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A novel photorearrangement of (coumarin-4-yl)methyl phenyl ethers

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ABSTRACT

In the present study, we describe synthesis and photochemical behaviour of the coumarinylmethyl phenyl ethers **1** and **6**–**10**. Irradiation of the compounds in polar solvents leads to *o*-, *p*- and *m*-hydroxybenzyl substituted coumarins as main products. A side reaction is the photosolvolysis of the ethers that gives the (coumarin-4-yl)methyl alcohol and the corresponding phenol. Detailed studies of the quantum yields and product distributions upon irradiation of **6** as a function of the solvents are indicative of a dominant role of an ionic pathway in photochemical conversions. The found photochemical rearrangement is a useful tool for the preparation of hydroxylated 4-benzylcoumarins. A series of such compounds have been synthesised.

1. Introduction

In the course of our studies on photoactivatable derivatives of vanilloid receptor ligands [1] we synthesised and photolysed the coumarinylmethyl capsaicin ether **1**. Compound **1** should be developed as so-called caged compound which upon illumination with UV/vis light releases temporally and spatially controlled the vanilloid capsaicin **2** [(*E*)-*N*-(4-hydroxy-3-methoxybenzyl)-8-methyl-non-6-enamide]. The biomolecule **2** is the pungent ingredient of chili peppers and is used in pain research as an activating ligand of heat-sensitive transduction channels in nociceptive neurons. However, contrary to our expectations light-induced reaction of **1** in aqueous buffer and quantification of the products by calibrated HPLC yielded the solvent-assisted photoheterolysis product **2** [2] only in small amounts (about 8%), but gave the novel rearrangement compound **4** as main product in a yield of 34% (Scheme 1).

To our knowledge, photochemical rearrangements of (coumarin-4-yl)methyl aryl ethers have not been described. However, well-known is the Photo-Claisen rearrangement [3] which was reported for the first time for allyl phenyl ethers and for benzyl phenyl ethers [4], and later also for naphthylmethyl phenyl ethers [5]. The reaction is usually carried out in nonpolar solvents and involves commonly an intramolecular radical process within a solvent cage to give a mixture of *ortho*- and *para*-rearranged products [3,5]. In the case of naphthylmethyl phenyl ethers (*o*-hydroxybenzyl)- and (*p*-hydroxybenzyl)naphthalenes are formed. The excitation energy is mainly localised in the phenyloxy and not in the arylmethyl chromophore.

Furthermore, thermal sigmatropic rearrangements of 3-(aryloxymethyl)coumarins at high temperatures (240 °C) resulting in 3-(*o*-hydroxybenzyl)- or 3-(*p*-hydroxybenzyl)-coumarins have been reported [6], but the corresponding 4-(aryloxymethyl)coumarins failed to undergo any such rearrangement [7].

The novel photorearrangement of the (coumarin-4-yl)-methyl phenyl ethers is of considerable interest both as a preparative method and for its theoretical implications. With the aim to get more information about this reaction we investigated the photochemical behaviour of **1** and of a series of various simply substituted (coumarin-4-yl)methyl phenyl ethers. Here, we present the results of the studies.

2. Experimental

2.1. Materials

Capsaicin (**2**) was obtained from Sigma (Germany). 4-(Bromomethyl)-7-methoxycoumarin (**5**), 7-methoxy-4-methylcoumarin

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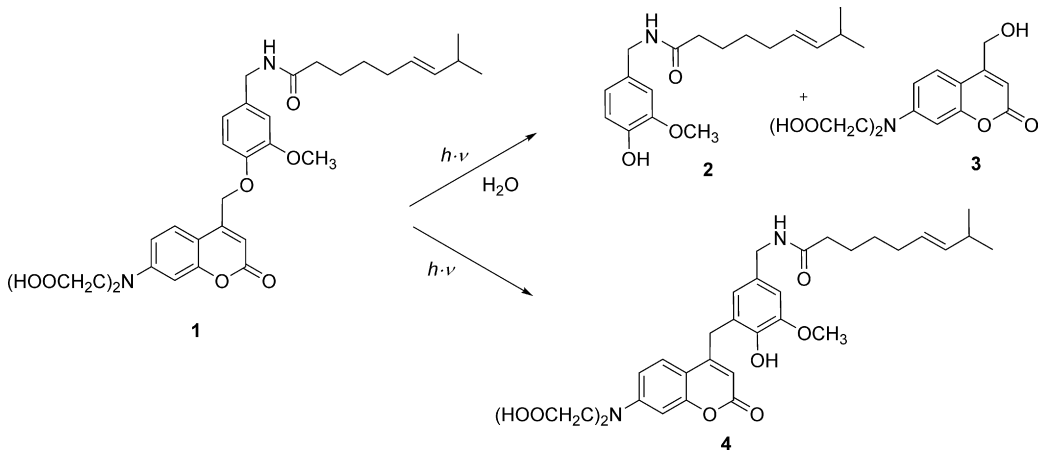


Scheme 1. Photochemical rearrangement of **1**.

(**20**), 7-methoxycoumarin (**22**), phenol, 2-methylphenol, 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2-methoxyphenol, thiophenol, aniline, and trifluoroacetic acid (TFA) were purchased from Aldrich (Germany). The remaining chemicals were of the highest grade commercially available and were used without further purification. 7-[Bis(*tert*-butoxycarbonylmethyl)amino]-4-(bromomethyl)coumarin was prepared as described previously [8]. TLC plates (silica gel 60 F_{254}) were purchased from E. Merck (Germany). Silica gel for flash chromatography was from J.T. Baker (The Netherlands). CH_3CN from Riedel-deHaen (Germany) was HPLC grade. Water was purified with a Milli-Q-Plus system (Millipore, Germany). The synthetic and analytical procedures with the coumarinylmethyl phenyl ethers were performed under yellow light provided by sodium vapor lamps.

2.2. Instrumentation

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV 300 spectrometer. Chemical shifts are given in parts per million (ppm) using the residue solvent peaks as reference relative to TMS. *J* values are given in Hz. Mass spectra were measured by electrospray ionization (ESI-TOF) mass spectrometry on an Acquity UPLC system coupled to LCT Premier (Waters) or on an Agilent 6220 ESI-TOF spectrometer (Agilent Technologies, U.S.A.). UV/vis spectra were recorded on a UV/vis spectrophotometer Lambda 9 (PerkinElmer). Fluorescence spectra were taken on a Jasco FP-6500 spectrometer. Phosphorescence was measured on a Fluoromax-4P spectrofluorometer (HORIBA Jobin Yvon). Analytical reversed-phase HPLC (RP-HPLC) was carried out on a Shimadzu LC-20 system (flow rate: 1 mL min^{-1}) equipped with a DAD-UV detector and a fluorescence detector (λ_{exc} = 320 nm, λ_{em} = 420 nm) by using a Nucleodur 100-5 C18 ec column, 100 Å, 5 μm, 250 mm × 4 mm, Macherey-Nagel (Germany). The given retention times (t_R) with exception of those of compounds **1** and **4** are related to a linear gradient of 20–95% B in A in 30 min (eluent A, H_2O/0.1% TFA; eluent B, CH_3CN). Preparative RP-HPLC was run on a Shimadzu LC-8A system (flow rate: 10 mL min^{-1}) with a UV/vis detector (SPD-6AV, λ_{det} = 320 nm) over a Nucleodur 100-5 C18 ec column (100 Å, 5 μm, 250 mm × 21 mm) from Macherey-Nagel (Germany). Photolysis of all synthesised photoprotected compounds in solution was performed by using a high-pressure mercury lamp (HBO 500, Oriel, U.S.A.) with controlled light intensity and metal interference filter (334 nm, Oriel, U.S.A.). For all experiments, UV and fluorescence quartz cuvettes with a path length of 1 cm and a cross-sectional area of 1 cm^2 were used. During irradiation, the solutions in the cuvettes were mixed by a magnetic stirrer. The melting points are uncorrected.

2.3. Synthesis

2.3.1. (*E*)-{7-[Bis(*tert*-butoxycarbonylmethyl)amino] coumarin-4-yl}methyl 2-methoxy-4-[(8-methylnon-6-enamido) methyl]-phenyl ether

