JOC Article
pubs.acs.org/joc

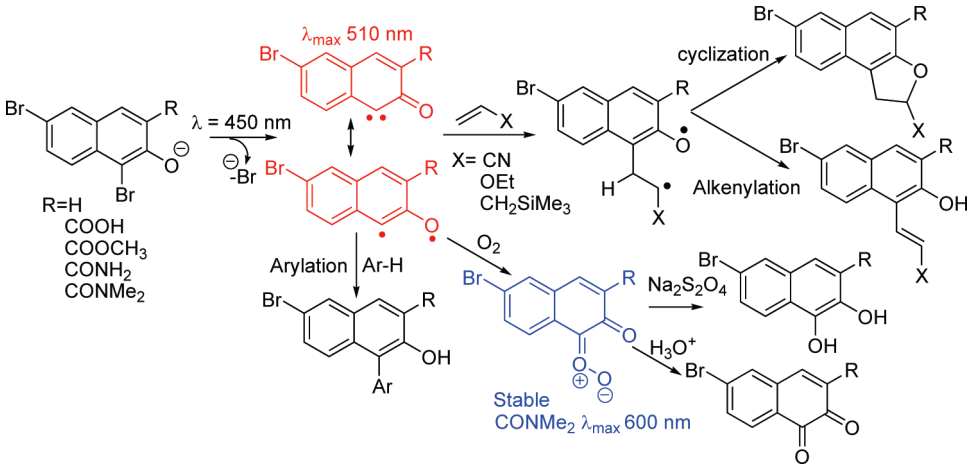
Selective Arylation, Alkenylation, and Cyclization of Dibromonaphthols, Using Visible Light, via Carbene Intermediates

Daniela Verga, Filippo Doria, Mariella Mella, and Mauro Freccero*

Dipartimento di Chimica Organica, Università di Pavia, V.le Taramelli 10, 27100 Pavia, Italy

mauro.freccero@unipv.it

Received April 16, 2009



The photoreactivity of several 3-substituted-1,6-dibromo-2-naphthols has been investigated in neat acetonitrile in the presence of diluted Et_3N and in aqueous buffered acetonitrile (pH 8, phosphate buffered), using visible light (450 nm). Hydrobromic acid loss in the presence of the base, for the unsubstituted naphthol, or heterolytic C−Br cleavage directly from the naphtholates, for the more acid 3-substutited naphthols (R = $COOCH_3$, $CONH_2$, $CONMe_2$), generates electrophilic carbene intermediates, which have been successfully trapped by molecular oxygen, pyrrole, acrylonitrile, ethyl vinyl ether, and allyltrimethylsilane. Product distribution analysis reveals three types of products arising from (i) arylation, (ii) alkenylation, and (iii) cyclization reactions. The generation and the reactivity of α-ketocarbene intermediates, as electrophilc diradicals, has been supported by laser flash photolysis, with the detection of both the carbene (λ_{max} 510 nm) and 1,2-naphthoquinone-*O*-oxide (R = $CONMe_2$, λ_{max} 600 nm) in the presence of O_2.

Introduction

The carbon−halogen bond cleaving process in aromatic halides, triggered by photoexcitation in protic media, has been studied for several decades[1] by product studies,[2] diagnostic chemical trapping, steady-state measurements, and time-resolved detection.[3] Such a process has found interesting applications in the degradation of organic pollutants mainly in water, using UV−vis light,[4] and more recently for synthetic purposes in organic protic solvents.[5] Three main reaction pathways have been identified: (i)

(1) (a) Schutt, L.; Bunce, N. J. In *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W. M., Lenci F., Eds.; CRC Press: Boca Raton, 2004, Chapters 38 and 39 and references therein. (b) Grimshaw, J.; De Silva, A. P. *Chem. Soc. Rev.* **1981**, *10*, 181–203.

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

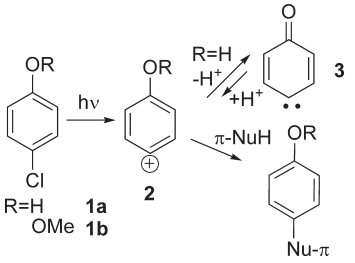
(3) (a) Grabner, G.; Richard, C.; Kohler, G. *J. Am. Chem. Soc.* **1994**, *116*, 11470–11480. (b) Bonnichon, F.; Grabner, G.; Guyot, G.; Richard, C. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1203−1210. (c) Arnold, B. R.; Scaiano, J. C.; Bucher, G. F.; Sander, W. *J. Org. Chem.* **1992**, *57*, 6469–6474.

(4) (a) Sykora, J.; Pado, M.; Tatarko, M; Izakovic, M. *J. Photochem. Photobiol. A* **1997**, *110*, 167–175. (b) Skurlatov, Y. I.; Ernestova, L. S.; Vichutinskaya, E. V.; Samsonov, D. P.; Semenova, I. V.; Rodko, I. Y.; Shvidky, V. O.; Pervunina, R. I.; Kemp, T. J. *J. Photochem. Photobiol. A* **1997**, *107*, 207–213.

(5) (a) Lazzaroni, S.; Protti, S.; Fagnoni, M.; Albini, A. *Org. Lett.* **2009**, *11*, 349–352. (b) Fagnoni, M.; Albini, A. *Acc. Chem. Res.* **2005**, *38*, 713–721. (c) Dichiarante, V.; Fagnoni, M. *Synlett* **2008**, 787–800.

DOI: 10.1021/jo900793b Published on Web 06/12/2009

SCHEME 1 Photogeneration of 4-Oxocyclohexa-2,5-dienylidene Carbene (3) and 4-Hydroxyphenyl Cation (2) from Chlorophenol 1a and Chloroanisole 1b

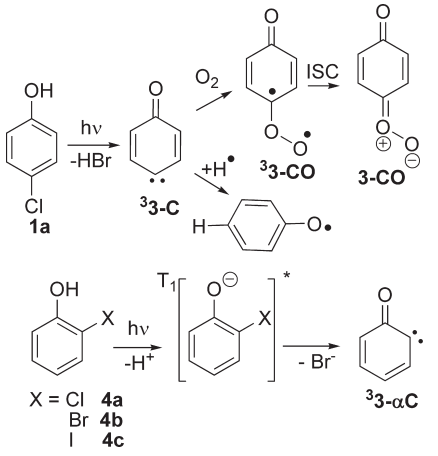


photohomolysis,[6] (ii) photoinduced electron transfer in the presence of a suitable donor followed by the cleavage of the resulting radical anion,[7] and more recently (iii) heterolysis with the generation of aryl cations.[5,8] The generation of aryl cations has found promising synthetic applications in the formation of new C−C bonds[5b] by photoexcitation of halophenols and haloanilines in protic solvents, in the presence of π-nucleophiles as traps.[8−10] In more detail, the photoreactivity of 4-chlorophenol (**1a**) and 4-chloroanisole (**1b**) has been rationalized as the result of a heterolytic process generating 4-oxocyclohexa-2,5-dienylidene carbene (**3**)[3,11] and 4-hydroxyphenyl cation (**2**) (Scheme 1).[9a]

The ketocarbene **3** arises from the 4-hydroxyphenyl cation (**2**) by a deprotonation process. Fast deprotonation, in the presence of bases, precludes the phenyl cation chemistry, since it efficiently generates the carbene. In these conditions the chemistry of the triplet carbene ^{3}**3-C**, which includes oxygen trapping and hydrogen abstraction, becomes dominant (Scheme 2).

More recently, the photochemistry of *o*-halophenols such as 2-chlorophenol (**4a**), 2-bromophenol (**4b**), and 2-iodophenol (**4c**) have been thoroughly investigated in aqueous solution by Grabner's group.[12] The chemical processes occurring after photoheterolysis of the *o*-halophenols are ring contraction, hydrolysis, and α-ketocarbene (^{3}**3-αC**) formation. Since the last process is much more efficient for iodo and bromo derivatives than for the chlorophenol, the authors

SCHEME 2 Photoreactivity of 4-Chlorophenol (1a) and 2-Halophenols (4a−4c)



suggest that the reaction pathway arising from the α-ketocarbene has to be a triplet excited state chemistry, which is favored by the internal heavy atom effect.[12b] The α-ketocarbene 2-oxocyclohexa-3,5-dienylidene (^{3}**3-αC**) has been assigned on the basis of its reactivity and on its spectroscopic characteristics by LFP.[12a] The typical α-ketocarbene reactions are addition to O_2 to yield *o*-benzoquinone-*O*-oxide and H-abstraction. This chemical behavior mirrors that of the related 4-oxocyclohexa-2,5-dienylidene, mentioned above,[3a] and that of 4-iminocyclohexa-2,5-dienylidene.[13] Such a photoreactivity is even more general, since it has also been extended to bromonaphthols (**5a** and **5b**, Scheme 3).[14] In fact, we have recently shown that there is a parallelism between the photoreactivity of the carbenes **3** and ^{3}**5-C**, arising from the photoactivation of halophenols (such as **1** and **4**) and 6-bromonaphthols (**5**), respectively. The carbene ^{3}**5-C** exhibits a strong electrophilic diradical character at both oxygen and C-6 carbon and has been trapped by electron-rich alkenes, aromatics, and heteroaromatics. (Scheme 3).[14]

The above preliminary study had prompted us to further investigate the photoreactivity of 3-substituted-1,6-dibromo-2-naphthols (**6a**−**6e** in Chart 1; compounds with the same letters share the same X substituent at C-3) and ethers (**7a** and **7c**). The dibromonaphthols **6a**−**6e** may in principle photogenerate carbenes at the C6 atom, such as ^{3}**5-C** (Scheme 2), or an α-ketocarbene at the C1 atom (such as **6-C**, Chart 1). In order to (i) evaluate both the regioselectivity of the photodehalogenation process [C(1)-Br vs C(6)-Br; see Chart 1 for numbering] and the subsequent reactions involving carbene intermediates (**6-C** vs **5-C**), we have investigated the photolysis of the 3-substituted-1,6-dibromo-2-naphthols **6a**−**6e**, in the presence of alkenes, aromatics, and O_2 by both product distribution analysis and laser flash photolysis.

