Intramolecular [2+2] Photocycloaddition of Bichromophoric Derivatives of 3,5-Dihydroxybenzoic Acid and 3,5-Dihydroxybenzonitrile

Norbert Hoffmann,* Jean-Pierre Pete

Laboratoire des Réactions Sélectives et Applications, UMR CNRS et Université de Reims Champagne-Ardenne, UFR Sciences, B.P. 1039, 51687 REIMS, cedex 2, France
Fax +33(0)326913166; E-mail: norbert.hoffmann@univ-reims.fr

Received 18 December 2000

Dedicated to Professor Howard E. Zimmerman on the occasion of his 75th birthday

Abstract: The irradiation of 3-alkenyloxy-5-hydroxybenzoic acid derivatives **1a**–**d** yields highly functionalized alkyloxyenone derivatives when the reaction is carried out in the presence of acid. A higher reactivity is observed for the corresponding 3-alkenyloxy-5-hydroxybenzonitrile compounds **7a**, **b**, which also react in neutral reaction media. In the first step of the reaction, a [2+2] photocycloaddition occurs. The following steps, leading to stable final products, need acid catalysis in the case of the substrates **1a**–**d**. The irradiation of the benzonitrile derivative **7b** also furnishes the side product **9**, which results from a [2+3] photocycloaddition.

Key words: photochemistry, cycloaddition, arenes, acidic reaction medium, herbicides

In contrast to their groundstate reactions, photochemical reactions of aromatic compounds most frequently lead to non-aromatic products. Cycloadditions of alkenes to photochemically excited aromatic compounds yield complex polyfunctional molecules, which represent precious intermediates for the organic synthesis. Depending on the difference of redox potentials of the two reaction partners and the substitution pattern, [2+2], [2+3] or less frequently [2+4], cycloadducts can be obtained.[1] Until recently, organic chemists were particularly interested in the [2+3] photocycloaddition (also known as *meta*-photocycloaddition) and its application to organic synthesis especially to the total synthesis of natural products.[2] Recent studies reveal that [2+2] photocycloadditions (also known as *ortho*-photocycloaddition) frequently compete with [2+3] cycloadditions.[3] Earlier theoretic treatments showed that polar transition states are involved in [2+2] as well as in [2+3] photocycloadditions of alkenes to electronically excited aromatic compounds.[4] More recently, theoretical reports claim that rather unpolar diradical intermediates are involved in these reactions.[5]

In many cases however, the products resulting from [2+2] reactions were not fully characterized since they could only be isolated as complex mixtures. [2+2] Cycloadducts have been easily isolated when the olefinic or the aromatic reaction partner possessed electron withdrawing substituents,[6] and particularly with naphthalene derivatives as starting material.[7] Furthermore, the [2+2] photocycloaddition seems to be more efficient when the CN group is used instead of the COOR group as electron withdrawing substituent.[6h-j] Indeed, 2-hydroxy and 4-hydroxybenzonitrile derivatives react more efficiently than the corresponding hydroxybenzoic acid ones.

In connection with our interest in [2+2] photocycloaddition of alkenes to aromatic compounds, we have previously shown, that the intramolecular [2+2] photocycloaddition of alkenes to aromatic compounds can be favored in acidic media[8,9] and derivatives of salicylic acid could be transformed efficiently under these reaction conditions.[10] In this case, the initial intramolecular photocycloaddition leads to unstable [2+2] adducts which react via reversible thermal and photochemical rearrangements. The acid was shown to catalyze a final step leading to products of high stability.

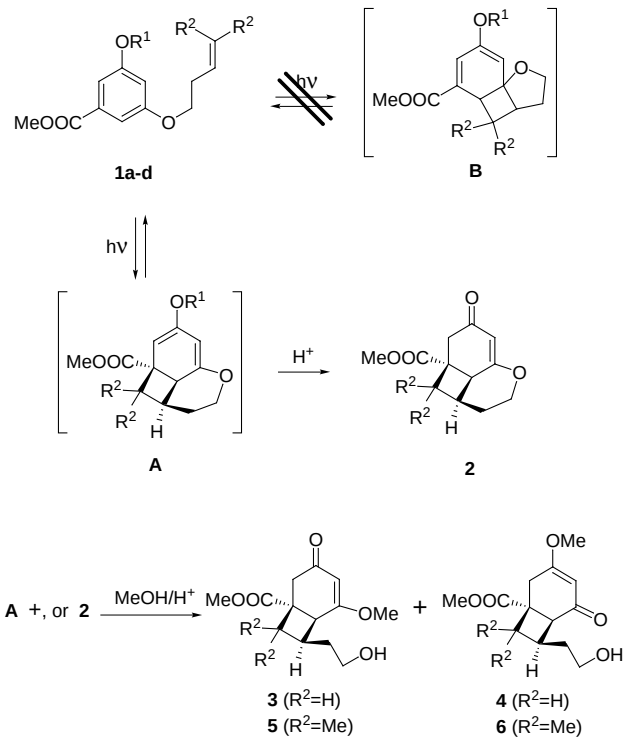
In a preliminary communication, we recently reported a new intramolecular [2+2] photocycloaddition of 3,5-dihydroxybenzoic acid derivatives.[11] This reaction was also favored by an acidic reaction media. In this article, we describe the influence of acidic conditions and the effect of the electron withdrawing substituents on the photochemical reactivity of bichromophoric compounds derived from 3,5-dihydroxybenzoic acid and 3,5-dihydroxybenzonitrile.

We started our investigation with the irradiation of a solution of 3,5-dihydroxybenzoic acid derivative **1a** in acetonitrile or methanol at $\lambda = 254$ nm (Scheme 1, Table 1). In both cases, no significant conversion could be observed. However, when sulfuric acid (6×10^{-3} mol L^{-1}) was added to the solution in acetonitrile, the tricyclic product **2** could be isolated in moderate yields (Scheme 1, Table 1, entries 1, 2). Unfortunately, the conversion rate was rather low. We wondered if this unfavorable result could be due to the presence of a free phenolic OH group in the substrate. However, the protection of this functional group in **1b** did not significantly improve the results. Somewhat better results were obtained when the irradiation was carried out at $\lambda = 300$ nm (Table 1, entry 3).

When methanol was used as the solvent instead of acetonitrile, the reaction and the conversion rate became more efficient and the product yields increased significantly. In this case, product **2** was transformed by acid catalyzed methanolysis into the more stable bicyclic products **3** and **4** (Scheme 1, Table 1, entry 4). Under the optimized reac-

Synthesis 2001, No. 8, 18 06 2001. Article Identifier:
1437-210X,E;2001,0,08,1236,1242,ftx,en;C20000SS.pdf.

