

The β Effect of Silicon in Phenyl Cations

Valentina Dichiarante, Andrea Salvaneschi, Stefano Protti, Daniele Dondi,
Maurizio Fagnoni,* and Angelo Albini

Department of Organic Chemistry, University of Pavia, viale Taramelli 10, 27100 Pavia, Italy

Received June 29, 2007; E-mail: fagnoni@unipv.it

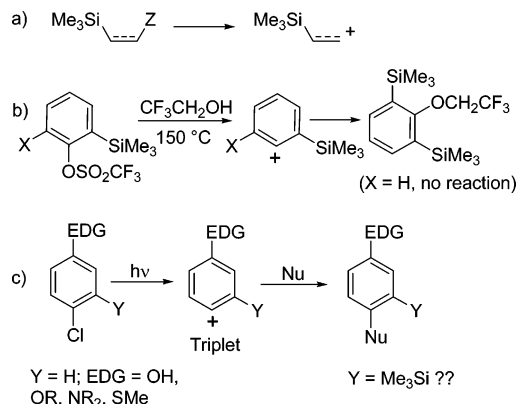
Abstract: Irradiation of chloroanisoles, phenols, and *N,N*-dimethylanilines bearing a trimethylsilyl (TMS) group in the *ortho* position with respect to the chlorine atom caused photolysis of the Ar–Cl bond and formation of the corresponding *ortho*-trimethylsilylphenyl cations in the triplet state. The β effect of silicon on these intermediates has been studied by comparing the resulting chemistry in alcoholic solvents with that of the silicon-free analogues and by computational analysis (at the UB3LYP/6-311+G(2d,p) level in MeOH). TMS groups little affect the photophysics and the photocleavage of the starting phenyl chlorides, while stabilizing the phenyl cations, both in the triplet (ca. 4 kcal/mol per group) and, dramatically, in the singlet state (9 kcal/mol). As a result, although triplet phenyl cations are the first formed species, intersystem crossing to the more stable singlets is favored with chloroanisoles and phenols. Indeed, with these compounds, solvent addition to give aryl ethers (from the singlet) competed efficiently with reduction or arylation (from the triplet). In the case of the silylated 4-chloro-*N,N*-dimethylaniline, the triplet cation remained in the ground state and trapping by π nucleophiles remained efficient, though slowed by the steric bulk of the TMS group. In alcohols, the silyl group was eliminated via a photoinduced protodesilylation during the irradiation. Thus, the silyl group could be considered as a *directing, photoremovable* group that allowed shifting to the *singlet* phenyl cation chemistry and was smoothly eliminated in the same one-pot procedure.

Introduction

Silicon-based substituents (e.g., the trimethylsilyl (TMS) group) are well-known to stabilize a positive charge present on a β position¹ and to facilitate the formation of alkyl and vinyl cations (Scheme 1a). Twenty years ago, this stabilization was exploited by Sonoda et al. for the generation of an elusive intermediate such as a phenyl cation in solution.² Thus, although the triflate of the 2-(trimethylsilyl)phenol was stable upon heating in TFE in the presence of 2,6-lutidine at 150 °C, the 2,6-bis(trimethylsilyl)-substituted analogue gave, under the same conditions, the corresponding trifluoroethyl ether quantitatively (Scheme 1b).^{2,3} The success of this reaction was ascribed to the hyperconjugative stabilization of the cation by the C–Si σ bonds, as confirmed by more recent calculations,⁴ as well as to the good leaving group.^{2,5}

Dinitrogen is a better leaving group than triflate anion, and both thermal and photochemical generation of phenyl cations from diazonium salts are documented, although the competition of radical paths may make the recognition of the mechanism

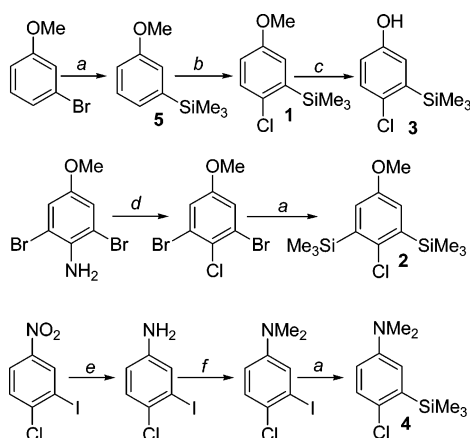
Scheme 1. β -Stabilizing Effect of Silicon on the Generation of (a) Alkyl and Vinyl Cations and (b) Phenyl Cations; (c) Application to the Case of Photogenerated Triplet Phenyl Cations



not obvious.⁶ Indeed, the effect of the TMS groups was calculated to be so strong that the 2,6-bis(trimethylsilyl)phenyl diazonium cation was predicted to decompose spontaneously at room temperature.^{2,7a} The focus of experimental and computational studies has been to individuate a substituent that

- (1) (a) Lambert, J. B. *Tetrahedron* **1990**, 46, 2677–2689. (b) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J.-H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, 32, 183–190.
- (2) Himeshima, Y.; Kobayashi, H.; Sonoda, T. *J. Am. Chem. Soc.* **1985**, 107, 5286–5288.
- (3) Phenyl triflate too was stable under harsh solvolytic conditions. See: (a) Subramanian, L. R.; Hanack, M.; Chang, L. W.; Imhoff, M. A.; Schleyer, P. v. R.; Effenberger, F.; Kurtz, W.; Stang, P. J.; Dueber, T. E. *J. Org. Chem.* **1976**, 41, 4099–4103. (b) Laali, K.; Szele, I.; Yoshida, K. *Helv. Chim. Acta* **1983**, 66, 1710–1720.
- (4) Laali, K. K.; Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **2002**, 67, 2913–2918.
- (5) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1985**, 107, 5285–5286.

- (6) (a) Gasper, S.; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, 117, 5206–5211. (b) Milanesi, S.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2005**, 70, 603–610. (c) Zollinger, H. *Diazo Chemistry*; VCH: Weinheim, Germany, 1994; Vol. 1. (d) Ussing, B. R.; Singleton, D. A. *J. Am. Chem. Soc.* **2005**, 127, 2888–2899.
- (7) (a) Nicolaides, A.; Smith, D. M.; Jensen, F.; Radom, L. *J. Am. Chem. Soc.* **1997**, 119, 8083–8088. (b) Aschi, M.; Harvey, J. N. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1059–1061. (c) Hori, K.; Sonoda, T.; Harada, M.; Yamazaki-Nishida, S. *Tetrahedron* **2000**, 56, 1429–1436. (d) Ambroz, H. B.; Kemp, T. J. *Chem. Soc. Rev.* **1979**, 8, 353–365.

