ChemPubSoc Europe

DOI: 10.1002/chem.201603522

CHEMISTRY
A European Journal
Full Paper

Reaction Mechanisms |*Hot Paper*|

Photochemistry of *N*-Arylsulfonimides: An Easily Available Class of Nonionic Photoacid Generators (PAGs)

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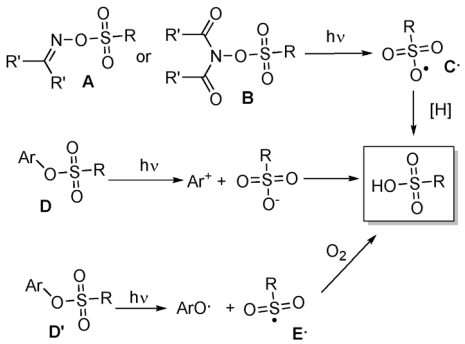
Abstract: The photochemical behavior of differently substituted *N*-arylsulfonimides was investigated. Homolysis of the S–N bond took place as the exclusive path from the singlet state to afford both *N*-arylsulfonamides and photo-Fries adducts, the amount of which depended on reaction conditions and aromatic substituents. Sulfinic and sulfonic acids were released upon irradiation under deaerated and oxygenated conditions, respectively. The nature of the excited states and intermediates involved were proved by laser flash photolysis and EPR experiments. These results highlighted the potential of such compounds as nonionic photoacid generators able to photorelease up to two equivalents of a strong acid for each mole of substrate.

Introduction

The photorelease of acids (especially strong sulfonic acids) is widely recognized as an important tool in materials science and micro-/nanoelectronics.[1] Aromatic iodonium or sulfonium salts are known to be excellent photoacid generators (PAGs),[2] but their thermal stability is, in some cases, counterbalanced by their limited solubility in polymer matrices,[3] which makes the development of nonionic PAGs desirable. Likewise, a deep understanding of the mechanism involved in the release of the acidic moiety from these substrates is fundamental for developing new and more efficient PAGs.

The mechanism of photorelease of sulfonic acids in (commercially available) nonionic PAGs may follow different pathways, as summarized in Scheme 1.[4] The homolytic cleavage of the O–N bond in iminosulfonates **A**[5] or imidosulfonates **B**[6,7] generates a sulfonyloxy radical (**C**•), which, upon hydrogen abstraction, gives the desired sulfonic acid. Recently, we discovered that the photoheterolytic cleavage of the Ar–O bond in electron-rich aryl mesylates and triflates (**D**) released the same strong acids.[8] However, photolysis of other sulfonates, such as aryl tosylates **D′** (R = Ar′), takes place through homolysis of the ArO–S bond,[9] and the thus-formed sulfonyl radical (**E**•) gives a sulfonic acid through the addition of oxygen present in solution (Scheme 1). In all of the abovementioned cases, one equivalent of acid is released per equivalent of PAG. In a few cases, however, PAGs able to generate more than one equivalent of acid, through either multi-[10] or one-photon processes,[11] have been reported.



Scheme 1. Possible mechanisms of photorelease of sulfonic acids from nonionic PAGs.

We report herein a new class of potential nonionic PAGs able to release one (or more) equivalent(s) of strong sulfonic acids smoothly, namely, *N*-arylsulfonimides **1a**–**j**. Compounds belonging to this class were recently investigated as potential inhibitors of tryptophan-2,3-dioxygenase in cancer therapy,[12] as hepatitis C virus inhibitors,[13] and as herbicides.[14] In the field of organic synthesis, the sulfonyl group is currently adopted to protect the amino group.[15] However, to the best of our knowledge, the potential of sulfonimides as PAGs was preliminary investigated only by Sasaki and Kawamura, who reported the release of variable amounts of sulfonic and sulfinic acids (depending on the reaction conditions) from both alkyl- and phenyl-substituted sulfonimides.[16]

N-Arylmethanesulfonimides with different aromatic substituents (**1a**–**g**) were initially tested, along with trimethylphenyl derivative **1h**, *N*-(4-acetylphenyl)-*N*-(*p*-tolylsulfonyl)-*p*-toluenesulfonamide (**1i**), and *N*-(4-acetylphenyl)-1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide (**1j**).

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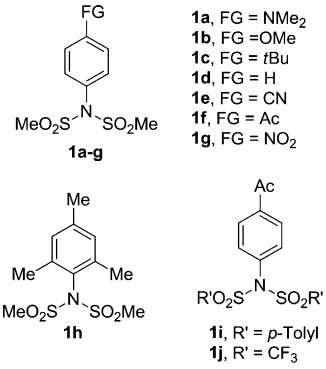
Supporting information for this article and ORCID(s) of the author(s) are available on the WWW under http://dx.doi.org/10.1002/chem.201603522.



Results

Photochemical experiments on 1 a–j

The examined sulfonimides were easily prepared from the corresponding anilines (see the Supporting Information for further details). Preliminary irradiation experiments ($\lambda = 254$ nm, 2 h) were carried out on compound **1 b** in medium to polar solvents under deaerated conditions (Table 1). Good photoreactivity for such a substrate was observed in THF, ethyl acetate, and acetonitrile (Φ_{-1} in the 0.1–0.2 range). The presence of protic solvents (MeOH or water) did not increase the consumption of **1 b**, which was photostable in acetone. The product distribution is quite complex and all of the compounds formed arose from the cleavage of the N–S bond, as in the case of desulfonylated derivatives **2 b** and **5 b**, or from a photo-Fries rearrangement (products **3 b**, **4 b**, and **6 b**). The presence of a protic medium, however, increased the amounts of desulfonylated adducts (Table 1).