ISSN 0039-7881

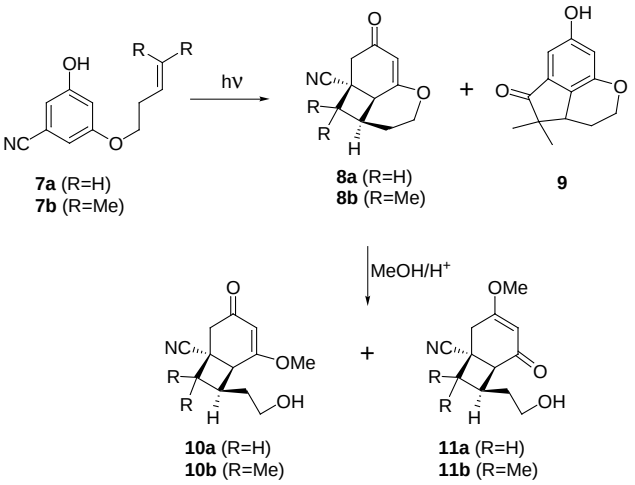


Scheme 1

tion conditions, compounds **1c** and **1d** could be similarly transformed into **5** and **6** (Table 1 entries 5, 6). Structural elucidation for the regioisomers **3** and **4** was carried out by NMR spectroscopy (HMBC pulse sequence).

Interestingly, and in contrast to the photoreactivity of 3-alkenyloylanisol,[8a-d] the first step of the reaction, a [2+2] photocycloaddition of the alkene moiety to the electronically excited aromatic part occurs with formation of a bridged tetrahydropyran **A** rather than a tetrahydrofuran **B** intermediate. This regioselectivity is similar to that observed for the [2+2] photocycloaddition of alkenes to α,β-unsaturated carbonyl compounds. The electron withdrawing substituent is essential to overcome an unfavorable entropic effect and activates the aromatic π system for the [2+2] photocycloaddition. The former 5-hydroxy or methoxy group is transformed by an acid-catalyzed reaction into a carbonyl group of a vinyloguous ester function **2**. We also noted that the reaction became more efficient when it was carried out in methanol as a protic solvent (Table 1, entries 4–6). In this case, the more stable bicyclic products **3**, **4**, **5** and **6** were produced by acid-catalyzed opening of the tetrahydropyran ring in **A** or **2**.

The considerable increase of reactivity in the presence of acid might be due to an efficient displacement of a reversible [2+2] photocycloaddition as previously observed for *O*-alkenyl resorcinol derivatives.[8a-d] The increase of the electrophilic character of the ester group by protonation in the excited state can also be envisaged. For these reasons, and as noted above, we anticipated that the replacement of the ester by a cyano substituent might increase the efficiency of the [2+2] photocycloaddition process. Indeed, irradiation of compound **7a** in methanol even in absence of acid furnished the tricyclic compound **8a** in good yield (Scheme 2, Table 2, entries 1, 2). It should also be noted that the conversion was significantly higher than for the corresponding benzoic ester derivative **1a**. This result confirms the higher reactivity of benzonitrile derivatives with respect to their analogues in the benzoic acid series. Similarly, compound **7b** possessing a 4-methylpent-3-enyl side chain, also yielded the corresponding tricyclic ketone **9** (Table 2, entry 2).



Scheme 2

Table 1 Irradiation of 3,5-Dihydroxybenzoic Acid Derivatives **1a**–**d** (Scheme 1) in the Presence of Acid (H_2SO_4, 6×10^{-3} mol L^{-1}).

Entry	Substrate	Solvent	R^1	R^2	Conversion (%)	Yield[a] (%)	Wavelength of irradiation (λ, nm)
1	**1a**	CH_3CN	H	H	50	**2** 47	254
2	**1b**	CH_3CN	Me	H	52	**2** 57	254
3	**1b**	CH_3CN	Me	H	57	**2** 65	300
4	**1b**	CH_3OH	Me	H	82	**3** 64, **4** 16	300
5	**1c**	CH_3OH	Me	Me	100	**5** 38, **6** 10	300
6	**1d**	CH_3OH	H	Me	100	**5** 48, **6** 12	300

[a] Based on transformed starting material.

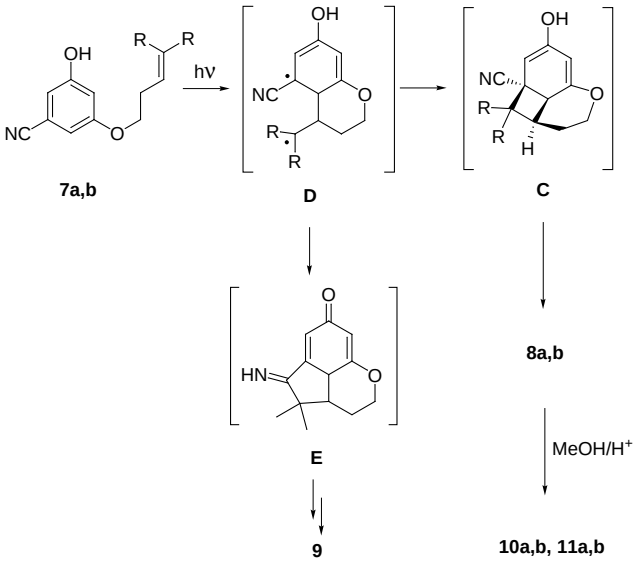
Table 2 Irradiation of 3,5-Dihydroxybenzonitrile Derivatives **7a**, **b** (Scheme 2) in MeOH as Solvent (λ = 300 nm)

Entry	Substrate	R	*c* (H_2SO_4) (mol L^{-1})	Conversion (%)	Yield[a] (%)
1	**7a**	H	0	90	**8a** 62
2	**7b**	Me	0	93	**8b** 39, **9** 11
3	**7a**	H	6.10^{-3}	82	**10a** 48, **11a** 21
4	**7b**	Me	6.10^{-3}	90	**10b** 48, **11b** 16, **9** 22

[a] Based on transformed starting material.

When the reaction of **7a** and **7b** was carried out in the presence of acid, the bicyclic products **10a**, **11a**, and **10b**, **11b** and **9** were isolated in higher yields (Table 2, entries 3, 4). The photochemical conversion was as fast as under neutral reaction conditions.

The formation of products **8a**, **b**, **10a**, **b** and **11a**, **b** can be described by the same mechanism as in the case of **1a**–**d** (Scheme 3). After intramolecular [2+2] photocycloaddition in acetonitrile, ketonization of the enol or the enolether, intermediate **C**, leads to the tricyclic vinyloguous ester **8a**, **b**.[12] A further stabilization of the final products occurred via methanolysis under acidic conditions. We determined that this step is not photo-assisted as the methanolysis of **8a** carried out in the dark and in the presence of acid yielded the corresponding **10a** and **11a** in similar proportions.

