

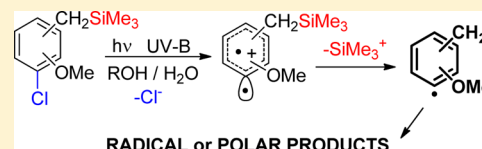
Methoxy-Substituted α,n -Didehydrotoluenes. Photochemical Generation and Polar vs Diradical Reactivity

Carlotta Raviola, Davide Ravelli, Stefano Protti, and Maurizio Fagnoni*

Photogreen Lab, Department of Chemistry, University of Pavia, V. Le Taramelli 12, 27100 Pavia, Italy

S Supporting Information

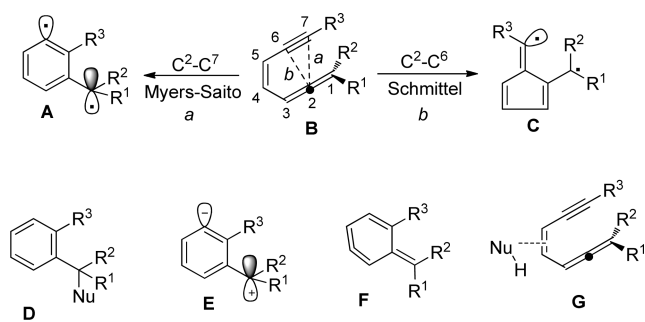
ABSTRACT: The photoreactivity of differently substituted (chloromethoxybenzyl)trimethylsilanes in alcohols and alcohol/water mixtures has been investigated by means of a combined computational and experimental approach. Subsequent elimination of the chloride anion and the trimethylsilyl cation gives the corresponding methoxy-substituted α,n -didehydrotoluenes (α,n -MeO-DHTs). The rate of desilylation is evaluated through the competition with arylation via phenyl cation (ca. 10^8 s⁻¹). $\alpha,2$ -MeO- and $\alpha,4$ -MeO-DHTs show a purely radical behavior (H abstraction from the solvent, methanol), while $\alpha,3$ -MeO-DHT shows mainly a ionic chemistry, as when the parent $\alpha,3$ -DHT is thermally generated. This is likely due to triplet–singlet surfaces crossing occurring during desilylation.



INTRODUCTION

$\alpha,3$ -Didehydrotoluenes (**A**) have been the subject of intense attention in recent years, in particular due to their potential application in medicine as antitumor agents,¹ as well as to the involved mechanistic issues. These diradicals have been generated by a cycloaromatization process (the Myers–Saito reaction)² starting from an enyne–allene (**B**; Scheme 1, path

Scheme 1. Thermal Route to $\alpha,3$ -Didehydrotoluenes from Enyne–Allenes via the Myers–Saito Reaction (Path a) and the Competing Schmittel Cyclization (Path b) and Proposed Intermediates (E–G) Invoked in the Formation of Products D



a).³ The parent $\alpha,3$ -didehydrotoluene ($R^1 = R^2 = R^3 = H$) as well as a few derivatives having substituents in position 1 (that become the α -substituents in the product; Scheme 1) or on the 3–5-positions (that become the aromatic substituents) have been generated.⁴

The mechanistic debate results from the fact that the main products from $\alpha,3$ -didehydrotoluene (**A**) arise from ionic addition to give **D**, not from radical reactions (minor path). Various mechanisms were considered for rationalizing this unexpected behavior. A resonance structure between an open-shell diradical (**A**) and a closed-shell zwitterion (**E**) was

rejected by Carpenter, since the mixing of these two electronic structures is symmetry forbidden in this heterosymmetric diradical.⁵ He further considered a closed-shell cyclic allene (**F**) fairly close in enthalpy to the open-shell singlet $\alpha,3$ -diradical, but this was also discarded because of the failed trapping and its involvement was not supported by theoretical calculations. Direct nucleophile assistance during cyclization (see formula **G**) was likewise incompatible with experiments. Recently, Carpenter suggested the occurrence of a nonadiabatic surface crossing from the ground state to the first excited-state singlet surface (that has a zwitterionic character) during the cycloaromatization process as responsible for the formation of such “ionic addition” products.⁶

An in-depth examination of these diradicals and their chemistry thus seemed advisable.^{4,7} However, it has proven difficult to change systematically the range of didehydrotoluenes (**A**) available from enyne–allenes (**B**) via the Myers–Saito reaction, because some of the substituents introduced in **B** completely suppressed the rearrangement³ and other compounds underwent a different rearrangement, the Schmittel cyclization to give **C** (Scheme 1, path b).⁸ At any rate, a major stumbling block is that this cycloaromatization gives access exclusively to the $\alpha,3$ - but not to the $\alpha,2$ - and $\alpha,4$ -didehydrotoluene isomers. This situation obviously called for an alternative approach.