A mixture of 7-[bis(*tert*-butoxycarbonylmethyl)amino]-4-(bromomethyl)coumarin (48.2 mg, 0.1 mmol) and capsaicin (30.4 mg, 0.1 mmol) was stirred in DMF (1 mL) for 24 h at room temperature in the presence of K_2CO_3 (72.6 mg, 0.2 mmol). The reaction mixture was filtered and evaporated. The residue was dissolved in CH_2Cl_2, washed with water (3×), dried with $MgSO_4$, evaporated and purified by preparative RP-HPLC. The desired product was eluted using a linear gradient 45–95% B in A in 60 min; eluent A, H_2O; eluent B, CH_3CN. The main fraction with a retention time of 58.1 min was collected, evaporated *in vacuo*, redissolved in CH_3CN/H_2O, and lyophilised to give 39.5 mg (56%) of a yellow solid, mp 130–132 °C; TLC, R_f 0.45 (*n*-hexane/THF = 1:1); ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92 (6H, d, J = 6.7, 2 × CH_3), 1.29 (2H, quintet, J = 7.4, CH_2CH_2CH=CH), 1.42 (18H, s, 2 × 3 × CH_3), 1.51 (2H, quintet, J = 7.4, $CH_2CH_2CH_2CH_2$), 1.94 (2H, q, J = 7.0, CH_2CH=CH), 2.11 (2H, t, J = 7.3, CH_2CONH), 2.20 [1H, sextet, J = 6.6, $CH(CH_3)_2$], 3.78 (3H, s, OCH_3), 4.20 (6H, m, CH_2NH and 2 × CH_2N), 5.29 (2H, s, Coum-CH_2), 5.31–5.38 (2H, m, CH=CH), 6.21 (1H, s, CoumH-3), 6.47 (1H, d, J = 2.2, CoumH-8), 6.59 (1H, dd, J = 9.0 and 2.2, CoumH-6), 6.76 (1H, d, J = 8.5, PhH-5), 6.91 (1H, s, PhH-3), 7.06 (1H, d, J = 8.3, PhH-6), 7.64 (1H, d, J = 8.9, CoumH-5), 8.22 (1H, t, J = 5.8, NH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 22.5 (2 × CH_3), 24.9 ($CH_2CH_2CH_2CH_2$), 27.7 (6 × CH_3), 28.6 (CH_2CH_2CH=CH), 30.3 [$CH(CH_3)_2$], 31.6 (CH_2CH=CH), 35.2 (CH_2CONH), 41.7 (CH_2NH), 53.5 (2 × CH_2N), 55.6 (OCH_3), 66.0 (Coum-CH_2), 81.1 [2 × $C(CH_3)_3$], 98.1 (CoumC-8), 106.6 (CoumC-3), 107.2 (CoumC-4a), 109.0 (CoumC-6), 111.6 (PhC-3), 113.8 (PhC-6), 119.2 (PhC-5), 125.5 (CoumC-5), 126.6 (CH_2CH=CH), 133.4 (PhC-4), 137.3 (CH_2CH=CH), 145.8 (PhC-1), 149.0 (PhC-2), 151.3 (CoumC-7), 151.7 (CoumC-4), 155.0 (CoumC-8a), 160.5 (CoumC-2), 168.8 (2 × *C*O*O*t-Bu), 171.9 (CONH); HRMS (ESI): $C_{40}H_{54}N_2O_9$, m/z [M+Na]$^+$ calcd 729.3727; found: 729.3695; elemental analysis calcd (%) for $C_{40}H_{54}N_2O_9$ (706.9): C, 67.97; H, 7.70, N, 3.96; found: C, 67.87; H, 7.68; N, 3.82.

2.3.2. (*E*)-7-{[Bis(carboxymethyl)amino]coumarin-4-yl}methyl 2-methoxy-4-[(8-methylnon-6-enamido)methyl]-phenyl ether (**1**)

(*E*)-7-{[Bis(*tert*-butoxycarbonylmethyl)amino]coumarin-4-yl} methyl 2-methoxy-4-[(8-methylnon-6-enamido)-methyl]-phenyl ether (30 mg, 0.042 mmol) was stirred in a mixture (10 mL) of TFA/CH_2Cl_2/H_2O (74:25:1) at room temperature for 30 min. The

solvents were evaporated, and the residue was coevaporated two times with diethyl ether, dissolved in CH_3CN/H_2O and lyophilised to give 25.6 mg (100%) of the desired product as a yellow solid: mp 155–160 °C (dec.); t_R = 13.55 min (analytical HPLC, 20–95% B in A in 20 min, eluent A, 0.1% TFA/H_2O; eluent B, CH_3CN); $\lambda_{max}{}^{em}$ (CH_3CN/HEPES buffer = 5:95, pH 7.2)/nm 484; ϕ_f = 0.12; ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92 (6H, d, J = 6.8, 2 × CH_3), 1.29 (2H, quintet, J = 7.6, CH_2CH$_2$CH=CH), 1.51 (2H, quintet, J = 7.3, CH$_2$CH_2CH$_2$CH$_2$), 1.94 (2H, q, J = 7.0, CH_2CH=CH), 2.12 (2H, t, J = 7.3, CH_2CONH), 2.20 [1H, sextet, J = 6.7, CH(CH$_3$)$_2$], 3.79 (3H, s, OCH$_3$), 4.19 (2H, d, J = 5.7, CH_2NH), 4.22 (4H, s, 2 × CH$_2$N), 5.29 (2H, s, Coum-CH_2), 5.32–5.35 (2H, m, CH=CH), 6.19 (1H, s, CoumH-3), 6.47 (1H, d, J = 2.1, CoumH-8), 6.60 (1H, dd, J = 9.0 and 2.3, CoumH-6), 6.76 (1H, d, J = 8.4, PhH-5), 6.91 (1H, s, PhH-3), 7.06 (1H, d, J = 8.2, PhH-6), 7.62 (1H, d, J = 9.1, CoumH-5), 8.22 (1H, t, J = 5.7, NH), 13.13 (2H, br s, 2 × COOH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 22.5 (2 × CH_3), 24.8 (CH$_2$CH_2CH$_2$CH$_2$), 28.6 (CH_2CH$_2$CH=CH), 30.3 [CH(CH$_3$)$_2$], 31.6 (CH_2CH=CH), 35.2 (CH_2CONH), 41.7 (CH$_2$NH), 53.2 (2 × CH$_2$N), 55.6 (OCH$_3$), 66.0 (Coum-CH_2), 97.9 (CoumC-8), 106.4 (CoumC-3), 107.0 (CoumC-4a), 109.0 (CoumC-6), 111.6 (PhC-3), 113.9 (PhC-6), 119.2 (PhC-5), 125.5 (CoumC-5), 126.6 (CH$_2$CH=CH), 133.4 (PhC-4), 137.3 (CHCH=CH), 145.8 (PhC-1), 149.0 (PhC-2), 151.3 (CoumC-7), 151.7 (CoumC-4), 155.1 (CoumC-8a), 160.5 (CoumC-2), 171.5 (2 × COOH), 171.9 (CONH); HRMS (ESI): $C_{32}H_{38}N_2O_9$, m/z [M−H]$^-$ calcd 593.2505; found: 593.2483; elemental analysis calcd (%) for $C_{32}H_{38}N_2O_9$ × 0.5 H_2O (603.67): C, 63.67; H, 6.51; N, 4.64; found: C, 63.52; H, 6.13; N, 4.66.

2.3.3. (E)-6-{{7-[Bis(carboxymethyl)amino]coumarin-4-yl}-methyl}-2-methoxy-4-[(8-methylnon-6-enamido)-methyl]-phenol (**4**)

1 (30.2 mg, 0.05 mmol) was dissolved in a semipreparative quartz cuvette with 15 mL CH_3CN/H_2O (1:1) and irradiated using a high-pressure mercury lamp (HBO 500) with controlled light intensity and 400 nm long pass filter (Thorlabs, Germany) for 40 min. HPLC showed starting compound **1** (10%), **4** (34%), capsaicin (8%) and other products. The solvent was evaporated and the residue was purified by RP-HPLC. The desired product **4** was eluted using a linear gradient 20–95% B in A in 60 min; eluent A, 0.1% TFA/H_2O; eluent B, CH_3CN. The main fraction with a retention time of 36.3 min was collected, evaporated, and lyophilised to give 3.9 mg (13%) of a yellow solid: mp 113–117 °C (dec.); t_R = 12.76 min (analytical HPLC, 20–95% B in A in 20 min, eluent A, 0.1% TFA/H_2O; eluent B, CH_3CN); λ_{max} (CH_3CN/HEPES buffer = 5:95, pH 7.2)/nm 378.5 (ε/dm^3 mol^{-1} cm^{-1} 17,700); $\lambda_{max}{}^{em}$ (CH_3CN/HEPES buffer = 5:95, pH 7.2)/nm 462; ϕ_f = 0.24; ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.92 (6H, d, J = 6.8, 2 × CH_3), 1.28 (2H, quintet, J = 7.3, CH_2CH$_2$CH=CH), 1.48 (2H, quintet, J = 7.4, CH$_2$CH_2CH$_2$CH$_2$), 1.92 (2H, q, J = 7.4, CH_2CH=CH), 2.07 (2H, t, J = 7.3, CH_2CONH), 2.19 [1H, sextet, J = 6.4, CH(CH$_3$)$_2$], 3.78 (3H, s, OCH$_3$), 3.96 (2H, s, Coum-CH_2) 4.12 (2H, d, J = 6.1, CH_2NH), 4.17 (4H, s, 2 × CH$_2$N), 5.27–5.37 (2H, m, CH=CH), 5.73 (1H, s, CoumH-3), 6.40 (1H, s, CoumH-8), 6.52 (1H, dd, J = 9.0 and 1.6, CoumH-6), 6.59 (1H, s, PhH-5), 6.75 (1H, s, PhH-3), 7.66 (1H, d, J = 9.0, CoumH-5), 8.15 (1H, t, J = 5.5, NH), 8.76 (1H, s, OH), 13.29 (2H, br s, 2 × COOH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 22.5 (2 × CH_3), 24.9 (CH$_2$CH_2CH$_2$CH$_2$), 28.7 (CH_2CH$_2$CH=CH), 30.3 [CH(CH$_3$)$_2$], 31.0 (Coum-CH_2), 31.6 (CH_2CH=CH), 35.2 (CH_2CONH), 41.7 (CH$_2$NH), 53.7 (2 × CH$_2$N), 55.7 (OCH$_3$), 97.8 (CoumC-8), 108.6 (CoumC-3), 108.9 (CoumC-4a), 109.1 (CoumC-6), 109.6 (PhC-3), 120.6 (PhC-5), 123.3 (PhC-6), 125.9 (CoumC-5), 126.6 (CH$_2$CH=CH), 130.4 (PhC-4), 137.3 (CHCH=CH), 142.6 (PhC-1), 147.5 (PhC-2), 151.0 (CoumC-7), 155.1 (CoumC-8a), 155.8 (CoumC-4), 160.6 (CoumC-2), 171.7 (2 × COOH), 171.9 (CONH); HRMS (ESI): $C_{32}H_{38}N_2O_9$, m/z [M−H]$^-$ calcd 593.2505; found: 593.2485.