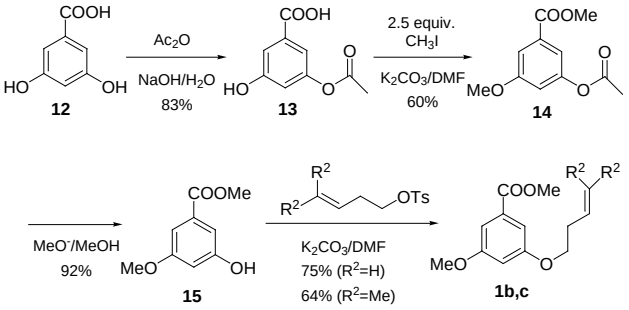


Scheme 3

The unexpected formation of the tricyclic ketone **9** might have resulted from an initial photochemical electron transfer mechanism (PET)[13] and C-C bond formation between the olefinic partner and the electronically excited aromatic moiety leading to a biradical intermediate **D**.[14] (**D** may also be a precursor of intermediate **C**.) Such an addition of an alkene to a nitrile group would lead to intermediate **E** possessing a cyclohexanedienone moiety and an imine function. The final product **9** would then result from tautomerization and hydrolysis. The electron transfer is certainly favored by the trialkylsubstitution of the double bond, which makes it more reductive.

The [2+2] photocycloaddition of 3,5-dihydroxybenzonitrile and 3,5-dihydroxybenzoic acid derivatives provides an easy access to polyfunctional cyclohexanediones of synthetic interest. Furthermore, compounds like **3**, **4**, **5** and **6** possess great interest in agrochemistry. They can be considered as derivatives of 5-disubstituted 1,3-cyclohexanedione included in the central part of the leading structure of new herbicides (inhibitors of acetyl-CoA carboxylase of monocotyledonous plants).[15]

The synthesis of the starting compounds **1a**–**d** and **7a**, **b** requires a mono *O*-alkylation of 3,5-dihydroxybenzene derivatives. For instance, in the case of methyl 3,5-dihydroxybenzoate, the selectivities of these reactions are low. It seems that the mono *O*-alkylated compounds are more reactive than their corresponding dihydroxy benzoic acid derivatives. Therefore, isolated yields of the mono alkylated compounds are rather low and considerable amounts of dialkylated products are also isolated as by products.[16] However, monoacylation of 3,5-dihydroxybenzoic acid (**12**) in aqueous medium can be very selective and efficient,[17] and compounds **1b** and **1c** have been prepared from **13** as depicted in Scheme 4. Compound **14** was obtained by dimethylation of **13** in basic conditions. The selective deprotection of one phenolic function was carried out by methanolysis of **14**. The resulting phenol derivative **15** was alkylated with but-3-en-1-yl tosylate or 4-methylpent-3-en-1-yl tosylate to yield **1b** or **1c**, respectively. Alkylation of phenols with tosylates in the presence of K_2CO_3 in DMF appeared to be the most efficient method and the overall synthesis can be easily applied to the preparation of **1b** on a multigram scale.



Scheme 4

We have described a new intramolecular [2+2] photocycloaddition type with 3-*O*-alkenyl-5-hydroxybenzoic acid derivatives **1a**–**d** and corresponding 3-*O*-alkenyl-5-hydroxybenzonitrile derivatives **7a**, **b**. In the case of the benzoic acid derivatives, the reaction must be carried out in acidic media in order to be observed and to obtain stable

polyfunctional final products. The initial [2+2] photocycloaddition process is followed by acid catalyzed consecutive reactions. The benzonitrile derivatives are more reactive and strained tricyclic products **8a**, **b** could be isolated in good yield, when the reaction was carried out in methanol and in absence of acid. With benzonitrile **7b**, we also obtained the side product **9** involving the cyclization of a biradical intermediate on the nitrile group.

^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC 250 (250 MHz for ^{1}H and 62 MHz for ^{13}C) or Bruker DRX 500 (500 MHz for ^{1}H and 126 MHz for ^{13}C). Chemical shifts are given in ppm relative to TMS as an internal standard. IR spectra were recorded with MIDAC Prospect IR (FTIR). MS spectra were recorded with JEOL D-300. UV spectra were recorded with a UVKON 941 PLUS (KONTRON Instruments). Preparative chromatography was carried out with Merck art 9385 Kieselgel 60. Irradiations of the solution were carried out in quartz tubes (Φ = 1 cm), with a Rayonet apparatus (model RPR-100) from the Southern New England Ultraviolet Company. Solutions were degassed with Ar before irradiation.

Synthesis of Compounds 1a–d and 7a, b, General Procedure

The phenol (45 mmol) and the tosylate of the corresponding alkenol (45 mmol) were dissolved in DMF (50 mL) followed by addition of K_2CO_3 (15 g). In the case of the synthesis of **1a** and **1d**, 2 equiv (90 mmol) of methyl 3,5-dihydroxybenzoate were used. The mixture was stirred at 80 °C for about 3 h. Most of the DMF was evaporated under reduced pressure and the residue was treated with H_2O and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2. In the case of the synthesis of **1a**, **b** and **7a**, **b** (mono alkylation of methyl 3,5-dihydroxybenzoate or 3,5-dihydroxybenzonitrile[18]), the aqueous phase was carefully acidified with concd HCl prior to extraction. The combined organic phases were dried ($MgSO_4$). After evaporation of CH_2Cl_2, the residue was purified by flash chromatography (EtOAc–petroleum ether).

Compound **1a**
Yield: 47%; mp 63–64 °C.

IR (KBr): ν = 3412, 3083, 2950, 2880, 1694, 1614, 1501, 1451, 1325, 1260, 1159, 1051, 766 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.19 (dd, 1H, *J* = 1.0, 2.5 Hz), 7.14 (dd, 1H, *J* = 1.0, 2.5 Hz), 6.64 (t, 1H, *J* = 2.5 Hz), 6.28 (br s, 1H), 5.88 (ddt, 1H, *J* = 10.5, 17.0, 6.5 Hz), 5.06–5.22 (m, 2H), 4.02 (t, 2H, *J* = 7 Hz), 3.90 (s, 3H), 2.54 (tq, 2H, *J* = 7.0, 1.0 Hz).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 167.3, 160.2, 157.0, 134.2, 131.8, 117.2, 109.3, 107.8, 107.3, 67.6, 52.4, 33.5.

MS (70eV): *m/z* (%) = 222 (61) [M$^+$], 191 (26), 168 (100), 137 (94), 136 (52), 126 (29).

Anal. Calcd for $C_{12}H_{14}O_4$ (222): C, 64.86; H, 6.31. Found: C, 64.67; H, 6.77.

Compound **1b**
Yield: 75%.