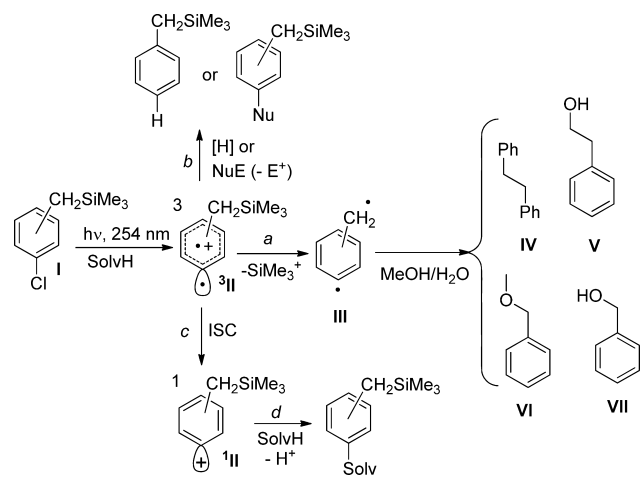
Indeed, the above limitations can be overcome by using an alternative path, as recently found in our laboratory, which involves the elimination of two substituting groups in a one-photon-induced process from an aromatic precursor. Thus, irradiation of (*n*-chlorobenzyl)trimethylsilanes (**I**) in protic media causes the photoheterolytic cleavage of the Ar–Cl bond from the triplet state and the formation of a triplet phenyl cation (³**II**). The desired α,n -DHT isomers (**III**, $n = 2–4$) are

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obtained by detachment of the electrofugal group (Me_3Si^+ , Scheme 2, path a).⁹

Scheme 2. Generation of α,n -DHTs Starting from (*n*-Chlorobenzyl)trimethylsilanes via Phenyl Cations



The three isomeric parent α,n -DHTs formed in this way gave a different distribution of products. In aqueous methanol, $\alpha,4$ - and $\alpha,2$ -DHT diradicals showed primarily a radical reactivity, with hydrogen abstraction to yield radicals that then coupled (to form bibenzyl IV and phenethyl alcohol V). On the other hand, a “polar” solvent addition (to give benzyl ether VI and benzyl alcohol VII in aqueous methanol) was the main process observed with the $\alpha,3$ -DHT isomer, consistent with the results from thermal generation.²

This finding was appealing, because the introduction of substituents in aromatic compounds is facile, and this suggests that a large-scope variation (and, in principle, a tuning) of the properties of these intermediates is possible in this way. Notice, however, that this requires that the two groups are eliminated as indicated in Scheme 2. In fact, in contrast to the Myers–Saito cyclization where the two radical sites are formed simultaneously in a single process, the photochemical generation involves two subsequent processes, and elimination of the Me_3Si^+ group has to be fast enough to overcome competitive pathways at the triplet phenyl cation (^3II) level. Apart from trapping by π -bond nucleophiles (NuE) when present, accessible paths include hydrogen abstraction from the solvent (path b) and, most importantly, intersystem crossing (ISC) to the singlet phenyl cation (^1II), a fast process (followed by solvent addition) when this is more stable than the triplet (Scheme 2, paths c and d).^{10,11}

Conditions for a convenient generation of DHTs thus are that (i) heterolysis of the Ar–Cl bond via triplet $^3\text{Ar-Cl}$ is efficient and (ii) no competitive processes from the triplet phenyl cation occur. As mentioned above, these include hydrogen abstraction from the solvent, which depends on the intrinsic reactivity of the cation, and ISC to the singlet, which is avoided if the ground state of the phenyl cation is a triplet. As for the first condition, previous work has demonstrated that photoheterolytic cleavage is a quite general process and occurs with all chlorobenzene derivatives bearing an (even weakly) electron-donating substituent, such as the trimethylsilylmethyl group above.⁹ The second condition requires a detailed examination of each case. A further bonus is that the introduction of an additional electron-donating group on the

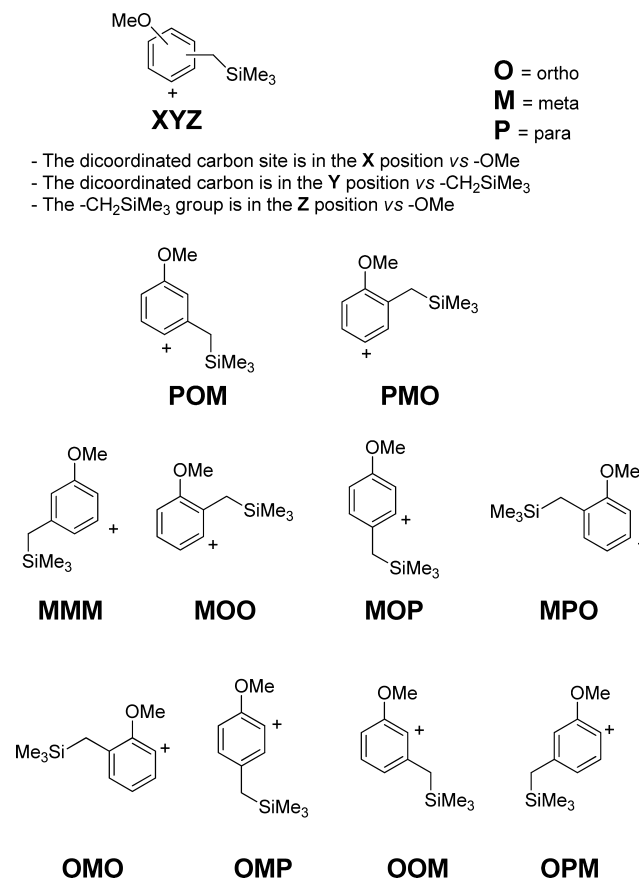
aromatic ring is expected to induce a red shift in the absorption of the (chlorobenzyl)trimethylsilanes, allowing the adoption of a longer irradiation wavelength, thus avoiding 254 nm and its carcinogenic effects.