2.3.4. Coumarinylmethyl phenyl ethers (**6–10**), general procedure

A mixture of 4-(bromomethyl)-7-methoxycoumarin **5** (2.69 g, 10 mmol), K_2CO_3 (1.38 g, 10 mmol), and the corresponding phenol (25 mmol) was stirred and refluxed in acetone (60 mL) under N_2 for 22 h. The mixture was cooled, filtered, and the solvent was removed. The residue was dissolved in AcOEt (50 mL) and washed three times with saturated aqueous NaCl-solution. The organic phase was dried with $MgSO_4$, evaporated, and crystallised from EtOH.

*2.3.4.1. 7-Methoxy-4-(phenoxymethyl)coumarin (**6**).* Colourless solid; yield: 1.97 g (70%); mp 116–117 °C (lit. [9], 112–114 °C); TLC, R_f 0.75 (*n*-hexane/THF = 1:1); t_R = 20.01 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.87 (3H, s, OCH$_3$), 5.39 (2H, s, CH$_2$), 6.41 (1H, s, CoumH-3), 6.98–7.03 (2H, m, CoumH-6 and PhH-4), 7.05 (1H, d, J = 2.1, CoumH-8), 7.14 (2H, d, J = 8.1, PhH-2 and PhH-6), 7.37 (2H, t, J = 8.1, PhH-3 and PhH-5), 7.79 (1H, d, J = 9.0, CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 55.9 (CH$_3$), 65.1 (CH$_2$), 100.9 (CoumC-8), 108.9 (CoumC-3), 110.4 (CoumC-4a), 112.2 (CoumC-6), 114.9 (PhC-2 and PhC-6), 121.4 (PhC-4), 126.0 (CoumC-5), 129.6 (PhC-3 and PhC-5), 151.4 (CoumC-4), 155.0 (CoumC-8a), 157.6 (PhC-1), 160.0 (CoumC-2), 162.5 (CoumC-7); HRMS (ESI): $C_{17}H_{14}O_4$, m/z [M+H]$^+$ calcd 283.0965; found: 283.0963; elemental analysis calcd (%) for $C_{17}H_{14}O_4$ (282.3): C, 72.33; H, 5.00; found: C, 72.00; H, 5.25.

*2.3.4.2. 7-Methoxy-4-(o-tolyloxymethyl)coumarin (**7**).* Colourless solid; yield: 2.1 g (72%); mp 175–176 °C (lit. [9], 164–165 °C); TLC, R_f 0.51 (*n*-hexane/AcOEt = 4:1); t_R = 21.95 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.25 (3H, s, CH$_3$), 3.87 (3H, s, OCH$_3$), 5.38 (2H, s, CH$_2$), 6.41 (1H, s, CoumH-3), 6.91 (1H, dt, J = 1.8 and 6.6, PhH-5), 7.00 (1H, dd, J = 2.4 and 9.0, CoumH-6), 7.05 (1H, d, J = 2.4, CoumH-8), 7.15–7.21 (3H, m, PhH-3, PhH-4 and PhH-6), 7.81 (1H, d, J = 8.7, CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 16.0 (Ph-CH$_3$), 56.0 (OCH$_3$), 65.0 (CH$_2$), 100.9 (CoumC-8), 108.6 (CoumC-3), 110.4 (CoumC-4a), 111.9 (PhC-4), 112.2 (CoumC-6), 121.0 (PhC-5), 125.8 (CoumC-5), 126.0 (PhC-2), 127.0 (PhC-6), 130.6 (PhC-3), 151.7 (CoumC-4), 155.0 (CoumC-8a), 155.5 (PhC-1), 160.1 (CoumC-2), 162.5 (CoumC-7); HRMS (ESI): $C_{18}H_{16}O_4$, m/z [M+H]$^+$ calcd 297.1121; found: 297.1119; elemental analysis calcd (%) for $C_{18}H_{16}O_4$ (296.3): C, 72.96; H, 5.44; found: C, 72.71; H, 5.49.

*2.3.4.3. 4-(2,6-Dimethylphenoxymethyl)-7-methoxycoumarin (**8**).* Colourless solid; yield: 2.2 g (70%); mp 154–155 °C; TLC, R_f 0.68 (*n*-hexane/AcOEt = 4:1); t_R = 22.99 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.25 (6H, s, CH$_3$), 3.87 (3H, s, OCH$_3$), 5.10 (2H, s, CH$_2$), 6.56 (1H, s, CoumH-3), 6.95 (1H, dd, J = 2.4 and 9.0, CoumH-6), 6.98–7.01 (1H, m, PhH-4), 7.05 (1H, d, J = 2.4, CoumH-8), 7.08 (2H, d, J = 7.5, PhH-3 and PhH-5), 7.78 (1H, d, J = 9.0 CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 16.0 (CH$_3$), 55.9 (OCH$_3$), 68.7 (CH$_2$), 100.9 (CoumC-8), 108.4 (CoumC-3), 110.3 (CoumC-4a), 112.2 (CoumC-6), 124.4 (PhC-4), 125.9 (CoumC-5), 128.9 (PhC-3 and PhC-5), 130.6 (PhC-2 and PhC-6), 152.2 (CoumC-4), 155.0 (CoumC-8a), 155.1 (PhC-1), 160.2 (CoumC-2), 162.5 (CoumC-7); HRMS (ESI): $C_{19}H_{18}O_4$, m/z [M+H]$^+$ calcd 311.1278; found: 311.1273; elemental analysis calcd (%) for $C_{19}H_{18}O_4$ (310.3): C, 73.53; H, 5.85; found: C, 73.33; H, 5.81.

*2.3.4.4. 7-Methoxy-4-(2,4,6-trimethylphenoxymethyl)coumarin (**9**).* Colourless solid; yield: 2.3 g (71%); mp > 159 °C (dec.); TLC, R_f 0.69 (*n*-hexane/AcOEt = 2:1); t_R = 17.55 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.20 (9H, s, CH$_3$), 3.87 (3H, s, OCH$_3$), 5.05 (2H, s, CH$_2$), 6.54 (1H, s, CoumH-3), 6.87 (2H, s, PhH-3 and PhH-5), 6.95 (1H, dd, J = 2.4 and 9.0, CoumH-6), 7.43 (1H, d, J = 2.4, CoumH-8), 7.67 (1H, d, J = 8.7, CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 16.0 (Ph-CH$_3$-2 and Ph-CH$_3$-6), 20.3 (Ph-CH$_3$-4), 55.9 (OCH$_3$), 68.8 (CH$_2$), 100.9 (CoumC-8), 108.4 (CoumC-3), 110.4 (CoumC-4a), 112.2 (CoumC-6), 125.9 (CoumC-5), 129.3 (PhC-3 and PhC-5), 130.1

(PhC-2 and PhC-6), 133.1 (PhC-4), 152.2 (CoumC-4), 152.9 (PhC-1), 155.0 (CoumC-8a), 160.2 (CoumC-2), 162.4 (CoumC-7); HRMS (ESI): $C_{20}H_{20}O_4$ *m/z* $[M+H]^+$ calcd 325.1434; found: 325.1430; elemental analysis calcd (%) for $C_{20}H_{20}O_4$, (324.4): C, 74.06; H, 6.21; found: C, 73.98; H, 6.16.

*2.3.4.5. 7-Methoxy-4-(2-methoxyphenoxymethyl)coumarin (**10**).* Colourless solid; yield: 2.5 g (80%); mp 167–169 °C; TLC, R_f 0.38 (petroleum ether/AcOEt = 2:1); t_R = 25.73 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.81 (3H, s, Ph-OCH_3), 3.87 (3H, s, 3H, Coum-OCH_3), 5.35 (2H, s, CH_2), 6.41 (1H, s, CoumH-3), 6.88–7.05 (5H, m, CoumH-6, CoumH-8, PhH-4, PhH-5, and PhH-3), 7.18 (1H, d, *J* = 7.5, PhH-6), 7.79 (1H, d, *J* = 8.7, CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 55.7 (Ph-OCH_3), 56.0 (Coum-OCH_3), 65.9 (CH_2), 100.9 (CoumC-8), 108.8 (CoumC-3), 110.5 (CoumC-4a), 112.3 and 112.4 (CoumC-6 and PhC-3, PhC-4 or PhC-5), 114.2 (PhC-6), 120.7 (PhC-3, PhC-4 or PhC-5), 122.0 (PhC-3, PhC-4 or PhC-5), 126.1 (CoumC-5), 147.0 (PhC-1), 149.2 (PhC-2), 151.7 (CoumC-4), 155.0 (CoumC-8a), 160.2 (CoumC-2), 162.5 (CoumC-7); HRMS (ESI): $C_{18}H_{16}O_5$, *m/z* $[M+H]^+$ calcd 313.1071; found: 313.1071; elemental analysis calcd (%) for $C_{18}H_{16}O_5 \times 0.5\ H_2O$ (321.11): C, 67.28; H, 5.33; found: C, 67.90, H, 5.19.