Results and Discussion

Photoreactivity of 1,6-DiBr-2-naphthol (6a). Selectivity of the Dehalogenation Process. The photoreactivity of **6a** was

(6) (a) Park, Y.-T.; Song, N. W.; Kim, Y.-H.; Hwang, C.-G.; Kim, S. K.; Kim, D. *J. Am. Chem. Soc.* **1996**, *118*, 11399–11405. (b) Grimshaw, J.; De Silva, A. P. *J. Chem. Soc.* **1979**, 193–194. (c) Grimshaw, J.; De Silva, A. P. *J. Chem. Soc., Chem. Commun.* **1980**, 302–303. (d) Grimshaw, J.; De Silva, A. P. *Can. J. Chem.* **1980**, *58*, 1880–1888.

(7) (a) Takeda, N.; Poliakov, P. V.; Cook, A. R.; Miller, J. R. *J. Am. Chem. Soc.* **2004**, *126*, 4301–4309. (b) Costentin, C.; Robert, M.; Saveant, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 16051–16057. (c) Chami, Z.; Gareil, M.; Pinson, J.; Saveant, J.-M.; Thiebault, A. *J. Org. Chem.* **1991**, *56*, 586–595. (d) Bunce, N. J.; Pilon, P.; Ruzo, L. O.; Sturch, D. J. *J. Org. Chem.* **1976**, *41*, 3023–3025.

(8) (a) Manet, I.; Monti, S.; Grabner, G.; Protti, S.; Dondi, D.; Dichiarante, V.; Fagnoni, M.; Albini, A. *Chem.—Eur. J.* **2008**, *14*, 1029–1039. (b) Dichiarante, V.; Fagnoni, M.; Mella, M.; Albini, A. *Chem.—Eur. J.* **2006**, *12*, 3905–3915.

(9) (a) Manet, I.; Monti, S.; Fagnoni, M.; Protti, S.; Albini, A. *Chem.—Eur. J.* **2005**, *11*, 140–151. (b) Guizzardi, B.; Mella, M.; Fagnoni, M.; Freccero, M.; Albini, A. *J. Org. Chem.* **2001**, *66*, 6353–6363.

(10) (a) Guizzardi, B.; Mella, M.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2003**, *68*, 1067–1074. (b) Guizzardi, B.; Mella, M.; Fagnoni, M.; Albini, A. *Tetrahedron* **2000**, *56*, 9383–9389.

(11) (a) Sander, W.; Mueller, W.; Sustmann, R. *Angew. Chem.* **1988**, *100*, 577–579. (b) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583–1621. (c) Wenk, H. H.; Hubert, R.; Sander, W. *J. Org. Chem.* **2001**, *66*, 7994–7999.

(12) (a) Bonnichon, F.; Richard, C.; Grabner, G. *Chem. Commun.* **2001**, 73–74. (b) Bonnichon, F.; Grabner, G.; Richard, C.; Lavedrine, B. *New J. Chem.* **2003**, *27*, 591–596.

(13) Othmen, K.; Boule, P.; Szczepanik, B.; Rotkiewicz, K.; Grabner, G. *J. Phys Chem. A* **2000**, *104*, 9525–9534.

(14) Pretali, L; Doria, F.; Verga, D.; Profumo, A; Freccero, M. *J. Org. Chem.* **2009**, *74*, 1034–1041.

SCHEME 3

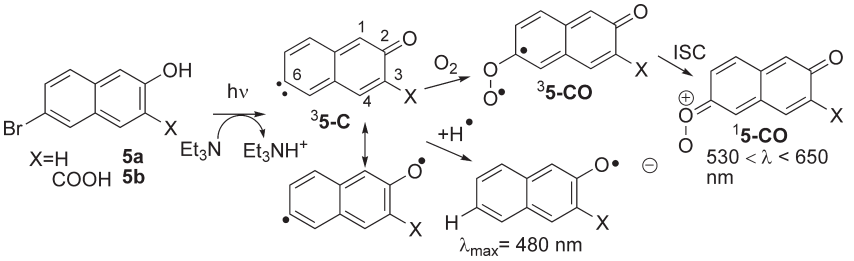
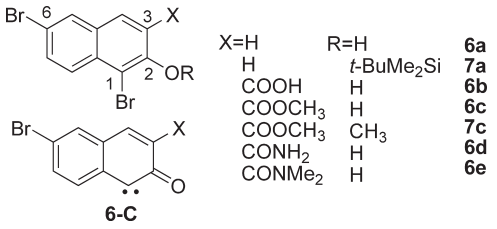


CHART 1



first explored in 1×10^{-3} M solutions using four lamps (15 W) centered at 310 nm, in the presence of different traps (1×10^{-1} M) such as allyltrimethylsilane, acrylonitrile, and pyrrole, in acetonitrile (ACN). Similarly to 6-Br-naphthols, in the absence of Et_3N, no reactivity was observed after 5 h of irradiation.[14] The irradiations were also run in the presence of Et_3N (2×10^{-3}M), in neat ACN and MeOH, and using NaPi (phosphate) buffer pH 8, in aqueous ACN (1:1) and MeOH (1:1). The choice of using Et_3N had been suggested by our previous investigation,[14] where we have shown that the reaction yields for the photoalkylation and -arylation of 6-Br-2-naphthols at C6 (see Chart 1 for numbering) are systematically improved by addition of Et_3N as base. The addition of the base in ACN, unlike for 6-Br-2-naphthols, causes a moderate red shift in the UV−vis spectrum of 1,6-dibromo-2-naphthol (λ_{max} = 350 nm), extending the absorption up to 450 nm. Taking advantage of this red shift, the photoreactivity was explored using two different wavelengths, centered at 310 and 450 nm, in O_2-free solution. The addition of Et_3N to neat ACN, similarly to 6-bromo-2-naphthol, switched on the reactivity, but the product distribution was wavelength-dependent. In more detail, the photolysis carried out in ACN in the presence of Et_3N (2×10^{-3} M) using 4 lamps centered at 450 nm activates selectively the heterolysis of the C1−Br bond with a low conversion of **6a** into **5a** (20% yield) after 3 h of irradiation. An almost identical conversion was achieved also in aqueous ACN buffered by NaPi at pH 8. The addition of Et_3N to neat MeOH, afforded a quantitative conversion to **5a** by a clean reductive dehalogenation process. In the presence of both allyltrimethylsilane (1×10^{-1} M) and Et_3N, beside the main product **5a**, we isolated **8a** (20% yield by HPLC), also recovering unreacted **6a** (<10%). The ratio **5a**/**8a** is a function of the Et_3N concentration, rising with the Et_3N concentration, as reported in Table 1.

In contrast, the photolysis of **6a** carried out in ACN in the presence of Et_3N (2×10^{-3} M) using 4 lamps centered at 310 nm (irradiation time, 1 h) activated the heterolysis of both C1−Br and C6−Br bonds, with the generation of a crude photolysate containing **5a** (20%) and 2-naphthol (15%). The irradiation at the same wavelength in the presence of both Et_3N and allyltrimethylsilane (1×10^{-1} M) gave a reaction mixture composed of 2-naphthol as the main product (30% yield), **8a** (24%), and 6-allylnaphthalen-2-ol (22%).[14] The TBS ether **7a** was not reactive under the irradiation conditions described above.

The irradiation of **6a** at 450 nm, in ACN, after 1 h in the presence of both O_2 and Et_3N generates a greenish reaction mixture, which was bleached by HCl addition. The main product in the resulting mixture was the naphthoquinone **9** (33% yield), identified by comparison to an authentic sample synthesized according a published procedure.[15] The very same greenish reaction mixture was also bleached with a mild reducing agents, such as aqueous $Na_2S_2O_4$ solution. In this case, a comparable conversion into the dihydroquinone **10** (36% yield)[16] was observed.