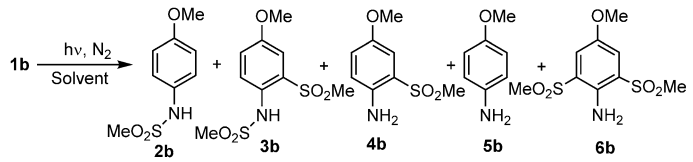
With these positive results in hand, we extended our investigation to other sulfonimides. For the photophysical properties (see Table S1 in the Supporting Information for further details), compounds **1 a–j** showed two absorption maxima in the UV region at $\lambda \approx 250$–300 and 210–240 nm, with the exception of **1 g** and **1 i**, which exhibited single absorption bands at $\lambda = 260$ and 240 nm, respectively (Figures S1–S10 in the Supporting Information). All of the sulfonimides tested showed a low ($\Phi_F < 0.02$) or negligible fluorescence emission, except for cyano derivative **1 e** ($\Phi_F \approx 0.1$). In view of the satisfactory Φ_{-1} value obtained for **1 b**, photochemical experiments on **1 a–j** were carried out in deaerated acetonitrile. As depicted in Table 2, a complex mixture of desulfonylated derivatives **2** and **5** and Fries adducts **3**, **4** and **6** resulted, along with sulfonyl anilines **7**. All of the *p*-substituted derivatives **1 a–g** were consumed, with a disappearance quantum yield $\Phi_{-1} > 0.1$; amino and acetyl derivatives **1 a** and **1 f** were the most reactive in the series (Φ_{-1} ca. 0.3), whereas **1 g** was an exception (almost photostable).

Potentiometric titration and ionic chromatography analyses were also carried out on the resulting solutions (Figures S13–S31 in the Supporting Information). Sulfinic acids were the only acid formed and their amount was comparable to that of desulfonylated products **2**, **4**, and **5**. To hamper the formation of Fries adducts and to increase the release of acids, we tested methanesulfonimide **1 h**, in which the *ortho* and *para* positions had methyl groups. As expected, no Ar–S bonds were formed in the reaction and only compounds **2 h** and **5 h** were obtained, along with 71% yield of CH_3SO_2H (Table 2). We then tested compounds **1 i** and **1 j**. In both cases, the Φ_{-1} value was in the same order as that observed for **1 f** (ca. 0.25). The photochemical behavior of **1 i** was very similar to that of **1 f** (and included *ipso*-substituted adduct **7 i**) and a significant amount of *p*-toluenesulfinic acid (along with traces of acetic acid) was detected by chromatographic analyses. In contrast, no Fries rearrangement was observed in the case of compound **1 j**, and a mixture of weak acids (H_2SO_3 and HF) was released in place of expected CF_3SO_2H (Table 2). Gaseous fluoroform (CHF_3) and hexafluoroethane were also revealed in this photolyzed solution by means of IR and GC-MS analyses (see Figures S11 and S12 in the Supporting Information).[8]

Photolysis of compounds **1 a–j** was then repeated under oxygenated conditions (Table 3). As it is apparent from comparing the results in Tables 2 and 3, the presence of oxygen did not affect the Φ_{-1} value. The scenario dramatically changed, however, upon analyzing the amount and nature of the acids released. Methanesulfonic acid (up to two equivalents) was formed from compounds **1 a–h** and, similarly, a quantitative amount of *p*-toluenesulfonic acid was released from **1 i**. In the case of **1 f**, the result in air-equilibrated solution is very similar to that observed under oxygenated conditions. Compound **1 j** gave the same acids formed in deaerated conditions, albeit in a higher amount.

To gain a deeper insight into the mechanism, we monitored the evolution of the photoproduct distributions obtained from compound **1 b** under deaerated conditions after different irradiation times (see

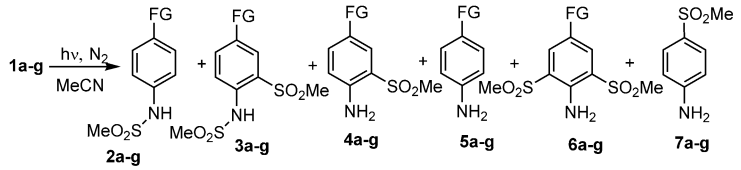
Table 1. Irradiation of sulfonimide **1 b** in neat solvents.[a]



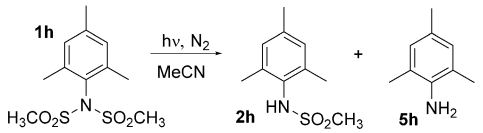
Solvent	Φ_{-1}[b]	Products, yield[c] [%]	Desulf./Fries[d]
AcOEt	0.14	**2 b**, 25; **3 b**, 26; **5 b**, 9; **6 b**, 16	44/56
THF	0.08	**2 b**, 29; **3 b**, 5; **5 b**, 10; **6 b**, 16.	64/36
MeCN	0.21	**2 b**, 22; **3 b**, 12; **5 b**, 11; **6 b**, 20	50/50
MeCN/MeOH (1:1)	0.16	**2 b**, 33; **3 b**, 6; **5 b**, 30; **6 b**, 14	75/25
MeCN/H_2O (1:1)	0.10	**2 b**, 30; **3 b**, 7; **5 b**, 16; **6 b**, 11	70/30
acetone	< 0.01	–	–

[a] Conditions: A solution of **1 b** (10^{-2} M, nitrogen purged) in the chosen solvent was irradiated for 2 h at $\lambda = 254$ nm (4×15 W Hg lamps). [b] Disappearance quantum yield (Φ_{-1}) measured on a N_2-purged 10^{-2} M solution of **1 b** in the chosen solvent ($\lambda = 254$ nm, 1×15 W Hg lamp). [c] Product yields calculated on the basis of the amount of **1 b** consumed. In each case, compound **4 b** was detected in < 1% yield. [d] Ratio between the yields of desulfonylated compounds **2 b** and **5 b** versus photo-Fries adducts **3 b**, **4 b**, and **6 b**.