IR (film): ν = 3081, 2951, 2843, 1723, 1599, 1439, 1327, 1238, 1161, 1061, 766 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.18 (d, 2H, *J* = 2.5 Hz), 6.64 (t, 1H, *J* = 2.5 Hz), 5.80 (ddt, 1H, *J* = 10.5, 17.0, 6.5 Hz), 5.17 (dq, 1H, *J* = 17.0, 1.5), 5.11 (dq, 1H, *J* = 10.5, 1.5 Hz), 4.04 (t, 2H, *J* = 7 Hz), 3.90 (s, 3H), 3.81 (s, 3H), 2.55 (dt, 2H, *J* = 1.5, 7.0 Hz).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 166.8, 160.6, 160.0, 134.2, 132.0, 117.1, 107.8, 107.2, 106.3, 67.5, 55.5, 52.2, 33.5.

MS (70eV): *m/z* (%) = 236 (67) [M$^+$], 205 (24), 182 (100), 154 (38), 151 (45), 124 (21), 123 (22).

UV ($c = 4.07 \times 10^{-5}$ mol/L, MeCN): λ_{max}, nm (ε): 305 (3600), 250 (6600), 208 (39000).

Anal. Calcd for $C_{13}H_{16}O_4$ (236): C, 66.10; H, 6.78. Found: C, 65.65; H, 6.98.

Compound **1c**
Yield: 64%.

IR (film): ν = 2935, 1723, 1600, 1436, 1302, 1238, 1159, 1055, 767 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.15–7.20 (m, 2H), 6.64 (t, 1H, *J* = 2.5 Hz), 5.21 (t/sept, 1H, *J* = 7.0, 1.5 Hz), 3.95 (t, 2H, *J* = 7.0 Hz), 3.90 (s, 3H), 3.82 (s, 3H), 2.47 (q, slightly broaden, 2H, *J* = 7.0 Hz), 1.73 (s, slightly broaden, 3H), 1.66 (s, slightly broaden, 3H).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 166.9, 160.6, 160.1, 134.5, 132.0, 119.4, 107.8, 107.1, 106.2, 68.0, 55.5, 52.1, 28.1, 25.7, 17.8.

MS (70eV): *m/z* (%) = 264 (15) [M$^+$], 233 (12), 183 (100), 182 (73), 151 (37), 135 (10), 123 (13).

HRMS: calcd for ($C_{15}H_{20}O_4$): 264.1362. Found: 264.1364.

Compound **1d**
Yield: 42%; mp 73–74 °C.

IR (KBr): ν = 3433, 3074, 2986, 2932, 2878, 1698, 1611, 1501, 1451, 1346, 1258, 1150, 1047, 764 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ =7.19 (dd, 1H, *J* = 1.5, 2.5 Hz), 7.14 (dd, 1H, *J* = 1.5, 2.5 Hz), 6.64 (t, 1H, *J* = 2.5 Hz), 6.41 (br s, 1H), 5.19 (t/sept, 1H, *J* = 7.0, 1.5 Hz), 3.93 (t, 2H, *J* = 7.0 Hz), 3.90 (s, 3H), 2.46 (q, slightly broaden, 2H, *J* = 7.0 Hz), 1.73 (s, slightly broaden, 3H), 1.65 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 164.4, 160.2, 157.0, 134.6, 131.7, 119.3, 109.2, 107.6, 107.2, 68.0, 52.4, 28.1, 25.7, 17.8.

MS (70eV): *m/z* (%) = 250 (13) [M$^+$], 219 (16), 168 (100), 168 (47), 151 (12), 149 (12), 137 (52), 136 (28).

Anal. Calcd for $C_{14}H_{18}O_4$ (250): C, 67.20; H, 7.20. Found: C, 67.38; H, 7.35.

Compound **7a**
Yield: 28%; mp 77–79 °C.

IR (KBr): ν = 3303, 3083, 2948, 2888, 2238, 1601, 1445, 1352, 1217, 1179, 1051, 851, 675 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.72–6.78 (m, 2H), 6.66 (t, 1H, *J* = 2.2 Hz), 5.86 (ddt, 1H, *J* = 11.5, 17.0, 6.5 Hz), 5.08–5.75 (m, 2H), 4.00 (t, 2H, *J* = 7.0 Hz), 2.53 (q, 2H, *J* = 7.0 Hz).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 160.4, 157.5, 133.8, 118.6, 117.5, 112.6, 111.6, 110.5, 107.6, 67.7, 33.2.

MS (70eV): *m/z* (%) = 189 (61) [M$^+$], 161 (17), 148 (30), 135 (100), 118 (30).

UV ($c = 4.79 \times 10^{-5}$ mol/L, MeOH): λ_{max}, nm (ε): 303 (4200), 247 (6300), 208 (39000).

Anal. Calcd for $C_{11}H_{11}NO_2$ (189): C, 69.84; H, 5.82; N, 7.41. Found: C, 69.41; H, 5.89; N, 7.32.

Compound **7b**
Yield: 39%; mp 64–66 °C.

IR: (KBr), ν = 3366, 3081, 2926, 2236, 1593, 1441, 1346, 1215, 1173, 1049, 845, 675 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.05 (br s, 1H), 6.71–6.76 (m, 2H), 6.63–6.66 (m, 1H), 5.17 (m, 1H), 3.90 (t, 2H, *J* = 7.0 Hz), 2.46 (q, slightly broaden, 2H, *J* = 7.0 Hz), 1.73 (s, 3H), 1.66 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 160.5, 157.7, 134.9, 119.0, 118.7, 112.7, 111.5, 110.3, 107.5, 68.1, 27.9, 25.7, 17.8.

MS (70eV): *m/z* (%) = 218 (45) [M^+ + 1], 161 (42), 148 (55), 136 (47), 135 (79), 118 (100).

Anal. Calcd for $C_{13}H_{15}NO_2$ (217): C, 71.89; H, 6.91; N, 6.45. Found: C, 71.68; H, 6.94; N, 6.26.

Irradiation of Compounds 1a–d and 7a, b

Four quartz tubes each containing 16 mL of **1a–d** or **7a, b** (0.5 mmol) and in the case of acidic reaction media H_2SO_4 (0.1 mmol) were irradiated (Rayonet, T = 30 °C). After about 3 h, the reaction was stopped and the solvent was evaporated. When the reaction was carried out in acidic conditions, $NaHCO_3$ was added prior to evaporation. The residue was subjected to flash chromatography (petroleum ether–EtOAc, 1:1, v/v) or (EtOAc). Yields of isolated products are given in Tables 1 and 2.