The formation of the adducts **8a** (which still contains the TMS moiety), **5a** (Scheme 4), and the naphthoquinone **9** or its dihydroquinone **10** (depending on the reaction workup) in the presence of O_2 occurs selectively by direct irradiation of the naphtholate anion **6a**$^-$ at longer wavelength. These evidence suggest that the photoreactivity may be ascribed to the carbene **6-C** as intermediate. In addition, the complete absence of the 1-allyl-6-bromo-naphthalen-2-ol among the photoproducts, which should arise from the trapping of an aryl cation intermediate, followed by a desilylation due to the loss of the TMS cation, ruled out the aryl cation as a possible reactive intermediate.

Photoreactivity of 3-Substituted 1,6-DiBr-2-naphthols (6b−6e) in the Presence of Allyltrimethylsilane. We also investigated the photoreactivity of the 3-substituted naphthols **6b**−**6e** in neat ACN in the presence of Et_3N (2×10^{-3}M) and allyltrimethylsilane (1×10^{-1} M) by visible-light irradiation 450 nm. The efficiency of the photoreaction involving the acid **6b** is very low, even in the presence of a higher concentration of Et_3N (2×10^{-2} M), and the photoproducts arising from the photodehalogenation of the amide **6d** were very difficult to isolate and purify by column chromatography because of an almost identical retention time. The methylether **7c** was stable under irradiations for several hours. Therefore, we investigate the photoreactivity of **6c** and **6e**, isolating the resulting photoproducts by preparative chromatography. Three types of adducts have been identified, which result from (i) reductive dehalogenation (**5b**, **5c**), (ii) alkylation (**8e**, **11c**, and **11e**), and (iii) cyclization

(15) Grugni, M.; Cassin, M.; Colella, G.; De Munari, S; Pardi, G.; Pavesi, P. *PCT Int. Appl. WO 066923*, **2006**; *Chem. Abstr.* **2006**, *145*, 103543.

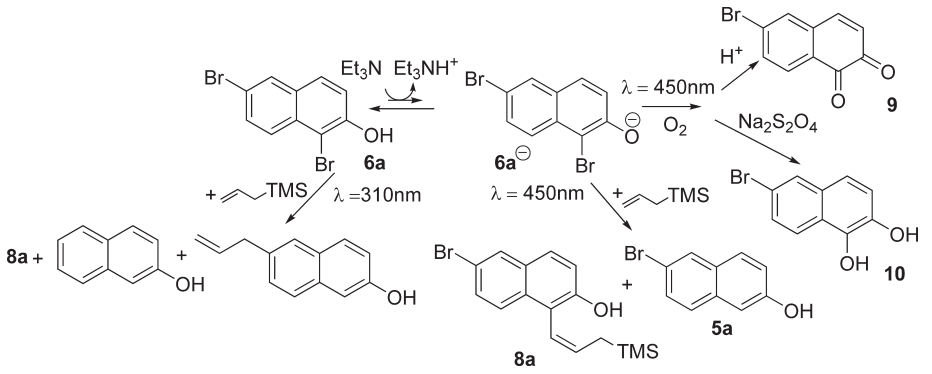
(16) (a) Burke, T. R.; Lim, B.; Marquez, V. E.; Li, Z. H.; Bolen, J. B.; Stefanova, I.; Horak, I. D. *J. Med. Chem.* **1993**, *36*, 425–432. (b) Horst, T. *Z. Chem.* **1973**, *13*, 216.

TABLE 1. Photoreactivity of 6a, 6c, and 6e in ACN or Aqueous ACN in the Presence of Allyltrimethylsilane and Et_3N or in Buffered Conditions (pH 8)[a]

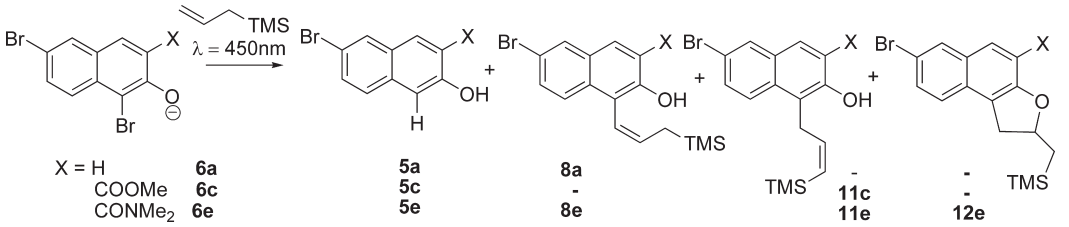
compd	irradiation time (h, λ 450 nm)	conversion (%)	products (% yield)
6a	3	30[b]	**5a** (10), **8a** (20)
		22[c]	**5a** (4), **8a** (18)
6c	3	80[b]	**5c** (60), **11c** (17)
		60[c]	**5c** (40), **11c** (14)
6e	1	37[c,d]	**5e** (trace), **8e** (13), **11e** (10), **12e** (14)
6e	2	58[c,d]	**5e** (trace), **8e** (≤5%), **11e** (32), **12e** (18)

[a] **6a**, **6c**, and **6e** concn = 1×10^{-3} M; allyltrimethylsilane concn = 0.1 M. [b] Et_3N concn = 2×10^{-2} M. [c] Et_3N concn = 2×10^{-3} M, [d] 1:1 MeCN/NaPi buffer pH 8, 2×10^{-3} M.

SCHEME 4



SCHEME 5



reactions (**12e**) (Scheme 5). Conversion and product yields for the reactants **6c** and **6e** are reported and compared to the data for **6a** in Table 1. The alkylation adducts **8e** and **12e** are both primary photoproducts since they are detected from the beginning of the irradiation (< 30 min). Longer irradiation time (≥1 h) causes a decrease of **8e** and an increase of both 11e and **12e**. Therefore, **11e** has to be considered a secondary product arising from **8e**. The alkylation reaction is stereospecific since the alkenes **8a**, **8e**, **11c**, and **11e** exhibit a *cis* configuration of the double bond, as suggested by NOE experiments on both **8e** and **11c** (see Supporting Information), which display a NOE effect between the alkene protons. In addition, the coupling constant $^3J_{H,H}$ of the alkene protons in **8a** is identical to that in **8e** (11 Hz), and that of **11e** is identical to that in **11c** (14 Hz).

These data suggest that the photodehalogenation is more efficient (higher product yields with lower irradiation time) for the 3-substituted derivatives **6c** and **6e** in comparison to that of the unsubstituted 1,6-diBr-2-naphthol (**6a**), as a result of a more intense absorbance for the 3-derivatives **6c** and **6e** at 450 nm. Such a red shift is caused by a higher concentration of the naphtholate anions $\mathbf{6c}^-$ and $\mathbf{6e}^-$, due to the lower pK_a values of **6c** and **6e**, in comparison to that of **6a** (pK_a 7.9[17] to 8.9[18]). In order to evaluate the acidity of these 3-substituted derivatives and to support such an hypothesis, we decided to run pK_a measurement experiments. Because of the insolubility of **6c** in water or in aqueous solution, it was not possible to run the pK_a measurement for the ester derivative. The different solubility of **6e** allowed the experimental measurement of the pK_a value in 20% v/v ACN/H_2O. The UV−vis spectra of **6e** (Supporting Information) is a function of the pH value. The band centered at 355 nm is ascribed to the absorbance of neutral naphthol **6e**. With the increasing of the pH value, the ground-state deprotonation generated a new band centered at 390 nm, with a tail up to 450 nm. The pK_a of the ground state was carried out by monitoring the pH dependence of anionic $\mathbf{6e}^-$ absorption. The sigmoid titration curve fitted to a Boltzman function[19] gave a pK_a of 6.82. The low pK_a for the amide **6e**, together with the photoreactivity of both **6c** and **6e** at 450 nm, suggests that the selectivity of the photodehalogenation (C1−Br vs C6−Br) is complete when the naphtholates $\mathbf{6c}^-$ and $\mathbf{6e}^-$ are directly irradiated. In other words, the conjugate bases of **6c** and **6e** undergoes selective C1−Br photoheterolysis.

(17) Rosenberg, J. L.; Brinn, I. M. *J. Phys. Chem.* **1972**, *76*, 3558–3562.

(18) Rosenberg, J. L.; Brinn, I. M. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 448–452.

(19) Albert, A.; Serjeant, E. P. In *The Determination of Ionization Constants*, 3rd ed.; Chapman and Hall: New York, 1984.

SCHEME 6

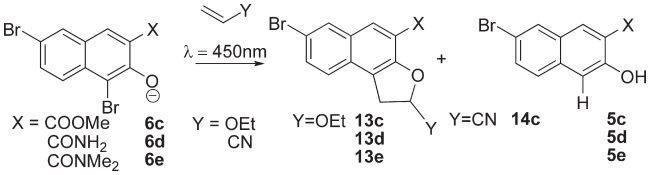


TABLE 2. Photoreactivity of 6c−e in ACN or Aqueous ACN in the Presence of Ethyl Vinyl Ether (EVE) and Et_3N

alkene (0.1 M)	compd	Y	conversion (%)	products (% yield)
EVE	**6c**[a]	OCH_2CH_3	85[c]	**5c** (60), **13c** (25)
			41[d]	**5c** (20), **13c** (21)
acrylonitrile	**6c**[a]	CN	55[c]	**5c** (50), **14c** (5)
			25[d]	**5c** (20), **14c** (5)
EVE	**6d**[b]	OCH_2CH_3	85[c]	**5d** (60), **13d** (25)
			47[d]	**5d** (26), **13d** (21)
EVE	**6e**[b]	OCH_2CH_3	51[d]	**5e** (10), **13e** (41)

[a] Irradiation time = 3 h. [b] Irradiation time = 2 h, concn of **6c−e** = 1×10^{-3} M. [c] Et_3N concn = 2×10^{-2} M. [d] Et_3N concn = 2×10^{-3}M.