*2.3.4.6. 7-Methoxy-4-(phenylthiomethyl)coumarin (**11**).* This compound was prepared from **5** (1.08 g, 4 mmol), K_2CO_3 (0.55 g, 4 mmol) and thiophenol (0.88 g, 8 mmol) in 35 mL acetone as described for **6**–**10**. Crystallisation from EtOH yielded 0.84 g (2.8 mmol, 70%) of **11** as a colourless solid, mp 124–125 °C (lit. [9], 108–109 °C); TLC, R_f 0.56 (*n*-hexane/AcOEt = 2:1); t_R = 20.29 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.86 (3H, s, OCH_3), 4.41 (2H, s, CH_2), 6.07 (1H, s, CoumH-3), 6.97–6.99 (2H, m, CoumH-6 and Coum H-8), 7.25–7.38 (5H, m, PhH-2-6), 7.86 (1H, d, *J* = 9.3, CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 33.5 (CH_2), 55.9 (OCH_3), 101.0 (CoumC-8), 111.2 (CoumC-4a), 111.3 (CoumC-3), 112.1 (CoumC-6), 126.8 (CoumC-5), 127.0 (PhC-4), 129.1 (PhC-2 and PhC-6), 130.1 (PhC-3 and PhC-5), 134.1 (PhC-1), 151.6 (CoumC-4), 155.2 (CoumC-8a), 159.8 (CoumC-2), 162.4 (CoumC-7); HRMS (ESI): $C_{17}H_{14}O_3S$, *m/z* $[M+H]^+$ calcd 299.0736; found: 299.0732.

2.3.4.7. 7-Methoxy-4-(phenylaminomethyl)coumarin (12). **12** was prepared following the procedure described for **11** from **5** (1.08 g, 4 mmol), K_2CO_3 (0.55 g, 4 mmol) and aniline (1.12 g, 12 mmol). Crystallisation (EtOH) gave 0.79 g (2.8 mmol, 70%) of the product as a colourless solid, mp 171–172 °C (lit. [10], 173–174 °C); TLC, R_f 0.41 (*n*-hexane/AcOEt = 2:1); t_R = 17.78 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.87 (3H, s, OCH_3), 4.51 (2H, d, *J* = 5.7, CH_2), 6.16 (1H, s, CoumH-3), 6.29 (1H, t, *J* = 5.7, NH), 6.58 (1H, t, *J* = 7.5, PhH-4), 6.61 (2H, d, *J* = 7.8, PhH-2 and PhH-6), 6.99 (1H, dd, *J* = 8.7 and 2.4, CoumH-6), 7.03 (1H, d, *J* = 2.4, CoumH-8), 7.09 (2H, t, PhH-3 and PhH-5), 7.85 (1H, d, *J* = 8.7, CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 43.1 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 108.6 (CoumC-3), 111.4 (CoumC-4a), 112.1 (CoumC-6), 112.2 (PhC-2 and PhC-6), 116.4 (PhC-4), 125.8 (CoumC-5), 129.0 (PhC-3 and PhC-5), 148.0 (PhC-1), 154.4 (CoumC-4), 155.0 (CoumC-8a), 160.3 (CoumC-2), 162.4 (CoumC-7); HRMS (ESI): $C_{17}H_{15}NO_3$, *m/z* $[M+H]^+$ calcd 282.1125; found: 282.1118; elemental analysis calcd (%) for $C_{17}H_{15}NO_3$ (281.31): C, 72.58; H, 5.37; N 4.98; found: C, 72.28; H, 5.52; N, 4.91.

*2.3.5. General procedure for photoreactions of compounds **6–8** and **10***

1 mmol of the coumarinylmethyl phenyl ethers **6**–**8** and **10** were solved in CH_3CN (300 mL) in a glass reactor (*V* = 500 mL) and irradiated with a 140 W high-pressure mercury arc lamp (XL 151, λ > 325 nm) for 40 min. Evaporation of the solvent furnished a mixture of products that was analysed by analytical RP-HPLC using a linear gradient 20–95% B in A in 30 min, eluent A, 0.1% TFA/H_2O; eluent B, CH_3CN. Quantification of the peak areas showed the above discussed yields of the photorearrangement and photolysis products. Separation of the products was achieved by preparative RP-HPLC using a linear gradient 20–95% B in A in 60 min; eluent A, 0.1% TFA/H_2O; eluent B, CH_3CN. Given yields are related to the amounts of purified isolated products.

*2.3.5.1. 4-(2-Hydroxybenzyl)-7-methoxycoumarin (**13**).* Colourless solid; yield: 70.6 mg (25%); mp 197 °C; TLC, R_f 0.31 (*n*-hexane/AcOEt = 2:1); t_R = 15.79 min; ^{1}H NMR (300 MHz, DMSO-d_6,): δ 3.85 (3H, s, OCH_3), 4.04 (2H, s, CH_2), 5.85 (1H, s, CoumH-3), 6.76 (1H, t, *J* = 7.5, PhH-5), 6.88 (1H, d, *J* = 7.8, PhH-3), 6.95 (1H, dd, *J* = 2.1 and 8.7, CoumH-6), 7.00 (1H, d, *J* = 2.1, CoumH-8), 7.09 (1H, d, *J* = 7.5, PhH-6), 7.10 (1H, t, *J* = 7.5, PhH-4), 7.80 (1H, d, *J* = 9.0, CoumH-5), 9.65 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 31.2 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 110.7 (CoumC-3), 112.1 (CoumC-6), 112.5 (CoumC-4a), 115.3 (PhC-3), 119.2 (PhC-5), 122.9 (PhC-1), 126.3 (CoumC-5), 128.1 (PhC-4), 130.5 (PhC-6), 154.9 (PhC-2), 155.0 (CoumC-8a), 155.8 (CoumC-4), 160.3 (CoumC-2), 162.3 (CoumC-7); HRMS (ESI): $C_{17}H_{14}O_4$, *m/z* $[M+H]^+$ calcd 283.0965; found: 283.0966.

*2.3.5.2. 4-(4-Hydroxybenzyl)-7-methoxycoumarin (**14**).* Colourless solid; yield: 33.9 mg (12%); mp 212–213 °C; TLC, R_f 0.24 (*n*-hexane/AcOEt = 2:1); t_R = 14.38 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.84 (3H, s, OCH_3), 4.03 (2H, s, CH_2), 6.02 (1H, s, CoumH-3), 6.71 (2H, d, *J* = 8.4, PhH-2 and PhH-6), 6.93 (1H, dd, *J* = 2.1 and 8.7, CoumH-6), 6.98 (1H, d, *J* = 2.1, CoumH-8), 7.11 (2H, d, *J* = 8.4, PhH-3 and PhH-5), 7.73 (1H, d, *J* = 8.7, CoumH-5), 9.31 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 36.2 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 111.2 (CoumC-3), 112.1 (CoumC-6), 112.3 (CoumC-4a), 115.4 (PhC-2 and PhC-6), 126.6 (CoumC-5), 127.0 (PhC-4), 129.9 (PhC-3 and PhC-5), 155.1 (CoumC-8), 156.1 (PhC-1), 156.2 (CoumC-4), 160.3 (CoumC-2), 162.3 (CoumC-7); HRMS (ESI): $C_{17}H_{14}O_4$, *m/z* $[M+H]^+$ calcd 283.0965; found: 283.0966.

*2.3.5.3. 4-(Hydroxymethyl)-7-methoxycoumarin (**15**).* Colourless solid; yield: 20.6 mg (10%) from **6**; mp 185–186 °C (lit. [11], 187 °C); TLC, R_f 0.12 (*n*-hexane/AcOEt = 2:1); t_R = 7.92 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.85 (3H, s, OCH_3), 4.73 (2H, d, *J* = 3.6, CH_2), 5.60 (1H, t, *J* = 4.5, OH), 6.30 (1H, s, CoumH-3), 6.93 (1H, dd, *J* = 2.4 and 8.7, CoumH-6), 7.00 (1H, d, *J* = 2.4, CoumH-8), 7.61 (1H, d, *J* = 8.7, CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 55.9 (OCH_3), 59.1 (CH_2), 100.8 (CoumC-8), 107.4 (CoumC-3), 110.7 (CoumC-4a), 112.1 (CoumC-6), 125.4 (CoumC-5), 154.8 (CoumC-4), 156.7 (CoumC-8a), 160.5 (CoumC-2), 162.3 (CoumC-7); MS (ESI): $C_{11}H_{10}O_4$, *m/z* $[M+H]^+$ calcd 207.1; found: 207.1.

