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Photochemical Arylation Reactions by 4-Chlorothioanisole

Simone Lazzaroni,[a] Daniele Dondi,[a,b] Maurizio Fagnoni,[a] and Angelo Albini*[a]

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The photochemistry of 4-chlorothioanisole (**1**) was investigated in various solvents, and it was found to involve the reduction to thioanisole as the main process. This occurs by heterolytic fragmentation of the triplet state of **1** and formation of the triplet 4-thiomethoxyphenylium ion, as supported by DFT calculations. The cation is trapped by alkenes and, less efficiently, by benzene, resulting in new examples of the recently emerging arylation reactions by S_N1 substitution of phenyl halides. The products from alkenes involve the phenonium ion as a further intermediate. The product distribution differs from the analogous reactions via 4-methoxyphenylium for including a larger proportion of 4-(β-substituted alkyl)- rather than 4-allylthioanisoles derivatives in alcohols, for the lower fraction of rearranged α-substituted 4-alkylthioanisoles and for the formation of some 4-cyclopropylthioanisole with allyltrimethylsilane. The difference is accounted for by the more developed dipolar character of the C–C cyclopropane bonds in the intermediate phenonium, as indicated by DFT calculations.

Introduction

In recent years, we have been involved in the photochemistry of electron-donating (usually *para*) substituted phenyl halides and of some of the corresponding esters, viz. phenyl mesylates, triflates, and phosphates.[1] In polar media, these compounds, for example 4-chlorophenol, -anisole, and -aniline, underwent photoheterolysis of the carbon–halogen bond (of the carbon–oxygen bond for the esters). The cleavage occurred in the triplet state and generated the corresponding phenyl cations, likewise as the triplet entity.[1b,1c,1e,2] The cations demonstrated to be quite useful in synthesis because in the triplet multiplicity these did not add to n-nucleophiles, but only to π-nucleophiles. This allowed the irradiation to be carried out in a polar solvent as required for efficient heterolysis, for example in an alcohol, yet avoiding addition of the phenyl cation to the solvent and obtaining selective addition to alkenes and aromatics.

In some cases mixtures are obtained, but in other cases the yields and selectivity are high. The synthetic potential of this arylation process appears to be remarkable and seems to be competitive with palladium-catalyzed methods.[1a] This encouraged us to explore the scope of the reaction. An obvious issue for the development of this method was a change in the electron-donating substituent, and to the previously investigated –OR and–NR_2 groups, a –SR group was added for study. Accordingly, we explored the photochemistry of 4-chlorothioanisole (**1**) in neat solvents and in the presence of various π-nucleophiles and we were gratified to find that functionalized thioanisoles could be conveniently obtained in this way.

Results

Irradiation in Neat Solvents

The photoreactivity of **1** was examined in 0.05 M solutions in four solvents, viz., acetonitrile, methanol, 2,2,2-trifluoroethanol (TFE), as well as in $MeCN/H_2O$ (5:1). The irradiation was carried out in the presence of triethylamine (0.05 M) to buffer the acid that is liberated during the course of the reaction (though this had only a marginal effect on the results). Compound **1** was consumed, and the only practically product formed was anisole **2** (Scheme 1a). To facilitate the comparison of the results, the experiments were carried out by irradiating for a fixed time (16 h), as shown in Table 1. The progress of the reaction was somewhat hampered by the formation of a film sticking to the walls of the irradiation vessel during the irradiation, which was a result of the separation of a small amount of a non-identified, sulfur-containing product. This made it difficult to arrive at 100% conversion, particularly with alcohol as the solvent.

The quantum yield of the reaction was then determined through separate, low (<20%) conversion experiments by comparison with potassium ferrioxalate actinometer and

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[a] Department of Organic Chemistry, University of Pavia,
Via Taramelli 10, 27100 Pavia, Italy
Fax: +39-0382-987323
E-mail: angelo.albini@unipv.it
[b] Interuniversity Consortium INCA, Research Unit at the University of Pavia,
Via Taramelli 10, 27100 Pavia, Italy