We report below an investigation of the photochemistry of methoxy-substituted (chlorobenzyl)trimethylsilanes, as a first attempt to evaluate the significance of this approach to DHTs. In recent years, we have demonstrated that chloroanisoles are excellent photochemical precursors of aryl cations.^{10–12} However, the position of the methoxy group with respect to the halogen greatly affects the energy of the resulting phenyl cation and it is not obvious whether the triplet or the singlet will be the lowest state.¹¹ Thus, introducing a donating group is not per se a guarantee that a DHT will be formed efficiently.

RESULTS

Choice of the Model Compounds. Ten isomeric methoxy(trimethylsilylmethyl)phenyl cations are possible (see Chart 1). The choice of the model compounds for the

Chart 1. Isomeric Methoxy(trimethylsilylmethyl)phenyl Cations



experimental investigation was made on the basis of a computational study, by determining which of the corresponding phenyl cations has a triplet ground state. The complete active space self-consistent field (CASSCF) method, a multiconfigurational approach that has previously been demonstrated to handle and describe properly the electronic structure of such intermediates, was adopted.^{13c} The resulting energy values were then refined to take into account the solvent effect (adopting the C-PCM model) and the dynamic electron

correlation term (MP2 theory). A detailed description of the theoretical approach is available in the Supporting Information. Briefly, the computational study on phenyl cations was carried out at the CASSCF (8,9)/6-31g(d) level of theory, with the three π and the three π^* orbitals of the aromatic ring, the σ/σ^* pair of the C_{α} -Si bond, and the orbital at the dicoordinated carbon included in the active space. The role of the lone pair on the oxygen atom was initially considered by adopting larger active spaces, but it was found that its contribution was negligible, while heavily affecting the computational cost. We thus decided not to include it in the active space.

The results are reported in Figure 1, in which the relative stabilities of the triplet and singlet phenyl cations of Chart 1 are shown and compared with those of the related monosubstituted phenyl cations.

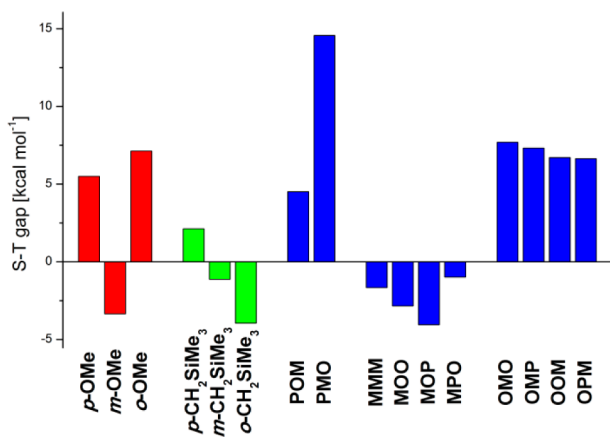


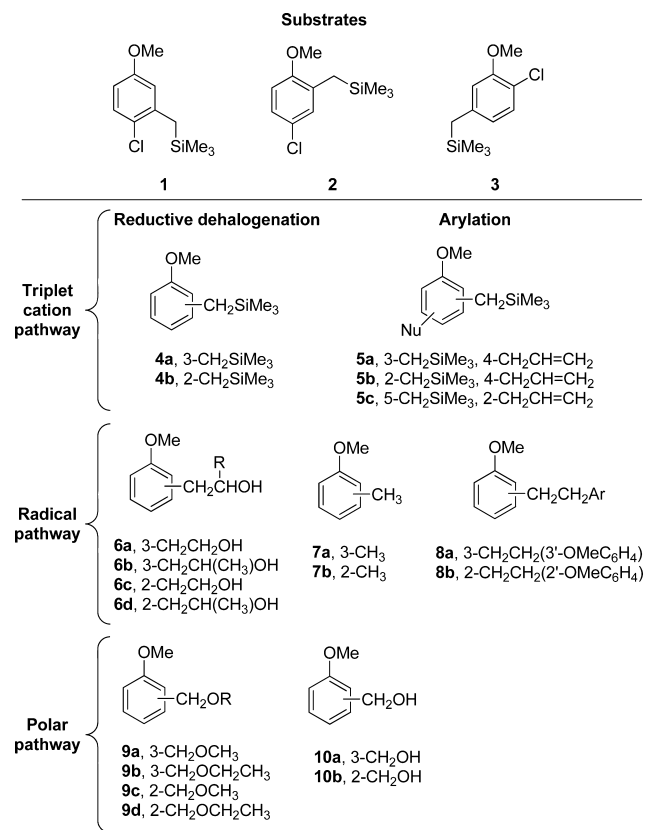
Figure 1. Singlet–triplet (S-T) gaps for the monosubstituted (red, green) and disubstituted (blue) phenyl cations studied. A positive bar indicates a triplet ground-state cation.

It is apparent that intermediates bearing the dicoordinated carbon in the meta position with respect to the methoxy group (indicated by an M as the first character of the abbreviations used in Figure 1 and in Chart 1) have a singlet ground state, independent of the position of the $-CH_2SiMe_3$ group with respect to the dicoordinated carbon (second character) and also independent of the position of the methoxy group with respect to the trimethylsilylmethyl group (third character). Likewise, the monosubstituted *m*-methoxyphenyl cation also has a singlet ground state.