*2.3.5.4. 4-(3-Hydroxybenzyl)-7-methoxycoumarin (**17**).* Colourless solid; yield: 14.1 mg (5%); t_R = 14.66 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.84 (3H, s, OCH_3), 4.08 (2H, s, CH_2), 6.10 (1H, s, CoumH-3), 6.63 (1H, d, *J* = 8.1, PhH-4), 6.68 (1H, s, PhH-2), 6.74 (1H, d, *J* = 7.8, PhH-6), 6.92 (1H, dd, *J* = 2.1 and 8.7, CoumH-6), 6.99 (1H, d, *J* = 2.4, CoumH-8), 7.12 (1H, t, *J* = 7.8, PhH-5), 7.71 (1H, d, *J* = 9.0, CoumH-5), 9.36 (1H, s, Ph-OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 37.0 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 111.6 (CoumC-3), 112.1 (CoumC-6), 112.3 (CoumC-4a), 113.8 (PhC-4), 115.6 (PhC-2), 119.5 (PhC-6), 126.7 (CoumC-5), 129.6 (PhC-5), 138.6 (PhC-1), 155.1 (CoumC-8a), 155.5 (CoumC-4), 157.5 (PhC-3), 160.3 (CoumC-2), 162.3 (CoumC-7); HRMS (ESI): $C_{17}H_{14}O_4$, *m/z* $[M+H]^+$ calcd 283.0965; found: 283.0968.

*2.3.5.5. 7-Methoxy-4-methyl-3-phenoxycoumarin (**18**).* Colourless solid; yield: 7.1 mg (2.5%); t_R = 23.41 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.07 (3H, s, CH_3), 3.88 (3H, s, OCH_3), 6.97–7.07 (5H,

m, PhH-2, PhH-4, PhH-6, CoumH-6 and CoumH-8), 7.32 (2H, t, J = 7.8, PhH-3 and PhH-5), 7.74 (1H, d, J = 8.4, CoumH-5); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 11.6 (CH_3), 60.0 (OCH_3), 100.8 (CoumC-8), 112.6 (CoumC-6), 113.0 (CoumC-4a), 115.0 (PhC-2 and PhC-6), 122.4 (PhC-4), 126.7 (CoumC-5), 129.7 (PhC-3 and PhC-5), 141.3 (CoumC-3), 152.4 (CoumC-8a), 156.5 (PhC-1), 156.9 (CoumC-4), 160.3 (CoumC-2), 161.7 (CoumC-7); HRMS (ESI): $C_{17}H_{14}O_4$, m/z $[M+H]^+$ calcd 283.0965; found: 283.0963.

*2.3.5.6. 3-(4-Hydroxyphenyl)-7-methoxy-4-methylcoumarin (**19**).* Colourless solid; yield: 4.2 mg (1.5%); t_R = 20.27 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.25 (3H, s, CH_3), 3.87 (3H, s, OCH_3), 6.82 (2H, d, J = 8.4, PhH-2 and PhH-6), 6.92–6.97 (1H, m, CoumH-6), 7.00 (1H, s, CoumH-8), 7.10 (2H, d, J = 8.4, PhH-3 and PhH-5), 7.73 (1H, d, J = 8.4, CoumH-5); 9.56 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 16.5 (CH_3), 55.9 (OCH_3), 100.4 (CoumC-8), 112.1 (CoumC-6), 113.7 (CoumC-4a), 114.8 (PhC-2 and PhC-6), 123.2 (CoumC-3), 125.0 (PhC-4), 126.9 (CoumC-5), 131.5 (PhC-3 and PhC-5), 147.6 (CoumC-4), 153.6 (CoumC-8a), 156.9 (PhC-1), 160.4 (CoumC-2), 161.9 (CoumC-7); HRMS (ESI): $C_{17}H_{14}O_4$, m/z $[M+H]^+$ calcd 283.0965; found: 283.0963.

2.3.5.7. 4-(2-Hydroxy-3-methylbenzyl)-7-methoxycoumarin. Colourless solid; yield: 32.6 mg (11%); mp 165 °C; TLC, R_f 0.40 (n-hexane/AcOEt = 2:1); t_R = 20.5 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH_3), 3.85 (3H, s, OCH_3), 4.10 (2H, s, CH_2), 5.78 (1H, s, CoumH-3), 6.72 (1H, t, J = 7.5, PhH-5), 6.93 (1H, d, J = 7.8, PhH-6), 6.96 (1H, dd, J = 2.4 and 9.0, CoumH-6), 7.00 (1H, d, J = 2.4, CoumH-8), 7.02 (1H, d, J = 8.7, PhH-4), 7.79 (1H, d, J = 8.7, CoumH-5), 8.53 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 16.7 (CH_3), 31.8 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 110.6 (CoumC-3), 112.1 (CoumC-6), 112.6 (CoumC-4a), 119.7 (PhC-5), 123.7 (PhC-3), 125.0 (PhC-1), 126.3 (CoumC-5), 128.1 (PhC-6), 129.6 (PhC-4), 152.9 (PhC-2), 154.9 (CoumC-8a), 155.9 (CoumC-4), 160.3 (CoumC-2), 162.3 (CoumC-7); HRMS (ESI): $C_{18}H_{16}O_4$, m/z $[M+H]^+$ calcd 297.1121; found: 297.1130.

2.3.5.8. 4-(4-Hydroxy-3-methylbenzyl)-7-methoxycumarin. Colourless solid; yield: 35.5 mg (12%); mp >180 °C (dec.); TLC, R_f 0.31 (n-hexane/AcOEt = 2:1); t_R = 19.07 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.08 (3H, s, CH_3), 3.84 (3H, s, OCH_3), 3.99 (2H, s, CH_2), 6.02 (1H, s, CoumH-3), 6.71 (1H, d, J = 8.1, PhH-5), 6.91 (1H, dd, J = 2.4 and 8.7, CoumH-6), 6.92 (1H, d, J = 8.7, PhH-6), 6.98 (1H, d, J = 2.4, CoumH-8), 7.00 (1H, s, PhH-2), 7.72 (1H, d, J = 8.7, CoumH-5), 9.19 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 16.0 (CH_3), 36.3 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 111.2 (CoumC-3), 112.0 (CoumC-6), 112.3 (CoumC-4a), 114.7 (PhC-5), 124.0 (PhC-2), 126.6 (CoumC-5), 126.8 (PhC-3), 127.1 (PhC-6), 131.0 (PhC-1), 154.1 (PhC-4), 155.1 (CoumC-4), 156.2 (CoumC-8a), 160.3 (CoumC-2), 162.2 (CoumC-7); HRMS (ESI): $C_{18}H_{16}O_4$, m/z $[M+H]^+$ calcd 297.1121; found: 297.1115.

2.3.5.9. 4-(3-Hydroxy-4-methylbenzyl)-7-methoxycoumarin. Colourless solid; yield: 8.6 mg (3%); mp 123–126 °C; TLC, R_f 0.39 (n-hexane/AcOEt = 2:1); t_R = 19.72 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.06 (3H, s, CH_3), 3.84 (3H, s, OCH_3), 4.04 (2H, s, CH_2), 6.10 (1H, s, CoumH-3), 6.65 (1H, s, PhH-2), 6.67 (1H, d, J = 6.9, PhH-5), 6.91 (1H, dd, J = 2.4 and 8.7, CoumH-6), 6.99 (1H, d, J = 2.1, CoumH-8), 7.00 (1H, d, J = 7.2, PhH-6), 7.68 (1H, d, J = 8.7, CoumH-5), 9.20 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 15.6 (CH_3), 36.8 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 111.5 (CoumC-3), 112.1 (CoumC-6), 112.3 (CoumC-4a), 114.8 (PhC-2), 119.4 (PhC-5), 122.3 (PhC-4), 126.7 (CoumC-5), 130.7 (PhC-6), 135.6 (PhC-1), 155.1 (CoumC-8), 155.5 (PhC-3), 155.7 (CoumC-4), 160.3 (CoumC-2), 162.3 (CoumC-7); HRMS (ESI): $C_{18}H_{16}O_4$, m/z $[M+H]^+$ calcd 297.1121; found: 297.1121.

2.3.5.10. 4-(3-Hydroxy-2-methylbenzyl)-7-methoxycoumarin. Colourless solid; yield: 7.4 mg (3%); mp 160–161 °C; TLC, R_f 0.39 (n-hexane/AcOEt = 2:1); t_R = 19.52 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.08 (3H, s, CH_3), 3.83 (3H, s, OCH_3), 4.06 (2H, s, CH_2), 6.16 (1H, s, CoumH-3), 6.85 (1H, d, J = 8.7, PhH-6), 6.89 (1H, t, J = 8.7, PhH-5), 6.93 (1H, dd, J = 2.4 and 8.7, CoumH-6), 7.02 (1H, d, J = 2.1, CoumH-8), 7.09 (1H, d, J = 8.5, PhH-4), 7.73 (1H, d, J = 8.7, CoumH-5), 9.32 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 15.4 (CH_3), 36.8 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 111.5 (CoumC-3), 112.1 (CoumC-6), 112.3 (CoumC-4a), 113.2 (PhC-4), 119.8 (PhC-5), 124.5 (PhC-2), 126.7 (CoumC-5), 129.9 (PhC-6), 136.1 (PhC-1), 154.9 (CoumC-4), 155.6 (PhC-3), 155.7 (CoumC-8a), 160.1 (CoumC-2), 162.4 (CoumC-7); HRMS (ESI): $C_{18}H_{16}O_4$, m/z $[M+H]^+$ calcd 297.1121; found: 297.1118.