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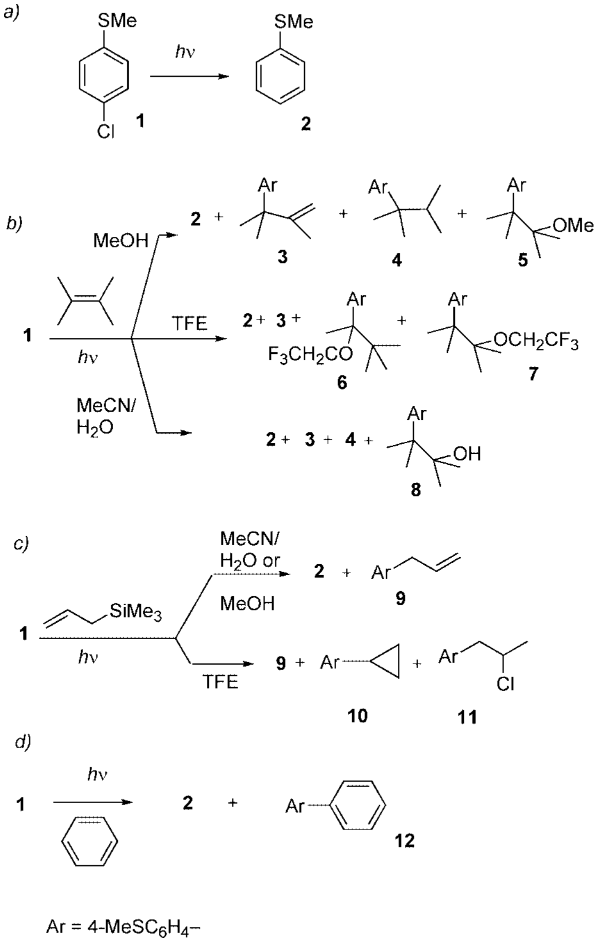


Scheme 1. Products from the irradiation of **1**: *a*) in neat solvent; *b*) in the presence of DMB; *c*) in the presence of ATMS; *d*) in the presence of benzene.

Table 1. Products from the irradiation of **1** in neat solvents and the quantum yield of the reaction (Φ_r).

Solvent	Consumed **1** [%][a]	Product yield [%][a]	Φ_r
MeOH	85	**2** (63)	0.38
TFE	86	**2** (37)	0.13
MeCN/H_2O	100	**2** (50)	0.29
MeCN	44	**2** (14)	[b]

[a] The consumption and the product yields (referred to the initial amount of reagent after 16 h of irradiation) were determined by GC. [b] Difficult to measure owing to some filming on the walls, see text.

was found to attain the maximum value (0.38) in methanol (Table 1). Compound **1** showed a modest fluorescence in solution and phosphorescence at 77 K in glass, both of them similar in shape and somewhat less intensive than that of thioanisole **2**.

Irradiation in the Presence of π-Nucleophiles

We next explored the irradiation of compound **1** in the presence of representative π-nucleophiles (again with equimolar triethylamine). Allyltrimethylsilane (ATMS), 2,3-dimethyl-2-butene (DMB), and benzene were chosen for this purpose. The products formed are shown in Scheme 1 and the yields obtained (again by irradiation for the fixed time of 16 h) are reported in Table 2. In the presence of the traps, the formation of a film on the walls of the vessel was much reduced, and in general the reactions could be carried out to completion.

Table 2. Products from the irradiation of **1** in the presence of π-nucleophiles.

Additive 1 M	Solvent	Consumed **1**[a] [%]	Yield of products formed [%][a]
DMB	MeOH	100	**2** (11), **3** (5), **4** (6), **5** (30)
	TFE	100	**2** (8), **3** (26), **6**(5), **7**(27)
	MeCN/H_2O	100	**2** (16), **3** (5), **4** (6), **8** (40)
ATMS	MeOH	92	**2** (14), **9** (24)
	TFE	100	**9** (31), **10** (7), **11** (8)
	MeCN/H_2O	100	**2** (14), **9** (29)
Benzene	MeOH	62	**2** (29), **12** (6)
	TFE	57	**2** (7), **12** (22)
	MeCN/H_2O	72	**2** (26), **12** (33)

[a] The consumption and the product yields (referred to the initial amount of reagent after 16 h irradiation) were determined by GC.

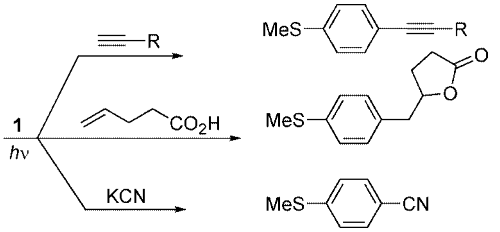
With 1 M DMB (Scheme 1b), compound **1** was in part reduced to thioanisole (**2**), but in part converted into alkylated thioanisoles with a distribution that depended on the solvent. Thus, in MeOH, an alkene 2,3-dimethyl-3-[4-(thiomethoxy)phenyl]-1-butene (**3**) and the corresponding alkane, 2,3-dimethyl-2-[4-(thiomethoxy)phenyl]butane (**4**), were formed in low yield, but the main single product was an ether resulting from a three-component combination: 2,3-dimethyl-2-[4-(thiomethoxy)phenyl]-3-methoxybutane (**5**, 30%).