Compound **2** (R = H)

IR (film): ν = 2953, 2859, 1732, 1645, 1393, 1265, 1221, 1182 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 5.63 (d, 1H, *J* = 1.5 Hz), 4.23 (ddd, 1H, *J* = 2.3, 4.2, 10.7 Hz), 4.15 (ddd, 1H, *J* = 1.5, 10.7, 12.5 Hz), 3.75 (s, 3H), 3.40 (ddd, 1H, *J* = 1.0, 3.9, 9.1 Hz), 3.10 (dp, 1H, *J* = 7.6, 9.5 Hz), 2.57 (ddd, 1H, *J* = 3.9, 7.3, 11.4 Hz), 2.48 (d, 1H, *J* = 18.7 Hz), 2.33 (d, 1H, *J* = 18.7 Hz), 2.15 (ddd, 1H, *J* = 1.0, 9.1, 10.5 Hz), 2.04 (ddt, 1H, *J* = 9.4, 14.0, 1.9 Hz), 1.62 (dddd, 1H, *J* = 4.2, 8.8, 12.8, 14.0 Hz).

^{13}C NMR (62 MHz, acetone-d_6): δ = 194.0, 176.2, 175.9, 108.9, 69.0, 52.8, 46.0, 40.5, 38.7, 37.9, 30.7, 30.0.

MS (70eV): *m/z* (%) = 223 (90) [M^+ + 1], 222 (100) [M^+], 207 (35), 163 (92), 149 (27), 124 (94), 123 (66).

HRMS: calcd for $C_{12}H_{14}O_4$: 222.0892. Found: 222.0899.

Compound 3

IR (film): ν = 3420, 3946, 2861, 1728, 1644, 1605, 1217 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 5.58 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.40–3.50 (m, 1H), 2.98 (ddd, 1H, *J* = 5.7, 8.5, 9.5 Hz), 2.50–2.60 (m, 3H), 2.55 (d, 1H, *J* = 17 Hz), 2.28 (d, 1H, *J* = 17 Hz), 1.72 (t, 1H, *J* = 10 Hz), 1.65 (sext, 1H, *J* = 6.5 Hz), 1.20–1.35 (m, 2H).

^{13}C NMR (126 MHz, acetone-d_6): δ = 195.8, 176.1, 175.3, 104.0, 62.0, 59.8, 55.9, 52.8, 42.8, 41.9, 35.6, 35.1, 33.6.

MS (70eV): *m/z* (%) = 255 (46) [M^+ + 1], 195 (35), 181 (76), 182 (100), 154 (54), 151 (32), 123 (34).

Anal. Calcd for $C_{13}H_{18}O_5$ (254): C, 61.42; H, 7.09. Found: C, 61.02; H, 7.20.

Compound **4** (isolated in a mixture with **3**)

^{1}H NMR (500 MHz, acetone-d_6): δ = 5.56 (d, 1h, *J* = 1.5 Hz), 3.75 (s, 3H), 2.32 (d, 1H, *J* = 18 Hz), 1.91 (t, 1H, *J* = 12.0 Hz), 1.58 (sext, 1H, *J* = 6.5 Hz).

^{13}C NMR (126 MHz, acetone-d_6): δ = 196.9, 176.0, 175.9, 103.7, 60.3, 56.4, 52.8, 48.6, 42.8, 36.7, 35.7, 34.3, 32.8.

Compound **5**

IR (film): ν = 3408, 2935, 1723, 1636, 1605, 1217 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 5.45 (s, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.60 (d, 1H, *J* = 10.3 Hz), 3.45–3.55 (m, 3H), 2.66 (d, 1H, *J* = 18.0 Hz), 2.60 (dt, 1H, *J* = 10.3, 7.7 Hz), 2.39 (d, 1H, *J* = 18.0 Hz), 1.05 (s, 3H), 1.00 (s, 3H), 1.60 (m, 2H).

^{13}C NMR (62 MHz, acetone-d_6): δ = 196.8, 176.6, 175.1, 103.6, 61.2, 55.8, 52.0, 50.0, 43.6, 42.7, 38.3, 37.9, 30.9, 28.0, 19.4.

MS (70eV): *m/z* (%) = 283 (8) [M^+ + 1], 251 (8), 205 (15), 184 (42), 183 (100), 182 (46), 155 (26), 154 (45), 151 (62), 139 (33), 124 (41), 123 (46).

Anal. Calcd for $C_{15}H_{22}O_5$ (282): C, 63.83; H, 7.80. Found: C, 63.29; H, 7.34.

Compound **6** (isolated as a mixture with **5**)

^{1}H NMR (250 MHz, acetone-d_6): δ = 3.79 (s, 3H), 3.74 (s, 3H), 1.09 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (62 MHz, acetone-d_6): δ = 103.4, 61.79, 56.5, 44.8, 44.0, 27.6, 18.7.

Compound **8a**

Mp 128 °C.

IR (KBr): ν = 2986, 2926, 2232, 1649, 1614, 1395, 1215 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 5.65 (d, 1H, *J* = 1.5 Hz), 4.28 (ddd, 1H, *J* = 1.5, 3.5, 8.5 Hz), 4.21, (ddd, 1H, *J* = 1.3, 8.5, 10.0 Hz), 3.52 (ddd, 1H, *J* = 4.5, 9.5, <1 Hz), 3.40 (ddt, 1H, *J* = 7.5, 15.0, 9.5 Hz), 2.63 (d, 1H, *J* = 18.5 Hz), 2.65 (ddd, 1H, *J* = 3.0, 8.0, 11.0 Hz), 2.57 (d, 1H, *J* = 18.5 Hz), 2.37 (dd, 1H, *J* = 10.0, 11.5 Hz), 2.14 (ddt, 1H, *J* = 9.5, 14.5, 1.5 Hz), 1.68 (dddd, 1H, *J* = 4.8, 8.0, 12.8, 15.5 Hz).

^{13}C NMR (62 MHz, acetone-d_6): δ = 191.9, 174.2, 124.2, 108.9, 68.8, 39.9, 38.6, 34.3, 30.2, 29.7.

MS (70eV): *m/z* (%) = 189 (5) [M^+], 124 (9), 123 (100).

HRMS: calcd for $C_{11}H_{11}NO_2$: 186.0808. Found: 186.0790.

Anal. Calcd for $C_{11}H_{21}NO_2$ (189): C, 69.84; H, 5.82; N, 7.41. Found: C, 69.29; H, 5.88; N, 7.27.

Compound **8b**

Mp 153 °C.

IR (KBr): ν = 2967, 2934, 2234, 1649, 1615, 1360, 1177 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 5.46 (d, 1H, *J* = 1.5 Hz), 4.31 (m, 1H, *J* = 10.5 Hz), 4.20 (m, 1H, *J* = 10.5 Hz), 3.48 (dd, 1H, *J* = 1.5, 10.0 Hz), 3.13 (q, 1H, *J* = 10.0), 2.72 (d, 1H, *J* = 19.0 Hz), 2.56 (d, 1H, *J* = 19 Hz), 1.75–2.01 (m, 2H), 1.33 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (62 MHz, acetone-d_6): δ = 192.6, 175.3, 123.7, 107.5, 68.2, 46.4, 41.0, 40.3, 36.9, 34.4, 29.4, 23.9, 20.0.