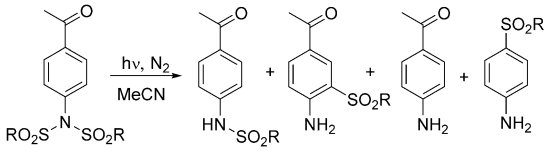
Table 2. Irradiation of sulfonimides **1a–j** in MeCN.[a]



1	Φ_{-1}[b]	Products, yield[c] [%]	H^+ [%][d]	Acids, yield[e] [%]
1a	0.31	**3a**, 82; **6a**, 10	<1	CH_3SO_2H, <1
1b	0.21	**2b**, 22; **3b**, 12; **5b**, 11; **6b**, 20	46	CH_3SO_2H, 45
1c	0.09	**2c**, 21; **4c**, 55; **5c**, 12	99	CH_3SO_2H, 96
1d	0.10	**2d**, 32; **5d**, 14; **7d**, 9	75	CH_3SO_2H, 74
1e	0.10	**2e**, 17; **4e**, 53; **5e**, 22	125	CH_3SO_2H, 116
1f[f]	0.28	**2f**, 80; **4f**, 8; **5f**, 7	[g]	[g]
1f	0.28	**2f**, 36; **4f**, 18; **5f**, 18; **7d**, 4	98	CH_3SO_2H, 93
1g	<0.01	[h]	<1	[i]



1h	0.13	**2h**, 56; **5h**,9	72	CH_3SO_2H, 71



1i	0.24	**2i**, 17; **4i**, 38; **5f**, 28; **7i**, 13	128	$CH_3C_6H_4SO_2H$, 116; CH_3COOH, 11
1j	0.22	**2j**, 5; **5f**, 78	319	H_2SO_3, 123; HF, 44

[a] Conditions: A solution of **1a–j** (10^{-2} M, nitrogen purged) in MeCN was irradiated for 2 h at $\lambda = 254$ nm. [b] Measured on a 10^{-2} M solution of **1a–j** in nitrogen-purged MeCN ($\lambda = 254$ nm). [c] Determined by HPLC or GC analyses. [d] Determined by potentiometric titration. [e] Determined by HPLC ion chromatography analyses. [f] Irradiation for 15 min. [g] Not determined. [h] No photoproducts detected. [i] No acid released.

Figure 1 and Table S2 in the Supporting Information). Compounds **2b** and **3b** were initially formed, but their concentration settled to almost constant values during irradiation, with the concomitant accumulation of anilines **5b** and **6b** (Figure 1). Similar behavior was found for **1f**. In this case, sulfonamide **2f** was obtained in 80% yield after 15 min of irradiation. Prolonged photolysis (2 h) caused the consumption of **2f** in favor of the formation of anilines **4f**, **5f**, and **7d** (Table 2).

Photochemical experiments on 2a–j and 3a,b

To determine the presence of secondary photochemical paths, our investigation proceeded with the exploration of sulfonamides **2** and Fries adducts **3** in MeCN (Table S3 in the Supporting Information). Compounds **2b–j** and **3a,b** are slightly more fluorescent than the corresponding sulfonimides **1b–j** and the Φ_{-1} values are, on average, lower than the corresponding sulfonimides, with notable exceptions for **2e** ($\Phi_{-1} = 0.2$) and **2j** ($\Phi_{-1} = 0.4$). Again, the presence of oxygen did not significantly affect the efficiency of consumption (Table S3 in the Supporting Information). Irradiation experiments were performed on nitrogen-saturated solutions of sulfonamides **2a**, **2b**, and **2f** in MeCN. Photolysis of **2a** gave Fries-adduct **4a** (91% yield) as the only photoproduct (Scheme S1 in the Supporting Information). An almost selective conversion of **2b** to anisidine **5b** was observed, whereas in the case of **2f** a mixture of Fries adduct **4f** and desulfonylated aniline **5f**, along with a minor amount of *ipso*-substituted product **7d**, was obtained. Finally, irradiation of Fries-adduct **3b** gave exclusively compound **6b** in 89% yield (Scheme 2).

Laser flash photolysis (LFP) and EPR experiments

Compounds **1b** and **1f** were further examined by means of time-resolved UV absorption spectroscopy. LFP experiments at $\lambda = 266$ nm on a nitrogen-saturated solution of **1b** (5×10^{-4} M) in acetonitrile revealed the formation of two intense absorptions located at $\lambda = 300$–340 and 440–460 nm (Figure 2a). The time evolution of the transient spectrum revealed the presence of different transient species, with the predominant contribution of a long-lived intermediate ($\tau \approx 100$ μs) in both absorption bands. However, two short-lived intermediates characterized by lifetimes of $\tau = 6$ and 1.8 μs were also identified at $\lambda = 300$–340 and 440–460 nm, respectively (see inset in Figure 2a and Figure S35 in the Supporting Information). Finally, a residual absorption band located at 370–400 nm can be observed about 50 μs after the laser pulse (Figure 2b).

When the same experiments were repeated in an oxygen-saturated solution, a modification of the transient absorption profile was observed; both of the

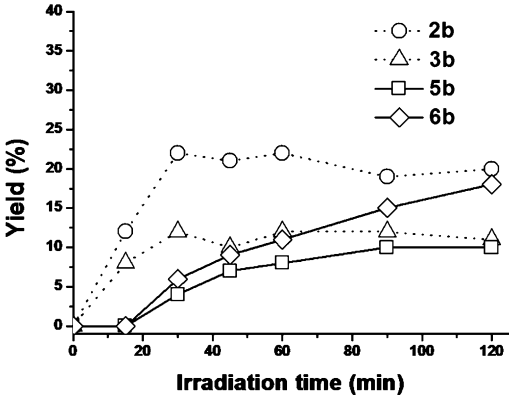
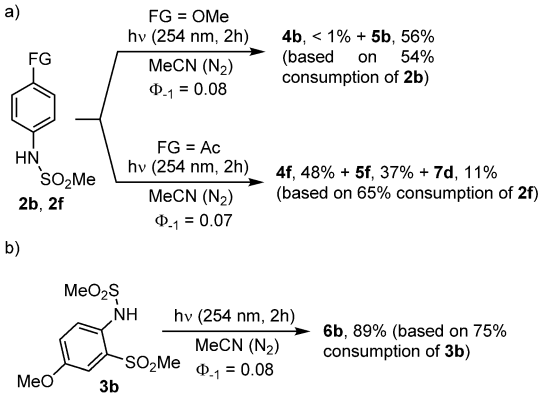


Figure 1. Yields of photoproducts obtained from irradiation of **1b** at different times. Conditions: A solution of **1b** (10^{-2} M, nitrogen purged) in acetonitrile at $\lambda = 254$ nm (4×15 W Hg lamps). Product yields calculated on the basis of the initial concentration of **1b** (see Table S3 in Supporting Information for further details).