These derivatives were thus not experimentally studied. The other cations all had a triplet ground state. Among these, the two isomers having the dicoordinated carbon para to the methoxy group (POM and PMO) were selected, also because we previously demonstrated^{10–12} that *p*-chloroanisoles were the best precursors for triplet phenyl cations, as well as OPM, the only potential precursor of an $\alpha,4$ -DHT.⁹ Accordingly, (2-chloro-5-methoxybenzyl)trimethylsilane (**1**), (5-chloro-2-methoxybenzyl)trimethylsilane (**2**), and (4-chloro-3-methoxybenzyl)trimethylsilane (**3**; see Chart 2, top), the putative precursors of the above phenyl cations, were synthesized and tested in the present work.

Experimental Study. Substrates **1–3** were prepared from the corresponding benzyl chlorides through the coupling of the corresponding Grignard reagents with trimethylsilyl chloride (TMSCl; see the Supporting Information for further details). The UV absorption spectra of **1–3** showed an absorption

Chart 2. Substrates 1–3 (Top) and the Products Considered in This Work (Bottom), Classified According to the Pathway Involved in Their Formation



maximum around 285–290 nm with a clear vibronic structure attributed to a nonpolar $\pi-\pi^*$ transition (with a slight blue shift observed for compound **3**; see Figure S1 in the Supporting Information).^{10,13} Thus, 310 nm lamps were convenient for the photolysis experiments (rather than the 254 nm lamp used for the unsubstituted chlorobenzylsilanes). Compounds **1–3** were all weakly fluorescent ($\Phi_F < 0.05$ in all of the solvents tested). Irradiation of **1–3** (0.025 M) was carried out in neat alcohols (MeOH, EtOH) and alcohol/water mixtures (MeOH/H₂O, 4/1 v/v; EtOH/H₂O, 2/1 v/v) by using a multilamp reactor equipped with 10 Hg phosphor-coated lamps (λ_{em} centered at 310 nm).

In order to acquire further insight, the reactions were also carried out in the presence of a π -bond nucleophile (allyltrimethylsilane, ATMS). As previously reported,^{10–12,14} ATMS is capable of trapping triplet phenyl cations to give allylated derivatives **5a–c** upon Me_3Si^+ loss from the phenonium ion intermediate.^{10–12,14} The competition between the addition to ATMS and the desilylation from the phenyl cation will give insight into the rate of formation of DHTs. The measured disappearance quantum yield (Φ_{-1}) of compounds **1** and **2** in methanol was around 0.5, significantly higher than that of the parent 4-chloroanisole,¹¹ while Φ_{-1} for compound **3** was comparable (0.05) to that of the corresponding 2-chloroanisole (see Table 1).¹⁰

The photoproducts can be grouped in two different classes as shown in Chart 2 (bottom):

- silyl-containing products, viz. those resulting from the reductive dehalogenation (products **4**) and from arylation (in the presence of ATMS, products **5**).

Table 1. Irradiation of 1–3 in Neat Solvent and in the Presence of Allyltrimethylsilane (ATMS)^a

halide	solvent	conversion (%)	cation product	yield (%)			DHT/cation ^c	polar/radical
				DHT product				
				diradical	polar			
1, $\Phi_{-1} = 0.41^b$	MeOH	100	4a, 18	6a, 15; 7a, 2; 8a, 4		1.17	0	
	MeOH/H ₂ O 4/1	90	4a, 21	6a, 7; 7a, 3; 8a, 2		0.57	0	
	EtOH	100	4a, 24	6b, 12; 7a, 4; 8a, 1		0.71	0	
	EtOH/H ₂ O 2/1	100	4a, 20	6b, 12; 7a, 7; 8a, 3		1.10	0	
	MeOH, 0.2 M ATMS	100	4a, 13; 5a, 16	8a, 1		0.03	0	
	MeOH, 1 M ATMS	100	4a, 9; 5a, 24			0		
2, $\Phi_{-1} = 0.55^b$	MeOH	100	4b, 6	6c, 8; 7b, 3; 8b, 5	9c, 18	5.67	1.13	
	MeOH/H ₂ O 4/1	100	4b, 17	7b, 4; 8b, 5	9c, 18	1.59	2.00	
	EtOH	100	4b, 7	6d, 18; 7b, 4; 8b, 7	9d, 4	4.71	0.14	
	EtOH/H ₂ O 2/1	100	4b, 17	6d, 24; 7b, 6; 8b, 6	9d, 5; 10b, 6	2.76	0.31	
	MeOH, 0.2 M ATMS	100	4b, 4; 5b, 7 ^d	6c, 4; 7b, 1; 8b, <1	9c, 9	1.27	1.80	
	EtOH, 0.2 M ATMS	100	4b, 6; 5b, 7	6d, 7; 7b, 4; 8b, 4	9d, 3	1.38	0.20	
3, $\Phi_{-1} = 0.05^b$	EtOH, 1 M ATMS	100	4b, 5; 5b, 17	6d, 1; 7b, 3; 8b, <1		0.18	0	
	MeOH	80	4a, 67	8a, <1		0		
	MeOH/H ₂ O 4/1	26	4a, 91			0		
	EtOH	100	4a, 53	7a, 2		0.04	0	
	EtOH/H ₂ O 2/1	54	4a, 66	6b, 20; 7a, 7		0.41	0	
	MeOH, 0.2 M ATMS	72	4a, 67			0		

^aConditions: 0.025 M solution of 1–3 (in the presence of ATMS where indicated) in the chosen solvent irradiated at 310 nm. $t_{\text{irr}} = 2\text{--}8$ h (see Supporting Information for further details). Yields were based on consumed 1–3 and determined by GC analysis. ^bQuantum yields of disappearance (Φ_{-1}) of 1–3 (10^{-2} M in MeOH) were measured at 254 nm. ^cRatio between DHT vs phenyl cation derived products. ^dA partial secondary desilylation of 5 to the corresponding 4-(2-propenyl)-1-methoxy-2-methylbenzene was observed (see the Supporting Information for details).

