Pergamon

Tetrahedron 58 (2002) 7933–7941

TETRAHEDRON

New photochemical rearrangements and extrusion reactions of aromatic compounds induced by an intramolecular [2+2] photocycloaddition between a naphthalene and a resorcinol moiety

Norbert Hoffmann*

Laboratoire des Réactions Sélectives et Applications, UMR 6519, CNRS et Université de Reims Champagne-Ardenne, UFR Sciences B.P. 1039, F-51687 Reims cedex 2, France

Received 10 May 2002; revised 5 July 2002; accepted 23 July 2002

Abstract—An intramolecular [2+2] photocycloaddition between a naphthalene and a resorcinyl moiety was followed by an acid catalyzed rearrangement leading to tricyclic tetrahydrofuran derivatives. The reaction was efficient when the irradiation was carried out at 300 nm. For the first time, an extrusion of a $RCOCH_3$ (R=H or alkyl) fragment from the tetrahydrofuran ring was observed when the tricyclic tetrahydrofuran derivatives were irradiated at 254 nm. Reaction rate and yield depended on the substitution pattern. In particular, significantly different quantum yields were measured in the case of different diastereoisomers.

1. Introduction

Photochemical cycloadditions of electronically excited aromatic compounds with alkenes have been studied intensively because they lead to polyfunctionalized products with a variety of different architectures which can be used for organic synthesis.[1] Depending on the difference of redox potentials of the reaction partners, and the substitution pattern, [2+2], [2+3] or less frequently [2+4] cycloadducts are obtained.[2] Most frequently, studies have focused on the [2+3] photocycloaddition.[3] However, recent investigations revealed that [2+2] photocycloadditions frequently compete with [2+3] cycloadditions.[4] In earlier studies, and especially in the absence of electron withdrawing substituents on the aromatic ring, the [2+2] reaction products were not fully characterized since they were isolated as complex mixtures. Theoretical studies showed that polar transition states of similar structure are involved in the [2+2] as well as in the [2+3] photocycloaddition of alkenes and electronically excited benzene derivatives.[5] However, more recent theoretical reports stated that rather unpolar, diradical intermediates are formed.[6] Based on theoretical results, a clear prediction of the competition between [2+2] and [2+3] is not yet possible.

Recently, we reported that the efficiency of such reactions can be significantly increased when the reaction is carried out in acidic reaction media. In this context, we studied the photochemical reactivity of bichromophoric derivatives of salicylic acid,[7] 3,5-dihydroxybenzonitrile,[8] 3,5-dihydroxybenzoic acid[8,9] and derivatives of resorcinol and 1,2,4-trihydroxyphenol.[10–12] All of them possessed an olefinic side chain. For most of them, no significant photochemical reactivity in neutral media could be observed.

In order to extend the scope of this methodology, we replaced the olefinic moiety by a naphthyl substituent. Although [2+2] photocycloadditions between naphthalene derivatives and olefines are quite frequently observed,[13,14] there have been no reports on photocycloaddition between a benzene ring and a naphthalene ring system. Recently, we observed photochemical rearrangements induced by a [2+2] photocycloaddition which preferentially occurred in acidic media.[15] In order to elucidate mechanistic aspects, we carried out a photophysical study mainly based on measurements of fluorescence lifetimes of different derivatives. Once again, the first reaction step was a reversible [2+2] photocycloaddition which was followed by an acid catalyzed rearrangement. In contrast to corresponding resorcinol derivatives possessing an olefinic side chain,[11] exciplexes were important intermediates of the reaction. In some cases, these intermediates offered additional deactivation pathways so that the reaction became less efficient. The mechanism of the main reaction is shown in Scheme 1.

In this article, different reaction conditions are described in order to improve the yield and to elucidate further mechanistic aspects. Further on, particular attention is paid to the consecutive photochemical extrusion which

Keywords: arenes; cycloadditions; diastereoselection; photochemistry; rearrangements.

* Fax: +33-326913166; e-mail: norbert.hoffmann@univ-reims.fr

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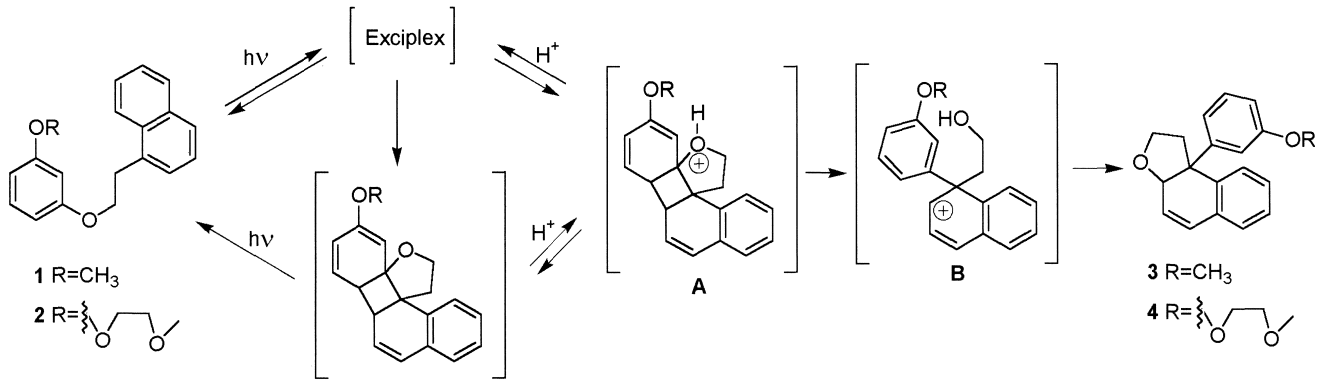
PII: S0040-4020(02)00902-X



Scheme 1. Mechanism of the [2+2] photocycloaddition induced rearrangement of bichromophoric naphthalene-tethered resorcinol ethers.

occurred when **1** or the products of the main reaction were irradiated at 254 nm.