SCHEME 7

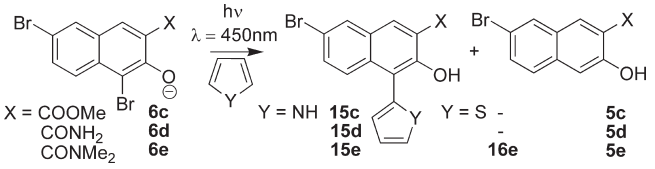


TABLE 3. Photoreactivity of 6c−e in the Presence of Pyrrole and Thiophene in ACN and Aqueous ACN, NaPi Buffered (pH 8.0)[a]

heterocycle	compound	Y	conversion (%)	Products (% yield)
pyrrole	**6c**[b]	NH	64[d]	**5c** (40), **15c** (24)[d]
			30[e]	**5c** (10), **15c** (20)[e]
pyrrole	**6d**[c]	NH	100[d]	**5d** (50), **15d** (50)[d]
			70[e]	**5d** (20), **15d** (50)[e]
pyrrole	**6e**[c]	NH	74[e]	**5e** (10), **15e** (64)[e]
			70[f]	**5e** (−),**15e** (70)[f]
thiophene	**6e**[c]	S	50[e]	**5e** (10), **15e** (40)[e]
			45[f]	**5e** (trace), **15e** (45)[e]

[a] Pyrrole and thiophene concn = 0.1 M; **6c−e** concn = 1×10^{-3} M. [b] Irradiation time 3 h. [c] Irradiation time 2 h. [d] Et_3N concn = 2×10^{-2} M. [e] Et_3N concn = 2×10^{-3} M. [f] 1:1 MeCN/NaPi buffer pH 8 2×10^{-3} M.

Photoreactivity of 3-Substituted 1,6-DiBr-2-naphthols in the Presence of Ethyl Vinyl Ether and Acrylonitrile. We also investigated the photoreactivity of the 3-substituted naphthols **6c−e** in neat ACN in the presence of Et_3N (2×10^{-3} M) and both ethyl vinyl ether (EVE) and acrylonitrile (1×10^{-1} M), as prototypes of electron-rich and -poor alkenes, by visible-light irradiation (450 nm). Two types of adducts have been isolated and characterized. They result from (i) reductive dehalogenation (**5c−e**) and (ii) cyclization reactions (**13c−e**, **14c**) (Scheme 6).

Photoarylation of 3-Substituted 1,6-DiBr-2-naphthols in the Presence of Heterocycles. The photoreactivity of the 3-substituted naphthols **6c−e** was also investigated in the presence of pyrrole and thiophene and Et_3N in neat ACN and in aqueous acetonitrile, buffered at pH 8 (Scheme 7). Reaction conditions and product yields are listed in detail in Table 3. The main adducts (**5c−e**) were generated by a reductive dehalogenation process, using a high concentration of Et_3N ($\geq 2 \times 10^{-2}$ M) in ACN. In contrast, the arylation adducts became dominant when running the photoreaction at a lower concentration of Et_3N ($\leq 2 \times 10^{-3}$ M). The irradiation in buffered aqueous acetonitrile (1:1, pH 8) generated a quantitative conversion of the reactant into the photoarylation adduct, without detectable photodehalogenation product.

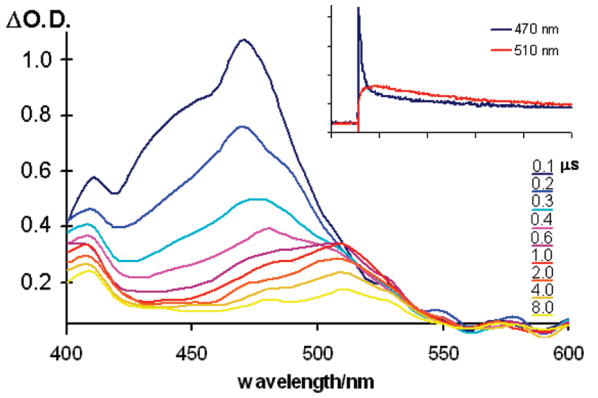
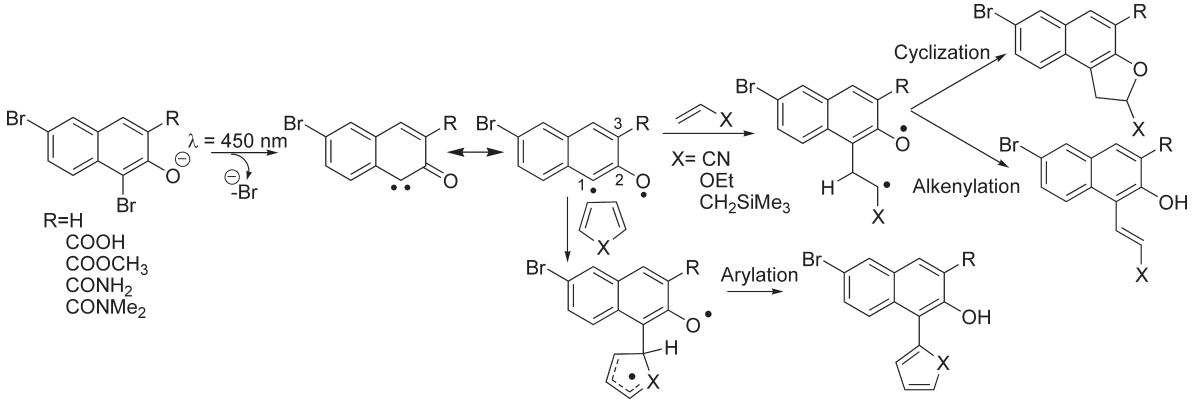


FIGURE 1. Transient absorption spectra of **6a** in 1:1 H_2O/ACN solution, buffered at pH 8, in the absence of O_2 (solution purged with argon). The spectra were taken 0.1, 0.2, 0.3, 0.4, 0.6, 1, 2, 4, and 8 μs after the laser pulse, respectively. The inset shows the decay traces monitored at 470 and 510 nm.

SCHEME 8



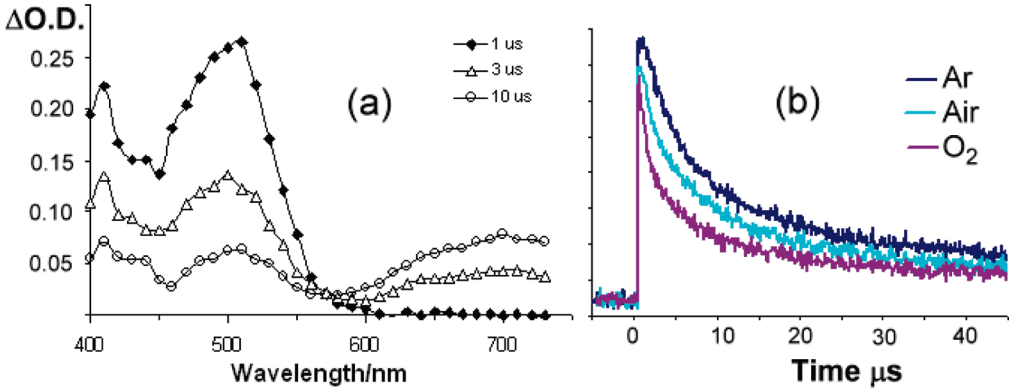


FIGURE 2. (a) Transient absorption spectra of **6a** in 1:1 H_2O/ACN solution, buffered at pH 8, in the presence of O_2 (air-equilibrated solution). The spectra were taken 1, 3, and 10 μs after the laser pulse, respectively. (b) Decay traces monitored at 510 nm in solutions purged with argon, air and O_2.

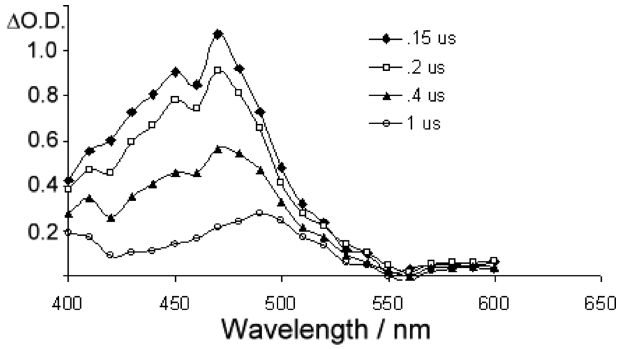


FIGURE 3. Transient absorption spectra of **6a** in neat ACN in the presence of Et_3N in the absence of O_2 (solution purged with air). The spectra were taken 0.15, 0.2, 0.4, and 1.0 μs after the laser pulse, respectively.