MS (70eV): *m/z* (%) = 217 (15) [M^+], 189 (15), 159 (12), 146 (11), 123 (100).

HRMS: calcd for $C_{13}H_{15}NO_2$: 217.1103. Found: 217.1100.

Compound **9**

Mp 176 °C (recrystallized from acetone–petroleum ether).

IR (KBr): ν = 3233, 2963, 2870, 1692, 1618, 1480, 1316, 1148, 1082, 855 cm^{-1}.

^{1}H NMR (500 MHz, acetone-d_6): δ = 8.50 (br s, 1H), 6.50 (d, 1H, *J* = 1.8 Hz), 6.37 (d, 1H, *J* = 1.8 Hz), 4.45 (ddd, 1H, *J* = 2.0, 11.5, 13.0 Hz), 4.21 (ddd, 1H, *J* = 2.0, 11.5, 13 Hz), 2.96 (dd, 1H, *J* = 5.0, 12 Hz), 2.00 (ddt, 1H, *J* = 13.0, 5.0, 2.0 Hz), 1.63 (dq, 1H, *J* = 4.0, 12.5 Hz), 1.17 (s, 3H), 0.81 (s, 3H).

^{13}C NMR (126 MHz, acetone-d_6): δ = 209.5, 160.0, 155.1, 136.2, 131.0, 107.8, 101.3, 68.4, 51.9, 43.7, 23.8, 22.5, 22.1.

MS (70eV): *m/z* (%) = 218 (95) [M^+], 203 (54), 190 (100), 175 (45), 162 (56), 157 (23), 147 (62), 119 (25), 115 (46).

Anal. Calcd for $C_{13}H_{14}O_3$ (218): C, 71.56; H, 6.42. Found: C, 71.47; H, 6.20.

Compound **10a**

IR (film): ν = 3391, 2942, 2236, 1640, 1597, 1387, 1215 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 5.63 (s, 1H), 3.80 (s, 3H), 3.40–3.62 (m, 4H), 3.17–3.35 (m, 1H), 3.07–3.17 (m, 1H), 2.66 (d, 1H, *J* = 17.0 Hz), 2.52–2.63 (m, 1H), 2.48 (d, 1H, *J* = 17.0 Hz), 1.97 (dd, 1H, *J* = 10.5, 12.0 Hz), 1.69 (dt, 1H, *J* = 7.5, 6.0 Hz).

^{13}C NMR (62 MHz, acetone-d_6): δ = 193.4, 173.8, 124.3, 104.4, 59.7, 56.3, 44.1, 41.3, 37.1, 34.8, 34.2, 31.5.

MS (70eV): *m/z* (%) = 222 (100) [M^+ + 1], 204 (19), 155 (25), 151 (26), 150 (77), 149 (69), 121 (69).

HRMS: calcd for $C_{12}H_{15}NO_3$: 221.1052. Found: 217.1049.

Anal. Calcd for $C_{12}H_{15}NO_3$ (221): C, 65.16; H, 6.79; N, 6.33. Found: C, 64.68; H, 7.04; N, 6.19.

Compound **11a** (isolated as a mixture with **10a**)

^{1}H NMR (250 MHz, acetone-d_6): δ = 5.62 (m, 1H), 3.82 (s, 3H), 2.68 (d, 1H, *J* = 17.0 Hz), 2.49 (d, 1H, *J* = 17.0 Hz), 2.16 (dd, 1H, *J* = 10.0, 11.5 Hz), 160 (dt, 1H, *J* = 8.5, 6.5 Hz).

^{13}C NMR (62 MHz, acetone-d_6): δ = 194.7, 174.1, 124.6, 104.1, 60.1, 56.7, 49.5, 37.7, 35.3, 34.1, 33.4, 31.6.

Compound **10b**
Mp 128−130 °C (recrystallized from acetone–petroleum ether).

IR (KBr): ν = 3432, 2942, 2884, 2223, 1640, 1607, 1391, 1215 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 5.57 (s, 1H), 3.78 (s, 3H), 3.41–3.75 (m, 3H), 2.70–2.91 (m, 2H), 2.76 (d, 1H, *J* = 17.5 Hz), 2.55 (d, 1H, *J* = 17.5 Hz), 1.62 (q, 1H, *J* = 7.0 Hz), 1.36 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (62 MHz, acetone-d_6): δ = 194.2, 174.7, 123.2, 104.1, 60.7, 56.2, 43.8, 43.4, 40.2, 39.8, 38.3, 30.8, 29.4, 18.8.

MS (70eV): *m/z* (%) = 250 (28) [M^+ + 1], 204 (7), 150 (100), 121 (16).

Anal. Calcd for $C_{14}H_{19}NO_3$ (249): C, 67.47; H, 7.63; N, 5.62. Found: C, 67.16; H, 7.58; N, 5.53.

Compound **11b** (isolated as a mixture with **10b**)
^{1}H NMR (250 MHz, acetone-d_6): δ = 3.83 (s, 3H), 1.32 (s, 3H), 1.11 (s, 3H).

^{13}C NMR (62 MHz, acetone-d_6): δ = 195.6, 175.6, 123.8, 103.7, 61.1, 56.7, 45.5, 45.3, 44.4, 43.3, 40.0, 30.1, 28.6, 17.8.

Methyl 3-*O*-Acetyl-5-methoxybenzoate (14)[19]
Compound **13** (10 g, 50 mmol) (synthesized according to the literature procedure[17]) and K_2CO_3 (21 g) were suspended in DMF (50 mL). CH_3I (16 g, 113 mmol) was added at 0 °C and the resulting mixture was stirred at r.t. for about 4 h. After evaporation of the solvent at reduced pressure, the residue was treated with H_2O. The aqueous phase was extracted with Et_2O (4 times). The combined organic phases were dried ($MgSO_4$). After evaporation of the solvent, the residue was recrystallized from Et_2O–petroleum ether.

Yield: 6.8 g (60%); mp 51–52 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.44 (dd, 1H, *J* = 1.0, 2.5 Hz), 7.37 (dd, 1H, *J* = 1.0, 2.5 Hz), 6.83 (t, 1H, *J* = 2.5 Hz), 3.88 (s, 3H), 3.83 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 169.1, 166.0, 160.2, 132.0, 120.2, 115.2, 112.8, 111.9, 55.6, 52.3, 21.0.

Methyl 3-Hydroxy-5-methoxybenzoate (15)[20]
Compound **14** (4 g, 17.9 mmol) was dissolved in MeOH (100 mL). Na (approx. 0.5 g) was added and the resulting solution was kept at r.t. for 1 h. After evaporation, Et_2O, then H_2O were added to the residue. The aqueous phase was extracted with Et_2O, acidified with diluted HCl and again extracted with Et_2O. The combined organic phases were washed with H_2O and dried ($MgSO_4$). After evaporation of the solvent, the residue was recrystallized from EtOAc–petroleum ether.