- silicon-free products, arising either via benzyl radicals (products 6–8) or via polar addition (9 and 10) from an *o,n*-MeO-DHT diradical intermediate.

The product distributions obtained in the irradiation experiments under conditions where the substrate was fully consumed (less than 4 h in neat alcohol, 2 h in alcohol–water for 1 and 2, much longer for 3; see the Supporting Information for details) are gathered in Table 1. Thus, irradiation of 1 in both methanol and ethanol yielded a mixture of (3-methoxybenzyl)trimethylsilane (4a) and of the corresponding phenethyl alcohols 6a,b along with a minor amount (<10% overall yield) of 3-methylanisole (7a) and of 1,2-diarylethane 8a. The addition of water to the mixture had a limited effect. Neither benzyl ethers 9a,b nor benzyl alcohol 10a was observed. On the other hand, in the presence of ATMS (0.2 M) the formation of 6–8 was almost completely suppressed, and allylarene 5a became the main product (with a yield increasing with the ATMS concentration), along with some 4a.

Compound 2 was found to react efficiently regardless of the solvent used. In contrast to compound 1, polar products such as benzyl ethers 9c,d and benzyl alcohol 10b were formed in variable amounts and were the main products in MeOH-containing media (Table 1). Diradical products were mainly formed in ethanol with a limited effect of the presence of water. Trapping with ATMS gave the corresponding allylanisole 5b, but small amounts of DHT-derived products were obtained even when using 1 M ATMS.

Isomer 3 reacted much less efficiently, and the presence of water further slowed down the conversion. Dechlorination of 3 to 4a was the only observed pathway, in the presence of ATMS as well. Of the silicon-free products, only 6b was obtained in a significant yield (20%) in EtOH/H₂O, along with a minor amount of 3-methylanisole (7a).

Mechanism. A rationalization to the product distribution obtained was sought for by computational methods. Thus, the nature of the excited states involved in the photochemistry of compounds 1–3, as well as the structure of the intermediates formed along the competing paths, was examined. The study of the ground state (S_0) and the lowest lying singlet and triplet excited states (S_1 and T_1 , respectively) clearly demonstrated that heterolytic C–Cl cleavage was feasible exclusively from the T_1 state. Since these results essentially duplicate conclusions from our previous work on simpler derivatives,^{9c} details are reported in the Supporting Information only (see section 2.2).

The phenyl cation intermediates formed by dechlorination of 1–3 from the triplet state were then examined. The aromatic rings in triplets ($^3\mathbf{11}^+ \text{--} ^3\mathbf{13}^+$) are planar with a geometry close to that of a regular hexagon.

More varied is the situation of the singlet phenyl cations, which were also studied for the sake of comparison. Thus, in $^1\mathbf{11}^+$ and $^1\mathbf{13}^+$ a marked puckering of the ring and an out-of-plane displacement of the dicoordinated carbon are evident, while in $^1\mathbf{12}^+$ the dicoordinated carbon remains in the plane and a (limited) distortion involves the adjacent carbon atoms (Figure 2).¹⁵

As for the electronic structure, $^3\mathbf{11}^+ \text{--} ^3\mathbf{13}^+$ can be described to a good approximation by a single configuration (the coefficient of the lowest eigenvector is >0.94 in every case). Accordingly, the localization of the two unpaired electrons is easily determined, as shown in Figure 3: viz., one of the SOMOs is located at the dicoordinated carbon, while the second is part of the π cloud, making $^3\mathbf{11}^+ \text{--} ^3\mathbf{13}^+$ straightforward examples of the typical radical/radical-cation character of triplet phenyl cations. A detailed description of the electronic structure of the corresponding singlet phenyl cations has been included in the Supporting Information (see section 2.3 for details).

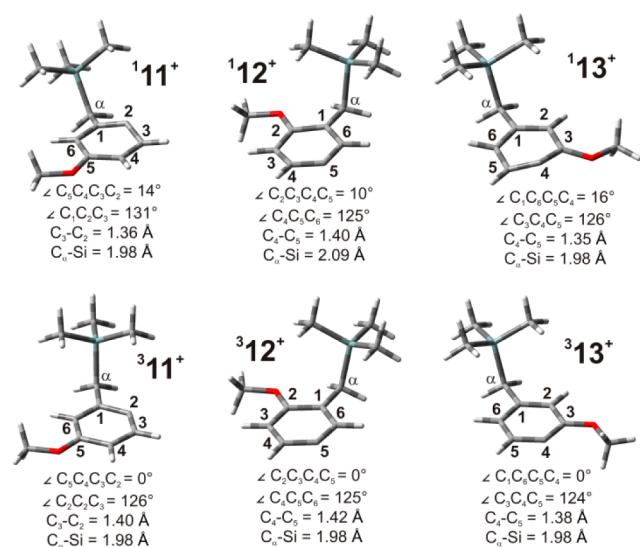


Figure 2. Optimized geometries at the CASSCF/6-31G(d) level and relevant parameters calculated for phenyl cations 11^+ – 13^+ .