Chart 1. Preparation of Silylated Phenyl Chlorides 1–4^a

^a (a) TMSCl, Mg, THF reflux; (b) SO_2Cl_2 , CHCl_3 , room temperature 60% for the two steps; (c) BBr_3 , CH_2Cl_2 $-78 \rightarrow 25^\circ\text{C}$ 2h, 54%; (d) NaNO_2 , HCl , 0°C , then CuCl , 52%; (e) SnCl_2 , ethanol/ethylacetate 5:2, 63%; (f) NaBH_4 , CH_2O , 51%.

would make generation of such an unstable species possible, with little interest in the ensuing reactions, which were actually limited to solvolysis.

As a matter of fact, the synthetic application of phenyl cations has been little explored because general and simple methods for their thermal generation are not available.⁸ Recently, however, there has been an increased interest in the *photoinduced* generation of this intermediate, and a novel chemistry has been revealed. The reactions observed depend on which spin state of the cation is formed, and this in turn depends on the precursor and on the mode of generation. To summarize, phenyldiazonium ion fragments and gives either the singlet or the triplet phenyl cation, according to the substituents, while the irradiation of electron-donating substituted phenyl chlorides, phosphate, or sulfonate esters in a polar solvent offers a straightforward access to triplet phenyl cations (Scheme 1c).⁹ The singlet is a localized cation with a vacant σ orbital at the dicoordinated carbon atom,^{7b} while the triplet state has a diradical character with single occupancy of the σ orbital and the charge delocalized on the aromatic ring.^{4,7}

Singlet phenyl cations are unselective electrophiles, and reaction via this path mostly results in solvolysis, forming Ar–O or Ar–N bonds when the reaction is carried out in alcohols or acetonitrile, respectively.^{6,10} Triplet phenyl cations react selectively with π nucleophiles (olefins and aromatics) forming new Ar–C bonds.⁹ With this large scope access, it becomes feasible to study the effect a silyl group has on the *chemistry* of the phenyl cation, in addition to that on its formation.

As a contribution toward this issue, we report here the photocleavage of some phenyl chlorides that are structurally related to the above-mentioned thermally labile phenyl triflates (one or two TMS group(s) in ortho with respect to the leaving group; Chart 1). The comparison of the photochemistry of these phenyl chlorides with that of the silicon-free analogues allows assessing the β effect of silicon.

Results

Four silylated phenyl chlorides were studied in this work, namely, 2-chloro-5-methoxyphenyltrimethylsilane (**1**), 2-chloro-5-methoxy-1,3-bis-trimethylsilylbenzene (**2**), 4-chloro-3-trimethylsilylphenol (**3**), and (4-chloro-3-trimethylsilylphenyl)-dimethylamine (**4**) (Chart 1). Silanes **1–4** were prepared from the corresponding phenyl halides via coupling of the Grignard reagent with trimethylsilylchloride (TMSCl) as illustrated in Chart 1.

Preparative Irradiation. Compounds **1–4** were irradiated in protic solvents (methanol, 2,2,2-trifluoroethanol (TFE), and water/acetonitrile mixtures) (i.e., under the conditions found to favor the heterolytic dissociation of the Ar–Cl bond with the silicon-free analogues).⁹ The experiments were carried out both in neat solvents and in the presence of a π nucleophile, either an alkene (allyltrimethylsilane, ATMS) or an aromatic (benzene). Since acidity was liberated in the reaction, an equivalent amount of a buffering agent such as cesium carbonate was added in some cases. This avoided undesired thermal desilylation either of the starting compounds or of the end products, which otherwise took place to some extent. Most of the irradiations were carried out until a high or complete consumption of the starting material was reached, but irradiations at shorter times were also performed to check for the occurrence of secondary processes. The product mixture was analyzed both as such and after full desilylation by treatment with Bu_4NF .

Compounds **1–4** showed a very weak fluorescence ($\Phi_F < 0.05$) both in MeCN and in TFE solutions, similar to that of the corresponding silicon-free analogues.^{11,12} Phosphorescence at 77 K in glass was likewise similar in shape and somewhat less intensive.

Photochemistry of 2-Chloro-5-methoxyphenyltrimethylsilane (1). Irradiation of compound **1** (0.05 M) in all of the solvents tested caused an efficient dechlorination (Table 1). In MeOH in the presence of Cs_2CO_3 , photoreduction to form anisole **5** and, mainly, solvolysis to give dimethoxy derivative **7** took place. Prolonged irradiation (up to 16 h) caused a partial desilylation of **7** to give **7a** (Scheme 2). In the presence of benzene (1 M), some arylation took place and biphenyl **12a** (10%) was formed, though photosubstitution remained by far the main path. Irradiation for a shorter time evidenced the formation of (4-methoxybiphenyl-2-yl)trimethylsilane **12** as an intermediate (Scheme 3).

In TFE, reduction to give anisoles **5** and **5a** (the latter desilylated) took place along with solvolysis to trifluoroethyl-ether **9a**. The silicon containing ether **9** was detected at a shorter irradiation time (Scheme 2). With 1 M benzene, **12a** was isolated in a satisfactory yield (60%) at the expense of the other photoproducts (Scheme 3). Furthermore, allylated derivatives **14** and **14a** were obtained in a poor yield in the presence of ATMS (0.5 M).

In water/acetonitrile (1:5) mixture, acetanilide **15** (67% yield) was the main product (accompanied by **5**) and the product distribution did not change with 1 M benzene (Scheme 2).