2. Results and discussion

When irradiated at 254 nm, compounds **1** and **2** reacted readily to yield **3** and **4**, respectively (Schemes 1 and 2). In the case of **1**, the reaction had to be carried out in the presence of acid in order to induce a proton catalyzed rearrangement via intermediates **A** and **B** (Scheme 1).[15] However, compound **2** also reacted in the absence of acid but with significantly lower quantum yield (Φ (formation of **4**): 0.004 (neutral), 0.14 ($c(H_2SO_4)$: 6×10^{-3} M)).[15] The formation of product **4** was attributed to a ligating stabilization of the protonated intermediate **A** by the methoxyethoxy group. In this case, small proton concentrations (e.g. traces of water in the solvent) were sufficient to catalyze the rearrangement of the [2+2] photocycloadduct leading to the final products.

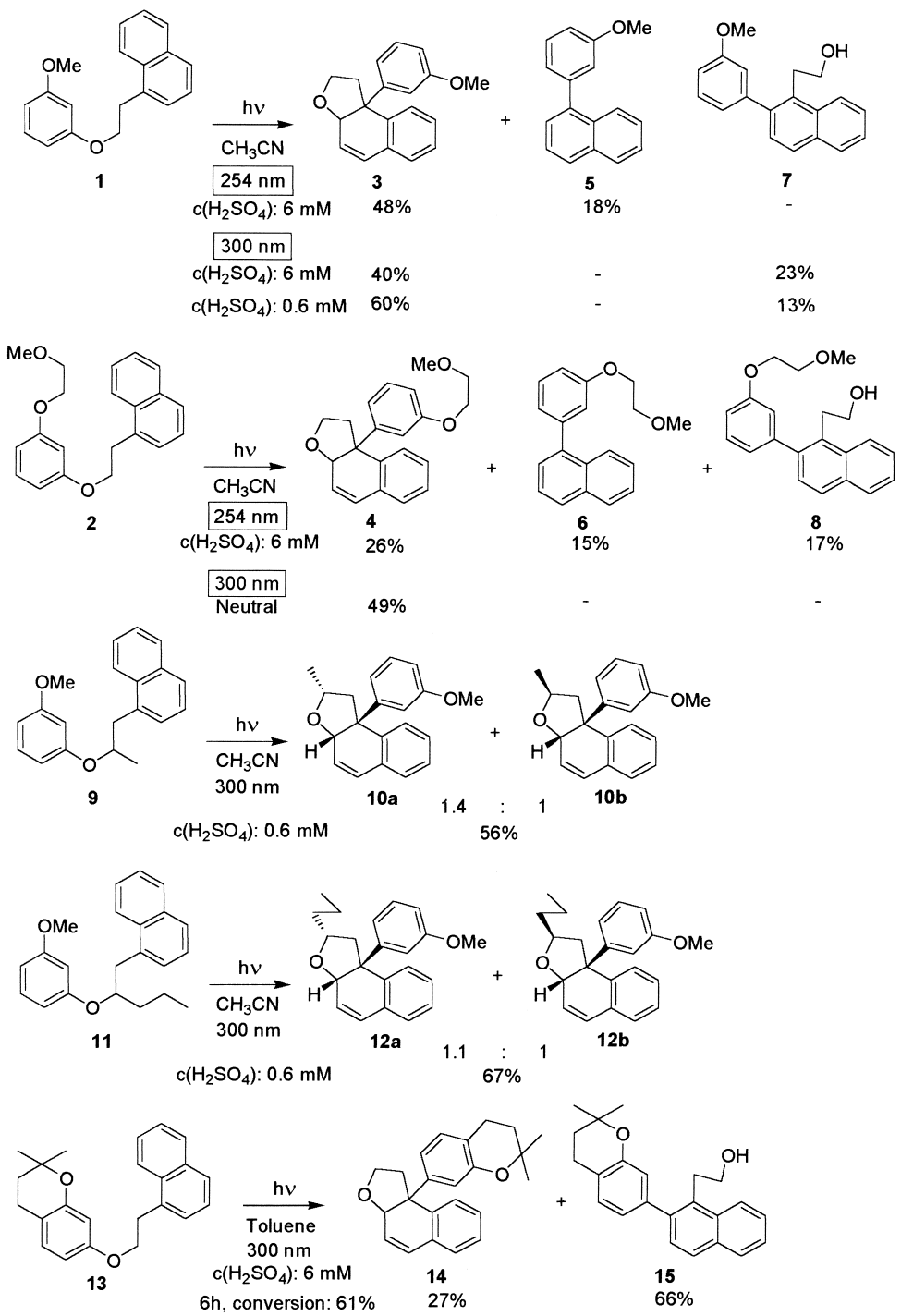
It was also shown that compounds **3** and **4** (Scheme 2) yielded products **5** and **6** upon irradiation at 254 nm. Compounds **7** and **8** are formed via an acid catalyzed rearrangement of **3** and **4** in the ground state.[15]