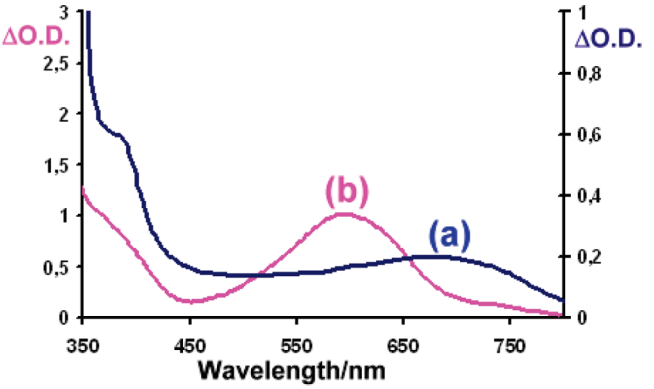


FIGURE 4. Absorption spectra of a solution of (a) **6a** and (b) **6e** in neat ACN in the presence of Et_3N, in the presence of O_2 (solution purged with O_2), measured after 50 laser shots, which have been assigned to the fairly stable carbonyloxides **6a-CO** and **6e-CO**.

The products arising from the photoheterolysis of the naphtholates and the further reactions of cyclization, alkenylation, and arylation in the absence of oxygen can be rationalized, according Scheme 8, with the generation of a reactive α-ketocarbene with diradical character at both C1 and O2 atoms. In order to support such an hypothesis we ran a LFP investigation with the aim to directly detect such a reactive intermediate.

Detection of Intermediates by Laser Flash Photolysis. The photolysis of an ACN aqueous solution of 1,6-diBr-2-naphthol (**6a**), buffered at pH 8 and purged with argon, results in a transient spectrum exhibiting at pulse end an absorption centered at 470 nm (Figure 1). At longer times (>1 μs), the transient spectrum is transformed into a less intense and red-shifted band, centered at 510 nm. The insert in Figure 1 shows the parallel time course of the absorbances at 470 and 510 nm. At the longer wavelength, the formation kinetics of this transient is seen, and this buildup is mirrored by the decay at 470 nm. In addition, the 510 nm absorbing species was quenched by both isopropyl alcohol (IPA) and pyrrole.

Irradiation of an air- and oxygen-saturated ACN aqueous solution of 1,6-diBr-2-naphthol (**6a**) buffered at pH 8 produces a pulse-end spectrum very similar to that reported in Figure 1. The primary absorption was completely bleached after the 0.2 μs laser pulse, leaving the secondary absorption substantially unmodified (Figure 2a). A closer inspection on a much shorter time scale (0.2 μs) revealed that both the transient species detected at 470 and 510 nm were quenched by O_2. The pseudo-first-order decay rate constants at both 470 and 510 nm were found to be proportional to the oxygen concentration (for instance, see decay traces monitored at 510 nm in Figure 2b).

In an aqueous ACN solution of 1,6-diBr-2-naphthol (**6a**) saturated by oxygen, a third broad absorption, rising from the transient centered at 510 nm, became detectable a longer wavelength (Figure 2a). Its lifetime was longer than 100 μs.

The transient spectrum generated from flashing an argon-saturated ACN solution of **6a** in the presence of Et_3N (2×10^{-3}M) displays two similar transients, the first one with two maxima at 450 and 470 nm and a second one, exhibiting a much longer lifetime, centered at 490 nm (see Figure 3).

Similarly to the aqueous acetonitrile, both of the transient species detected at 470 and 490 nm are quenched by O_2. The latter is also quenched by pyrrole. In addition, at much longer time after the pulse (>2 μs) in an ACN oxygen-saturated solution, a third broad absorption (very similar to that in Figure 2a) became detectable. This species is stable for several hours in ACN solution, and its spectrum can be recorded by classical visible detection (Figure 4a).

Such a species is instantaneously bleached by both addition of acidic water or a reducing $Na_2S_2O_4$ solution. The

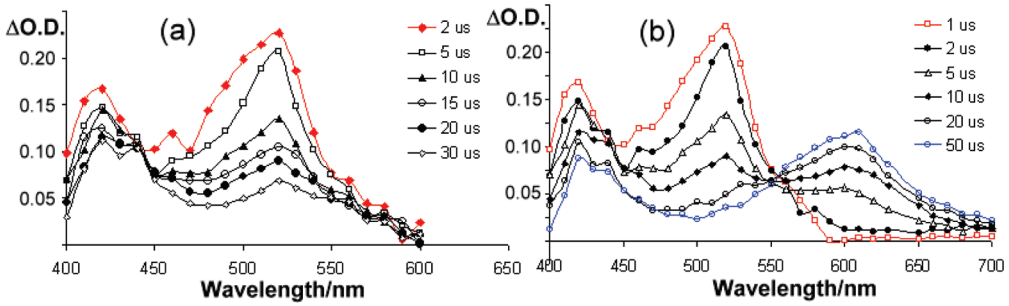
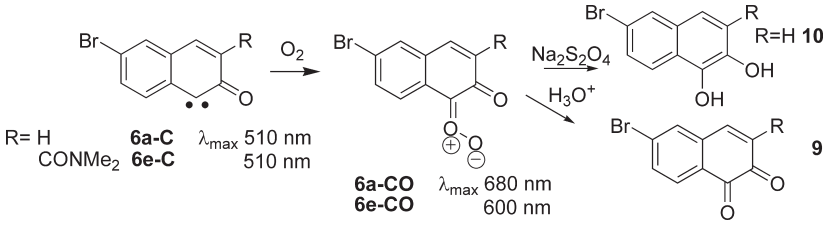


FIGURE 5. (a) Transient absorption spectra of **6e** in 1:1 H_2O/ACN solution, buffered at pH 8, in the absence of O_2 (solution purged with argon). The spectra were taken 2, 5, 10, 15, 20, and 30 μs after the laser pulse. (b) Transient absorption spectra of **6e** in 1:1 H_2O/ACN solution, buffered at pH 8, in O_2 equilibrated solutions. The spectra were recorded 1, 2, 5, 10, 20, and 50 μs after the laser pulse.

SCHEME 9



main products detected by HPLC after aqueous or reductive quenching are the naphthoquinone **9** and the dihydroquinone **10**, respectively. The quenching experiments in the presence of pyrrole and oxygen suggest that the transient absorbing at shorter wavelength (470 nm) is the triplet excited state of 1,6-dibromonaphthol and the second absorption (510 nm) has to be ascribed to the carbene **6a-C** (Scheme 9). Since the species exhibiting the broad spectrum is generated from the carbene **6a-C** in the presence of O_2, it has to be the carbonyloxide **6a-CO**. Such a hypothesis is further supported by the HPLC product distribution analysis, which reveals the formation of the naphthoquinone **9** an the dihydroquinone **10** under aqueous acid and reducing quenching, respectively.

Photolysis of an argon-saturated ACN aqueous solution of 4,7-dibromo-3-hydroxy-naphthalene-2-carboxylic acid dimethylamide (**6e**), buffered at pH 8, results in a transient spectrum exhibiting an end pulse absorption centered at 510 nm (Figure 5).

This transient was quenched by O_2. In the presence of O_2 the formation of a second transient species at longer wavelength was clear, with an absorption centered at 600 nm (Figure 5b).

The only difference in comparison to the aqueous solution was the persistence of the blue transient (λ_{max} 600 nm) for several hours (Figure 4b). Similarly to the reactivity of 1,6-diBr-2-naphthol (**6a**), the latter species was instantaneously bleached by addition of either acid water or a reducing $Na_2S_2O_4$ solution. Therefore, the blue-colored specie has to be ascribed to the analogue carbonyl oxide **6e-CO** (Scheme 9).

Conclusions

We have described the photoreactivity of 3-substituted-1,6-dibromo-2-naphthols both in acetonitrile and in aqueous acetonitrile. Under slightly basic conditions the photodehalogenation of the acid naphthols (**6c**−**e**, $pK_a \leq 7$) occurs by direct irradiation of the naphtholate anions, using visible light ($\lambda = 450$ nm). Using visible light, the heterolytic fragmentation of the C1−Br bond is selective. Such a fragmentation generates an electrophilic carbene, which has been directly detected by laser flash photolysis and trapped by several alkenes, heterocycles, and molecular oxygen. The generation of the resulting photoproducts, according to the reactions of arylation, cyclization, and alkenylation, has been rationalized taking into account the key feature of the carbene, which reacts as a diradical at both C1 and O2 atoms. The reactivity of the carbene with pyrrole and O_2 has been monitored by LFP, allowing also the detection of stable carbonyloxides.