Photochemistry of 2-Chloro-5-methoxy-1,3-bis-trimethylsilylbenzene (2). Chloride **2** (0.025 M, a saturated solution)

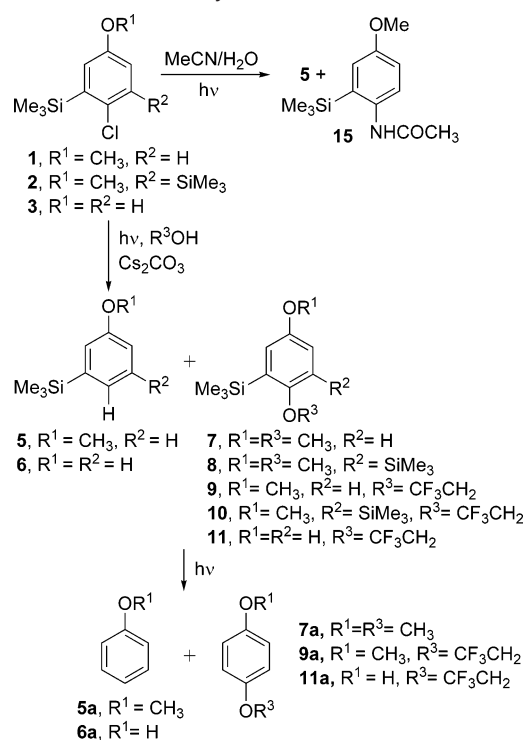
(8) Stang, P. J. In *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: New York, 1997; pp 451–460.
 (9) (a) Fagnoni, M.; Albini, A. *Acc. Chem. Res.* **2005**, *38*, 713–721. (b) Fagnoni, M. *Lett. Org. Chem.* **2006**, *3*, 253–259.
 (10) Dichiarante, V.; Dondi, D.; Protti, S.; Fagnoni, M.; Albini, A. *J. Am. Chem. Soc.* **2007**, *129*, 5605–5611.

(11) Manet, I.; Monti, S.; Fagnoni, M.; Protti, S.; Albini, A. *Chem.–Eur. J.* **2005**, *11*, 140–151.
 (12) Freccero, M.; Fagnoni, M.; Albini, A. *J. Am. Chem. Soc.* **2003**, *125*, 13182–13190.

Table 1. Photolysis of **1** (0.05 M) and **2** (0.025 M) in the Presence of Various Nucleophiles^a

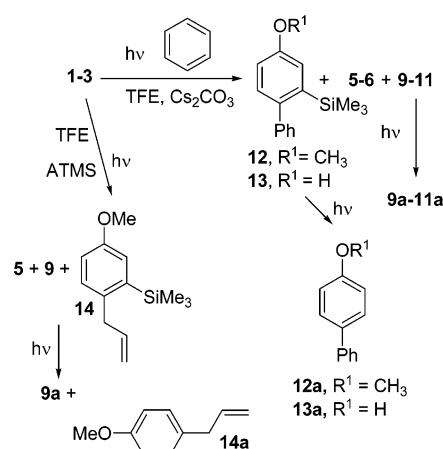
aryl chloride	solvent	nucleophile	t_{irr} , h (conversion, %)	products (yield %) ^b		
				reduced	substituted	arylated
1	MeOH	none	9 (78) 16 (100)	5 (19) 5 (28)	7 (48) 7 (55) 7a (15)	
1	MeOH	C ₆ H ₆ 1 M	6 (78) ^c	5 (20)	7 (46)	12a (10)
1	TFE	none	7 (100)	5 (23) 5a (18)	9a (44)	
1	TFE	C ₆ H ₆ 1 M	7 (100)	5a (3)	9a (25)	12a (60)
1	TFE	ATMS 0.5 M	12 (100)	5 (22)	9a (53)	14 (11) 14a (8)
1	H ₂ O/MeCN 1:5 ^d	none	23 (90)	5 (21)	15 (67)	
1	H ₂ O/MeCN 1:5 ^d	C ₆ H ₆ 1 M	20 (86)	5 (14)	15 (65)	
2	MeOH	none	16 (100)		8 (51)	
2	TFE	none	1 (100) ^c		9a (3.5) 10 (94) 9a (100)	
			8 (100)		10 (73)	
2	TFE	C ₆ H ₆ 1 M	1.5 (100)		9a (4)	
2	TFE	ATMS 0.5 M	2 (88) ^c		10 (75) 9a (38) 10 (23)	
			4 (100) ^c			

^a Cesium carbonate (0.025 M for **1** and 0.0125 M for **2**) added. ^b Yields were based on the initial amount of reagent and determined by GC. ^c Sample treated with Bu₄NF before analysis. ^d No base added.

Scheme 2. Irradiation of Aryl Halides **1–3** in Neat Solvents

was completely consumed within 5 h when irradiated in neat MeOH, and the disilylated derivative **8** was formed as the only isolated product in 51% yield (Table 1, Scheme 2). In TFE, irradiation caused likewise solvolysis of the chlorine atom and both **10** and **9a** were formed (**10** was completely converted to **9a** upon prolonged irradiation). Solvolysis to **10** remained the main process, in the presence of either 1 M benzene or ATMS with no competing C-arylation, and also in this case full desilylation occurred upon doubling the irradiation time from 2 to 4 h.

Photochemistry of 4-Chloro-3-trimethylsilylphenol (3). Photolysis of compound **3** in alcohols (Table 2) gave reduced

Scheme 3. Irradiation of Aryl Halides **1–3** in the Presence of π Nucleophiles

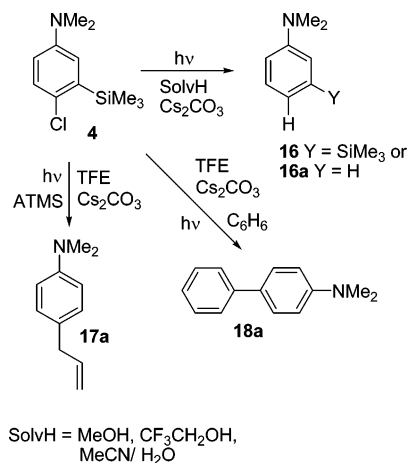
6 exclusively in MeOH and mainly ether **11a** in TFE. Biphenyl **13a** was a minor product (8% yield) in the presence of benzene, where at low conversion silylated **13** was also detected.

Photochemistry of (4-Chloro-3-trimethylsilylphenyl)-dimethylamine (4). Aniline **4** (Table 2) gave silylated aniline **16**, along with a small amount of **16a** in MeOH, with no change in the presence of benzene (Scheme 4). In TFE, **16** and **16a** were likewise formed, although in a lower yield, but in this solvent arylation took place to a small extent with benzene (**18a**) and in a good yield with ATMS (**17a**, 62%). Again, aniline **16** was the only product in MeCN/H₂O mixed solvents. Noteworthy, no solvolysis took place upon irradiation of aniline **4**, contrary to the case of anisoles and phenols **1–3**.