In order to perform the reaction in a more selective way, the irradiation of **1** and **2** was now carried out at 300 nm (Scheme 2). In this way, electronic excitation was mainly performed on the naphthalene moiety (λ_{max} (**1**): 282, 224 nm; λ_{max} (**2**): 282, 224, 202 nm). Since the products **3** and **4** possess benzene rings, undesired secondary reactions and side reactions should be reduced (λ_{max} (**3**): 266, 218 nm; λ_{max} (**4**): 265, 219 nm). Indeed, the formation of **5** or **6** was not observed in both cases. Furthermore, the yield of **3** and **4** increased. In the case of the reaction of **1**, the yield of compound **3** was further increased and the formation of the side product **7** could be reduced when the concentration of sulfuric acid was diminished to 0.6 mM. Further reduction of acid concentration, however, considerably slowed the reaction rate. The formation of **7** was caused by the higher temperature (~40°C) in the Rayonet reactor when the reaction was carried out at 300 nm (compare the reaction conditions for this transformation in the ground state[15]). Compound **2** could be transformed into **4** without formation of side products. In this case, the formation of **8** was avoided by the absence of acid. Similar substrates **9** and **11** carrying alkyl substituents on the tether were transformed in the same way by irradiation at 300 nm in the presence of acid (Scheme 2). In both cases, mixtures of diastereomers **10a**,**b** and **12a**,**b**, respectively, were isolated. While the reaction of **11** was almost stereo unselective, **10a** was formed with 17% de in the reaction of **9**. The corresponding side products resulting from acid catalyzed rearrangements of **10a**,**b** and **12a**,**b** in the ground state were formed only in minor quantities (≤10%) and were not isolated.

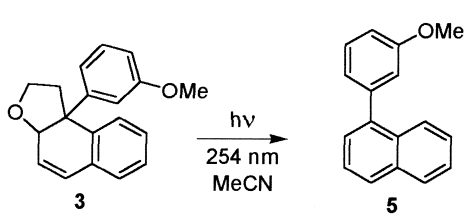
Under the same conditions, compound **13** reacted slowly and very unselectively. No product could be identified. In order to increase the selectivity, the reaction was carried out in toluene. Aromatic solvents may act as filter to cut low wavelength parts of the emission spectrum of the light source. In a very slow but selective reaction, compound **14** was isolated with modest yield (27% with respect to transformed substrate) while **15** was obtained in high yield (66% with respect to transformed substrate). Due to lower light intensity in connection with the filter effect, the conversion of **13** was additionally slowed and the primarily formed product **14** was transformed into **15** via a ground state reaction during the prolonged reaction time.

As mentioned above, compound **3** underwent an extrusion reaction when irradiated at 254 nm (Scheme 3). This reaction did not need acid catalysis. Aside from elimination of molecules such as N_2, CO, CO_2, SO_2 or several anhydrates, photochemical extrusion from five membered rings has not frequently been described.[16] In the case of **3**, we wondered whether the C_2H_4O fragment eliminated during the reaction was acetaldehyde or ethylene oxide. Our preliminary investigation of this reaction[15] using the purpal test[17] indicated that acetaldehyde was formed. However, the concomitant formation of ethylene oxide could not be excluded. Additional investigations giving insight into the mechanism of this reaction are now described.

In order to check whether a triplet or singlet species is involved in the reaction, the irradiation of **3** was performed at 254 nm in the presence of piperylene (*c*: 0.4 M) which is considered an efficient triplet quencher. This triplet quencher possess a lower triplet energy than **3** (styrene derivative).[18] Compared to the transformation in absence of piperylene, only a slight decrease in conversion was observed. Therefore, a singlet reaction can be postulated



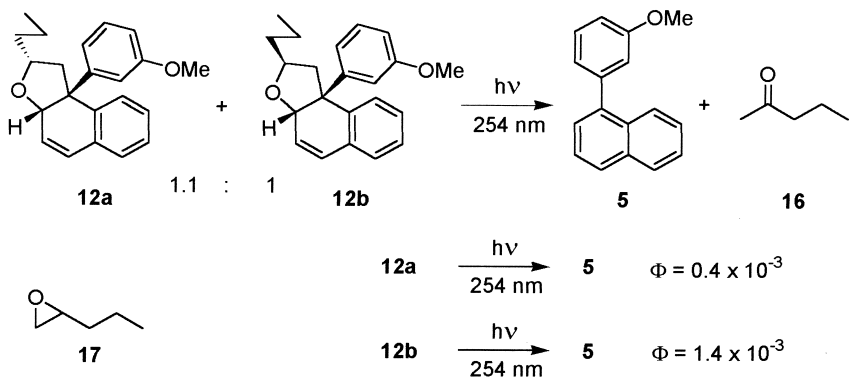
Scheme 2. Photochemical reactions of naphthalene-tethered resorcinol ethers by irradiation at 254 or 300 nm.



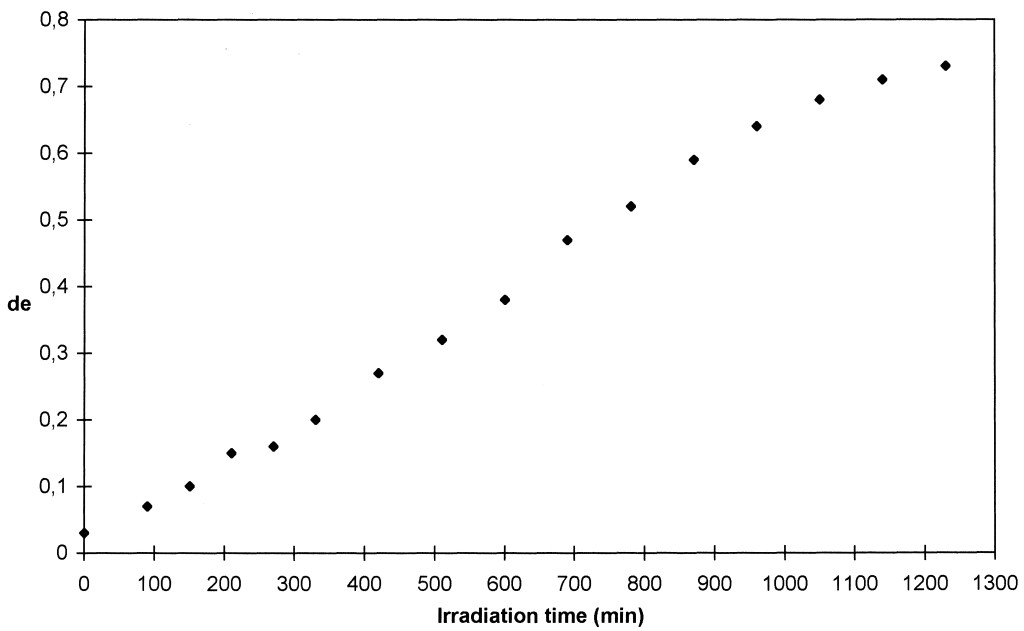
Scheme 3. Photochemical extrusion of a C_2H_4O fragment from the tricyclic tetrahydrofuran derivative **3**.[15]

when the substrate is excited by light absorption. Furthermore, when irradiated in acetone as solvent, a degradation of **3** but no significant formation of **5** was observed. Efficient triplet sensitization can therefore also be excluded.[18] From these results, it can be concluded that the extrusion is a singlet reaction.