Experimental Section

2-Naphthol and **5a** are commercially available products. The substituted naphthols **5c**−**e**,[20,21] **6a**,[22] **6b**,[23] 6-allylnaphthalen-2-ol,[14] and 6-bromonaphthalene-1,2-dione (**9**)[15] are known products; **9** was synthesized via standard published procedure.[15]

Methyl 4,7-Dibromo-3-hydroxynaphthalene-2-carboxylate (6c). Compound **6b** (3.0 g, 8.68 mmol) dissolved in Et_2O (50 mL) was added dropwise to a solution of CH_2N_2 (546 mg, 13.0 mmol) in Et_2O. A light yellow solid precipitated. The suspension was stirred for 1 h a room temperature. The solid was filtered and pure **6c** was obtained (2.174 g, yield 70%). Mp 205.4−206.9 °C. ^{1}H NMR ($CDCl_3$): δ 4.08 (s, 3H), 7.69 (dd, J = 9.1, 1.9 Hz, 1H), 7.97 (d, J = 1.9 Hz, 1H), 8.06 (d, J = 9.1 Hz, 1H), 8.38 (s, 1H), 11.29 (s, 1H, -OH). ^{13}C NMR ($CDCl_3$): δ 53.1, 107.2, 114.9, 118.3, 127.6, 128.2, 130.6, 131.1, 133.5, 134.6, 153.4, 169.5. Anal. Calcd for $C_{12}H_8Br_2O_3$: C, 40.04; H, 2.24; Br, 44.39; O, 13.33. Found: C, 40.15; H, 2.17; Br, 44.34.

(20) Li, X.; Hewgley, J. B.; Mulrooney, C. A.; Yang, J.; Kozlowski, M. C. *J. Org. Chem.* **2003**, *68*, 5500–5511.
(21) Zitscher, A. U.S. Patent 1850526, **1932**; *Chem. Abstr.* **1932**, 26035.
(22) (a) Vyas, P. V.; Bhatt, A. K.; Ramachandraiah, G.; Bedekar, A. V. *Tetrahedron Lett.* **2003**, *44*, 4085–4088. (b) Koelsch, F. C. *Org. Synth.* **1940**, *20*, 12–21.
(23) Murphy, R. A.; Kung, H. F.; Kung, M. P.; Billings, J. *J. Med. Chem.* **1990**, *33*, 171–178.

4,7-Dibromo-3-hydroxynaphthalene-2-carboxamide (6d). Compound **6c** (100 mg, 0.279 mmol) was dissolved in NH_3 32%/CH_3CN (8:2, 10 mL). This solution was stirred at rt. After 24 h the reaction mixture was cooled at 0 °C, and HCl 10% was added until pH 1−2 was reached. A solid precipitated. The solid was filtered and dried under vacuum. Pale yellow crystals were obtained (91 mg, yield 95%). Mp > 235 °C dec. ^{1}H NMR (DMSO): δ 7.82 (dd, J = 9.1, 2.0 Hz, 1H), 7.98 (d, J =9.1 Hz, 1H), 8.05 (d, J = 2.0 Hz, 1H), 8.44 (bs, 1H), 8.59 (s, 1H), 9.21 (bs, IH), 13.88 (s, 1H). ^{13}C NMR (DMSO): δ 105.8, 117.1, 117.4, 127.1, 127.8, 128.4, 130.9, 132.9, 133.1, 154.7, 171.5. Anal. Calcd for $C_{11}H_7Br_2NO_2$: C, 38.30; H, 2.05; Br, 46.32; N, 4.06; O, 9.28. Found: C, 38.37; H, 1.98; Br, 46.30; N, 4.15.

4,7-Dibromo-3-hydroxy-*N*,*N*-dimethylnaphthalene-2-carboxamide (6e). Compound **6c** (500 mg, 1.40 mmol) was dissolved in $NHMe_2$ 40%, water solution (20 mL) and stirred at rt for 24 h. The reaction mixture was cooled at 0 °C, and HCl 10% was added until pH 1−2 was reached. After a few minutes a solid precipitated. The solid was filtered and dried under vacuum. The reaction mixture was purified by chromatography on silica gel 60 HR, eluting with cyclohexane/ethyl acetate = 7:3. The product was obtained as white crystals (233 mg, yield 45%). Mp 193.5−194.9 °C. ^{1}H NMR ($CDCl_3$): δ 3.22 (s, 6H), 7.68 (dd, J = 9.1, 1.9 Hz, 1H), 7.72 (s, 1H), 7.94 (d, J = 1.9 Hz, 1H), 8.03 (d, J = 9.1 Hz, 1H), 9.17 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 37.6, 107.7, 118.4, 121.8, 127.2, 127.6, 128.5, 130.3, 132.2, 132.3, 150.9, 169.6. Anal. Calcd for $C_{13}H_{11}Br_2NO_2$: C, 41.86; H, 2.97; Br, 42.84; N, 3.75; O, 8.58. Found: C, 41.76; H, 3.05; Br, 42.82; N, 3.78.

***tert*-Butyl(1,6-dibromonaphthalen-2-yloxy)dimethylsilane (7a).** To a solution of **6a** (100 mg, 0.331 mmol) and imidazole (42 mg, 0.622 mmol) in CH_2Cl_2 (10 mL) was added TBDMSCl (90 mg, 0.596 mmol). After the mixture stirred overnight at rt, H_2O (5 mL) was added. The phases were separated, and the aqueous phase was extracted twice with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (cyclohexane/CH_2Cl_2 = 98:2), yielding **7a** as a colorless oil (138 mg, yield 98%). ^{1}H NMR ($CDCl_3$): δ 0.34 (s, 6H), 1.12 (s, 9H), 7.15 (d, J = 8.9 Hz, 1H), 7.60−7.63 (m, 2H), 7.94 (d, J = 1.8 Hz, 1H), 8.10 (d, J = 9.1 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ −4.0, 18.4, 25.7, 112.1, 118.2, 121.9, 127.4, 128.3, 129.7, 130.5, 130.8, 132.0, 150.9. Anal. Calcd for $C_{16}H_{20}Br_2OSi$: C, 46.17; H, 4.84; Br, 38.39; O, 3.84; Si, 6.75. Found: C, 46.24; H, 4.73; Br, 38.46; Si, 6.74.

Methyl 4,7-Dibromo-3-methoxynaphthalene-2-carboxylate (7c). Compound **6c** (100 mg, 0.279 mmol) was dissolved in anhydrous THF (10 mL) containing K_2CO_3 (46 mg, 0.335 mmol) and 2.5% 18-crown-6 (2 mg, 0.838×10^{-2} mmol). The suspension was stirred for 10 min, and CH_3I (48 mg, 0.335 mmol, 0.021 mL) was added. The mixture was stirred at rt for 4 h, and a second portion of CH_3I (48 mg, 0.335 mmol, 0.021 mL) was added. After 5 h, the solvent was evaporated, and water was added to the residue. The K_2CO_3 and 18-crown-6 were dissolved, and the product remained in suspension. The white solid was filtered and dried under vacuum (101 mg, yield 97%). Mp 132.2−133.9 °C. ^{1}H NMR ($CDCl_3$): δ 4.01 (s, 3H), 4.03 (s, 3H), 7.74 (dd, J = 9.1, 1.9 Hz, 1H), 8.05 (d, J = 1.9 Hz, 1H), 8.15 (d, J = 9.1 Hz, 1H), 8.26 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 52.2, 61.8, 117.3, 120.1, 125.9, 128.2, 130.4, 130.6, 130.7, 132.2, 132.8, 153.2, 164.9. Anal. Calcd for $C_{13}H_{10}Br_2O_3$: C, 41.75; H, 2.69; Br, 42.73; O, 12.83. Found: C, 41.83; H, 2.60; Br, 42.70.

General Procedure for the Irradiation of 6a in the Presence of Allyltrimethylsilane. An argon-purged solution of **6a** (91 mg, 0.3 mmol), freshly distilled allyltrimethylsilane (3.43 g, 30 mmol), and Et_3N (607 mg, 6 mmol) in 300 mL of CH_3CN was irradiated for 3 h by using argon-purged solutions in Pyrex tubes (20 mL) and a multilamp reactors fitted with four 15 WT8 PREHEAT COOL WHITE 4500 K lamps, with maximum emission centered at 450 nm. Chromatographic separation (cyclohexane/ethyl acetate = 98:2) following solvent removal by vacuum concentration gave 20 mg of **8a** (20%, yield) and 9 mg of **5a** (11%, yield). The other preparative irradiations were performed under similar conditions (Supporting Information)

(*Z*)-6-Bromo-1-(3-(trimethylsilyl)prop-1-enyl)naphthalen-2-ol (8a). Colorless oil. ^{1}H NMR ($CDCl_3$): δ −0.09 (s, 9H), 1.51 (d, J = 8.4 Hz, 2H), 5.61 (s, 1H), 6.31 (dt, J = 11.0, 8.4 Hz, 1H), 6.41 (d, J = 11.0 Hz, 1H), 7.24 (d, J = 8.9 Hz,1H), 7.51 (dd, J = 9.0, 1.8 Hz, 1H), 7.63−7.67 (m, 2H), 7.93 (s, J = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ −1.9, 20.8, 115.8, 116.8, 118.0, 118.5, 126.0, 127.9, 129.3, 129.8, 129.9, 131.3, 136.2, 149.6. Anal. Calcd for $C_{16}H_{19}BrOSi$: C, 57.31; H, 5.71; Br, 23.83; O, 4.77; Si, 8.38. Found: C, 57.40; H, 5.75; Br, 23.62; Si, 8.49.