In TFE, alkene **3** (26%) and two solvent incorporating products viz. 2,2-dimethyl-3-[4-(thiomethoxy)phenyl]-3-(2,2,2-trifluoroethoxy)butane (**6**, 5%) and isomeric 2,3-dimethyl-2-[4-(thiomethoxy)phenyl]-3-(2,2,2-trifluoroethoxy)-butane (**7**, 27%) were formed along with a little amount of **2** (8%). In MeCN/H_2O, the main product was an alcohol, 2,3-dimethyl-3-[4-(thiomethoxy)phenyl]butan-2-ol (**8**), formed in 40% yield along with a small amount of alkylated products **3** and **4** and 16% of reduced **2**.

In the presence of 1 M ATMS (Scheme 1c), compound **1** gave 4-allylthioanisole (**9**) as the main product along with some thioanisole (**2**) both in methanol and in MeCN/H_2O (5:1). In TFE, the results were somewhat different in that reduced **2** was no longer formed and main product **9** was accompanied by small amounts of two additional products viz. 4-cyclopropylthioanisole (**10**, 7%) and 4-(2-chloropropyl)thioanisole (**11**, 8%).

The photochemical reaction in the presence of 1 M benzene (Scheme 1d) was less efficient and starting compound **1** was not fully converted in 16 h. The products were thioanisole (**2**) and 4-phenylthioanisole (**12**), with the former more abundant in methanol, the latter in TFE, and the two forming in about the same yield in mixed MeCN/H_2O solvent.

Finally, we notice that during systematic studies of the reaction of phenylium ions with alkynes,[3] nonconjugated unsaturated acids[4] and cyanide,[5] the corresponding thiomethoxyaryl derivatives were obtained by irradiation of compound **1** (Scheme 2).



Scheme 2. Products from the irradiation of **1** in the presence of various nucleophiles.

Computational Studies

The experimental work was complemented by DFT calculations. These were carried out at the UB3LYP/6-311G++ (2d,p) level, known to be suitable for sulfur-containing compounds. The structure and energy of the proposed intermediate, 4-thiomethoxyphenylium ion (^{1,3}**13**$^+$) were examined in both spin states. It resulted that the triplet was the ground state in the gas phase, with a gap ΔE_{S-T} = 8.1 kcal/mol. Solvation effects calculated with the CPCM method (acetonitrile as solvent) on the optimized geometries showed that singlet state ^{1}**13**$^+$ was somewhat more stabilized than triplet ^{3}**13**$^+$, decreasing the gap to 7.1 kcal/mol, but leaving the order unchanged. The optimized geometry of both states was essentially the same as that of the respective nonsubstituted cations,[1c,2a–2c] with the triplet state characterized by a planar, hexagonal structure, and the singlet state differing by a puckering inwards of C-1 (Figure 1). In particular, there was a close likeness to corresponding 4-methoxyphenylium ions **14**$^+$.

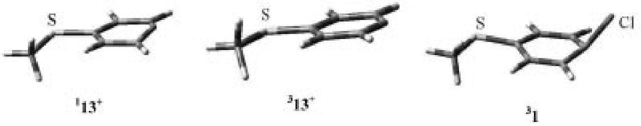
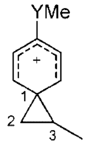


Figure 1. Optimized geometry of singlet and triplet 4-thiomethoxyphenylium ion (^{1,3}**13**$^+$) and of triplet 4-chlorothioanisole (^{3}**1**).

The exploration was extended to the energy and geometry of the putative precursor of the cation, triplet chlorothioanisole ^{3}**1** and to the ensuing chemistry of such an intermediate. As for ^{3}**1**, this was characterized by a conspicuous out-of-plane deformation of the C–Cl bond (Figure 1). To calculate the C–Cl bond dissociation energy in this excited state, the bond was stretched up to 4 Å in increments of 0.1 Å (in MeCN bulk, CPCM method as above). The cleavage was endothermic by 6.4 kcal/mol and no maximum was encountered along the path.

