992**, *35*, 4665–4675; T. Hayashi, Y. Katsuro, Y. Okamoto, M. Kumada, *Tetrahedron Lett.* **1981**, *22*, 4449–4452.

[9] In contrast to the singlet states, triplet phenyl cations behave as selective electrophiles and react with π, not n nucleophiles; see reference [10].

[10] S. Milanesi, M. Fagnoni, A. Albini, *Chem. Commun.* **2003**, 216–217.

[11] B. Guizzardi, M. Mella, M. Fagnoni, M. Freccero, A. Albini, *J. Org. Chem.* **2001**, *66*, 6353–6363; M. Mella, P. Coppo, B. Guizzardi, M. Fagnoni, M. Freccero, A. Albini, *J. Org. Chem.* **2001**, *66*, 6344–6352; B. Guizzardi, M. Mella, M. Fagnoni, A. Albini, *Tetrahedron* **2000**, *56*, 9383–9389; B. Guizzardi, M. Mella, M. Fagnoni, A. Albini, *Chem. Eur. J.* **2003**, *9*, 1549–1555; A. Fraboni, M. Fagnoni, A. Albini, *J. Org. Chem.* **2003**, *68*, 4886–4893.

[12] S. Protti, M. Fagnoni, M. Mella, A. Albini, *J. Org. Chem.* **2004**, *69*, 3465–3473.

[13] J. W. Meyer, G. S. Hammond, *J. Am. Chem. Soc.* **1972**, *94*, 2219–2228; M. R. Sandner, E. Hedaya, D. J. Trecker, *J. Am. Chem. Soc.* **1968**, *90*, 7249–7254.

[14] D. Bellus in *Advances in Photochemistry, Vol. 8* (Eds.: J. N. Pitts, Jr., G. Hammond, W. A. Noyes, Jr.), Wiley-Interscience, New York, **1971**, pp. 109–159; J. L. Stratenus, E. Havinga, *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 434–436; E. Elhalem, B. N. Bailey, R. Docampo, I. Ujvari, S. H. Szajnman, J. B. Rodriguez, *J. Med. Chem.* **2002**, *45*, 3984–3999.

[15] a) Y.-S. Chang, J.-S. Jang, M. L. Deinzer, *Tetrahedron* **1990**, *46*, 4161–4164; b) Q.-Y. Chen, Z.-T. Li, *J. Org. Chem.* **1993**, *58*, 2599–2604; c) S. Knapp, J. Albaneze, H. J. Schugar, *J. Org. Chem.* **1993**, *58*, 997–998.

[16] E. Havinga, R. O. De Jongh, W. Dorst, *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 378–383.

[17] R. S. Givens, L. W. Kueper III, *Chem. Rev.* **1993**, *93*, 55–66.

[18] a) M. Nakamura, Y. Okamoto, S. Takamuku, *Chem. Commun.* **1996**, 209–210; b) M. Shi, K. Yamamoto, Y. Okamoto, S. Takamuku, *Phosphorus Sulfur Silicon Relat. Elem.* **1991**, *60*, 1–14; c) M. Nakamura, A. Ouchi, M. Miki, T. Majima, *Tetrahedron Lett.* **2001**, *42*, 7447–7449.

[19] Palladium-catalyzed arylation of allyltrimethylsilane starting from aryl iodides led to allyl aromatic compounds in low to good selectivities according to the conditions used,[20] whereas aryl triflates afforded arylated allylsilanes.[21]

[20] T. Jeffery, *Tetrahedron Lett.* **2000**, *41*, 8445–8449.

[21] K. Olofsson, M. Larhed, A. Hallberg, *J. Org. Chem.* **1998**, *63*, 5076–5079.

[22] Methoxyphenyl esters exhibited the long-wavelength band at 275–280 nm, with virtually no absorption at 310 nm, thus poorly matching the spectrum of the lamp (see Experimental Section). In contrast, aminophyenyl esters strongly absorbed at 310 nm ($\varepsilon \approx 1200–2500$ mol^{-1}dm^{3}cm^{-1}).