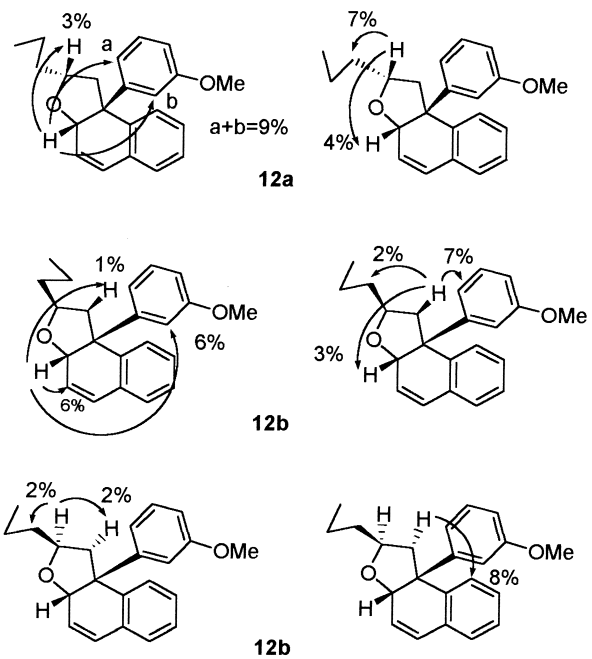
Further information was obtained from the irradiation of **12a**,**b** (Scheme 4). Traces of ketone **16** were detected by GC while the corresponding epoxide **17** could not be detected. Since **16** undergoes reactions like Norrish Type I and Type



Scheme 4. Photochemical extrusion of pentane-2-one **16** from the diastereomeric tricyclic tetrahydrofuran derivatives **12a** and **12b**.



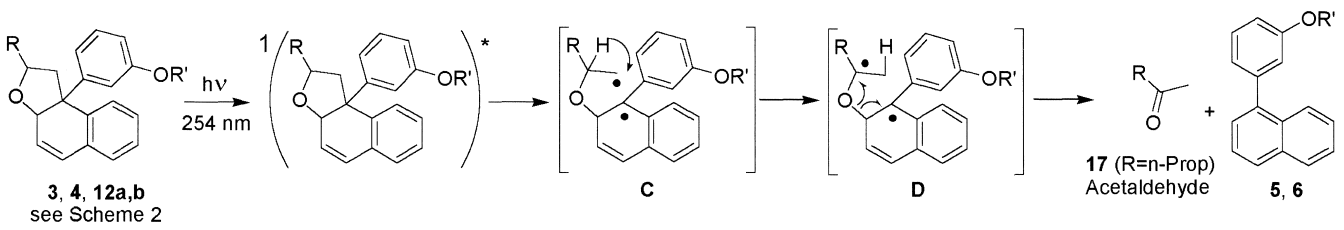
Scheme 5. Diastereomeric excess of **12a** depending on the irradiation time of the 1.1/1 mixture of **12a** and **12b**. The irradiation was carried out at 254 nm.



Scheme 6. Determination of the configuration of **12a** and **12b** by of NOE detection.

II when irradiated at 254 nm, only traces of this compound could be detected.

During the irradiation of a 1.1/1 mixture of both diastereoisomers **12a** and **12b** at 254 nm, it was observed that **12b** reacted significantly faster than **12a**. The diastereomeric excess for **12a** of 75% was attained at the plateau (Scheme 5). After 11 h of irradiation, the reaction rates of both isomers were identical since the concentration of **12b** had become very low. The two diastereomers **12a** and **12b** were then separated by HPLC and characterized separately. Their structure was determined by NMR (NOE-effects) (Scheme 6). Since both diastereomers have similar UV spectra, the rate difference could not be explained by different light absorption. Each isomer was then irradiated under the same conditions to determine the quantum yield using the photochemical addition of water to *N*,*N*′-dimethyluracil as actinometer.[19] The values are given in Scheme 4. No interconversion of **12a**,**b** or formation of other diastereoisomers (e.g. isomers resulting from a trans fusion of the tetrahydrofuran ring) could be detected. Further on, both isomers **12a** and **12b** were transformed into **5** with about the same product yields



Scheme 7. Mechanism of the extrusion of pentane-2-one **16** or acetaldyde from the tricyclic tetrahydrofuran derivatives **3**, **4** and **12a**,**b**.

(detected by GC) but with significantly different quantum yields.

Based on these results, the mechanism depicted in Scheme 7 can be proposed for the extrusion reaction of compounds **3**, **4** and **12a**,**b**. After excitation to the S_1 state, a fragmentation of a C–C bond occurs leading to the biradical **C** possessing a dibenzylic radical moiety. **C** undergoes 1,2 hydrogen shift which transforms the primary radical into the more stable tertiary alkoxyalkyl radical moiety of intermediate **D**.[20] The fragmentation of a C–O bond then leads to ketone **17** or acetaldehyde and to the final products **5** or **6**. Since the reaction occurs at the S_1 state, a concerted mechanism can not be excluded. In this context it has to be noted that the efficiency of the reaction strongly depends on the substitution of the tetrahydrofuran moiety. The product quantum yields for the transformation of compound **3** (Scheme 3) are much higher than those for the transformation of compounds **12a**,**b**. Furthermore, significant differences in quantum yields and consequently reaction rates were observed between the diastereoisomers **12a** and **12b** (Schemes 4 and 5). Considerable rate differences depending on the substitution are frequently observed for concerted reactions.