Table 3. Irradiation of sulfonimides **1a–j** in MeCN under oxygenated conditions.[a]

	Φ_{-1}[b]	Conversion[c] [%]	H^+[d] [%]	Acids, yield[e] [%]
1a	0.29	100	72	CH_3SO_3H, 66
1b	0.21	92	149	CH_3SO_3H, 154
1c	0.08	74	172	CH_3SO_3H, 178
1d	0.08	70	157	CH_3SO_3H, 154
1e	0.10	80	190	CH_3SO_3H, 182
1f	0.28	100	199	CH_3SO_3H, 192
1f[f]	–	100	195	CH_3SO_3H, 185
1g	<0.01	<1	<1	–
1h	0.22	96	186	CH_3SO_3H, 182
1i	0.23	100	195	$CH_3C_6H_4SO_3H$, 200; CH_3COOH, <1
1j	0.22	100	698	H_2SO_3, 175; HF, 330

[a] Conditions: Solutions of **1a–j** (10^{-2} M, oxygen purged) in MeCN irradiated for 2 h at $\lambda = 254$ nm. [b] Measured on a 10^{-2} M solution of **1a–j** in oxygen-purged MeCN ($\lambda = 254$ nm). [c] Determined by HPLC or GC analyses. [d] Determined by potentiometric titration of the photolyzed solution with aqueous NaOH. [e] Determined by HPLC ion chromatography analyses. [f] Reaction carried out on an air-equilibrated solution.



Scheme 2. Irradiation of **2b**, **2f**, and **3b** (10^{-2} M, nitrogen purged) in MeCN.

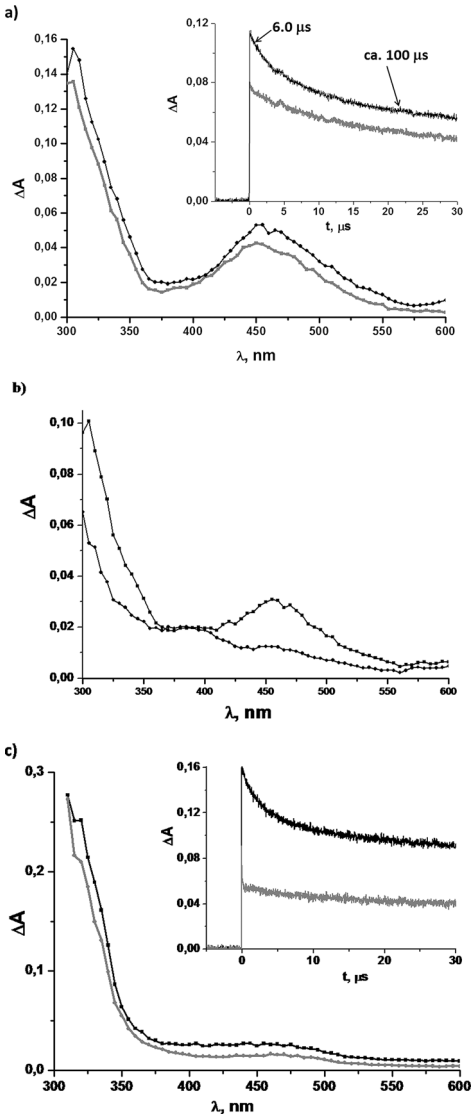


Figure 2. Transient absorption spectra of a solution of **1b** in nitrogen- (black) and oxygen-saturated (gray) acetonitrile a) recorded 6 µs after a 7 ns laser pulse ($\lambda = 266$ nm); inset: profile of the absorbance change observed at 330 nm; and b) recorded 50 (upper curve) and 450 µs after a 7 ns laser pulse ($\lambda = 266$ nm). c) Transient absorption spectra of a solution of **1i** in nitrogen- (black) and oxygen-saturated (gray) acetonitrile recorded 6 µs after a 7 ns laser pulse ($\lambda = 266$ nm); inset: profile of the absorbance change observed at $\lambda = 340$ nm.

short-lived species were quenched (Figure 2a and Figures S32 and S33 in the Supporting Information), and a modest lowering in the intensity of the remaining absorption bands resulted (see Figure S33 in the Supporting Information). Analogous results were obtained in the case of acetyl derivative **1f** (5×10^{-4} M in MeCN), for which again two absorption bands ($\lambda_{max} =$ 300–340 and 450–480 nm) were detected under nitrogen-saturated conditions. However, in this case, only two transient species contributed to both bands, namely, a short- ($\tau = 1.8$ µs) and long-lived ($\tau = 100$ µs) intermediate; the former was quenched in the presence of oxygen (see Figures S37–S40 in the Supporting Information).