(*Z*)-7-Bromo-3-hydroxy-*N*,*N*-dimethyl-4-(3-(trimethylsilyl)prop-1-enyl)naphthalene-2-carboxamide (8e). Colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 9H), 1.46 (dd, J = 8.5, 1.2 Hz 1H), 3.16 (s, 6H), 6.23 (dt, J = 11.1, 8.5 Hz, 1H), 6.41 (dd, J = 11.1, 1.2 Hz, 1H), 7.54 (dd, J = 9.0, 1.9 Hz, 1H), 7.66 (s, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.93 (d, J = 1.9 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ −1.8, 20.9, 30.8, 117.4, 118.6, 123.4, 126.4, 128.4, 130.3, 130.4, 130.8, 131.8, 135.0, 148.6, 169.9. Anal. Calcd for $C_{19}H_{24}BrNO_2Si$ C, 56.15; H, 5.95; Br, 19.66; N, 3.45; O, 7.87; Si, 6.91. Found: C, 56.13; H, 5.98; Br, 19.74; N, 3.38; Si, 7.04.

6-Bromonaphthalene-1,2-dione (9). Compound **9** was synthesized according to a published procedure.[15] Mp 166.5−167.8 °C. ^{1}H NMR (DMSO): δ 6.46 (d, J = 10.2 Hz, 1H), 7.62 (d, J = 10.2 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 8.2 Hz 1H), 7.89 (s, 1H). ^{13}C NMR (DMSO): δ 129.1, 129.3, 130.3, 130.9, 132.3, 133.0, 136.5, 142.7, 177.5, 179.8. Anal. Calcd for $C_{10}H_5BrO_2$: C, 50,67; H, 2,13; Br, 33,71; O, 13,50. Found: C, 50.60; H, 2.15; Br, 33.78.

6-Bromonaphthalene-1,2-diol (10).[16] To a solution of **9** (100 mg, 0.422 mmol) in acetonitrile (10 mL) was added a water solution of $Na_2S_2O_4$. The color of the solution instantaneously changed from orange to pale yellow. After 10 min, oxygen was bubbled into the resulting solution in order to removed the unreacted $Na_2S_2O_4$ in excess. The solvent was evaporated under reduced pressure. A pale yellow solid was obtained that was dried under vacuum (99 mg, yield 98%). Mp > 198 °C dec. ^{1}H NMR (DMSO): δ 7.18 (d, J = 8.7 Hz, 1H), 7.27 (d, J = 8.7 Hz, 1H), 7.44 (dd, J = 9.0, 2.0 Hz, 1H), 7.93 (d, J = 9.0 Hz 1H), 7.98 (d, J = 2.0 Hz 1H), 9.50 (bs, 2H). ^{13}C NMR (DMSO): δ 115.7, 118.1, 119.7, 123.3, 127.3, 129.0, 129.4, 129.5, 137.8, 140.7. Anal. Calcd for $C_{10}H_7BrO_2$: C, 50,24; H, 2,95; Br, 33,42; O, 13,38. Found: C, 50.37; H, 2.90; Br, 33.39.

(*Z*)-Methyl-7-bromo-3-hydroxy-4-(3-(trimethylsilyl)allyl)naphthalene-2-carboxylate (11c). The compound was purified by column chromatography and eluted with cyclohexane. White crystals. Mp 104.2−105.9 °C. ^{1}H NMR ($CDCl_3$): δ 0.31 (s, 9H), 3.96 (dd, J = 6.4, 2.4 Hz 2H), 4.05 (s, 3H), 5.64 (dd, J = 14.0, 2.4 Hz, 1H), 6.25 (dt, J = 14.0, 6.4 Hz, 1H), 7.61 (dd, J = 9.2, 2.0 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.98 (d, J = 2.0 Hz, 1H), 8.34 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 0.0, 28.5, 52.6, 114.5, 117.0, 120.9, 125.0, 128.0, 129.8, 130.1, 131.6, 132.0, 134.7, 146.0, 153.8, 170.2. m/z: 379 (100.0%), 394 (55.1%), 347 (48.6%), 281 (21.7%), 361 (10.9%), 334 (10.9%). Anal. Calcd for $C_{18}H_{21}BrO_3Si$: C, 54.96; H, 5.38; Br, 20.31; O, 12.20; Si, 7.14. Found: C, 54.90; 5.46; Br, 20.25; Si, 7.34.

(*Z*)-7-Bromo-3-hydroxy-*N*,*N*-dimethyl-4-(3-(trimethylsilyl)allyl) naphthalene-2-carboxamide (11e). Colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.30 (s, 9H), 3.24 (s, 6H), 3.96 (dd, J = 6.4, 1.8 Hz, 2H), 5.63 (d, J = 14.0, 1.8 Hz, 1H), 6.27 (dt, J = 14.0, 6.4 Hz, 1H), 7.59 (dd, J = 9.1, 2.0 Hz, 1H), 7.64 (s, 1H), 7.82 (d, J = 9.1, 1H), 7.92 (d, J = 2.0 Hz, 1H), 9.61 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 0.0, 28.5, 38.3, 117.0, 120.2, 121.3, 125.0, 126.6, 127.8, 130.0, 130.8, 130.9, 132.8, 146.1, 152.1, 171.2. Anal. Calcd for $C_{19}H_{24}BrNO_2Si$: C, 56.15; H, 5.95; Br, 19.66; N, 3.45; O, 7.87; Si, 6.91. Found: C, 56.02; H, 5.98; Br, 19.61; N, 3.53; Si, 6.97.

7-Bromo-2-trimethylsilanylmethyl-1,2-dihydro-naphtho[2,1-*b*]furan-4-carboxylic Acid Dimethylamide (12e). The compound was purified by repeating twice the chromatography separation in CH_2Cl_2/ethyl ether = 98:2 as eluent. Colorless oil. ^{1}H NMR ($CDCl_3$): δ 0.14 (s, 9H), 1.21 (dd, J = 14.2, 6.6 Hz, 1H), 1.43 (dd, J = 14.2, 8.2 Hz, 1H), 2.96 (s, 3H), 3.07 (dd, J = 15.3, 8.3 Hz, 1H), 3.16 (s, 3H), 3.61 (dd, J = 15.3, 9.0 Hz, 1H), 5.18−5.21 (m, 1H), 7.44 (d, J = 8.8 Hz, 1H), 7.55 (dd, J = 8.8, 1.6 Hz, 1H), 7.66 (s, 1H), 7.96 (d, J = 1.6 Hz, 1H). ^{13}C NMR DEPT ($CDCl_3$): δ −1.0 (CH_3), 25.6 (CH_2), 34.9 (CH_3), 36.8 (CH_2), 38.3 (CH_3), 83.7 (CH), 116.6 (C), 119.8 (C), 122.4 (C), 124.2 (CH), 126.6 (CH), 129.4 (C), 129.7 (C), 130.4 (CH), 130.8 (CH), 153.3 (C), 167.8 (C). Anal. Calcd for $C_{19}H_{24}BrNO_2Si$: C, 56.15; H, 5.95; Br, 19.66; N, 3.45; O, 7.87; Si, 6.91. Found: C, 56.23; H, 5.90; Br, 19.55; N, 3.41; Si, 6.97.

7-Bromo-2-ethoxy-1,2-dihydro-naphtho[2,1-*b*]furan-4-carboxylic Acid Methyl Ester (13c). The compound was purified by column chromatography and eluted with cyclohexane/ethyl acetate = 95:5. Yellow powder. Mp 105.0−106.1 °C. ^{1}H NMR ($CDCl_3$): δ 1.29 (t, 3H), 3.33 (dd, J = 16.6, 2.3 Hz, 1H), 3.58 (dd, J = 16.6, 6.8 Hz, 1H), 3.76−3.81 (m, 1H), 4.00 (*s*, 3H), 4.05−4.12 (m, 1H), 6.07 (dd, J = 6.8, 2.3 Hz, 1H), 7.47 (d, J = 8.9 Hz, 1H), 7.60 (dd, J = 8.9, 1.9 Hz, 1H), 8.04 (d, J = 1.9 Hz, 1H), 8.32 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.9, 35.0, 52.1, 64.6, 107.1, 116.1, 117.2, 120.2, 124.4, 129.3, 130.92, 131.2, 131.5, 131.9, 154.4, 165.2. Anal. Calcd for $C_{16}H_{15}BrO_4$: C, 54.72; H, 4.31; Br, 22.75; O, 18.22. Found: C, 54.80; H, 4.34; Br, 22.60.

7-Bromo-2-ethoxy-1,2-dihydro-naphtho[2,1-*b*]furan-4-carboxylic Acid Amide (13d). The compound was purified by silica gel column chromatography and eluted using cyclohexane/ethyl acetate = 7:3. White crystals. Mp 179.8−181.7 °C. ^{1}H NMR ($CDCl_3$): δ 1.30 (t, 3H), 3.39 (dd, J = 16.7, 2.1 Hz, 1H), 3.63 (dd, J = 16.7, 6.7 Hz, 1H), 3.76−3.82 (m, 1H), 3.99−4.05 (m, 1H), 6.11 (dd, J = 6.7, 2.1 Hz, 1H), 6.52 (bs, 1H), 7.47 (d, J = 8.9 Hz, 1H), 7.61 (dd, J = 8.9, 1.8 Hz, 1H), 7.67 (bs, 1H), 8.06 (d, J = 1.8 Hz, 1H), 8.48 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 15.0, 35.0, 65.0, 108.1, 116.95, 117.7, 119.1, 124.3, 129.9 130.6, 131.0, 131.9, 132.0, 152.4, 166.0. Anal. Calcd for $C_{15}H_{14}BrNO_3$: C, 53.59; H, 4.20; Br, 23.77; N, 4.17; O, 14.28. Found: C, 53.65; H, 4.18; Br, 23.82; N, 4.20.