Yield: 3.0 g (92%); mp 92–96 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.22 (dd, 1H, *J* = 1.5, 2.5 Hz), 7.13 (dd, 1H, *J* = 1.5, 2.5 Hz), 6.90 (br s, 1H), 3.90 (s, 3H), 3.79 (s, 3H).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 167.5, 160.7, 157.1, 131.6, 109.4, 107.1, 106.8, 55.5, 52.5.

Acknowledgement

The authors thank Dr. Karen Plé (UMR 6013, CNRS) for language corrections of the manuscript.

References and Notes

(1) (a) Bryce-Smith, D.; Gilbert, A.; Orger, B.; Tyrrell, H. *J. Chem. Soc., Chem. Commun.* **1974**, 334. (b) Leismann, H.; Mattay, J.; Scharf, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 3985. (c) Mattay, J.; Runsink, J.; Gersdorf, J.; Rumbach, T.; Ly, C. *Helv. Chim. Acta* **1986**, *69*, 442. (d) Müller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99.

(2) (a) Barentsen, H. M.; Talman, E. G.; Piet, D. P.; Cornelisse, J. *Tetrahedron* **1995**, *51*, 7469. (b) Barentsen, H. M.; Sieval, A. B.; Cornelisse, J. *Tetrahedron* **1995**, *51*, 7495. (c) Van der Eycken, E.; De Keukeleire, D.; De Bruyn, A.; Van der Eycken, J.; Gilbert, A. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 480. (d) Blakemore, D. C.; Gilbert, A. *Tetrahedron Lett.* **1994**, *35*, 5267. (e) Blakemore, D. C.; Gilbert, A. *Tetrahedron Lett.* **1995**, *36*, 2307. (f) Amey, D. M.; Gilbert, A.; Jones, D. T. *J. Chem. Soc., Perkin Trans. 2* **1998**, 213. (g) Weber, G.; Runsink, J.; Mattay, J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2333. (h) Mattay, J.; Rumbach, T.; Runsink, J. *J. Org. Chem.* **1990**, *55*, 5691. (i) Cornelisse, J. *Chem. Rev.* **1993**, *93*, 615. (j) Wender, P. A.; Dore, T. M.; de Long, M. A. *Tetrahedron Lett.* **1996**, *37*, 7687. (k) Wender, P. A.; Dore, T. M. *Tetrahedron Lett.* **1998**, *39*, 8589. (l) Zhang, C.; Bourgin, D.; Keese, R. *Tetrahedron* **1991**, *47*, 3059. (m) Baralotto, C.; Chanon, M.; Julliard, M. *J. Org. Chem.* **1996**, *61*, 3576. (n) Avent, A. G.; Bryne, P. W.; Penkett, C. S. *Org. Lett.* **1999**, *1*, 2073. (o) Wender, P. A.; Ternansky, R.; de Long, M.; Singh, S.; Olivero, A.; Rice, K. *Pure Appl. Chem.* **1990**, *62*, 1597. (p) Wender, P. A.; Siggel, L.; Nuss, J. M. *Comprehensive Organic Synthesis*, Vol. 5; Trost, B. M.; Fleming, I.; Paquette, L. A., Eds.; Pergamon Press: Oxford, **1991**, 645–673. (q) Wender, P. A.; Siggel, L.; Nuss, J. M. *Organic Photochemistry*, Vol. 10; Padwa, A., Ed.; Marcel Dekker: New York, **1989**, 357–473. (r) Wender, P. A.; Dore, T. M. *CRC Handbook of Photochemistry and Photobiology*; Horspool, W. M.; Song, P.-S., Eds.; CRC Press: Boca Raton, **1995**, 280–290.

(3) (a) Vízvárdi, K.; Toppet, S.; Hoonaert, G. J.; De Keukeleire, D.; Bakó, P.; Van der Eycken, E. *J. Photochem. Photobiol., A* **2000**, *133*, 135. (b) Van der Eycken, E.; De Keukeleire, D.; De Bruyn, A. *Tetrahedron Lett.* **1995**, *36*, 3573. (c) De Keukeleire, D. *Aldrichimica Acta* **1994**, *27*, 59. (d) De Keukeleire, D.; He, S.-L.; Blakemore, D.; Gilbert, A. *J. Photochem. Photobiol., A* **1994**, *80*, 233. (e) Gilbert, A.; Taylor, G. N.; bin Samsudin, M. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 869. (f) Mattay, J.; Leismann, H.; Scharf, H. D. *Chem. Ber.* **1979**, *112*, 577. (g) Kishikawa, K.; Akimoto, S.; Kohmoto, S.; Yamamoto, M.; Yamada, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 77. (h) Mani, J.; Schüttel, S.; Zhang, C.; Bigler, P.; Müller, C.; Keese, R. *Helv. Chim. Acta* **1989**, *72*, 487. (i) De Keukeleire, D.; He, S.-L. *Chem. Rev.* **1993**, *93*, 359.

(4) (a) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309. (b) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1977**, *33*, 2459. (c) Houk, K. N. *Pure Appl. Chem.* **1982**, *54*, 1633. (d) van der Hart, J. A.; Mulder, J. J. C.; Cornelisse, J. *J. Mol. Struct. (Theochem)* **1987**, *151*, 1. (e) van der Hart, J. A.; Mulder, J. J. C.; Cornelisse, J. *J. Photochem. Photobiol., A* **1991**, *61*, 3. (f) Stehouwer, A. M.; van der Hart, J. A.; Mulder, J. J. C.; Cornelisse, J. *J. Mol. Struct. (Theochem.)* **1992**, *92*, 333. (g) van der Hart, J. A.; Mulder, J. J. C.; Cornelisse, J. *J. Photochem. Photobiol., A* **1995**, *86*, 141.

(5) Clifford, S.; Bearpark, M. J.; Bernardi, F.; Olivucci, M.; Robb, M. A.; Smith, B. R. *J. Am. Chem. Soc.* **1996**, *118*, 7353.