[23] Some irradiations with mesylate **5** in the presence of ATMS were carried out under nonsensitized conditions at 254 nm and gave the same product distribution, although product **13** was not stable under prolonged irradiation. The use of the lamps at a wavelength of 310 nm prevented both product photodegradation and competititve absorption by benzene when this was used as the trap. A possible wavelength dependence of the reaction is under investigation.

[24] In these acetone-sensitized reactions in the presence of ATMS, the Paternò-Büchi oxetane was found as a by-product in a variable amount, particularly in the case of phosphate **8**.

[25] The presence of a protic polar medium (for example, water) could dramatically favor the photoheterolytic process, see: M. Freccero, M. Fagnoni, A. Albini, *J. Am. Chem. Soc.* **2003**, *125*, 13182–13190.

[26] 4-Methoxybiphenyl was obtained only in 7% yield in aprotic solvent after irradiation of 4-chloroanisole in the presence of benzene (1M). In TFE the yield did not exceed 70%.

[27] Triethylamine (0.05 M) buffers the acid liberated in the photolysis of the esters and avoids degradation and polymerization of the photoproducts, as indicated by experiments using cesium carbonate instead which led to the same product distribution.

However, the use of the MeCN/water mixed solvent made the use of a base unnecessary, thus supporting the idea that electron transfer between the amine and the triplet state of the aromatic reagents (very short lived in the halides, reference [25] and presumably also of the esters) is not involved in the arylation reaction.

[28] Attack of allyltrimethylsilane by cations is well known. The alternative formation of compounds **9** and **13** by a photo-generated aryl radical is excluded on two grounds. First, it has been reported that such a path operates only with strongly electrophilic aryl radicals (for example, 3,5-dinitrophenylradical[29]) and, then, only with a poor yield. Moreover, β fragmentation of the adduct radical leading to allylated derivatives is usually observed with an (Me$_3$Si)$_3$Si group rather than with other alkyl- or aryl-substituted silanes.[30] Second, purposely designed experiments disfavor this hypothesis. Thus, generation of an authentic 4-methoxyphenyl radical by photolysis of 4-bromoanisole in the presence of ATMS gave no allylated compounds but only anisole. Likewise, substituting 2,3-dimethylbutene for ATMS gave 2,3-dimethyl-3-(4-methoxyphenyl)-1-butene, 2,3-dimethyl-3-(4-methoxyphenyl)-2-(2,2,2-trifluoroethoxy)butane, 2,3-dimethyl-2-(4-methoxyphenyl)butane, and 2-(4-methoxyphenyl)-2-(2,2,2-trifluoroethoxy)-3,3-dimethylbutane from **5** in CF$_3$CH$_2$OH/Cs$_2$CO$_3$, in the same proportion as from 4-chloroanisole (see reference [12]). This reaction is difficult to envisage other than involving loss of a proton from (or solvent addition to) an adduct cation. (Further evidence is the fact that a cationic Wagner–Meerwein rearrangement has taken place in the last product).

[29] F. Ek, L.-G. Wistrand, T. Frejd, *J. Org. Chem.* **2003**, *68*, 1911–1918.

[30] L. Chabaud, P. James, Y. Landais, *Eur. J. Org. Chem.* **2004**, 3173–3199.

[31] The role of solvents, and in particular of alcohols, as hydrogen donors (and not as n nucleophiles) in the reaction with the triplet phenyl cation has been previously demonstrated, see Refs. [10–12].

[32] In rare instances, the Suzuki coupling occurred under microwave irradiation in the absence of a catalyst, see: N. E. Leadbeater, M. Marco, *Angew. Chem.* **2003**, *115*, 1445–1447; *Angew. Chem. Int. Ed.* **2003**, *42*, 1407–1409.

[33] Quartz allowed the absorption of all of the light emitted by the lamp.