3. Conclusion

Tricyclic tetrahydrofuran derivatives were obtained by an intramolecular [2+2] photocycloaddition between a resorcinol and a naphthalene moiety followed by an acid catalyzed rearrangement. The reaction could be optimized when the irradiation was carried out at 300 nm. In this case, mainly the naphthalene chromophore was excited while the products possessing benzene rings as chromophores remained at the ground state. Compounds which were less reactive in the first step of the reaction could be selectively transformed when toluene was used as solvent. Aromatic solvents act as filter for low wavelengths ($\lambda<300$ nm).

The tricyclic tetrahydrofuran derivatives obtained from the irradiation at 300 nm from naphthalene-tethered resorcinol ethers underwent further transformation when irradiated at 254 nm. An extrusion of ketones or aldehydes from a tetrahydrofuran ring was observed for the first time. The reaction proceeded at the S_1 state and did not need acid catalysis. The quantum yields depended on the substitution pattern. Significantly different quantum yields were observed for the diastereomers **12a** and **12b**. A stepwise mechanism explains the reaction but a concerted reaction can not be excluded. A polar mechanism is unlikely since no difference of the quantum yields was detected for the reactions in the presence or absence of acid (Scheme 3).

4. Experimental

4.1. General methods

^{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). Chemical shifts are given in ppm relative to tetramethylsilane as an internal standard. IR spectra were recorded with Nicolet Avatar 320. MS spectra were recorded with JEOL D-300. UV spectra were recorded with a UVKON 941 PLUS (KONTRON Instruments). GC was carried out on a Hewlett–Packard 6890HP or 5880HP with a capillary column (HP-1 or DB-1 from J&W Scientific). Preparative chromatography was carried out with Merck art 9385 Kieselgel 60. Semi-preparative HPLC was carried out on Hewlett Packard Series 1100 equipped with a UV detector (Polymer Laboratories, PL-ELS 1000) with a column: LiChrosorb Si 7m (length: 25 cm, ID: 9 mm, OD: 1/2 in.).

Irradiations of the solution were carried out in quartz tubes (∅=1 cm), with a Rayonet apparatus (model RPR-100) from the Southern New England Ultraviolet Company. RPR-3000 A or RPR-2537 A Lamps were used. Solutions were degazed with argon before irradiation.

1-(1-Naphthyl)-propan-2-ol and 1-(1-naphthyl)-pent-2-ol which were used for the synthesis of the corresponding tosylates were obtained by copper catalyzed addition of naphth-1-yl magnesium bromide to propylene oxide or 1-pentene oxide according to Ref. 21.

4.1.1. 1-(1-Naphthyl)-pent-2-ol. Mp 74–76°C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.04–8.09 (m, 1H), 7.87–7.91 (m, 1H), 7.78 (d, J=7.7 Hz, 1H), 7.48–7.60 (m, 2H), 7.36–7.45 (m, 2H), 3.35 (dd, J=4.0, 14.0 Hz, 1H), 3.06 (dd, J=8.5, 14.0 Hz, 1H), 1.35–1.67 (m, 4H), 1.70 (s, broad, 1H), 0.99 (t, J=6.0 Hz, 3H). ^{13}C NMR (62 MHz, $CDCl_3$): δ=134.8, 133.9, 132.1, 128.8, 127.6, 127.2, 125.9, 125.6, 125.4, 123.8, 71.6, 41.2, 39.3, 19.0, 14.1. IR (KBr): ν_{max}=3341, 3237, 3054, 2956, 2868, 1596, 1117, 774. MS (EI): m/z (%)=214 (45) [M^+], 154 (21), 141 (93), 128 (39), 115 (100). HMRS (EI): calcd for $C_{15}H_{18}O$ 214.1357, found 214.1352.

4.1.2. Synthesis of compounds 9. A suspension of 3-methoxyphenol (2.8 g, 22.5 mmol), 1-(1-naphthyl)-prop-2-yl tosylate (7.4 g, 22 mmol)[21] and K_2CO_3 (7.0 g, 51 mmol) in DMF (28 ml) was heated to 80°C for about 4 h. After evaporation of the solvent, the residue was treated with water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2. The organic phase was then washed subsequently with 10% NaOH and water. After drying over $MgSO_4$ and evaporation of the solvent, the residue was subjected to flash

chromatography (petroleum ether/ethyl acetate: 1/10). Yield: 1.28 g (20%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.12 (dd, J=8.0, 1.0 Hz, 1H), 7.90 (dd, J=6.5, 2.0 Hz, 1H), 7.79 (t, J=4.8 Hz, 1H), 7.49–7.61 (m, 2H), 7.45 (2d, J=5.0 Hz, 2H), 7.18 (t, J=8.0 Hz, 1H), 6.45–6.57 (m, 3H), 4.81 (sext, J=6.5 Hz, 1H), 3.77 (s, 3H), 3.65 (dd, J=6.5, 14.5 Hz, 1H), 3.31 (dd, J=6.5, 14.0 Hz, 1H), 1.38 (d, J=6.5 Hz, 3H). ^{13}C NMR (62 MHz, $CDCl_3$): δ=160.8, 159.1, 134.3, 133.8, 132.2, 129.8, 128.8, 127.7, 127.2, 125.9, 125.5, 125.4, 123.8, 108.1, 106.4, 102.4, 74.2, 55.1, 39.8, 19.8. IR (film): ν_{max}=3046, 2972, 2935, 2834, 1598, 1491, 1151, 778. MS (EI): m/z (%)=292 (42) [M^+], 169 (100), 153 (50), 151 (82), 141 (80), 128 (28), 115 (28). $C_{20}H_{20}O_2$: Calcd C 82.19, H 6.85; found C 80.99, H 6.85.