Steady State Measurements. The decomposition quantum yields (Φ_{-1}) of the silyl derivatives **1–4** (5×10^{-3} M) were determined by irradiation in MeOH and TFE at 254 nm. The results are gathered in Table 3. The Φ_{-1} values ranged from 0.1 to 0.3 in MeOH and 0.2 to 0.4 in TFE. The solvent effect on quantum yields was small, except that in the case of **1**, where the value in TFE was three times as much as that in MeOH. In Table 3, these values are compared to those measured for the

Table 2. Photolysis of **3** and **4** (0.05 M) in the Presence of Various Nucleophiles^a

aryl chloride	solvent	nucleophile	<i>t</i> _{irr} , h (conversion, %)	products (yield %) ^b		
				reduced	substituted	arylated
3	MeOH	none	4 (100)	6 (97)		
3	TFE	none	20 (100)	6 (13)	11a (52)	
				6a (9)		
3	TFE	C ₆ H ₆ 1 M	20 (100)	6 (9)	11a (38)	13a (8)
				6a (6)		
4	MeOH	none	1 (100)	16 (86)		
				16a (12)		
4	MeOH	C ₆ H ₆ 1 M	1.5 (100)	16 (87)		
				16a (6)		
4	TFE	none	1 (65)	16 (33)		
				16a (7)		
			3 (90)	16 (40)		
				16a (10)		
4	TFE	ATMS 0.5 M	6 (100)	16a (10)		17a (62)
4	TFE	C ₆ H ₆ 1 M	3 (100) ^c	16 (16)		18a (7)
				16a (32)		
4	H ₂ O/MeCN 1:5 ^d	none	18 (100)	16 (60)		

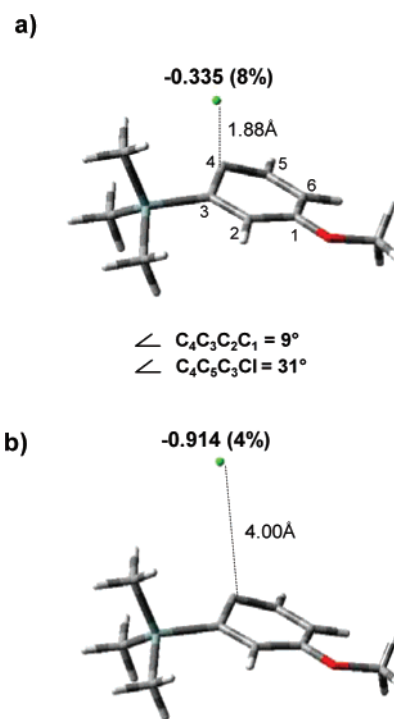
^{a–d} See Table 1.**Scheme 4.** Irradiation of Aniline **4****Table 3.** Quantum Yield of Photodecomposition (Φ_{-1}) of Phenyl Trimethylsilanes **1–4** in Alcohols

Ar–SiMe ₃	quantum yields (Φ_{-1}) ^a	
	MeOH	TFE
1	0.13 (0.1) ^b	0.43 (0.07) ^b
2	0.27 (0.1) ^b	0.29 (0.07) ^b
3	0.17 (0.66) ^c	0.20 (0.46) ^c
4	0.32 (0.95) ^d	0.30 (0.5) ^d

^a In parentheses, the quantum yield of the silicon-free analogue. ^b From ref 10. ^c This work. ^d From ref 13.

corresponding silicon-free aryl chlorides. The effect caused by introducing a silyl group was not uniform, with an enhancement with anisoles **1** and **2** and a marked decrease with chlorophenol **3** and aniline **4**.

Calculations. Further insight was sought by using DFT calculations, known from previous studies to be suitable for the generation and chemistry of phenyl cations.¹³ The geometries of the intermediates studied were optimized by using a B3LYP functional at the 6-311+G(2d,p) level (Supporting Information). Frequency calculations were performed at the same level of theory to check the minima. The solvent effect was evaluated

**Figure 1.** Geometries, Mulliken atomic charges, and spin density (in parentheses) on the Cl atom calculated in MeOH bulk at the CPCM-UB3LYP/6-311+G(2d,p)//UB3LYP/6-311+G(2d,p) level for (a) **31** (Ar–Cl bond: 1.88 Å) and (b) the same upon stretching the Ar–Cl bond up to 4.00 Å.

by carrying out single-point calculations on the optimized geometries in vacuo through the CPCM polarizable conductor calculation model¹⁴ by using methanol as solvent.

The properties of the triplet state of the precursor phenyl chlorides were examined for the case of **31** (in MeOH). Figure 1 shows the lowest-energy geometry of this state. As one may see, the Ar–Cl bond is virtually cleaved (1.88 Å), C₄ sticks out of the molecule plane (C₄–C₃–C₂–C₁ dihedral angle of 9°), and the C₄–Cl bond is further bent upward by an angle of 31° with the C₄–C₅–C₃ plane. This state cleaves heterolytically

(13) Guizzardi, B.; Mella, M.; Fagnoni, M.; Freccero, M.; Albini, A. *J. Org. Chem.* **2001**, 66, 6353–6363.(14) (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, 102, 1995–2001. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, 24, 669–681.

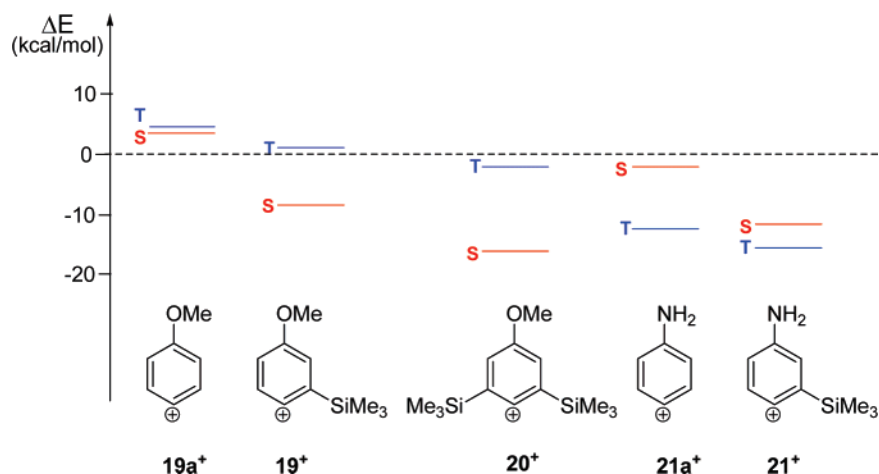
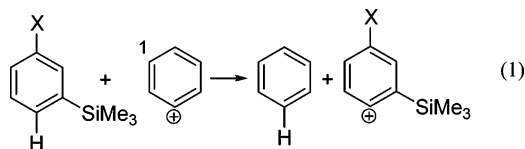


Figure 2. Relative energies of phenyl cations **19**–**21** by taking ${}^1\text{C}_6\text{H}_5^+ = 0$.

as indicated by the fact that, stretching the $\text{C}_4\text{--Cl}$ bond up to 4 Å, the chlorine atom acquired a full negative charge (−0.914) and only a 4% spin density.