Turning to compound **1i** (10^{-4} M in MeCN), an absorption spectrum with a strong maximum located in the $\lambda = 300$–340 nm region was observed, along with a weaker absorption band at $\lambda \approx 440$–470 nm (Figure 2c and Figures S42–S45 in the Supporting Information). Kinetic analysis revealed the presence of a long-lived intermediate ($\tau \approx 100$ µs) that was the main contributor to both maxima. However, as in the case of **1b**, we also found the presence of two oxygen-sensitive species, characterized by lifetimes of about 1.8 and 9.4 µs, respectively; the former present in both maxima, whereas the latter only contributed significantly to the absorption in the $\lambda = 300$–340 nm region. A residual absorption with broad bands at $\lambda = 300$–340 and 420–480 nm has been detected for all of the compounds examined, even 4000 µs after the laser pulse (Figures S36, S41, and S46 in the Supporting Information). EPR analyses were performed on solutions of **1f**, **1i**, and **1j** in deaerated benzonitrile. For compounds **1f** and **1i**, two species with similar g values (2.006 ± 0.0005) were observed during irradiation of the samples by a high-pressure Hg lamp (Figure 3 and Figure S47 in the Supporting Information). Analyses of **1f** carried out in

the presence of the spin-trapping agent *N-tert*-butyl-α-phenylnitrone (PBN) resulted in amplification of the generated species, giving a signal with hyperfine coupling constants of 13 (a_N) and (3 ± 0.5) G (a_H). In the case of **1 j**, a weak signal was observed only upon irradiating the sample in the presence of 2-methyl-2-nitrosopropane (MNP) as a spin trap, although in an amount below the limit of quantification (Figure S48 in the Supporting Information).

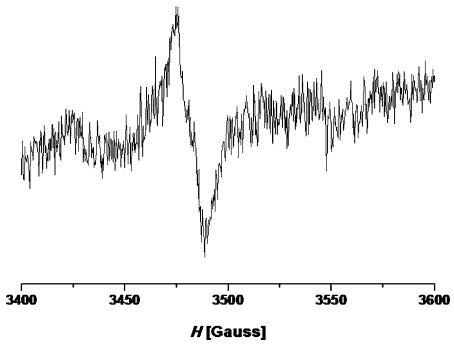


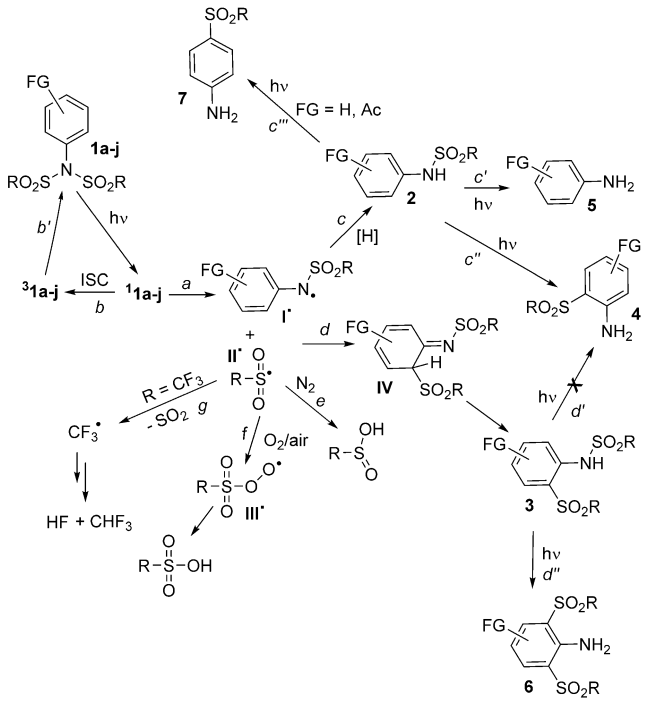
Figure 3. EPR spectra recorded during photolysis of **1 f** in deaerated benzonitrile.

Discussion

Photochemistry of compounds 1 a–j

A tentative mechanism for the photoreactivity of *N*-arylsulfonimides is shown in Scheme 3. Irradiation of **1 a**–**j** causes their excitation to the singlet excited state, ^{1}**1 a**–**j**. Then, homolytic fragmentation of one of the N–S bonds (Scheme 3, path a) takes place from ^{1}**1 a**–j to afford sulfamido (**I**•) and sulfonyl (**II**•) radicals. The presence of such species is strongly supported by both time-resolved absorption and EPR spectroscopy techniques. In particular, the long-lived transient spectrum with absorption maxima in the λ = 300–340 and 440–480 nm regions was assigned to **I**•, whereas methanesulfonyl and *para*-toluenesulfonyl radicals **II**• were characterized as the short-lived (6 and 9.4 μs, respectively), oxygen-sensitive signals in the λ = 300–340 nm region.[17] The presence of such sulfur-centered radicals was further confirmed by EPR analyses on **1 f**, for which the *g* factor value obtained for the methanesulfonyl radical (2.006 ± 0.0005) was in accordance with literature data (Figure 3).[18]

The very short lived transient species at λ = 440–460 nm for **1 b** can be safely assigned to its triplet state, by comparison with the absorption spectrum of the triplet state of anisidine.[19] Similarly, the 2 μs long, oxygen-sensitive, signals at λ = 300–340 and 440–480 nm were assigned to ^{3}**1 f** and ^{3}**1 j** (Figure S39).[20] However, the insensitivity of the photoreactions of **1 a**–**j** to oxygen (compare the similar Φ_{-1} values reported in Tables 2 and 3), and the observed photostability of **1 b** in acetone (a well-known triplet sensitizer), exclude fragmentation from this state (Scheme 3, paths b and b′). Notably, despite the presence of the acetyl substituent in derivatives **1 f**, **1 i** and **1 j** could increase the efficiency of intersystem crossing to make the triplet state accessible; no alteration of the reaction mechanism was observed. Once generated, radicals **I**• and **II**• can follow two competing pathways, namely, recombination to yield Fries rearrangement products **3** or escape from the solvent cage. In the former case, the formation of **3** (Scheme 3, path d) proceeded via intermediate **IV**,[21] which was characterized by LFP experiments by the residual λ = 370 nm absorption observed for **1 b** (see Figure 2 b). In contrast, sulfonamide **2** arises from hydrogen abstraction by radical **I**• from the reaction medium (Scheme 3, path c). The competition between these two pathways depends on the functional groups present in the aryl moiety and reaction media. Compound **3** is formed preferentially in less polar solvents (Table 1) and in the presence of electron-donating aromatic substituents (NMe_2, OMe; Table 2).