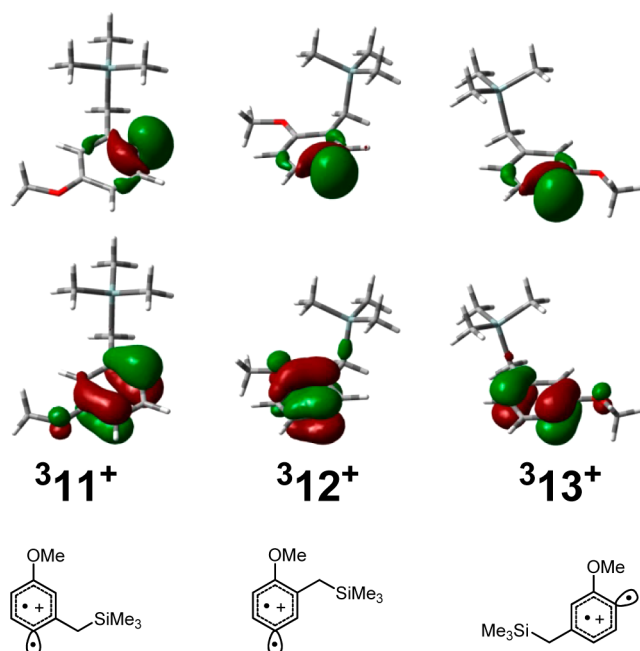


Figure 3. Singly occupied molecular orbitals (SOMOs) for triplet phenyl cations 311^+ – 313^+ as determined from CASSCF/6-31G(d) calculations.

The stabilization imparted by the methoxy group to phenyl cations 11^+ – 13^+ was quantified by using the isodesmic equation reported in Table 2 with the corresponding Me_3SiCH_2 -substituted phenyl cations as a reference. The results show that the stabilization by the methoxy group depends on the position on the ring and is much larger for triplets than for the corresponding singlets, particularly with 12^+ .

The likelihood of the detachment of the Me_3Si^+ group from cations 11^+ – 13^+ to form diradicals 14 – 16 was then evaluated by a relaxed PES (potential energy surface) scan: viz., by stretching the C_α – Si bond from the equilibrium geometry up to $\sim 3 \text{ \AA}$ by 0.1 \AA intervals (see section 2.8 in the Supporting Information for details). It is worth noting (see Figure 2) that

Table 2. Gibbs Free Energy (ΔG_{CASMP2} ; See Eq S1 in the Supporting Information) Changes for Phenyl Cations 11^+ – 13^+ According to the Isodesmic Equation Below, Calculated at the CASMP2/6-31G(d) Level of Theory in Bulk Methanol

species	ΔG_{CASMP2} (kcal mol ⁻¹)	
	$^1Ar^+$	$^3Ar^+$
11^+	–10.46	–18.93
12^+	–5.68	–21.39
13^+	–10.68	–15.19

the length of the C_α – Si bond at the equilibrium geometry in 12^+ (2.09 \AA) is in any case larger (by about 0.1 \AA) than in isomeric $1,311^+$, 312^+ , and $1,313^+$ (1.98 \AA). As shown in Figure 4, desilylation of 12^+ confronts the lowest energy barrier (around 16 kcal mol⁻¹), while for the other cations the barrier is higher, around 20–26 kcal mol⁻¹. Importantly, in the case of 12^+ a crossing between the singlet and triplet surfaces takes place during C_α – Si bond stretching. This results in a further desilylation path for the conversion of 312^+ to 15 via this surface crossing, confronting a barrier of around 24 kcal mol⁻¹ (Figure 4b).

A CASSCF analysis was then carried out on the diradicals arising through desilylation of the phenyl cations. All of these structures are planar and have the two SOMOs located in orthogonal orbitals (one at the dicoordinated carbon and the second delocalized over the π cloud; see section 2.4 in the Supporting Information for details), similarly to what was found for the unsubstituted derivatives.

As for the parent α,n -DHTs, the ground state is a singlet for the $\alpha,3$ -derivative (with a small S-T gap) and a triplet for the other two isomers. The present computational analysis confirmed the same trend, with a triplet ground state for derivatives 14 and 16 , while 15 (an $\alpha,3$ -MeO-DHT) has a singlet ground state. The isodesmic equation reported in Table 3 was then used to evaluate the stabilization imparted by the methoxy group with respect to the corresponding parent DHTs. As shown in Table 3, the effect is minimal, and the singlets are slightly more stabilized than the corresponding triplets.

DISCUSSION

The initial part of the reaction conforms to what has been observed in other phenyl halides, with efficient ISC to triplet states 31 – 33 (Scheme 3, path a)^{12,16} and heterolysis of the Ar – Cl bond (Scheme 3, path b; see section 2.2 in the Supporting Information for further details). All of the photoproducts obtained were chlorine-free; thus, the efficiency of path b (η_b) coincided with the quantum yield of reaction.¹⁷ The quantum yield of heterolytic dechlorination remains sufficiently high to make these reasonable precursors of MeO-DHTs, at least for the case of **1** and **2**. Note that the presence of the methoxy group in the ortho position with respect to the nucleofugal group $-Cl$ effectively suppressed the photoreactivity of the simpler model (4-chlorobenzyl)trimethylsilane (for which the measured disappearance quantum yield was $\Phi_{-1} = 0.71$).^{9a,18} The first intermediate formed was in every case a triplet phenyl cation (311^+ – 313^+), which was consistently lower in energy