As for the chemistry of the triplet phenylium ion, this was explored for the case of propene as the nucleophile. It was found that, similar to the previously studied 4-methoxyphenylium ion, ^{3}**13**$^+$ formed a triplet, diradical cation adduct with propene, then leading to a more stabilized cation adduct, viz. phenonium ion **15**$^+$ (stabilized by 86.8 kcal/mol with respect to ^{3}**13**$^+$ + propene). This was necessarily a singlet, and intersystem crossing must intervene in between. The geometry in this adduct, and in particular the C–C distances in the three-membered ring, were similar to those in oxa analogue **16**$^+$ (Table 3), but the (Mulliken) charge distribution was somewhat different. In the sulfur derivative, the positive charge was localized to a greater extent on the heteroatom and on the neighboring carbon atoms and to a lesser extent at C_1 with respect to the oxa analogue. This gave the C_1–C_2 and C_1–C_3 bonds a marked dipolar character in **15**$^+$ when in solution. In particular, the C_1–C_3 bond was more polarized by 28% in **15**$^+$ with respect to **16**$^+$ (as calculated from the Mulliken charges at the carbon atom, with the hydrogen summed in, see Table 3; Figure 2).

Table 3. C–C distances and Mulliken charges for the adduct between 4-thiomethoxy and 4-methoxyphenylium and propene (phenonium ions). Data refer to the optimized (UB3LYP/6-311G++(2d,p) structures.

 YMe 1 2 3	Y	$d(C_1–C_2)$	$d(C_1–C_3)$	$q(C_1)$	$q(C_2)$	$q(C_3)$
	O	1.58	1.65	0.21	–0.19	0.44
	S	1.58	1.66	0.06	–0.18	0.47

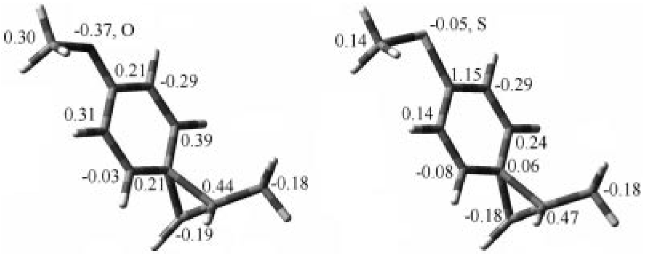
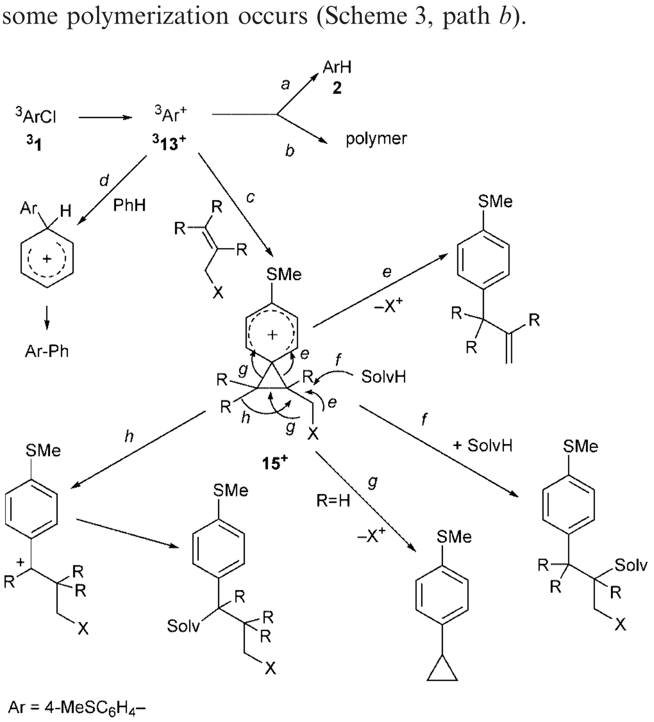


Figure 2. Optimized geometry and Mulliken charges (with the hydrogens summed in) for phenonium ions **16**$^+$ (left) and **15**$^+$ (right).

Discussion

Comparison with previous work suggests that the thioether functionality can be added to previously studied O- and N-bonded functionalities[1] that facilitate unimolecular fragmentation of the corresponding aryl chlorides from the triplet state. DFT calculations support that heterolytic cleavage of the C–Cl bond confronts a modest barrier (6.4 kcal/mol) in triplet 4-chlorothioanisole ^{3}**1** (triplet energy 74.0 kcal/mol from the phosphorescence spectrum) and the experiments show that the quantum yield of dechlorination ranges from ca. 0.1 to 0.4, that is more efficient than with 4-chloroanisole and less than with 4-chloro-*N*,*N*-dimethylaniline.