Scheme 3. Mechanism for the photochemical reactivity of *N*-arylsulfonimides **1 a**–**j**.

As previously reported,[22,23] the obtained *N*-arylsulfonamides are also photoactive, and both desulfonylation to the corresponding anilines **5** (Scheme 3, path c′) and Fries rearrangement products (**4**; Scheme 3, path c″) can be observed. The last pathway is favored for electron-rich sulfonamides, as in the case of **2 a**, which gives Fries-adduct **4 a** exclusively upon irradiation. On the other hand, when irradiating nonsubstituted **1 d**, photo-Fries rearrangement from primary photoproduct **2 d** results in the formation of either aniline **5 d** or *p*-substituted compounds **7 d** (Scheme 3, path c‴).

Compounds **7** were also obtained as minor products from acetyl derivatives **1 f** and **1 i**. In the latter case, we suggest that path c‴ (Scheme 3) is still involved and an aromatic *ipso* substitution occurs with the subsequent release of acetic acid

(Table 2). The radical-induced displacement of an acyl group was previously observed for 2-acetylbenzothiazoles[24a] and acylpyridines.[24b] Moreover, the photosubstitution of a chlorine atom for a sulfonyl group has also been reported in the photo-Fries rearrangement of *N*-chlorophenylsulfonamides, in which a chlorine cation is supposed to be lost at the end of the process.[23] The photoreactivity of photoproducts **3a** and **b** is instead limited to rearranged anilines **6a** and **b** (Scheme 3, path d''), whereas desulfonylation to compounds **4** (Scheme 3, path d') seems to have no role.

N-Arylsulfonimides as PAGs

For the release of acid, under deaerated conditions, the corresponding weak sulfinic acids are mainly released (Scheme 3, path e). However, the presence of oxygen prevents any Fries rearrangement from occurring and drives the process to the formation of radicals **III**$^{\bullet}$, which are precursors of sulfonic acids (Scheme 3, path f).[9] Thus, in the case of sulfonimides **1b–f**, **h**, and **i**, a strong acid is always photoreleased in high yields. Paradigmatic is the case of compound **1i**, for which almost two equivalents of *p*-toluenesulfonic acid were obtained from each mole of starting substrate.

Interestingly, no triflic acid was released upon irradiation of triflimide **1j** under oxygenated conditions. This is due to the facile loss of SO_2 (detected as H_2SO_3 by ion chromatography) from trifluoromethanesulfonyl radical **II**$^{\bullet}$ (Scheme 3, path g).[8] Secondary processes of the resulting trifluoromethyl radicals $F_3C^{\bullet}$ lead to the formation of fluoroform, hexafluoroethane, and the liberation of HF.[8] The presence of such radicals was confirmed by EPR analyses on **1j**. Indeed, the weak signal observed during irradiation in the presence of the spin-trapping agent MNP can be assigned to $F_3C^{\bullet}$ species (Figure S48 in the Supporting Information), according to data reported in the literature.[25]

Ionic gelation of alginate polymer induced by 1i as a proof of concept

To test the potential of the examined substrates as PAGs, light-activated ionic gelation of alginate polymer[26] was promoted by using sulfonimide **1i**. Irradiation at $\lambda = 310$ nm of a fine dispersion of 2 wt% sodium alginate in water, $CaCO_3$ (15 mmol L^{-1}), and **1i** (0.030 M) resulted in the acid-induced release of soluble Ca^{2+} ions that were capable of inducing the gelification of alginate to afford a gel capable of holding its weight in the inverted tube, as illustrated in Figure 4 and Figure S47 in the Supporting Information.

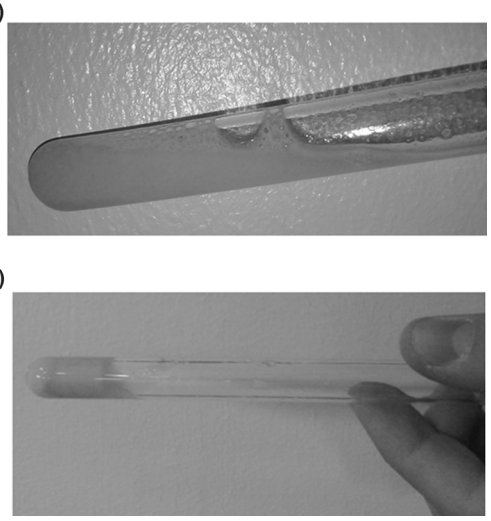


Figure 4. Quartz tube containing a suspension of sodium alginate (2 wt%), $CaCO_3$ (0.015 M) and **1i** (0.030 M) in water a) before irradiation, and b) after 6 h of irradiation at $\lambda = 310$ nm.

Conclusion

We presented herein a new class of nonionic PAGs able to release, upon irradiation, up to two equivalents of strong sulfonic acids (methanesulfonic and *p*-toluenesulfonic acids) for each mole of photoactive substrate. These compounds were efficiently obtained in a straightforward way from the corresponding commercially available anilines, and their absorption properties and photochemical behavior could be simply tuned by choosing suitable substituents.

Experimental Section

General

^{1}H NMR spectra were recorded with a 300 MHz spectrometer, and ^{13}C NMR spectra were recorded with a 75 MHz spectrometer. Assignments were made on the basis of ^{1}H and ^{13}C NMR spectra, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from tetramethylsilane (TMS).