The energy of the phenyl cations (**19**⁺–**21**⁺) was then calculated in MeOH for both the singlet and the triplet states. The isodesmic reaction in eq 1 was used to quantify the stabilization of the cation by both the *ortho*-TMS group and the para electron-donating group with respect to the parent singlet phenyl cation taken as the reference. The results are graphically shown in Figure 2, along with the data for the silicon-free cations (for details, see Supporting Information). It is apparent that the stabilization induced by the TMS group is dramatic and often larger than that exerted by the groups in para. It is noteworthy that the effect of the TMS is considerably greater for singlet than for triplet states. Thus, the 4-methoxyphenyl cation (**19a**⁺) is less stable than the parent cation in both the singlet and the triplet states, with the singlet slightly more stable. Introduction of a silyl group (cation **19**⁺) brings about a stabilization of 11.1 kcal/mol for the singlet and 4.3 kcal/mol for the triplet, so that the former is now by far (ca. 9 kcal/mol) the lowest state. A second TMS group as in the case of **20**⁺ further increases the singlet–triplet gap ($\Delta E_{\text{ST}} = -14.7$ kcal/mol), and **20**⁺ is stabilized by 17.1 kcal/mol with respect to ${}^1\text{C}_6\text{H}_5^+$. Analogously, with the aminophenyl cation **21**⁺,^{13,15} introduction of a silyl group stabilized the singlet with respect to **21a**⁺, although the triplet remained the lowest state. To summarize, each silyl group stabilized the triplet by 3–4 kcal/mol and the singlet by 9 kcal/mol.



Calculations on the Cation Reactivity. The same approach was used for predicting the reactivity of phenyl cations **19**⁺ and **21**⁺ with π nucleophiles, by calculating the potential energy surface (PES) for the reaction with ethylene (Figure 3).¹⁶ In the case of the triplets, a path leading to a distonic radical cation,

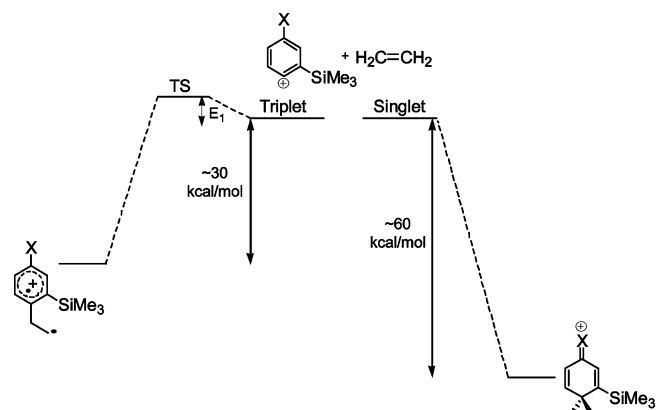


Figure 3. Stationary points on the PES for the addition of **319**⁺ (X = OMe) and **321**⁺ (X = NH₂) to ethylene.

about 30 kcal/mol below the reactants, was found for both **19**⁺ and **21**⁺ ($E_1 = 1.0$ and 2.0 kcal/mol, respectively), and a transition state was located on the PES. In the case of singlet cations, a strongly stabilized (60 kcal/mol) closed shell adduct cation (a phenonium ion) was formed through a barrierless process.

Discussion

Photogeneration of the Phenyl Cation. According to the literature, the effect of a TMS group on the photophysics of aromatics is varied.¹⁷ With polynuclear derivatives such as silylated naphthalenes,^{18a} pyrenes,^{18b} and anthracenes,^{18c} a marked enhancement of both fluorescence and phosphorescence quantum yield (proportional to the number of the silyl groups) was observed. However, in other cases (e.g., for porphyrin derivatives), both the fluorescence and phosphorescence quantum yield did not appreciably change.¹⁹ Closer to the compounds considered here, the photophysical parameters of trimethyl-*p*-tolylsilane did not significantly differ from those of toluene,

(15) 4-Amino-3-trimethylsilylphenyl cation was used as a model for 4-*N,N*-dimethylamino-3-trimethylsilylphenyl cation.
(16) Mella, M.; Coppo, P.; Guizzardi, B.; Fagnoni, M.; Freccero, M.; Albini, A. *J. Org. Chem.* **2001**, *66*, 6344–6352.

(17) For a review on organosilane photochemistry, see: Steinmetz, M. G. *Chem. Rev.* **1995**, *95*, 1527–1588.
(18) (a) Kyushin, S.; Ishikita, Y.; Matsumoto, H.; Horiuchi, H.; Hiratsuka, H. *Chem. Lett.* **2006**, 64–65. (b) Maeda, H.; Inoue, Y.; Ishida, H.; Mizuno, K. *Chem. Lett.* **2001**, 1224–1225. (c) Kyushin, S.; Ikarugi, M.; Goto, M.; Hiratsuka, H.; Matsumoto, H. *Organometallics* **1996**, *15*, 1067–1070.
(19) Horiuchi, H.; Tanaka, T.; Yoshimura, K.; Sato, K.; Kyushin, S.; Matsumoto, H.; Hiratsuka, H. *Chem. Lett.* **2006**, 662–663.

Table 4. Comparison of the Product Distribution between 4-Chloroanisole and Phenyl Chlorides **1**, **2**, and **4** upon Irradiation in Alcohols

aryl chloride	reduction/substitution		arylation/reduction + substitution	
	MeOH (neat)	TFE (neat)	TFE (benzene 1 M)	TFE (ATMS 0.5 M)
4-chloroanisole	78/22 ^a	73/27 ^a	92/8 ^a	93/7 ^a
1	29/71	48/52	68/32 (0/100) ^b	23/77
2	0/100	0/100	0/100	0/100
4	100/0	100/0	14/86	86/14

^a From ref 21. ^b In MeCN/water 5:1 as the solvent.