2.3.5.11. 4-(4-Hydroxy-3,5-dimethylbenzyl)-7-methoxycoumarin. Colourless solid; yield: 18.6 mg (6%); mp >179 °C (dec.); TLC, R_f 0.35 (n-hexane/AcOEt = 2:1); t_R = 17.83 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.12 (6H, s, 2 × CH_3), 3.84 (3H, s, OCH_3), 3.97 (2H, s, CH_2), 6.02 (1H, s, CoumH-3), 6.85 (2H, s, PhH-2 and PhH-6), 6.92 (1H, dd, J = 2.4 and 8.7, CoumH-6), 6.98 (1H, d, J = 2.4, CoumH-8), 7.73 (1H, d, J = 8.8, CoumH-5), 8.12 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 16.6 (2 × CH_3), 36.3 (Coum-CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 111.2 (CoumC-3), 112.0 (CoumC-6), 112.3 (CoumC-4a), 124.4 (PhC-3, PhC-5), 126.6 (CoumC-5), 127.2 (PhC-1), 128.6 (PhC-2 and PhC-6), 151.9 (PhC-4), 155.1 (CoumC-4), 156.1 (CoumC-8a), 160.3 (CoumC-2), 162.2 (CoumC-7); HRMS (ESI): $C_{19}H_{18}O_4$, m/z $[M+H]^+$ calcd 311.1278; found: 311.1273.

2.3.5.12. 4-(3-Hydroxy-2,4-dimethylbenzyl)-7-methoxycoumarin. Colourless solid; yield: 13.3 mg (4%); TLC, R_f 0.37 (n-hexane/AcOEt = 2:1); t_R = 18.3 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.05 (3H, s, Ph-CH_3-2), 2.17 (3H, s, Ph-CH_3-4), 3.86 (3H, s, OCH_3), 4.08 (2H, s, CH_2), 5.54 (1H, s, CoumH-3), 6.54 (1H, d, J = 7.5, PhH-6), 6.88 (1H, d, J = 7.5, PhH-5), 6.98 (1H, dd, J = 2.1 and 9.0, CoumH-6), 7.02 (1H, d, J = 2.1, CoumH-8), 7.76 (1H, d, J = 9.0, CoumH-5), 8.24 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 12.1 (Ph-CH_3-4), 16.7 (Ph-CH_3-2), 34.9 (CH_2), 55.9 (OCH_3), 100.9 (CoumC-8), 110.4 (CoumC-3), 112.2 (CoumC-6), 112.5 (CoumC-4a), 121.1 (PhC-6), 123.2 (PhC-4), 123.5 (PhC-2), 126.3 (CoumC-5), 127.7 (PhC-5), 133.4 (PhC-1), 153.2 (PhC-3), 154.9 (CoumC-4), 155.9 (CoumC-8a), 160.3 (CoumC-2), 162.4 (CoumC-7); HRMS (ESI): $C_{19}H_{18}O_4$, m/z $[M+H]^+$ calcd 311.1278; found: 311.1273.

2.3.5.13. 3-(4-Hydroxy-3,5-dimethylbenzyl)-7-methoxy-4-methylcoumarin. Colourless solid; yield: 9.3 mg (3%); TLC, R_f 0.50 (n-hexane/AcOEt = 2:1); t_R = 18.75 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.18 (6H, s, 2 × Ph-CH_3), 2.24 (2H, s, Coum-CH_3), 3.87 (3H, s, OCH_3), 6.82 (2H, s, PhH-2 and PhH-6), 6.96–6.99 (2H, m, CoumH-6 and CoumH-8), 7.72 (1H, d, J = 8.4, CoumH-5), 8.35 (1H, s, OH); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 16.5 (Coum-CH_3), 16.6 (2 × Ph-CH_3), 55.9 (OCH_3), 100.4 (CoumC-8), 112.1 (CoumC-6), 113.7 (CoumC-4a), 123.4 (PhC-1), 123.8 (PhC-3 and PhC-5), 125.2 (CoumC-3), 126.8 (CoumC-5), 130.0 (PhC-2 and PhC-4), 147.4 (CoumC-4), 152.8 (PhC-3), 153.6 (CoumC-8a), 160.4 (CoumC-2), 161.8 (CoumC-7); HRMS (ESI): $C_{19}H_{18}O_4$, m/z $[M+H]^+$ calcd 311.1278; found: 311.1270.

2.3.5.14. 4-(2-Hydroxy-3-methoxybenzyl)-7-methoxycoumarin. Colourless solid; yield: 37.5 mg (12%); mp >64 °C (dec.); TLC, R_f 0.72 (n-hexane/AcOEt = 3:1); t_R = 20.12 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.80 (3H, s, Ph-OCH_3), 3.84 (3H, s, Coum-OCH_3), 4.05 (2H, s, CH_2), 5.84 (1H, s, CoumH-3), 6.70 (1H, d, J = 7.4, PhH-4 or PhH-6), 6.73 (1H, t, J = 7.7, PhH-5), 6.88 (1H, d, J = 8.0, PhH-4 or PhH-6), 6.93 (1H, dd, J = 1.6 and 8.8, CoumH-6), 6.99 (1H, d, J = 1.6, CoumH-8), 7.79 (1H, d, J = 9.1, CoumH-5), 8.85 (1H, s, OH); HRMS

(ESI): $C_{18}H_{16}O_5$, *m/z* $[M+H]^+$ calcd 313.1071; found: 313.1070; elemental analysis calcd (%) for $C_{18}H_{16}O_5 \times 0.5\ H_2O$ (321.32): C, 67.28; H, 5.33; found: C, 67.91; H, 4.99.

2.3.5.15. 4-(4-Hydroxy-3-methoxybenzyl)-7-methoxycoumarin. Colourless solid; yield: 34.4 mg (11%); mp >115 °C (dec.); TLC, R_f 0.50 (*n*-hexane/AcOEt = 3:1); t_R = 17.73 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.72 (3H, s, Ph-OCH_3), 3.83 (3H, s, Coum-OCH_3), 4.03 (2H, s, CH_2), 6.01 (1H, s, CoumH-3), 6.66–6.71 (2H, m, PhH-5 and Ph-H6), 6.90 (1H, m, PhH-2), 6.92 (1H, dd, *J* = 2.4 and 8.5, CoumH-6), 6.98 (1H, d, *J* = 2.5, CoumH-8), 7.76 (1H, d, *J* = 9.2, CoumH-5), 8.87 (1H, s, OH); HRMS (ESI): $C_{18}H_{16}O_5$, *m/z* $[M+H]^+$ calcd 313.1071; found: 313.1072; elemental analysis calcd (%) for $C_{18}H_{16}O_5 \times 0.5\ H_2O$ (321.32): C, 67.28; H, 5.33; found: C, 67.70; H, 5.14.

2.3.5.16. 4-(3-Hydroxy-4-methoxybenzyl)-7-methoxycoumarin. Colourless solid; yield: 1.6 mg (0.5%); TLC, R_f 0.55 (*n*-hexane/AcOEt = 3:1); t_R = 18.38 min; HRMS (ESI): $C_{18}H_{16}O_5$, *m/z* $[M+H]^+$ calcd 313.1071; found: 313.1065.

2.3.5.17. 4-(3-Hydroxy-2-methoxybenzyl)-7-methoxycoumarin. Colourless solid; yield: 1.2 mg (0.4%); TLC, R_f 0.55 (*n*-hexane/AcOEt = 3:1); t_R = 18.62 min; HRMS (ESI): $C_{18}H_{16}O_5$, *m/z* $[M+H]^+$ calcd 313.1071; found: 313.1066.

*2.3.6. Photolysis of 7-methoxy-4-(2,4,6-trimethylphenoxymethyl)coumarin (**9**)*

32.4 mg (0.1 mmol) of compound **9** were dissolved in 15 mL CH_3CN and irradiated at λ = 334 nm in a semipreparative cuvette for 40 h. Evaporation of the solvent furnished a mixture of products that was analysed by analytical RP-HPLC. Quantification of the peak areas showed the above discussed yields of the photorearrangement and photolysis products. Separation of the rearrangement product 4-(3-hydroxy-2,4,6-trimethylbenzyl)-7-methoxycoumarin and **15** (2.9 mg, 14%) was achieved by preparative RP-HPLC using a linear gradient 20–95% B in A in 60 min; eluent A, 0.1% TFA/H_2O; eluent B, CH_3CN.

Data of *4-(3-hydroxy-2,4,6-trimethylbenzyl)-7-methoxycoumarin*: Colourless solid; yield: 1.6 mg (5%); t_R = 21.20 min; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.28 (6H, s, Ph-CH_3-2 and Ph-CH_3-4), 1.73 (3H, s, Ph-CH_3-6), 3.85 (3H, s, OCH_3), 4.08 (2H, s, CH_2), 5.55 (1H, s, CoumH-3), 6.66 (1H, d, *J* = 7.8, PhH-6), 6.91 (1H, d, *J* = 7.8, PhH-5), 6.97 (1H, dd, *J* = 2.1 and 9.0, CoumH-6), 7.02 (1H, d, *J* = 2.4, CoumH-8), 7.76 (1H, d, *J* = 8.7, CoumH-5), 8.23 (1H, s, OH); HRMS (ESI): $C_{20}H_{20}O_4$, *m/z* $[M+H]^+$ calcd 325.1434; found: 325.1428.