The photochemical reactions were performed by using nitrogen- or oxygen-saturated solutions in quartz tubes in a multilamp reactor equipped with 4×15 W Hg lamps (emission centered at $\lambda = 254$ nm) for irradiation. Quantum yields were measured at $\lambda = 254$ nm (1 Hg lamp, 15 W). Solvents of HPLC-grade purity were employed for all photochemicals reactions. The reaction course was followed by either GC (compounds **1c**, **1d**, and **1h**) or HPLC analyses (all other compounds) and the products formed were identified and quantified by comparison with calibration curves of authentic samples.

GC analyses were carried out by using a chromatograph equipped with a flame ionization detector (FID). A 30 m×0.25 mm×0.25 μm capillary column was used for the separation of analytes with nitrogen as a carrier gas at 1 mL min^{-1}. Injection into the GC system was performed in split mode and the injector temperature was 250 °C. The GC oven temperature was held at 120 °C for 2 min, increased to 250 °C by a temperature ramp of 10 °C min^{-1}, and held for 10 min. HPLC analyses were carried out on a HPLC apparatus equipped with two pumps and a UV detector (C-18 column: 300×3.9 mm; eluent: MeCN/water 30/70, flux 0.5 mL min^{-1}).

GC-MS analysis on an irradiated solution of compound **1i** was carried out by using a single quadrupole GC/MS system. A 30 m×0.25 mm×0.25 μm capillary column was used for the separation of analytes with helium as a carrier gas at 1 mL min^{-1}. Injection into

the GC system was performed in split mode and the injector temperature was 250 °C. The GC oven temperature was held at 120 °C for 2 min, increased to 250 °C by a temperature ramp of 10 °C min^{-1}, and held for 10 min. The transfer line temperature was 270 °C and the ion source temperature was 250 °C. Mass spectral analysis was carried out in full-scan mode.

The acidity liberated was determined on photolyzed solutions (5 mL) by dilution with water (25 mL) and titration with a 0.1 M aqueous solution of NaOH. Titrations were followed by using an Orion mod 250 potentiometer equipped with an Orion pH glass combined electrode mod 91–56. Ion chromatography analyses were performed by means of a Dionex GP40 instrument equipped with a conductimetric detector (Dionex 20 CD20) and an electrochemical suppressor (ASRS Ultra II, 4 mm) by using the following conditions: chromatographic column IONPAC AS23 (4 mm × 250 mm), guard column IONPAC AG12 (4 mm × 50 mm), eluent: $NaHCO_3$ 0.8 mM + Na_2CO_3 4.5 mM, flux: 1 mL min^{-1}; current imposed at detector: 50 mA. Commercially available sodium methanesulfinate, sodium *p*-toluenesulfinate, methanesulfonic acid, and *p*-toluenesulfonic acid monohydrate were used as standards. The presence of fluoroform and hexafluoroethane when irradiating **1j** was detected by IR[8] and GC-MS analyses (see Figures S11 and S12 in the Supporting Information).

Microsecond transient absorption experiments were performed by using a nanosecond LFP apparatus equipped with a 20 Hz Nd:YAG laser (25 ns, 25 mJ at $\lambda = 266$ nm) and a 150 W Xe flash lamp as the probe light. Samples were placed in a quartz cell (10 × 10 mm section) at a concentration adjusted to obtain an optical density (OD) value of 1.0 at $\lambda = 266$ nm.

EPR experiments were performed on a 0.01 M solution of the chosen compounds in freshly distilled benzonitrile. A Bruker EMX 10/12 spectrometer equipped with ER4102ST cavity was employed. The lamp (a high pressure 500 W Hg lamp) was focused on the window of the cavity by means of a crown glass lens (spot diameter about 4 cm). When spin-trapping agents (PBN and MNP) were present, a concentration of 10^{-1} M was used.

Synthesis of 2a–h

Compounds **2a**–**h** were prepared by following a known procedure.[27] A solution of the chosen aniline **5a**–**h** (10 mmol) and pyridine (0.90 mL, 11 mmol) in dry dichloromethane (25 mL) was cooled to 0 °C under a nitrogen atmosphere. Methanesulfonyl chloride (0.85 mL, 11 mmol) was added dropwise with stirring, then the mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with a 6 N aqueous solution of NaOH (50 mL) and water was added to the resulting mixture to dissolve the resultant salts. The layers were then separated: the aqueous phase was washed with CH_2Cl_2 (3 × 40 mL) and cooled to 0 °C. Upon subsequent acidification to pH 2.0 (by adding aqueous HCl (18%)) a white solid precipitated. The obtained product was collected on a sintered glass funnel, washed repeatedly with cold water, and then dried under vacuum; thus giving the desired compounds without need for further purification.

Synthesis of 2i

Compound **2i** was synthesized by adapting the procedure employed for the synthesis of *N*-arylmethanesulfonamides **2a**–**h**.[27] A solution of aniline **5i** (1.35 g, 10 mmol) and pyridine (1.50 mL, 19 mmol) in CH_2Cl_2 (35 mL) was cooled to 0 °C. *p*-Toluenesulfonyl chloride (2.28 g, 12 mmol) was added portionwise under stirring. The resulting mixture was then allowed to warm to room temperature and stirred overnight. The reaction was quenched with a 6 N aqueous solution of NaOH (50 mL), and water was added to the resulting mixture to dissolve the resultant salts. The layers were separated, the aqueous phase was washed with CH_2Cl_2 (3 × 40 mL), cooled to 0 °C, and upon subsequent acidification to pH 2.0 (by adding aqueous HCl 18%) a white solid precipitated. This solid was separated by filtration on a sintered glass funnel and washed with cold water to afford **2i** as a white solid (87%) without need for further purification.