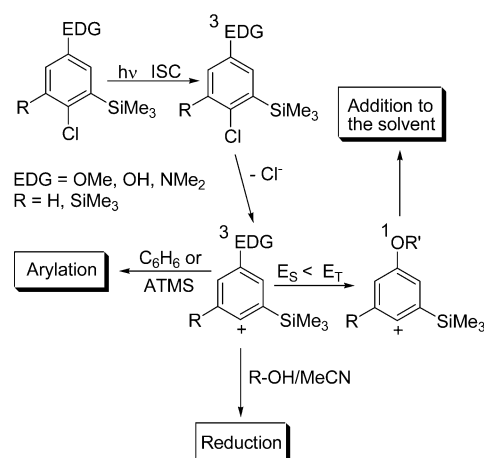
except for a slight red shift of the fluorescence and phosphorescence spectrum.²⁰

As a matter of fact, compounds **1–4** exhibited both fluorescence and phosphorescence similar to those of the corresponding silicon-free aromatic chlorides. It is reasonable to think that ISC is as efficient as with the parent phenyl chlorides ($\Phi_{ISC} \geq 0.7$) and their photoreaction ($\Phi_{-1} = 0.13$ to 0.43) in polar media proceeds from the triplet. Under these conditions, the process taking place is heterolytic fragmentation, as supported by DFT calculations in MeOH. This evidences that cleavage of **31** localizes the charge on the leaving Cl anion (Figure 1). It can be thus safely concluded that the phenyl cation is generated in the triplet state.

Although the silyl group affects the efficiency of the fragmentation, the process remain qualitatively the same, and any difference in the photoproduct distribution from phenyl halides **1–4** occurring upon introduction of TMS group(s) must be related to an effect on the cation rather than on the photochemical step. The main effect is on the energy of such an intermediate. The trimethylsilyl group stabilizes the singlet much more than the triplet (Figure 2) so that the former state is 9 and 17 kcal/mol below the latter in cations **19**⁺ and **20**⁺, respectively, whereas the triplet remains the lowest state with the aminophenyl cation **21**⁺, although the gap decreases.

Effect of the TMS Group on the Chemistry of Phenyl Cations. Previous evidence shows that the main fate of triplet phenyl cation is reduction either by H transfer from the solvent or by electron transfer from the starting aryl chloride, while the singlet adds nucleophilic solvents.^{9,13,16,21} The triplets are further distinguished by the selective attack to π nucleophiles. The effect of Si is apparent in Table 4, where the behavior of silylated and non-silylated phenyl chlorides is compared.

In the case of chloroanisole, where the singlet is slightly below the triplet, reduction predominates 3 to 1 over solvolysis. This can be attributed to the initial formation of the triplet **19a**⁺ that in part is reduced by reaction with the solvent and in part intersystem crosses to the singlet forming ethers by solvent addition.^{10,21} The sequential introduction of TMS groups makes solvolysis as important as reduction (with one group) and the sole process (with two groups), in accord with the fact that in silylated phenyl cations the singlet is strongly stabilized and the large exothermicity arguably increases the role of ISC.²²

Scheme 5. Overall Mechanism in the Irradiation of **1–4**

In parallel, the diagnostic triplet trapping by π nucleophiles is complete with chloroanisole, partial with **1** and insignificant with **2**.

With the silylated derivatives, trapping by π nucleophiles is intrinsically disfavored by the TMS group and **319**⁺ is in part reduced. Figure 3 shows that triplet addition to ethylene to form a diradical adduct that then evolves to the arylated product is viable for the silylated cation. However, in contrast to **319a**⁺ where the process is barrierless, a transition state was detected with **319**⁺ and **321**⁺ (1.0 and 2.0 kcal/mol, respectively). This can be reasonably attributed to the steric effect of the TMS group. Notice that addition to ethylene remains barrierless for the silylated singlets (Figure 3, right part), although, due to the unselective nature of these states, arylation via the singlet does not compete with solvolysis.

Some effect of the medium can be noticed. A more nucleophilic medium facilitates solvolysis both vs reduction (compare the experiments in neat alcohols, where solvolysis has a greater role in MeOH with respect to TFE) and vs arylation of benzene (see the results for **1** in MeCN–H₂O with respect to TFE, Table 4).

As hinted above, the picture does not apply to the irradiation of aniline **4**. Triplet cation **321**⁺ is stabilized by 3.5 kcal/mol with respect to the silicon-free cation, but this is not sufficient for reversing the order of the states. Triplet **321**⁺ remains the ground state cation, and reduction is the only path in neat solvents (Table 4). In the presence of a π nucleophile trapping occurs, inefficiently with benzene but in a good yield with ATMS. Apparently, steric hindrance by the TMS group inhibits the reaction at least with the former nucleophile (note the barrier in this process as shown in Figure 3).

The products distribution from 2-trimethylsilyl-4-hydroxyphenyl cation **22**⁺ was similar to that obtained from **20**⁺ in TFE, although the material balance was less satisfactory in the presence of π traps, while in MeOH reduction highly predominated. Deprotonation of **22**⁺ to yield a 4-oxocyclohexa-2,5-dienylidene carbene¹¹ might take place in this case, and part of the product might arise from that intermediate.

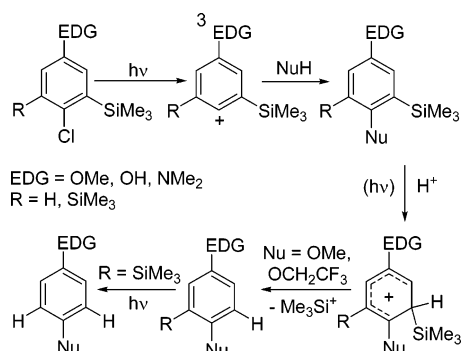
Summing up, the aryl-Cl cleavage in polar media is little affected and proceeds from the triplet as in the silicon-free analogues, thus giving the triplet phenyl cation (Scheme 5). The stabilization of the cation by the TMS group is much larger for the singlets, however. With the 4-methoxyphenyl cation, this makes the singlet by far the more stabilized state and the

(20) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 383–401.

(21) Protti, S.; Fagnoni, M.; Mella, M.; Albini, A. *J. Org. Chem.* **2004**, *69*, 3465–3473.

(22) Harvey's calculations²³ support that with phenyl cation the barrier to ISC is negligible when the process is strongly exothermic.

(23) Harvey, J. N.; Aschi, M.; Schwarz, H.; Koch, W. *Theor. Chem. Acc.* **1998**, *99*, 95–99.

Scheme 6. Photoinduced Protodesilylation of Substituted Phenyl Trimethylsilanes

chemical reactions involve that intermediate. With the 4-aminophenyl cation, the triplet remains the ground state and the chemistry observed arises from it.