(6) (a) Wagner, P. J.; McMahon, K. *J. Am. Chem. Soc.* **1994**, *116*, 10827. (b) Wagner, P. J.; Cheng, K.-L. *Tetrahedron Lett.* **1993**, *34*, 907. (c) Smart, R. P.; Wagner, P. J. *Tetrahedron Lett.* **1995**, *36*, 5131. (d) Wagner, P. J.; Smart, R. P. *Tetrahedron Lett.* **1995**, *36*, 5135. (e) Nuss, J. M.; Chinn, J. P.; Murphy, M. M. *J. Am. Chem. Soc.* **1995**, *117*, 6801. (f) Busson, R.; Schraml, J.; Saeyens, W.; Van der Eycken, E.; Herdewijn, P.; De Keukeleire, D. *Bull. Soc. Chim. Belg.* **1997**, *106*, 671. (g) de Haan, R. *Proefschrift*; Rijksuniversiteit te Leiden: Netherlands, **1996**. (h) Al-Qaradawi, S.; Gilbert, A.; Jones, D. T. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 485. (i) Cosstick, K. B.; Drew, M. G. B.; Gilbert, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1867. (j) Al-Qaradawi, S. Y.; Cosstick, K. B.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1145.

(7) (a) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811. (b) Döpp, D.; Memarian, H. R. *Chem. Ber.* **1990**, *123*, 315. (c) Döpp, D.; Erian, A. W.; Henkel, G. *Chem. Ber.* **1993**, *126*, 239. (d) Lanfermann, H.; Döpp, D. *J. Inform. Rec. Mats.* **1994**, *21*, 545. (e) Memarian, H. R.; Nasr-Esfahani, M.; Boese, R.; Döpp, D. *Liebigs Ann./Receuil* **1997**, 1023. (f) Al-Jalal, N. A. *J. Chem. Res., Synop.* **1995**, 44. (g) Al-Jalal, N. A.; Prichard, R. G.; McAuliffe, C. A. *J. Chem. Res. Synop.* **1994**, 452. (h) Mizuno, K.; Konishi, S.; Yoshimi, Y.; Sugimoto, A. *Chem. Commun.* **1998**, 1659. (i) Wagner, P. J.; Sakamoto, M. *J. Am. Chem. Soc.* **1989**, *111*, 9254. (j) Noh, T.; Kim, D.; Kim, Y.-J. *J. Org. Chem.* **1998**, *63*, 1212.

(8) (a) Hoffmann, N.; Pete, J. P. *Tetrahedron Lett.* **1996**, *37*, 2027. (b) Hoffmann, N.; Pete, J. P. *J. Org. Chem.* **1997**, *62*, 6952. (c) Hoffmann, N.; Pete, J. P. *J. Inform. Record.* **1998**, *24*, 133. (d) Verrat, C.; Hoffmann, N.; Pete, J. P. *Synlett* **2000**, 1166.

(9) For the influence of acidic media in similar reactions see: (a) Kalena, G. P.; Pradhan, P.; Banerji, A. *Tetrahedron Lett.* **1992**, *55*, 7775. (b) Kalena, G. P.; Pradhan, P.; Banerji, A. *Tetrahedron* **1999**, *55*, 3209. (c) Ohkura, K.; Kanazashi, N.; Seki, K. *Chem. Pharm. Bull.* **1993**, *41*, 239. (d) Ohkura, K.; Seki, K.; Hiramatsu, H.; Aoe, K.; Terashima, M. *Heterocycles* **1997**, *44*, 467. (e) Ohkura, K.; Noguchi, Y.; Seki, K. *Heterocycles* **1998**, *47*, 429. (f) Howell, N.; Pincock, J. A.; Stefanova, R. *J. Org. Chem.* **2000**, *65*, 6173. (g) Matohara, K.; Lim, C.; Yasutake, M.; Nogita, R.; Koga, T.; Sakamoto, Y.; Shinmyozu, T. *Tetrahedron Lett.* **2000**, *41*, 6803. (h) Mori, T.; Wada, T.; Inoue, Y. *Org. Lett.* **2000**, *2*, 3401.

(10) Hoffmann, N.; Pete, J. P. *Tetrahedron Lett.* **1995**, *36*, 2623.

(11) Hoffmann, N.; Pete, J. P. *Tetrahedron Lett.* **1998**, *39*, 5027.

(12) When **7b** was irradiated at $\lambda = 300$ nm in acetone, a decrease of the conversion rate and the amount of **8b** was observed. No formation of compound **9** could be detected. In contrast, when the reaction of **7a** was carried out in the presence of 1,3-cyclohexadiene (1.5 m/L, $E_T = 52.4$ kcal/mol; (Murov, S. L. *Handbook of Photochemistry;* Marcel Dekker: New York, **1973**) in acetonitrile–toluene (1:1), the formation of **8a** was not affected. These results led us to conclude that the formation of the products **8a** and **8b** results from a transformation of **7a** or **7b** in their singlet excited state.

(13) Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; VCH: New York, **1993**.

(14) (a) Kubo, Y.; Kusumoto, K.; Nakajima, S.; Inamura, I. *Chem. Lett.* **1999**, 113. (b) Kubo, Y.; Adachi, T.; Miyahara, N.; Nakajima, S.; Inamura, I. *Tetrahedron Lett.* **1998**, *39*, 9477. (c) Kubo, Y.; Yoshioka, M.; Kiuchi, K.; Nakajima, S.; Inamura, I. *Tetrahedron Lett.* **1999**, *40*, 527. (d) Kubo, Y.; Inoue, T.; Sakai, H. *J. Am. Chem. Soc.* **1992**, *114*, 7660. (e) Saito, I.; Shimozono, K.; Matsuura, T. *J. Am. Chem. Soc.* **1983**, *105*, 963. (f) Andersen, S.; Margaretha, P. *J. Photochem. Photobiol., A* **1998**, *112*, 135. (g) Schwebel, D.; Ziegenbalg, J.; Kopf, J.; Margaretha, P. *Helv. Chim. Acta* **1999**, *82*, 177.

(15) (a) Maier, A.; Golz, A.; Lichtenthaler, H. K.; Meyer, N.; Retzlaff, G. *Pestic. Sci.* **1994**, *42*, 153. (b) Liepa, A. J.; Wilkie, J. S.; Winkler, D. A.; Winzenberg, K. A. *Aust. J. Chem.* **1992**, *45*, 759. (c) Burton, J. D.; Gronwald, J. W.; Somers, D. A.; Connelly, J. A.; Gengenbach, B. G.; Wyse, D. L. *Biochem. Biophys. Res. Commun.* **1987**, *148*, 1039. (d) Rendina, A. R.; Felts, J. M. *Plant Physiol.* **1988**, *86*, 983.

(16) (a) Imai, H.; Uemori, Y. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1793. (b) Crombie, L.; Jamieson, S. V. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1467. (c) Gibson, H. W.; Nagvekar, D. S. *Can. J. Chem.* **1997**, *75*, 1375.

(17) Wagner, G. *Arch. Pharm. (Weinheim, Ger.)* **1959**, *292*, 282.

(18) McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289.

(19) Halton, D. D.; Morrison, G. A. *J. Chem. Res., Miniprint* **1979**, 301.

(20) Chakraborty, T. K.; Reddy, G. V. *J. Org. Chem.* **1992**, *57*, 5462.