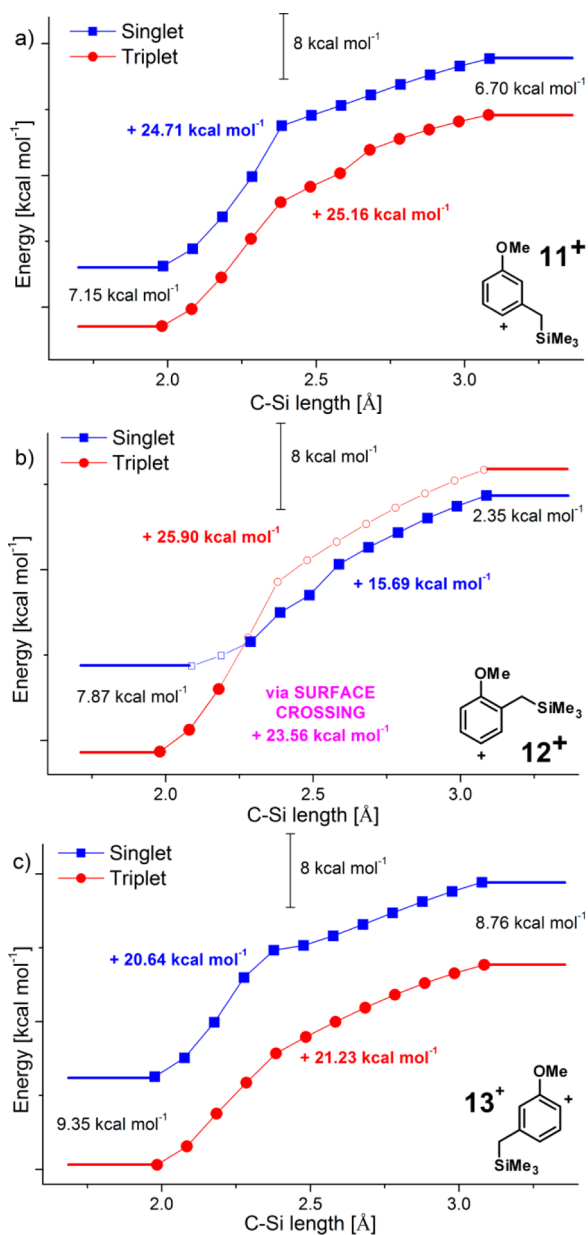


Figure 4. Energy profiles for the relaxed scans of the C_{α} -Si bond in (a) 11^+ , (b) 12^+ , and (c) 13^+ at the CPCM-CASSCF/6-31G(d) level of theory in bulk methanol.

than the corresponding singlet.^{10,11,19,20} Accordingly, the typical chemistry of triplet cations, viz. hydrogen abstraction from the alcoholic solvent (Scheme 3, path e) to form methoxybenzylsilanes **4a,b** and trapping in the presence of a sufficient amount of a π -bond nucleophile to give allylbenzenes **5a,b** (path f), was observed, with no solvolysis that would point to a role for singlet cations $11^+ - 13^+$ (Scheme 3, paths c and d). Cleavage of Me_3Si^+ from the triplet cations $311^+ - 313^+$ took place to give α,n -MeO-DHTs ($314 - 316$; path g).

The quantum yield of trapping of the phenyl cation by ATMS (Φ_{tr}) is thus given by eq 1.

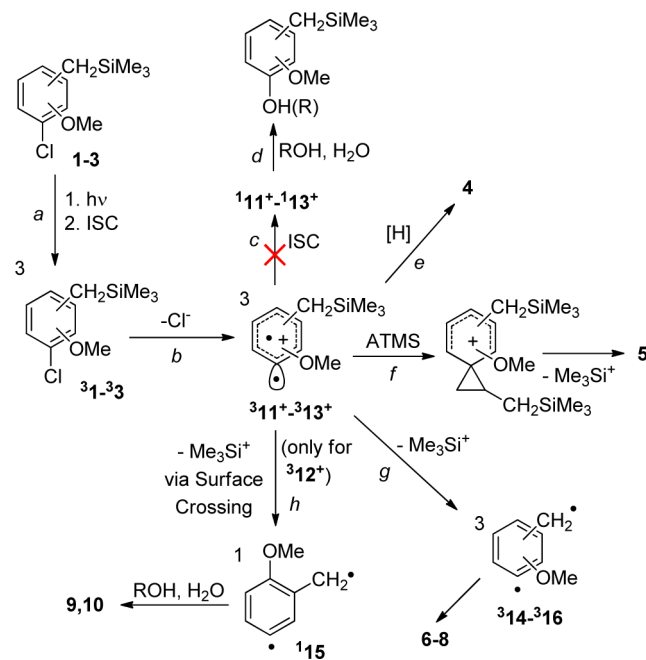
$$\Phi_{\text{tr}} = \eta_b k_f [\text{ATMS}] / \{k_g + k_e + k_f [\text{ATMS}]\} \quad (1)$$

Previous experiments on the 4-methoxyphenyl cation showed that the pseudounimolecular rate of reduction k_e is

Table 3. Gibbs Free Energy (ΔG_{CASMP2} ; See Eq. S1 in the Supporting Information) Changes for MeO-DHTs 14–16 According to the Isodesmic Reaction Illustrated Below, Calculated at the CASMP2/6-31G(d) Level of Theory in Bulk Methanol