Therefore, it seems safe to assume that in polar solvents 4-chlorothioanisole undergoes heterolytic cleavage from the triplet state and the first-formed intermediate is triplet thiomethoxyphenylium ion ^{3}**13^{+}**. Indeed, no 4-thiomethoxyphenyl ethers, the products expected from singlet cation ^{1}**13^{+}**, are formed in alcohol solvents. Previous studies with the corresponding chloroanisole and aniline showed that the main processes form triplet phenylium ions in neat solvents (at concentrations in the range of those presently used) was reduction (Scheme 3, path *a*). This may involve either direct hydrogen transfer from the solvent to cation Ar^{+} or previous reduction to the aryl radical (electron transfer from the halide $Ar^{+} + ArCl \rightarrow Ar^{\cdot} + ArCl^{\cdot +}$) and ensuing H transfer from the solvent.[1c,6] Reduction to **2** is in fact a major process (Table 1), whereas the other often observed process involving the cation and the starting halide, viz. formation of a biphenyl, does not take place here. However, the formation of films on the walls suggests that some polymerization occurs (Scheme 3, path *b*).



Scheme 3. Main paths in the photochemistry of **1**.

Calculations predict that analogous to what was observed with other phenylium ions[1] ^{3}**13^{+}** adds to π-nucleophiles such as alkenes. Indeed, arylation both of alkenes and of benzene occurred satisfactorily. Comparison of the results from **1** with those previously obtained with 4-chloroanisole[6] via triplet 4-methoxyphenylium ion (^{3}**14^{+}**) shows several common characteristics and some differences. Trapping by alkenes is efficient with both cations (Scheme 3, path *c*). As an example, the ratio addition/reduction is 3.7 for ^{3}**13^{+}** and 2.7 for ^{3}**14^{+}** with 1 M DMB in MeOH. The less nucleophilic benzene (Scheme 3, path *d*) is a poorer trap, at least when competing with reducing methanol, with an arylation/reduction ratio 0.2 and 0.4 for 1 M benzene in MeOH, but the ratio increased to 3.1 and 20 in TFE. The latter solvent favors ion separation, and the free ion clearly is a better electrophile under these conditions.

The arylation of alkenes proceeds via phenonium ion **15^{+}** (Scheme 3, path *c*) as a further intermediate. Also in this case, it is instructive to compare the reactivity of ion **15^{+}** with that of oxa analogue **16^{+}**. Thus, in the reaction with DMB (X = H) deprotonation (Scheme 3, path *e*) is the preferred process from methoxyphenonium **16^{+}** and allylbenzene (**3**) is the main product in MeOH (not in less basic MeCN). On the other hand, with thio analogue **15^{+}** nucleophilic addition of the solvent to give a β-alkoxy(hydroxy)-alkylbenzene (Scheme 3, path *f*) predominates in all of the solvents tested (MeOH, TFE, MeCN/H_2O), although its proportion decreases in TFE (ratio ether/allylbenzene 0.5 in MeOH and 1.8 in TFE for 4-$MeOC_6H_4Cl$, 6 in MeOH, and 1.2 in TFE for **1**). In the case of ATMS, the main process via both cations **15^{+}** and **16^{+}** is solvent-assisted desilylation, giving again an allylbenzene (Scheme 3, path *e*, X = Me_3Si). Indeed, this is the only process, except for the case of **15^{+}** in TFE, where a different reaction leading to a cyclopropyl derivative is observed as a minor process. This can be envisaged as an alternative elimination path (Scheme 3, path *g*) and has analogy in the known formation of cyclopropane from 3-chloropropylsilanes by an S_N1 process.[7,8] A third difference has to do with the role of the Wagner–Meerwein rearrangement (Scheme 3, path *h*). The rearranged/nonrearranged ratio is 1.6 for methoxy-substituted ion **16^{+}** and 0.2 for sulfur analogue **15^{+}**.