2.4. Photochemical and photophysical properties

2.4.1. Photochemical quantum yields

The differential photochemical quantum yields, ϕ_{dis}, were determined for **1** at 365 nm and for **6**–**10** at 334 nm by the relative method as previously described [12] using *E,E*-1,4-diphenylbuta-1,3-diene in *n*-hexane (ϕ = 0.11) as standard for **1** and (6,7-dimethoxycoumarin-4-yl)methyl diethyl phosphate (ϕ = 0.08) [13] in CH_3CN/0.01 M HEPES/KOH buffer (5:95, pH 7.2) as standard for compounds **6**–**10**. Identical absorbances for the references and **1** or **6**–**10** were used during photolysis. For kinetic investigations the irradiated solutions of **1**, **6**–**10**, and (6,7-dimethoxycoumarin-4-yl)methyl diethyl phosphate were analysed by analytical HPLC and those of *E,E*-1,4-diphenylbuta-1,3-diene by UV spectroscopy (λ = 328 nm).

2.4.2. Fluorescence quantum yields

The fluorescence quantum yields, ϕ_f, were determined at 25 °C by the relative method [14] versus quinine sulfate in 0.1N H_2SO_4 as a standard (ϕ_f = 0.545). At the excitation wavelength used, the absorbance values of the standard and the investigated compound were identical.

2.4.3. Triplet energy

Triplet energy of compound **6** was determined from phosphorescence measurements in diethyl ether/*i*-pentane/ethanol (5:5:2) at 77 K.

3. Results and discussion

3.1. Synthesis

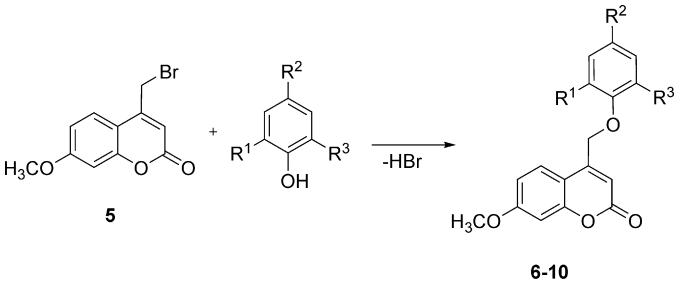
1 was prepared from 7-[bis(*tert*-butoxycarbonylmethyl)-amino]-4-(bromomethyl)coumarin [8] by reaction with capsaicin (**2**) using K_2CO_3 in dry DMF to yield the corresponding *tert*-butyl-protected derivative which was purified by reversed-phase HPLC on a preparative scale and then deprotected with TFA to generate **1** in 56% yield.

The (7-methoxycoumarin-4-yl)methyl phenyl ethers **6**–**10** – compounds **6** and **7** were already known [9] – were synthesised in 58–80% yields by condensation of the 4-(bromomethyl)-7-methoxycoumarin **5** with various substituted phenols in the presence of K_2CO_3 in acetone using standard literature procedures (Scheme 2).

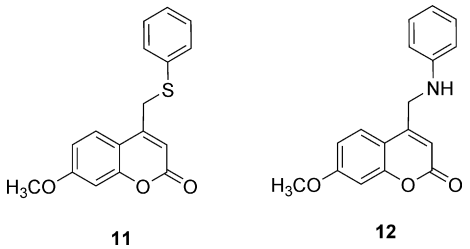
In order to check whether the rearrangement takes place also with coumarinylmethyl phenyl thioethers or (coumarinylmethyl)phenylamines, compounds **11** [9] and **12** [10] (structures see Scheme 3) were prepared by reaction of **5** and thiophenol or aniline in the presence of K_2CO_3 in acetone.

3.2. Photochemical and photophysical properties

Compounds **1** and **6**–**12** show typical absorption spectra. The long-wavelength absorption maxima, λ_{max}, of **1** are centred at 380 nm in aqueous buffer at pH 7.2 and those of **6**–**12** at 320–325 nm in CH_3OH/H_2O with molar extinction coefficients



Scheme 2. Synthesis of the ethers **6**–**10**.



Scheme 3. Structures of compounds **11** and **12**.

Table 1
Long-wavelength absorption maxima, λ_{max}, extinction coefficients at the absorption maxima, ε_{max}, and photochemical quantum yields, ϕ_{dis}, of compounds **1** and of **6**–**12** in CH_3OH/H_2O (1:1).

Compound	λ_{max} (nm)	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	ϕ_{dis}
1	381[a]	17,700[a]	0.33
6	323	14,200	0.63
7	325	13,300	0.55
8	324	14,600	0.38
9	324	14,500	0.30
10	325	12,200	0.46
11	323	12,900	n.d.[b]
12	321	14,400	n.d.[b]

[a] In CH_3CN/HEPES buffer (5:95), pH 7.2.
[b] n.d.: not determined.

Table 2
Long-wavelength absorption maxima, λ_{max}, extinction coefficients at the absorption maxima, ε_{max}, photochemical quantum yields, ϕ_{dis}, fluorescence maxima, λ_{max}^{em}, and fluorescence quantum yields, ϕ_f, of compound **6** in different solvents at room temperature.

Solvent	λ_{max} (nm)	ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)	ϕ_{dis}	λ_{max}^{em} (nm)	ϕ_f
CH_3OH/H_2O (1:1)	323	14,200	0.63	390	0.02
CH_3CN/H_2O (1:1)	323	14,200	0.55	396	0.02
CH_3OH	320	13,500	0.51	393	0.03
CH_3CN	320	13,600	0.17	393	0.04
CH_2Cl_2	322	14,700	0.21	391	0.05
Acetone	326	10,800	0.04	395	0.03

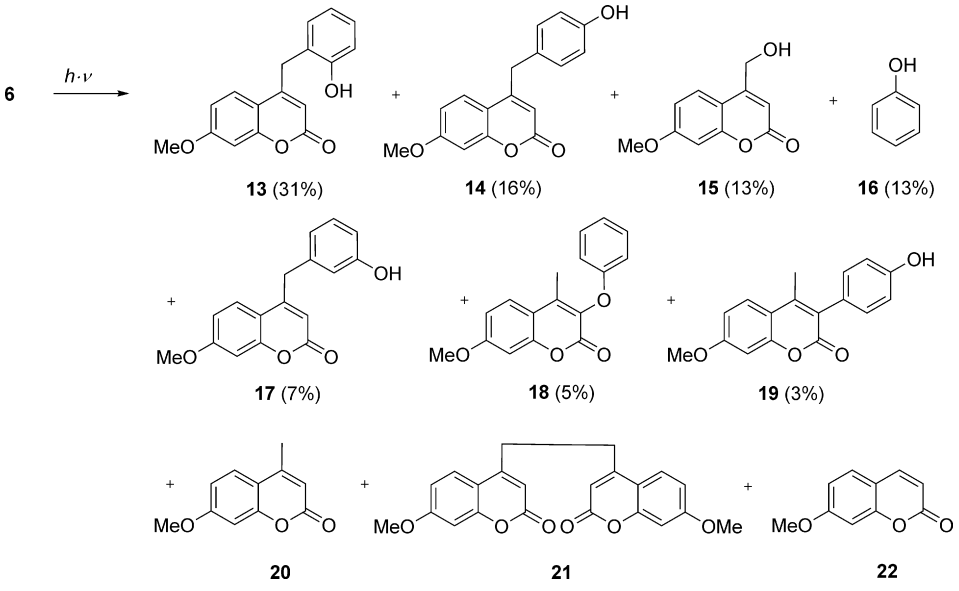
ε_{max} of 17,700 and 12,200–14,600 $dm^3\ mol^{-1}\ cm^{-1}$, respectively (Table 1). The absorption bands are assigned to the coumarin chromophore. Irradiation of compound **1** with light at 365 nm and of compounds **6**–**10** at 334 nm leads to photoreactions, mainly rearrangements and photocleavages. The photochemical quantum yields, ϕ_{dis}, for disappearance of **1** and **6**–**10** in CH_3OH/H_2O (1:1) solutions are relatively high (see Table 1). All values are reported at conversions between 5% and 10% to avoid internal filter effects that result because the products have the same chromophore as the starting materials.

The thioether **11** produced upon irradiation at 334 nm under identical conditions in CH_3OH/H_2O (1:1), CH_3CN or CH_3CN/H_2O (1:1) complex mixtures of photolysis products (probably radical-derived compounds) and no rearrangement product could be detected, while compound **12** failed to undergo any photocleavage or rearrangement under the described reaction conditions. The (phenoxymethyl)coumarins **6**–**10** exhibit only a weak fluorescence presumably due to short lifetimes in the S_1 states by the very rapid chemical reactions which involves only a low fractional rate in fluorescence.

The dependence of λ_{max}, ε_{max}, ϕ_{dis}, the fluorescence maxima, λ_{max}^{em}, and the fluorescence quantum yields, ϕ_f, upon the solvent system is presented exemplarily for compound **6** in Table 2. As expected λ_{max} values are essentially the same in protic and aprotic solvents and also the extinction coefficients vary with exception of that in acetone only weakly with the polarity of the solvents. The fluorescence data are similar in the investigated solvents as well. However, photochemical quantum yields of **6** are strikingly solvent dependent and the relative reactivity of **6** increased in the order of acetone $< CH_3CN < CH_2Cl_2 < CH_3OH < CH_3CN/H_2O < CH_3OH/H_2O$, that means polar protic solvents favour the photoreactivity probably due to stabilisation of ion pairs formed via photoheterolysis. The very low reaction quantum yield of **6** in acetone could result from formation of a triplet state coumarin by triplet sensitisation that gives no C–O bond cleavage as shown recently for unsubstituted 4-(phenoxymethyl)coumarin [15].