SPECIES	S-T gap [kcal mol ⁻¹]	ΔG_{CASMP2} [kcal mol ⁻¹]	
		$^1\alpha,n$ -DHT	$^3\alpha,n$ -DHT
	6.20 (T more stable)	-2.26	-1.67
	-1.81 (S more stable)	-0.48	-0.13
	5.34 (T more stable)	-2.26	-1.67

Scheme 3. Generation of MeO-DHTs 14–16 from Silanes 1–3



ca. $5 \times 10^7 \text{ s}^{-1}$ and k_f is $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.¹¹ The data in Table 1 thus show that the rate of desilylation from the cation k_g may reach the same value and increases from $k_g / (k_e + k_f [\text{ATMS}])$ ca. 1 for 11^+ up to 6 for 12^+ (in the last case k_h rather than k_g is likely involved).

As for the 2-methoxyphenyl cation **13**, some MeO-DHT-derived products are formed, at least in EtOH–H₂O. Furthermore, no trapping by ATMS occurs. The simplest explanation is that the rate of reduction (k_e) largely increases in

this case and severely limits any competitive path from the cation.

Of the two electron-donating groups (MeO- and Me₃SiCH₂-) present,²¹ it is the former that directs the reactivity of the system. In addition to the aforementioned effect on dechlorination, it determines the spin state of the resulting cation (see Chart 1 and Figure 1). The electron-donating group stabilizes the phenyl cation but has no appreciable effect on the energy of the resulting α,n -MeO-DHT. This makes the desilylation step from the triplets less favorable (energy barrier up to 26 kcal mol⁻¹) than when no methoxy group is present (<20 kcal mol⁻¹ when imposing a similar elongation to the C _{α} -Si bond; see Figure 4).^{9c} The products from **1** and **3** result exclusively from the “radical” path, viz. the MeO-DHT abstracts a hydrogen from the solvent (more efficiently, as one may expect, from EtOH than from MeOH), but this is not the case for the MeO-DHT derived from **2**. With this compound, products resulting from “ionic” addition to the corresponding MeO-DHT were significant (polar/radical ratio from 0.14 to 2, Table 1) and, as one may expect, were formed more efficiently in MeOH than in EtOH (see Table 1).²²

Whereas desilylation from ³11⁺ and ³13⁺ proceeds with spin conservation to yield ³14 and ³16, respectively, in the case of ³12⁺ a surface crossing (see Figure 4b) was detected in the Me₃Si⁺ cleavage, suggesting that the corresponding singlet $\alpha,3$ -MeO-DHT (¹15) is obtained directly from the cation (³12⁺, path h). It is worth noting that the crossing occurs at an early stage along the reaction coordinate describing C _{α} -Si bond breaking. Thus, the spin-orbit coupling matrix element for the T-S crossing point should be close to the value for the equilibrium geometry. Indeed, some reports in the literature dealing with simple derivatives demonstrated that, despite the fact that coupling constants are rather small in absolute terms, they are certainly large enough to efficiently mediate the transition of the triplet cation to the singlet, fully supporting the feasibility of path h.²³ Furthermore, the product distribution in Table 1 supports that the latter path is favored ($k_h \geq k_g$ resulting in a high yield of MeO-DHT-derived products). It seems that this is a general characteristic of $\alpha,3$ -DHT, whether thermally or photochemically generated.

CONCLUSION

Summing up, extending the photoreaction of (chlorobenzyl)-trimethylsilanes to derivatives bearing a methoxy substituent has revealed more details regarding the generation of didehydrotoluenes and each of the steps of the overall mechanism, which are the efficiency of the heterolytic ³Ar-X cleavage, the stabilization imparted by substituents to the phenyl cation Ar⁺ formed, the multiplicity of the lowest-lying state, and the effect on desilylation to give MeO-DHTs. $\alpha,2$ -MeO- and $\alpha,4$ -MeO-DHTs are accessible by the phenyl cation path and do behave as “pure” diradicals. However, despite the accessible triplet surface, $\alpha,3$ -MeO-DHT shows a zwitterionic behavior. It is tempting to attribute this to the role of the surface crossing (Figure 4b) in this case.

This work proved the versatility of photochemical generation with respect to the limited thermal access and a much greater suitability for testing computational predictions. The chemistry of such unusual species bears some analogy to that of diphenylcarbenes, with radical abstraction from the solvent when the lowest state is a triplet and ionic addition when it is a

singlet, although the product distribution depends on the medium.²⁴

It is hoped that a judicious choice of the substituent pattern will make it possible to optimize the fragmentation of phenyl chlorides to yield DHTs and tune the chemistry of such intermediates, a target that increases the interest for possible biological applications. Work in this direction is underway. Importantly for potential applications, this work demonstrated that the presence of an electron-donating substituent in compounds **1–3** allows for the use of UV-B irradiation in place of the more toxic UV-C (254 nm) used in our previous experiments with unsubstituted (*n*-chlorobenzyl)-trimethylsilanes.⁹

ASSOCIATED CONTENT

Supporting Information

Text, figures, and tables giving experimental procedures, sample spectra, and optimized geometries, energies, and CASSCF output data for all of the structures involved in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*M.F.: fax, +39 0382 987323; tel, +39 0382 987198; e-mail, fagnoni@unipv.it.

Notes

The authors declare no competing financial interest.

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