Synthesis of 2j

Compound **2j** was synthesized by adapting the procedure employed for the synthesis of *N*-alkyltrifluoromethanesulfonamides.[28] Trifluoromethanesulfonic anhydride (1.8 mL, 11 mmol) was added dropwise under stirring to a cooled solution (−78 °C) of **5f** (1.35 g, 10 mmol) and triethylamine (1.6 mL, 11 mmol) in dry CH_2Cl_2 (35 mL) under a nitrogen atmosphere. The mixture was stirred at −78 °C for 2 h, allowed to warm to room temperature, transferred to a separation funnel, and quenched with water (60 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL), then the organic phases were combined and treated with a 6 N aqueous solution of NaOH (50 mL) and water to dissolve the resultant salts. The layers were separated, the aqueous phase was washed with CH_2Cl_2 (3 × 40 mL), cooled to 0 °C, and upon acidification to pH 2.0 (by adding aqueous HCl (18%)) a white solid precipitated. This solid was separated by filtration on a sintered glass funnel and washed with cold water to afford **2j** as a white solid (70%) without need for further purification.

Synthesis of 1a–h

Compounds **1a**–**h** were obtained from **2a**–**h** by following a known procedure.[29] Methanesulfonyl chloride (0.57 mL, 7.4 mmol) was rapidly added to a solution of **2a**–**h** (5.0 mmol) and NaOH (5.2 mmol) in water (15 mL) under vigorous stirring. A white precipitate appeared instantaneously, then the resulting mixture was further stirred for 30 min and extracted with CH_2Cl_2 (3 × 20 mL). The organic phases were combined, washed with a 10% aqueous solution of NaOH (2 × 20 mL), dried over Na_2SO_4, and the solvent was evaporated to give **1a**–**h** as white solids.

Synthesis of 1i

Compound **1i** was synthesized by adapting a known procedure for the synthesis of *N*-aryl-*p*-toluenesulfonimides.[30] *p*-Toluenesulfonyl chloride (4.0 g, 21 mmol) was added portionwise under stirring at room temperature to a solution of aniline **5f** (1.35 g, 10 mmol) and triethylamine (4.2 mL, 30 mmol) in CH_2Cl_2 (30 mL). After 24 h of stirring, the mixture was quenched with water (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was washed sequentially with water (75 mL), a 10% aqueous solution of HCl (3 × 30 mL), water (2 × 50 mL), a 10% aqueous solution of NaOH (2 × 30 mL), and brine (2 × 30 mL) and dried with Na_2SO_4. The solvent was then evaporated to afford the crude product. After purification by column chromatography (eluent: cyclohexane/ethyl acetate, 9:1), compound **1i** was obtained as a white solid (77%).

Synthesis of 1j

Compound **1j** was synthesized by using a procedure employed for the synthesis of *N*-(4-vinylphenyl)-1,1,1-trifluoro-*N*-[(trifluorome-

thyl)sulfonyl]methanesulfonamide.[31] Trifluoromethanesulfonic anhydride (3.6 mL, 21 mmol) was added dropwise to a cooled solution (−78 °C) of **5 f** (1.35 g, 10 mmol) and triethylamine (4.0 mL, 30 mmol) in dry CH_2Cl_2 (35 mL) under a nitrogen atmosphere. The mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature, and then further stirred for another hour. The resulting mixture was diluted with dichloromethane (80 mL) and washed with a saturated aqueous solution of $NaHCO_3$ (3×30 mL) and brine (3×30 mL). The organic layer was then dried over Na_2SO_4 and the solvent was evaporated. The crude residue was thus purified by column chromatography (eluent: hexane/ethyl acetate, 95:5) to afford **1 j** as a white solid (83%).

Preparative irradiations

Preparative photochemical reactions were performed by using nitrogen-saturated solutions (0.012–0.052 M) in quartz tubes in a multilamp reactor equipped with 4×15 W Hg lamps (emission centered at $\lambda = 254$ nm) for irradiation. Workup of the photolytes involved concentration in vacuo (80–100 torr) and chromatographic separation. Solvents of HPLC purity were employed.

Photogelling of alginate polymer

Light-activated ionic gelation experiments followed a reported procedure.[26] The sample to be irradiated was prepared by combining $CaCO_3$ particles (15 mmol L^{-1}) with a suspension of sodium alginate (2.0 wt%) and **1 i** (dissolved in the minimum amount of MeCN) in distilled water. The resulting mixture was stirred overnight by using a magnetic stirring bar and then sonicated for 45 min at 20 kHz. Then an aliquot (2 mL) was placed in a 10 mL quartz tube and irradiated under stirring in a multilamp apparatus fitted with 10×15 W phosphor-coated lamps (emission centered at $\lambda =$ 310 nm).

Acknowledgements

We acknowledge Prof. A. Albini (University of Pavia) for fruitful discussions and Dr. S. Lazzaroni for experimental support in EPR analyses. This work has been supported by the Fondazione Cariplo (grant no. 2012-0186).

Keywords: photochemistry · radicals · reaction mechanisms · sulfonic acids · sulfonimides

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Received: July 26, 2016
Published online on ■■ ■■, 0000

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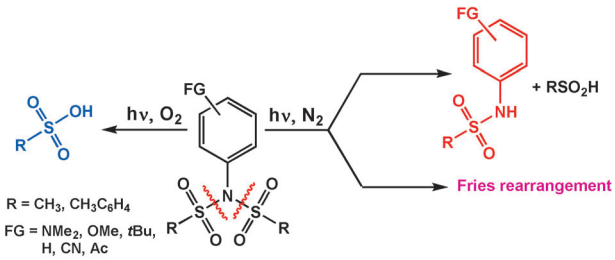

Two-for-one on acid generation: The photochemical behavior of differently substituted *N*-arylsulfonimides is described. Homolysis of the S–N bond takes place as the exclusive pathway from the singlet state to afford both *N*-arylsulfonamides and photo-Fries adducts, the amount of which depends on reaction conditions and aromatic substituents (see scheme). Sulfinic and sulfonic acids were likewise released under deaerated and oxygenated conditions, respectively.

Reaction Mechanisms

*E. Torti, S. Protti, D. Merli, D. Dondi, M. Fagnoni**

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Photochemistry of *N*-Arylsulfonimides: An Easily Available Class of Nonionic Photoacid Generators (PAGs)