Under these reaction conditions, elimination of tosylate leading to 1-(1-naphthyl)-prop-1-ene was an important side reaction. Yield: 1.55 g (42%).

4.1.3. Synthesis of compound 11. A suspension of 3-methoxyphenol (2.6 g, 21 mmol), 1-(1-naphthyl)-pent-2-yl tosylate (7.5 g, 20 mmol)[21] and K_2CO_3 (6.5 g, 47 mmol) in DMF (25 ml) was heated to 80°C for about 4 h. After evaporation of the solvent, the residue was treated with water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2. The organic phase was then washed subsequently with 20% NaOH and water. After drying over $MgSO_4$ and evaporation of the solvent, the residue was subjected to flash chromatography (petroleum ether/ethyl acetate: 10/1). Yield: 1.22 g (18%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.09–8.13 (m, 1H), 7.88–7.92 (m, 1H), 7.76 (dd, J=3.5, 6.0 Hz, 1H), 7.48–7.61 (m, 2H), 7.45 (d, J=3.5 Hz, 1H), 7.44 (d, J=6.0 Hz, 1H), 7.16 (t, J=8.2 Hz, 1H), 6.51 (dt, J=2.5, 8.2 Hz, 2H), 6.40 (t, J=2.5 Hz, 1H), 4.68 (ddt, J=4.5, 11.5, 6.5 Hz, 1H), 3.72 (s, 3H), 3.52 (dd, J=6.5, 14.5 Hz, 1H), 3.40 (dd, J=6.5, 14.5 Hz, 1H), 1.31–1.87 (m, 4H), 0.95 (t, J=7.5 Hz, 3H). ^{13}C NMR (62 MHz, $CDCl_3$): δ=160.8, 159.8, 134.5, 133.8, 132.3, 129.7, 128.8, 127.7, 127.1, 125.9, 125.44, 125.42, 123.8, 108.3, 106.5, 102.4, 78.5, 55.1, 37.7, 36.5, 18.7, 14.1. IR (film): ν_{max}=3062, 2957, 2871, 2834, 1598, 1489, 1151, 778. MS (EI): m/z (%)=320 (9) [M^+], 252 (9), 196 (28), 179 (33), 167 (47), 141 (100), 128 (25), 123 (22), 115 (22). $C_{22}H_{24}O_2$: Calcd C 82.50, H 7.50; found C 82.10, H 7.70.

4.1.4. Synthesis of compound 13. A suspension of 2,2-dimethylchroman-7-ol[22] (2.6 g, 14.5 mmol), 2-(1-naphthyl)-ethyl tosylate (5 g, 15 mmol) and K_2CO_3 (5 g, 36 mmol) in DMF (20 ml) was heated to 80°C for about 4 h. After evaporation of the solvent, the residue was treated with water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2. The organic phase was then washed subsequently with 20% NaOH and water. After drying over $MgSO_4$ and evaporation of the solvent, the residue was subjected to flash chromatography (petroleum ether/ethyl acetate: 20/1). Yield: 2.7 g (56%). ^{1}H NMR (250 MHz, $CDCl_3$): δ=8.09–8.13 (m, 1H), 7.86–7.93 (m, 1H), 7.78 (t, J=5.0 Hz, 1H), 7.48–7.59 (m, 1H), 7.45 (d, J=4.5 Hz, 1H), 7.45 (d, J=5.3 Hz, 1H), 6.96 (d, J=8.3 Hz, 1H), 6.46 (dd, J=2.5, 8.3 Hz, 1H), 6.40 (d, J=2.5 Hz, 1H), 4.29 (t, J=6.5 Hz, 2H), 3.58 (t, J=7.5 Hz, 2H), 2.72 (t, J=6.5 Hz, 2H), 1.79 (t, J=7.5 Hz, 2H), 1.34 (s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): δ=158.2, 154.6, 134.2, 133.8, 132.0, 129.8, 128.8, 127.2, 126.9, 126.0, 125.5 (2×), 123.6, 113.1, 107.2, 102.5, 74.2, 67.9, 32.9, 32.8, 26.8 (2×), 21.7. IR (film): ν_{max}=3046, 2973, 2930, 2873, 2851, 1619, 1504, 1151, 777. MS (EI): m/z (%)=332 (17) [M^+], 178 (8), 155 (100), 141 (9), 115 (8). $C_{23}H_{24}O_2$: Calcd C 83.13, H 7.23; found C 83.14, H 7.46.

4.2. Irradiation of compounds 1 and 2

Solutions of **1** (400 mg, 1.44 mmol) and H_2SO_4 (6.0 or 0.6 mM) in acetonitrile (120 ml) were distributed in to 8 quartz tubes and irradiated for 2.5 h (λ=300 nm). In the same way a solution of **2** (400 mg, 1.24 mmol) in acetonitrile (120 ml) were distributed in to 8 quartz tubes and irradiated for 2.5 h λ=300 nm. (For further conditions see Scheme 2. For irradiations at λ=254 nm see Ref. 15) The solvent was evaporated and the residue was subjected to flash chromatography (petroleum ether/ethyl acetate: first: 5/1, than 1/1). In the case of **1**, the evaporation was carried out in the presence of $NaHCO_3$.

4.2.1. Compound 3. Yield (in the presence of H_2SO_4 (6.0 mM)): 160 mg (40%). Yield (in the presence of H_2SO_4 (0.6 mM)): 240 mg (60%).