Loss of the TMS Group. An important point is that, as shown in Tables 1 and 2, irradiation led to partial or complete desilylation concurrently with reaction at the chlorinated carbon. Elimination of the Me₃Si⁺ is due to a photoinduced protidesilylation process in analogy to the previously reported photodesilylation of 2-trimethylsilyl-1,3-dimethoxybenzene in 1,1,1,3,3,3-hexafluoroisopropanol.²⁴ This process is another manifestation of the β -silyl effect in the stabilization of the cyclohexadienyl cation (Scheme 6). Note that the protidesilylation took place also thermally, but only in more acidic media.²⁵

With the present compounds **1–4**, neither dechlorination nor desilylation was observed in blank experiments (quartz tubes covered with aluminum foil during the irradiation). However, if the base was omitted, the acidity (HCl) liberated upon photolysis caused a thermal desilylation. On the other hand, when there was irradiation in the presence of a buffering agent (e.g., cesium carbonate or even water), desilylation took place as a secondary *photochemical* process. The proportion of the desilylation depended on the group replacing the chlorine atom in the reaction. Thus, a trimethylsilyl group in *ortho* either to a methoxy or to a trifluoroethoxy group was rapidly lost, whereas with C-substituted (allyl, phenyl) desilylation was slower, and it was noteworthy that *ortho*-trimethylsilyl acetanilides were totally recalcitrant to (photo)desilylation.

Conclusions

The β -silicon effect individuated two decades ago as a tool for the thermal generation of phenyl cations due to the large stabilization of the singlet state is of general application. In particular, this has been extended to a series of 2-trimethylsilylphenyl cations bearing an electron-donating group in **4** that are photochemically generated from the corresponding phenyl chlorides and exhibit a dramatic stabilization of the singlet, much less of the triplet state. In the most clear-cut cases, this leads to interchange of the *reactive* spin state of the cation and substitution of the singlet chemistry (solvolysis, and thus O- or N-arylation) for the triplet chemistry (reduction or C-arylation). Since (photo)desilylation then occurs smoothly, one may think of the silyl group as a *directing, photoremovable* group (Scheme

6). As an example, introduction of a TMS group makes the preparation of phenyl ethers from phenyl chlorides easy, and under the same conditions the TMS group is removed.

Experimental Section

General Procedure for the Photochemical Reactions of 1–4. A solution of the starting chlorides **1–4** (0.025–0.05 M) and an equivalent amount of Cs₂CO₃ (when required) was placed in quartz tubes, flushed with nitrogen, and irradiated. The solvent was removed from the photolyzed solutions, and the residue was purified by column chromatography (cyclohexane/ethyl acetate mixtures as eluant). Trapping experiments were carried out by adding the selected nucleophile (0.5–1.0 M) to the initial mixture.

Irradiation of 1 in Methanol. A solution containing 322 mg (1.5 mmol, 0.05 M) of **1** and 244 mg (0.75 mmol, 0.025 M) of Cs₂CO₃ in 30 mL of MeOH was irradiated for 16 h. Purification by column chromatography (cyclohexane as the eluant) afforded 80 mg of **5** (colorless oil, 30% yield), 22 mg of dimethoxybenzene (**7a**, 11% yield), and 88 mg of (2,5-dimethoxyphenyl)trimethylsilane (**7**, colorless oil, 28% yield).

5: ¹H NMR (CDCl₃) δ : 0.35 (s, 9H), 3.90 (s, 3H), 6.90–6.95 (m, 1H), 7.10–7.20 (m, 2H), 7.30–7.40 (m, 1H); ¹³C NMR (CDCl₃) δ : –1.6 (CH₃), 54.6 (CH₃), 113.4 (CH), 118.5 (CH), 125.1 (CH), 128.5 (CH), 141.7, 158.5; IR (neat) ν /cm^{–1}: 838, 1046, 1228, 1247, 1409, 1570, 2955; MS (*m/z*): 180 (M⁺, 20), 165 (100), 135 (25), 121 (5), 107 (5), 91 (10), 77 (5), 51 (2), 43 (5); Anal. Calcd for C₁₀H₁₆O₂Si: C, 66.61; H, 8.94. Found: C, 66.7; H, 8.8.

7: ¹H NMR (CD₃COCD₃)²⁶ δ : 0.25 (s, 9H), 4.75 (s, 3H), 4.80 (s, 3H), 6.80–6.95 (m, 3H); ¹³C NMR (CD₃COCD₃) δ : –0.7 (CH₃), 56.2 (CH₃), 56.4 (CH₃), 112.0 (CH), 116.0 (CH), 122.0 (CH), 129.8, 155.0, 159.9; IR (neat) ν /cm^{–1}: 837, 1221, 1480, 2953, 3421; Anal. Calcd for C₁₁H₁₈O₂Si: C, 62.81; H, 8.63. Found: C, 62.9; H, 8.5.

Irradiation of 1 in TFE in the Presence of ATMS. Quantities of 322 mg (1.5 mmol, 0.05 M) of **1**, 244 mg (0.75 mmol, 0.025 M) of Cs₂CO₃, and 2.4 mL (15 mmol, 0.5 M) of ATMS in 30 mL of TFE were irradiated for 7 h. Purification by column chromatography (neat cyclohexane) afforded 14 mg of **5** (colorless oil, 6% yield) and a mixture of 20 mg of 2-allyl-5-methoxyphenyltrimethylsilane (**14**, 7% yield) and 30 mg of **14a** (16%).

14: ¹H NMR (CDCl₃, from the mixture) δ : 0.35 (s, 9H), 3.50 (d, 2H, *J* = 6.3 Hz), 3.80 (s, 3H), 5.00–5.15 (m, 2H), 5.90–6.05 (m, 1H), 6.80–6.85 (m, 2H), 7.05 (d, 1H, *J* = 2.9 Hz); ¹³C NMR (CDCl₃, from the mixture) δ : 0.1 (CH₃), 39.1 (CH₂), 55.0 (CH₃), 113.4, 115.5 (CH₂), 120.3 (CH), 125.4, 130.2 (CH), 132.0 (CH), 138.2 (CH), 157.0; IR (from the mixture) ν /cm^{–1}: 837, 989, 1245, 1512, 1610, 2951.