In other words, 4-methoxy- and thiomethoxyphenylium ions ^{3}**14^{+}**, ^{3}**13^{+}** are similar electrophiles. In the alkene adduct (phenonium) ions, however, methoxy derivative **16^{+}** is more prone to base-induced proton (or silyl cation) transfer to the solvent, and thiomethoxy analogue **15^{+}** is prone to inter- and intramolecular nucleophilic addition. These pieces of evidence suggest that anchimeric assistance by the thiomethoxyphenyl group is less effective, or, as it can be also expressed, the phenylium–alkene interaction maintains more of a dipolar character, making nucleophile attack at the three-membered ring easier. This view is supported by the calculated geometry of the phenonium ion where it appears that, although the bond lengths in the spirocyclopropane ring change little, the C_1–C_3 bond is more polarized in **15^{+}** than in oxa analogue **16^{+}**. This facilitates both attack by an external nucleophile (Scheme 3, path *f*), and the second mode of elimination of the electrofugal group X^{+}, characterized by formation of a C–C σ bond with the distal carbon of the spirocyclopropane ring (Scheme 3, path *g*) rather than of a π bond with the vicinal carbon (Scheme 3, path *e*; the only elimination path from **16^{+}**, whereas both compete from **15^{+}**). On the other hand, the greater stabilization imparted to the phenonium ion by the methoxy group arguably lengthens the lifetime of this intermediate (or gives a greater role to the free cation in comparison to the ion pair). This makes it possible to undergo Wagner–Meerwein rearrangement for a larger fraction of ions.

In conclusion, the thioanisolium ion is conveniently generated by photolysis of 4-chlorothioanisole and adds to alkenes and benzene, widening the scope of the photochemical arylation by a photo-S_N1 reaction of aryl halides, which has been recently emerging. The products formed are the analogues of those isolated from 4-chloroanisole, as expected from the similar DFT calculated structure. However, with alkenes in alcohols, β-alkoxyalkylbenzenes are formed to a larger extent than with the oxa analogue and with allyltrimethylsilane a previously unobserved cyclization to a cyclopropylbenzene occurs. These are indications of the lower stabilization of the intermediate phenonium ion by the sulfur versus the oxygen atom in the 4-position.

Experimental Section

General Remarks: The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes by using a multilamp reactor fitted with six 15-W phosphor-coated lamps (maximum emission is 310 nm) for the irradiation. The reaction course was followed by thin-layer chromatography (TLC, cyclohexane/ethyl acetate) and gas chromatography (GC). Workup of the photolytes involved concentration in vacuo and chromatographic separation on silica gel. Allyltrimethylsilane, 2,3-dimethyl-2-butene, benzene, and 4-chlorothioanisole were freshly distilled before use. The solvents were used as received. No previous anhydrification was carried out as it was found that this did not affect the results. NMR spectra were recorded with a 300 MHz spectrometer. The structure attributions were made on the basis of analytical and spectroscopic data, in particular ^{1}H and ^{13}C NMR spectra, supported by DEPT-135 experiments.

Irradiation of 1 in Neat Solvent: A solution of **1** (0.05 M) was irradiated in the solvent chosen (MeOH; TFE; or MeCN/H_2O, 5:1) in the presence of triethylamine (0.05 M) for 16 h. The product distribution was analyzed by GC. Thioanisole was determined on the basis of calibration curves. A precipitate formed (≤3% of the initial weight) and was filtered and washed with methanol. This material contained sulfur and gave signals compatible with a sulfonium salt in accordance with a polymer from **1**.[9] IR: $\tilde{\nu}$ = 1630, 1500, 1235, 765 cm^{-1}. ^{1}H NMR large signals at δ = 2.4, 3.7, 7.0–7.4.

General Procedure for the Irradiation of 1 in the Presence of π Nucleophiles: Experiments were carried out as described above starting from **1** (100 μL, 0.75 mmol, 0.05 M) in the chosen solvent (15 mL) after adding the π-nucleophile (1 M of 2,3-dimethyl-2-butene, allyltrimethylsilane, or benzene) again in the presence of triethylamine (0.05 M).

Photochemical Reactions of 1 in the Presence of DMB

In Methanol: After 16 h of irradiation, evaporation and chromatographic separation (cyclohexane/ethyl acetate, 99:1) of the residue afforded 61 mg of compound **5** (30% yield) and a mixture containing 9 mg of **4** (6% yield) and 7 mg of **3** (5% yield) all of these slightly yellow viscous oils.