4.2.2. Compound 7. Yield (in the presence of H_2SO_4 (6.0 mM)): 90 mg (23%). Yield (in the presence of H_2SO_4 (0.6 mM)): 53 mg (13%).

4.2.3. Compound 4. Yield: 196 mg (49%).

Compounds **3**, **4** and **7** are characterized in Ref. 15.

4.3. Irradiation of compounds 9 and 11

Solutions of **9** (400 mg, 1.37 mmol) or **11** (400 mg, 1.25 mmol), H_2SO_4 (0.6 mM) in acetonitrile (120 ml) were distributed in to 8 quartz tubes and irradiated for 2.5 h at λ=300 nm. (For further conditions see Scheme 2). The solvent was evaporated in the presence of $NaHCO_3$ and the residue was subjected to flash chromatography (petroleum ether/ethyl acetate: 5/1). The diastereomers **12a** and **12b** were then separated by HPLC (hexane/ethyl acetate: 96/4).

4.3.1. Compounds 10a,b. Yield: 224 mg (56%). Ratio (**10a**/**10b**): 1.4/1. ^{1}H NMR (250 MHz, CD_3COCD_3): δ=7.35–7.42 (m, 1H, **10a**), 7.10–7.25 (m), 7.01–7.06 (m, **10b**), 6.90 (ddd, J=1.0, 2.5, 7.8 Hz, 1H, **10a**), 6.84 (t, J=2.5 Hz, 1H, **10a**), 6.63–6.82 (m), 6.17 (dd, J=5.3, 9.5 Hz, 1H, **10a**), 6.03 (dd, J=4.5, 9.8 Hz, 1H, **10b**), 4.65 (d, J=5.3 Hz, 1H, **10a**), 4.52 (dd, J=4.5, 0.5 Hz, 1H, **10b**), 4.19 (ddq, J=6.0, 9.2, 6.0 Hz, 1H, **10b**), 3.80 (ddq, J=5.0, 11.0, 6.0 Hz, 1H, **10a**), 3.70 (s, 2×3H, **10a**,**b**), 3.20 (dd, J=6.0, 13.5 Hz, 1H, **10b**), 3.05 (dd, J=5.5, 12.5 Hz, 1H, **10a**), 2.48 (dd, J=9.5, 12.5 Hz, 1H, **10a**), 2.13 (dd, J=9.0, 13.5 Hz, 1H, **10b**), 1.27 (d, J=6.0 Hz, 3H), 1.17 (d, J=6.5 Hz, 3H). ^{13}C NMR (62 MHz, CD_3COCD_3): δ=160.6 (**10b**), 160.4 (**10a**), 150.3 (**10b**), 140.8 (**10b**), 132.8 (**10a**), 131.3 (**10a**), 131.2 (**10b**), 130.2, 130.1, 129.8, 129.6, 129.3, 129.1, 128.4, 128.2, 128.0, 127.9, 127.5, 127.2, 126.8, 126.4, 119.9 (**10b**), 119.1 (**10a**), 114.3 (**10b**), 113.5 (**10a**), 111.8 (**10a**), 83.9 (**10b**), 80.3 (**10a**), 75.2 (**10a**), 72.7 (**10b**), 55.3, 54.5 (**10b**), 54.4 (**10a**), 49.8, 48.6, 17.2 (**10a**), 16.7 (**10b**). IR (film):

ν_{max}=3030, 2969, 2931, 2873, 2834, 1607, 1582, 1487, 1254, 1051, 784, 751, 699. MS (EI): *m/z* (%)=292 (95) [M^+], 275 (20), 251 (80), 236 (100), 222 (22), 174 (53), 165 (59), 149 (38), 131 (46), 115 (58). $C_{20}H_{20}O_2$: Calcd C 82.19, H 6.85; found C 81.34, H 6.92.

4.3.2. Compounds 12a,b. Yield: 267 mg (67%). Ratio (**12a/12b**): 1.1/1. **12a**. ^{1}H NMR (250 MHz, CD_3COCD_3): δ=7.41 (d, *J*=7.3 Hz, 1H), 7.15–7.28 (m, 3H), 7.12 (d, *J*=8.0 Hz, 1H), 6.90 (ddd, *J*=1.0, 2.5, 7.8 Hz, 1H), 6.85 (t, *J*=2.5 Hz, 1H), 6.72 (d, *J*=9.5 Hz, 1H), 6.71–6.77 (m, 1H), 6.18 (dd, *J*=5.3, 9.5 Hz, 1H), 4.61 (d, *J*=5.3 Hz, 1H), 3.70 (s, 3H), 3.61–3.73 (m, 1H), 3.08 (dd, *J*=12.3, 4.8 Hz, 1H), 2.49 (dd, *J*=12.3, 10.3 Hz, 1H), 1.25–1.70 (m, 4H), 0.89 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (62 MHz, CD_3COCD_3): δ=160.4, 148.7, 140.7, 132.9, 131.2, 130.1, 129.3, 128.4, 128.1, 127.5, 126.7, 119.1, 113.5, 111.8, 80.0, 79.1, 55.2, 54.0, 46.9, 38.9, 20.2, 14.5. UV (CH_3CN): $\lambda_{max}(\varepsilon)$=268 (10,200), 220 (3400). **12b** ^{1}H NMR (250 MHz, CD_3COCD_3): δ=7.10–7.25 (m, 4H), 7.00–7.07 (m, 1H), 6.70–6.85 (m, 3H), 6.65 (d, *J*=9.8 Hz, 1H), 6.02 (dd, *J*=4.5, 9.8 Hz, 1H), 4.58 (d, *J*=4.5 Hz, 1H), 4.00–4.12 (m, 1H), 3.72 (s, 3H), 3.16 (dd, *J*=6.0, 13.0 Hz, 1H), 2.17 (dd, *J*=9.3, 13.0 Hz, 1H), 1.28–1.52 (m, 4H), 0.89 (t, *J*=7.0 Hz, 3H). ^{13}C NMR (62 MHz, CD_3COCD_3): δ=160.5, 150.3, 143.2 131.4, 130.1, 129.8, 129.4, 129.0, 128.0, 127.2, 126.7, 120.1, 114.4, 111.6, 83.8, 76.7, 55.3, 54.2, 48.1, 38.6, 20.3, 14.4. UV (CH_3CN): $\lambda_{max}(\varepsilon)$=263 (10,100), 218 (3600). **12a**,**b**. IR (film): ν_{max}=3030, 2956, 2931, 2871, 2834, 1607, 1582, 1468, 1054, 784, 750, 699. MS (CI, NH_3): *m/z* (%)= 338 (14) [M^++NH_4], 321 (21) [M^++H], 320 (19) [M^+], 304 (26), 303 (100). $C_{22}H_{24}O_2$: Calcd C 82.50, H 7.50; found C 82.35, H 7.35.