7-Bromo-2-ethoxy-1,2-dihydro-naphtho[2,1-*b*]furan-4-carboxylic Acid Dimethylamide (13e). The compound was separated by column chromatography and eluted with cyclohexane/ethyl acetate = 7:3. White crystals. Mp 154.8−156.0 °C: ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 3H), 2.97 (s, 3H), 3.18 (s, 3H), 3.34 (dd, J = 16.7, 2.3 Hz, 1H), 3.59 (dd, J = 16.7, 6.8 Hz, 1H), 3.70−3.76 (m, 1H), 3.97−4.02 (m, 1H), 5.91 (dd, J = 6.8, 2.3 Hz, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.55 (dd, J = 8.8, 1.2 Hz, 1H), 7.68 (s, 1H), 7.97 (d, J = 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 15.0, 35.0, 35.4, 38.3, 64.5, 107.1, 117.1, 118.6, 122.4, 124.4, 126.7, 129.12, 130.0 130.6, 130.8, 151.9, 167.6. Anal. Calcd for $C_{17}H_{18}BrNO_3$: C, 56.06; H, 4.98; Br, 21.94; N, 3.85; O, 13.18. Found: C, 56.14; H, 4.95; Br, 21.84; N, 3.94.

7-Bromo-2-cyano-1,2-dihydro-naphtho[2,1-*b*]furan-4-carboxylic Acid Methyl Ester (14c). The compound was purified by column chromatography and eluted with cyclohexane/ethyl acetate = 8:2. Yellow pale crystals. Mp 171.4−173.2 °C. ^{1}H NMR ($CDCl_3$): δ 3.96−4.04 (m, 2H), 4.11 (s, 3H), 5.81 (dd, J = 10.1, 6.1 Hz, 1H), 7.59 (d, J = 8.8 Hz, 1H), 7.81 (dd, J = 8.8, 1.7 Hz, 1H), 8.21 (d, J = 1.7 Hz, 1H), 8.50 (s, 1H). ^{13}C NMR DEPT ($CDCl_3$): δ 34.1 (CH_2), 52.4 (-CH_3), 69.1 (CH), 116.4 (C), 117.4 (C), 118.5 (C), 124.1 (CH), 130.0 (C), 130.3 (C), 131.8 (CH), 132.6 (CH), 132.8 (CH), 154.1 (C), 164.4 (C). Anal. Calcd for $C_{15}H_{10}BrNO_3$: C, 54.24; H, 3.03; Br, 24.06; N, 4.22; O, 14.45. Found: C, 54.17; H, 3.09; Br, 24.04; N, 4.15.

Methyl-7-bromo-3-hydroxy-4-(1*H*-pyrrol-2-yl)naphthalene-2-carboxylate (15c). The compound was purified by column chromatography using cyclohexane/ethyl acetate = 8:2 as eluent. Yellow solid. Mp 169.7−171.2 °C. ^{1}H NMR ($CDCl_3$): δ 4.06 (s, 3H), 6.44−6.53 (m, 2H), 7.03−7.04 (m, 1H), 7.55 (dd, J = 9.2, 1.8 Hz, 1H), 7.97 (d, J = 1.8 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H), 8.35 (s, 1H), 9.09 (bs, 1H) 11.16 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 52.8, 108.7, 111.3, 114.3, 115.7, 117.6, 118.3, 124.0, 127.4, 128.3, 130.1, 131.0, 132.2, 134.4, 153.3, 170.3. Anal. Calcd for $C_{16}H_{12}BrNO_3$: C, 55.51; H, 3.49; Br, 23.08; N, 4.05; O, 13.87. Found: C, 55.45; H, 3.58; Br, 23.21; N, 3.94.

7-Bromo-3-hydroxy-4-(1*H*-pyrrol-2-yl)naphthalene-2-carboxamide (15d). Yellow solid. Mp > 165.0 °C dec. ^{1}H NMR (DMSO-d_6): δ 6.16−6.22 (m, 2H), 6.88−6.92 (m, 1H), 7.60 (dd, J = 9.2, 2.0 Hz, 1H), 7.76 (d, J = 9.2 Hz, 1H), 7.99 (d, J = 2.0 Hz, 1H), 8.26 (bs, 1H), 8.51 (s, 1H), 8.81 (bs, 1H), 10.96 (bs, 1H), 13.23 (s, 1H). ^{13}C NMR (DMSO): δ 107.7, 109.8, 116.0, 116.1, 116.7, 118.2, 123.2, 127.1, 127.3, 127.7, 130.4, 131.2, 134.0, 155.3, 172.3. Anal. Calcd for $C_{15}H_{11}BrN_2O_2$: C, 54.40; H, 3.35; Br, 24.13; N, 8.46; O, 9.66. Found: C, 54.30; H, 3.40; Br, 24.10; N, 8.42.

7-Bromo-3-hydroxy-*N*,*N*-dimethyl-4-(1*H*-pyrrol-2-yl)naphthalene-2-carboxamide (15e). The compound was purified by column chromatography and eluted with cyclohexane/ethyl acetate = 7:3. Green solid. Mp 179.6−181.0 °C. ^{1}H NMR ($CDCl_3$): δ 3.16 (s, 6H), 6.42−6.47 (m, 2H), 7.03−7.05 (m, 1H), 7.49 (dd, J = 9.1, 1.9 Hz, 1H), 7.61 (s, 1H), 7.88 (d, J = 1.9 Hz, 1H), 7.93 (d, J = 9.1 Hz, 1H), 8.81 (bs, 1H), 9.19 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 37.9, 108.9, 110.9, 115.4, 117.6, 119.0, 122.1, 123.4, 126.9, 127.0, 127.8, 130.2, 130.9, 132.4, 150.3, 170.7. Anal. Calcd for $C_{17}H_{15}BrN_2O_2$: C, 56.84; H, 4.21; Br, 22.24; N, 7.80; O, 8.91. Found: C, 56.73; H, 4.26; Br, 22.30; N, 7.79.

7-Bromo-3-hydroxy-4-thiophen-2-yl-naphthalene-2-carboxylic Acid Dimethylamide (16e). The compound was purified by column chromatography and eluted with cyclohexane/ethyl acetate = 95:5 (40%, yield) Yellow oil: ^{1}H NMR ($CDCl_3$): δ 3.22 (s, 6H), 7.15 (d, J = 3.3 Hz 1H), 7.26−7.28 (m, 1H), 7.51 (dd, J = 9.0, 1.8 Hz, 1H), 7.57−7.60 (m, 2H), 7.78 (s, 1H), 7.96 (d, J = 1.8 Hz, 1H), 8.70 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 38.3, 116.15, 117.69, 121.95, 126.57, 127.33, 127.39, 127.96, 128.25, 129.19, 130.09, 131.23 133.73, 134.27, 151.65, 170.10. Anal. Calcd for $C_{17}H_{14}BrNO_2S$: C, 54.27; H, 3.75; Br, 21.24; N, 3.72; O, 8.50; S, 8.52. Found: C, 54.21; H, 3.76; Br, 21.28; N, 3.70; S, 8.49.

Laser Flash Photolysis Experiments. These experiments were performed with a Nd:YAG laser used at the third harmonic of its fundamental wavelength as the excitation source. The laser delivered a maximum power of 5−8 mJ at 355 nm, with 10 ns pulse duration. The monitor system, arranged in a cross-beam configuration, consisted of a 275 W Xe arc lamp, an F/3.4 monochromator, and a five-stage photomultiplier. The signals were captured by means of a digitizing oscilloscope, and the data was processed on a PC system using a software developed in-house. Solutions for analysis were placed in a fluorescence cuvette (length 10 mm). The absorbance of each solution was adjusted to 1.2−1.5. Sample solutions were then sealed with a rubber serum cap and purged with Ar or O_2 for 5 min prior the experiment. Sample concentrations were adjusted such that their optical densities were 1.0−1.5 at the excitation wavelength.

Acknowledgment. Financial support from Miur (FIRB-Ideas RBID082ATK_003), Pavia University ("Fondo FAR 2008"), and "Consorzio CINMPIS" is gratefully acknowledged.

Supporting Information Available: UV−vis spectra of **6e**, in H_2O/ACN 8:2 and ACN solutions; ^{1}H NMR, and ^{13}C NMR spectra for the compounds **6c**−**6e, 7a**, **7c**, **8a**, **8e**, **9**, **10**, **11c**, **11e**, **12e**, **13c**−**13e**, **14c**, **15c**−**15e**, and **16e**. This material is available free of charge via the Internet at http://pubs.acs.org.