2,3-Dimethyl-3-[4-(thiomethoxy)phenyl]-1-butene (3): ^{1}H NMR (300 MHz, $CDCl_3$, from the mixture with **4**): δ = 1.5 (s, 6 H), 1.6 (s, 3 H), 2.5 (s, 3 H), 4.9 (br. s, 1 H), 5.0 (br. s, 1 H), 7.2–7.4 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.1 (CH_3), 20.0 (CH_3), 28.2 (2 CH_3), 40.1, 109.5 (CH_2), 126.4 (CH), 126.7 (CH), 128.5, 129.4, 130.3 ppm. IR (for the mixture): $\tilde{\nu}$ = 2968, 1476, 1110, 821 cm^{-1}.

2,3-Dimethyl-2-[4-(thiomethoxy)phenyl]butane (4): ^{1}H NMR (300 MHz, $CDCl_3$, from the mixture with **3**): δ = 0.8 (d, *J* = 6.8 Hz, 6 H), 1.25 (s, 6 H), 1.9 (m, 1 H), 2.45 (s, 3 H), 7.2–7.4 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.0 (CH_3), 17.8 (2 CH_3), 24.6 (2 CH_3), 38.1 (CH), 40.1, 126.4 (CH), 126.6 (CH), 127.8, 128.8 ppm. GC–MS: *m*/*z* = 208.

2,3-Dimethyl-2-[4-(thiomethoxy)phenyl]-3-methoxybutane (5): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.1 (s, 6 H), 1.4 (s, 6 H), 2.4 (s, 3 H), 3.2 (s, 3 H), 7.1–7.5 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.9 (CH_3), 19.8 (CH_3), 20.0 (CH_3), 24.3 (CH_3), 24.9 (CH_3), 45.0, 49.4 (CH_3), 78.4, 125.4 (CH), 128.8 (CH), 129.0 (CH), 129.2 (CH), 134.8, 144.5 ppm. IR (neat): $\tilde{\nu}$ = 2964, 1492, 1373, 1152, 1113, 1068, 812 cm^{-1}. $C_{14}H_{22}OS$ (238.28): calcd. C 70.54, H, 9.30; found C 70.2, H 9.1.

In Trifluoroethanol: After 16 h of irradiation, evaporation and chromatographic separation (cyclohexane/ethyl acetate, 99:1) of the residue afforded 39 mg of **3** (26% yield), 11 mg of **6** (5% yield), 57 mg of **7** (27% yield).

2,2-Dimethyl-3-[4-(thiomethoxy)phenyl]-3-(2,2,2-trifluoroethoxy)butane (6): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (s, 9 H), 1.6 (s, 3 H), 2.5 (s, 3 H), 3.7 (m, 2 H), 7.1–7.3 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.5 (CH_3), 19.2 (CH_3), 25.4 (CH_3), 38.6, 61.0 (q, *J* = 34 Hz, CH_2), 84.3, 125.2 (CH), 125.8 (q, *J* = 276 Hz, CF_3), 128.6 (CH), 136.9, 137.4 ppm. IR (neat): $\tilde{\nu}$ = 2962, 1597, 1492, 1281, 1163, 1133, 1103, 971, 824, 676 cm^{-1}. $C_{15}H_{21}F_3OS$ (306.27): calcd. C 58.80, H, 6.91; found C 58.4, H, 7.0.

2,3-Dimethyl-2-[4-(thiomethoxy)phenyl]-3-(2,2,2-trifluoroethoxy)butane (7): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.1 (s, 6 H), 1.45 (s, 6 H), 2.5 (s, 3 H), 3.65 (q, *J* = 8.6 Hz, 2 H), 7.15–7.5 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.7 (CH_3), 20.4 (CH_3), 24.1 (CH_3), 44.9 (CH_3), 60.3(q, *J* = 34 Hz, CH_2), 80.3, 125.8 (q, *J* = 276 Hz, CF_3), 129.0 (CH), 135.2, 143.4 ppm. IR (neat): $\tilde{\nu}$ = 2976, 1494, 1377, 1280, 1152, 972, 820 cm^{-1}. $C_{15}H_{21}F_3OS$ (306.27): calcd. C 58.80, H, 6.91; found C 58.6, H, 7.0.

In MeCN/H_2O: After 16 h of irradiation, purification (cyclohexane/ethyl acetate, 99:1) of the raw photolyte afforded 67 mg of **8** (40%) and a mixture containing 9 mg of **4** (6% yield) and 7 mg of **3** (5% yield) all as a slightly yellow viscous oils.