Spectroscopic data of compound **14a** in accordance with the literature.²⁷

Irradiation of 1 in MeCN/Water 5:1. A quantity of 322 mg (1.5 mmol, 0.05 M) of **1** in 30 mL of MeCN/water 5:1 was irradiated for 23 h (90% of **1** consumption). Purification by column chromatography (cyclohexane/ethyl acetate from 99:1 to 7:3 as the eluant) afforded 57 mg of **5** and 238 mg of 2-trimethylsilyl-4-methoxyacetanilide (**15**, colorless oil, 67% yield based on consumed **1**).

15: ¹H NMR (DMSO-*d*₆) δ : 0.25 (s, 9H), 2.00 (s, 3H), 3.80 (s, 3H), 6.90–7.05 (m, 3H), 9.10 (bs, 1H); ¹³C NMR (DMSO-*d*₆) δ : –0.7 (CH₃), 22.9 (CH₃), 55.1 (CH₃), 114.5 (CH), 119.6 (CH), 129.9 (CH), 135.2, 138.6, 157.0, 169.2; IR (neat) ν /cm^{–1}: 838, 1041, 1475, 1651, 2930, 3226; Anal. Calcd for C₁₂H₁₉NO₂Si: C, 60.72; H, 8.07. Found: C, 61.0; H, 7.6.

Irradiation of 2 in Methanol. A quantity of 216 mg (0.75 mmol, 0.025 M) of **2** in 30 mL of MeOH was irradiated for 5 h. Purification

(24) Lew, C. S. Q.; McClennan, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 11516–11520.

(25) Benkens, R. A.; Krysiak, H. R. *J. Am. Chem. Soc.* **1953**, *75*, 4528–4531.

(26) Crowther, G. P.; Sundberg, R. J.; Sarpeshkar, A. M. *J. Org. Chem.* **1984**, *49*, 4657–4663.

(27) Gomes, P.; Gosmini, C.; Périchon, J. *Org. Lett.* **2003**, *5*, 1043–1045.

by column chromatography (neat cyclohexane as the eluant) yielded 78 mg of 2,5-dimethoxy-1,3-bis(trimethylsilyl)benzene (**8**, colorless oil, 37% yield).

8: ^1H NMR (CDCl_3) δ : 0.35 (s, 18H), 3.70 (s, 3H), 3.85 (s, 3H), 7.00 (s, 2H); ^{13}C NMR (CDCl_3) δ : -0.0 (CH_3), 55.4 (CH_3), 63.6 (CH_3), 121.7 (CH), 132.9, 154.8, 164.9; IR (neat) ν/cm^{-1} : 837, 1207, 1247, 1379, 1577, 2953; Anal. Calcd for $\text{C}_{14}\text{H}_{26}\text{O}_2\text{Si}_2$: C, 59.52; H, 9.28. Found: C, 59.6; H, 9.1.

Irradiation of 2 in TFE in the Presence of Benzene. Quantities of 216 mg (0.75 mmol, 0.025 M) of **2**, 122 mg (0.375 mmol, 0.0125 M) of Cs_2CO_3 , and 3 mL (30 mmol, 1 M) of benzene in 30 mL of TFE were irradiated for 2.5 h. Purification by column chromatography (cyclohexane as the eluant) afforded 192 mg of 2-(2,2,2-trifluoroethoxy)-5-methoxy-1,3-bis(trimethylsilyl)benzene (**10**, colorless oil, 73% yield).

10: ^1H NMR (CD_3COCD_3) δ : 0.40 (s, 18H), 3.80 (s, 3H), 4.30 (q, 2H, $J = 8.6$ Hz), 7.05 (s, 2H); ^{13}C NMR (CD_3COCD_3) δ : 0.4 (CH_3), 56.0 (CH_3), 73.0 (CH_2 , q, $J = 33$ Hz), 123.5 (CH), 124.9 (CF_3 , q, $J = 276$ Hz), 134.2, 157.3, 162.4; IR (neat) ν/cm^{-1} : 839, 1073, 1163, 1280, 1381, 1576, 2955; Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{F}_3\text{O}_2\text{Si}_2$: C, 51.40; H, 7.19. Found: C, 51.5; H, 7.1.

Irradiation of 3 in TFE. Quantities of 300 mg (1.5 mmol, 0.05 M) of **3** and 244 mg (0.75 mmol, 0.025 M) of Cs_2CO_3 in 30 mL of TFE were irradiated for 18 h. Purification by column chromatography (cyclohexane/ethyl acetate 95:5 as the eluant) yielded 108 mg of **11a** (pale yellow oil, 38% yield).

11a: ^1H NMR (CDCl_3)²⁸ δ : 4.30 (q, 2H, $J = 8.2$ Hz), 5.10 (bs, 1H), 6.75–6.90 (m, 4H); ^{13}C NMR (CDCl_3) δ : 66.5 (CH_2 , q, $J = 35$

Hz), 115.7 (CH), 116.1 (CH), 122.9 (CF_3 , q, $J = 276$ Hz), 150.5, 151.0; IR (neat) ν/cm^{-1} : 1076, 1163, 1512, 1666, 3332; m/z (%): 192 [M^+] (100), 109 (80), 81 (55), 63 (5), 53 (15); Anal. Calcd for $\text{C}_8\text{H}_7\text{F}_3\text{O}_2$: C, 50.01; H, 3.67. Found: C, 50.2; H, 3.65.

Irradiation of 4 in TFE in the Presence of ATMS. Quantities of 342 mg of **4** (1.5 mmol, 0.05 M), 2.4 mL of ATMS (15 mmol, 0.5 M), and 244 mg (0.75 mmol, 0.025 M) of Cs_2CO_3 in 30 mL of TFE were irradiated for 6 h. Purification by column chromatography (cyclohexane/ethyl acetate 99:1 as the eluant) afforded 150 mg of **17a** (colorless oil, 62% yield). Spectroscopic data of compound **17a** in accordance with literature data.^{6b} MS (m/z): 161 (M^+ , 100), 160 (85), 145 (11), 134 (39), 117 (23), 91 (12).

Acknowledgment. Partial support of this work by MIUR, Rome, is gratefully acknowledged. We acknowledge Consorzio Interuniversitario Lombardo per l'Elaborazione Automatica (CILEA) for the free access to their supercomputer facilities.

Supporting Information Available: Details of the preparation of compounds **1–4**, **6**, **16**; NMR spectra of compounds **1–8**, **10**, **11a**, **15**, **16**; and details of the calculations on intermediates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA074778X

(28) Endo, Y.; Shudo, K.; Okamoto, T. *J. Am. Chem. Soc.* **1982**, *104*, 6393–6397.