4.4. Irradiation of compound 13

A solution of **13** (6 mM), H_2SO_4 (0.6 mM) in toluene (120 ml) were distributed in to 8 quartz tubes and irradiated for 6 h at λ=300 nm. The solution was slightly cloudy. The solvent was evaporated in the presence of $NaHCO_3$ and the residue was subjected to flash chromatography (petroleum ether/ethyl acetate: 1/5).

4.4.1. Compound 13. 157 mg (conversion: 61%).

4.4.2. Compound 14. Yield: 65 mg (27% with respect to the transformed compound **13**). ^{1}H NMR (250 MHz, CD_3COCD_3): δ=7.10–7.30 (m, 4H), 6.93 (d, *J*=8.0 Hz, 1H), 6.73 (dd, *J*=2.0, 8.0 Hz, 1H), 6.67 (d, *J*=9.8 Hz, 1H), 6.56 (d, *J*=2.0 Hz, 1H), 6.08 (dd, *J*=5.0, 10.0 Hz, 1H), 4.50 (d, *J*=5.0 Hz, 1H), 3.91 (dt, *J*=6.0, 7.5 Hz, 1H), 3.65 (dt, *J*= 6.5, 7.5 Hz, 1H), 2.85–2.96 (m, 1H), 2.68 (pent, *J*=6.5 Hz, 3H), 1.73 (t, *J*=6.5 Hz, 2H), 1.25 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (62 MHz, CD_3COCD_3): δ=154.6, 146.8, 141.8, 132.2, 130.4, 130.1, 129.1, 129.0, 128.2, 127.3, 126.6, 119.7, 116.1, 82.5, 74.6, 66.5, 53.4, 41.4, 33.2, 27.1, 27.0, 22.5. IR (film): ν_{max}=3023, 2973, 2926, 2870, 1619, 1569, 1451, 1152, 1121, 755. MS (EI): *m/z* (%)=332 (100) [M^+], 276 (20), 249 (14), 202 (15), 183 (14), 178 (39), 170 (57), 123 (49), 117 (33). $C_{23}H_{24}O_2$: Calcd C 83.13, H 7.23; found C 82.75, H 7.45.

4.4.3. Compound 15. Yield: 160 mg (66% with respect to the transformed compound **13**). ^{1}H NMR (250 MHz, CD_3COCD_3): δ=8.24 (d, *J*=8.5 Hz, 1H), 7.90 (dd, *J*=1.5, 8.0 Hz, 1H), 7.77 (d, *J*=8.5 Hz, 1H), 7.58 (ddd, *J*=1.5, 6.8, 8.3 Hz, 1H), 7.50 (ddd, *J*=1.5, 7.2, 8.0 Hz, 1H), 7.30 (d, *J*=8.5 Hz, 1H), 7.14 (dt, *J*=7.5, 0.5 Hz, 1H), 6.82 (dd, *J*=1.7, 7.5 Hz, 1H), 6.73 (d, *J*=1.7 Hz, 1H), 3.70–3.80 (m, 2H), 3.25–3.38 (m, 2H), 2.83 (t, *J*=6.8 Hz, 2H), 1.85 (t, *J*=6.8 Hz, 2H), 1.34 (s, 6H). ^{13}C NMR (62 MHz, CD_3COCD_3): δ=154.6, 142.6, 140.9, 134.1, 133.3, 132.3, 130.0, 129.4, 129.1, 127.1 (2×), 126.2, 125.4, 121.5, 120.5, 118.6, 74.8, 63.1, 33.8, 33.3, 27.1, 22.8. IR (film): ν_{max}=3416, 3053, 2968, 2926, 1616, 1564, 1453, 1155, 1121, 1039, 814, 751. MS (EI): *m/z* (%)=332 (71) [M^+], 277 (45), 258 (26), 245 (100), 231 (27), 215 (42), 202 (39), 241 (22), 115 (14).

4.5. Irradiation of compounds 12a and 12b

A solution of **12a**,**b** (40 mg, 0.15 mmol, ratio (**12a/12b**): 1.1/1) in acetonitrile (12 ml) was irradiated at λ=254 nm. The reaction was monitored by GC (Scheme 5). Solutions of diastereomerically pure **12a** or **12b** (5 mg, 0.02 mmol) were treated in the same way in order to check whether interconversion of formation of other diastereomers occurred. No such transformations could be detected.

4.6. Determination of the quantum yields

Solutions (Schemes 3 and 4) possessing an optical density of 3.5 (λ=254 nm, optical path=0.5 cm) were irradiated at λ=254 nm. until the conversion reached between 10 and 20%. *N*,*N*-dimethyluracil (formation of the monohydrate) was used as actinometer.[19]

Acknowledgements

The author thanks Professor Jean Pierre Pete for his support and Dr Karen Plé (UPRESA 6013, CNRS) for some language corrections of the manuscript.

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