2,3-Dimethyl-3-[4-(thiomethoxy)phenyl]butan-2-ol (8): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.2 (s, 6 CH_3), 1.4 (s, 6 CH_3), 2.5 (s, CH_3), 7.2–7.4 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (CH_3), 23.9 (CH_3), 25.2 (CH_3), 44.3, 74.0, 125.5 (CH), 128.2 (CH), 135.3, 142.8 ppm. IR (neat): $\tilde{\nu}$ = 3468, 2976, 1494, 1375, 1112, 822 cm^{-1}. $C_{13}H_{20}OS$ (224.26): calcd. C 69.59, H, 8.98; found C 69.2, H, 9.0.

Photochemical Reactions of 1 in the Presence of ATMS

In TFE: After 16 h of irradiation, evaporation, and chromatographic separation (cyclohexane/ethyl acetate, 99:1) of the residue, 38 mg of **9** (31% yield) as a yellow liquid and 9 mg of **10** (7% yield, admixed with some **9**), and a pure fraction containing 12 mg of **11** (8% yield) as a yellowish oil were obtained.

4-Allylthioanisole (9): ^{1}H NMR (300 MHz, $CDCl_3$, from the mixture): δ = 2.5 (s, 3 H), 3.4 (d, *J* = 6.6 Hz, 2 H), 5.2 (m, 2 H), 5.9 (m, 1 H), 7.15–7.3 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.2 (CH_3), 39.6 (CH_2), 115.8 (CH_2), 127.1 (CH), 129.0 (CH), 137.2 (CH, allyl), 135.6, 137.0 ppm. GC–MS: *m*/*z* = 164. The product was previously reported, but not spectroscopically characterized.[10]

4-Cyclopropylthioanisole (10): ^{1}H NMR (300 MHz, $CDCl_3$, from the mixture): δ = 0.7 (m, 2 H), 1.0 (m, 2 H), 1.9 (m, 1 H), 2.5 (s, 3 H), 7.1–7.3 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.0 (2 CH_2), 14.9 (CH), 16.5 (CH_3), 126.2 (CH), 127.3 (CH), 134.6, 141.2 ppm. IR (for the mixture): $\tilde{\nu}$ = 2921, 1493, 1091, 915, 800, 797 cm^{-1}. GC/MS: m/z = 164.

4-(2-Chloropropyl)thioanisole (11): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.5 (d, J = 6.5 Hz, 3 H), 2.5 (s, 3 H), 3.0 (ABX, 2 H), 4.2 (X, 1 H), 7.1–7.3 (AA′-BB′, 4 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 15.9 (CH$_3$), 24.5 (CH$_3$), 46.0 (CH$_2$), 58.3 (CH), 126.7 (CH), 129.7 (CH), 134.7, 136.6 ppm. IR (neat): $\tilde{\nu}$ = 2923, 1495, 1092, 798 cm^{-1}. $C_{10}H_{13}ClS$ (200.70): calcd. C 59.84, H, 6.53; found C 60.0, H, 6.7.

Photochemical Reactions of 1 in the Presence of Benzene

In Trifluoroethanol: A solution of **1** (100 µL, 0.75 mmol, 0.05 M), benzene (1.4 mL, 15 mmol, 1 M), and TEA (100 µL, 0.75 mmol) in TFE (15 mL) was irradiated for 16 h. Separation of the residue by column chromatography (cyclohexane/ethyl acetate, 99:1) gave 23 mg of **2** (16% yield) and 33 mg of the known compound **12** (22% yield) as a white solid, m.p. 98–100 °C.

4-Phenylthioanisole (12): ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.5 (s, 3 H), 7.3–7.4 (m, 4 H), 7.5–7.6 (m, 2 H), 7.7–7.8 (m, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 15.8 (CH$_3$), 126.7 (CH), 126.8 (CH), 127.1 (CH), 127.4 (CH), 128.7 (CH), 137.4, 137.9, 140.4 ppm. IR (neat): $\tilde{\nu}$ = 2917, 1265, 824, 753, 685 cm^{-1}.[11]

Quantum Yield Measurement: Quantum yields were measured on 2-mL samples of solutions as above in 1-cm optical path cuvettes by irradiating by means of a focalized high pressure mercury arc through an interference filter. The extent of the reaction was assessed by GC, the light absorbed by ferrioxalate actinomety.

Computational Study: Structure and energy were optimized at the UB3LYP/6-311G++(2d,p) level by using the Gaussian 03W package (see Supporting Information).[12]

Supporting Information (see footnote on the first page of this article): Coordinates and energies of the investigated intermediates are available.

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