3.3. Photochemical rearrangements

Table 2 shows that the best solvents for photoreactions of **6**–**10** are CH_3OH and mixtures of CH_3OH/H_2O and CH_3CN/H_2O. However, due to more side reactions in CH_3OH and the poor solubility of the compounds in CH_3OH/H_2O (1:1) and CH_3CN/H_2O (1:1) we decided to carry out the photoreactions in a preparative scale in wet CH_3CN. Irradiation of a 1 mmol solution of **6** in 300 mL undegassed acetonitrile in a reactor with a 140 W high-pressure mercury arc lamp at $\lambda > 325$ nm for 40 min afforded the *o*-, *p*- and *m*-hydroxybenzyl-substituted coumarins **13**, **14** and **17** together with the known alcohol **15** [11], phenol (**16**), and recovery of unreacted **6** (12%) as main products. The yield of the *meta*-rearranged product **17** is considerably lower than that of the *ortho*- and *para*-isomers **13** and **14**. Compounds **13** and **14** were obtained in a 1.8:1 ratio. Furthermore, small amounts of compounds **18** and **19** and traces (<1%) of **20**–**22** were obtained (Scheme 4). Yields were determined by HPLC. Derivatives **13**–**15**, **17**–**19** and **22** were isolated by preparative HPLC. Their structures were determined by NMR and mass spec-



Scheme 4. Photochemical reactions of compound **6**.

Table 3
Product distribution in % determined by calibrated HPLC after irradiation of compound **6** at λ = 334 nm in different solvent systems (50 μmol)[a].

Solvent	13	14	17	13 + 14 + 17
CH_3OH/H_2O (1:1)	46	21	7	73
CH_3CN/H_2O (1:1)	48	28	6	82
CH_3OH	45	26	6	77
CH_2Cl_2	36	22[b]		58
CH_3CN	35	20	7	62

[a] Irradiation time 5–10 min.
[b] Including **17** (HPLC peaks of **14** and **17** were not fully separable).

trometry. Compounds **20** and **21** were identified only by HPLC–MS and by comparison of their HPLC data with authentic reference samples. Compounds **13**–**17** are formed probably by ionic mechanisms. The formation of **15** results from photosolvolysis of **6** using traces of water in the solvent. In contrast the products **20** and **21** are clearly indicative of a radical pathway. The photoproduct distributions are a reflection of the participation of ionic and radical intermediates.

Similar irradiation of **7**, containing an *ortho*-methyl substituent at the phenyl moiety, for 40 min under identical conditions afforded the corresponding rearranged 2-hydroxy-3-methylbenzyl- (15%), 4-hydroxy-3-methylbenzyl- (17%), 3-hydroxy-4-methylbenzyl- (5%) and 3-hydroxy-2-methylbenzyl-substituted coumarins (5%) as well as *o*-cresol and the alcohol **15** (23%) as major products. As expected, the *ortho*-methyl substituent resulted in a lower *ortho*-selectivity relative to the parent compound **6**. The photorearrangement of the 4-(2,6-dimethylphenoxymethyl)-7-methoxycoumarin (**8**) produced the *para*- and *meta*-rearranged products 4-(4-hydroxy-3,5-dimethylbenzyl)- and 4-(3-hydroxy-2,4-dimethylbenzyl)coumarin with yields of 11% and 9%, respectively. Furthermore, 3-(4-hydroxy-3,5-dimethylbenzyl)-7-methoxycoumarin (9%) was isolated. Here, the main reaction products were the cleavage products 2,6-dimethylphenol and the alcohol **15** (26%). The results show that the yields of rearranged products are reduced by introduction of methyl substituents in one or both *ortho*-positions of the phenyl moiety. In general, the *meta*-rearrangement shows a low preference. Photoreaction to 2,4,6-trimethylphenol and **15** (28% yield) were also predominant at irradiation of **9**, containing three methyl groups positioned in the two *ortho*- and the *para*-positions. The *meta*-rearranged product 4-(3-hydroxy-2,4,6-trimethylbenzyl)coumarin was isolated with a yield of only 13%.

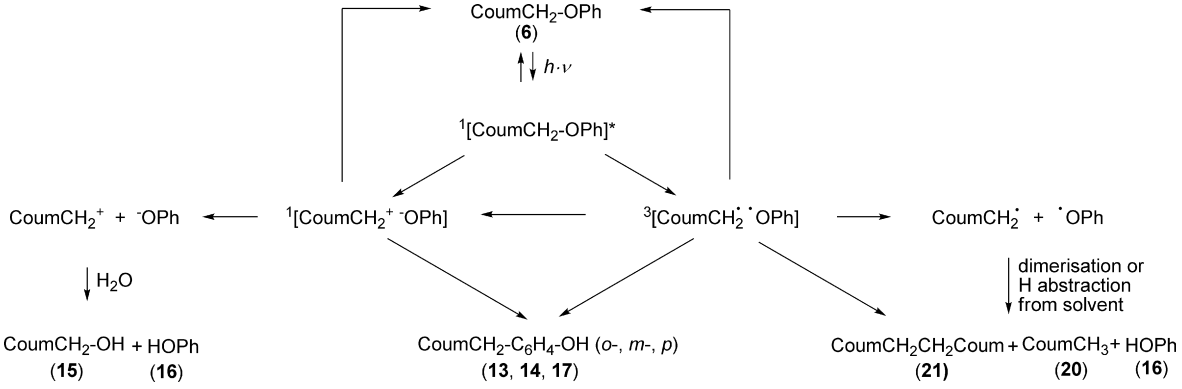
Analogue photoproducts as in the case of the methyl-substituted phenyl coumarinylmethyl ether **7** were also observed for the coumarinylmethyl ether **10** of the corresponding methoxy-substituted phenol. Irradiation of a 1 mmol solution of **10** in CH_3CN at λ > 325 nm gave the *ortho*- and *para*-rearranged products with yields of each 18% and the two isomeric *meta*-rearranged products with a yield of together 3%.

With the aim to characterise the photoreaction of the coumarinylmethyl phenyl ethers in detail and to optimise the conditions of the photochemical rearrangements we determined the distribution of the major photoproducts upon irradiation of **6** with 334 nm light in a cuvette at high conversion runs in various solvents. As shown in Table 3 the photorearrangements of **6** are strikingly solvent dependent and the yields of rearranged products are increased in the order of $CH_2Cl_2 < CH_3CN < CH_3OH/H_2O < CH_3OH < CH_3CN/H_2O$, that means polar protic solvents favour the photoreaction. The three rearranged photoproducts are barely fluorescent and are stable to the reaction conditions for at least as long as any of the irradiation times. At 334 nm the rearrangement product yields were significantly higher than those in the reactor at λ > 325 nm. In CH_3CN/H_2O (1:1) the total amount of rearranged products achieved 82%.

In order to obtain information about mechanistic aspects we determined the triplet energy of compound **6** (E_T = 63 kcal mol^{-1}) using phosphorescence measurements at 77 K and examined the photoreaction of **6** in CH_3CN in the presence of the triplet sensitizer acetone (E_T = 82 kcal mol^{-1}) [16] and the triplet quencher cyclohexa-1,3-diene (E_T = 52 kcal mol^{-1}) [16]. We found that both reagents had no effects with respect to the formation of the rearranged products **13**, **14**, and **17** and the cleavage products **15** and **16**. From these results, we conclude that the photochemical conversions proceed via excited singlet states. When photoreaction of **6** was performed in dry nitrogen-degassed CH_3CN solutions at 334 nm the product yields of **15** and **16** were definite lower and the total rate of the photoreactions was also diminished.

3.4. Mechanism

Scheme 5 summarises the mechanistic conclusions reached from the study of the product distribution, solvent dependencies on quantum yields, and photophysical properties of the coumarinylmethyl phenyl ethers. All of the parameters are clearly indicative of a dominant role of an ionic pathway in the phototransformations and we assume that the photoreactions proceed in analogy to the conversion of coumarinylmethyl esters via a photochemical S_N1 mechanism [2]. Indications of the involvement of triplet states were not found. This finding is consistent with results of Yamaji et al. which show that 4-(phenoxymethyl)coumarin is uncleavable in the triplet state by using laser flash photolysis [15]. We propose that the first step is the formation of the excited singlet state of the coumarin chromophore. The second step is mainly the heterolytic bond cleavage to give the singlet ion pair ^{1}[CoumCH$_2^+$ $^-$OPh]. Imaginable is also homolytic cleavage from S_1 to form the radical pair followed by single-electron transfer to form the ion pair. There were insufficient data for us to distinguish between these pathways. In



Scheme 5. Main phototransformation pathways for the photolysis of (coumarin-4-yl)methyl phenyl ethers in aqueous solvents. The transformations of **6** are shown.

the case of the ion-derived rearrangements the coumarinylmethyl cation attacks the *ortho*-, *meta*- or *para* position of the phenolate anion in the solvent cage to form the hydroxybenzylcoumarins. The reaction competes with the escape from the solvent cage to give the solvent-separated coumarinylmethyl cation and phenolate anion, which then react with water to yield the product alcohol **15** in addition to the phenol derivatives. The formation of radical-derived compounds **20** and **21** is explainable from the radical pair by hydrogen-abstraction from the solvent or by dimerisation. The very low yields of **20** and **21** show that this pathway is not favoured.

4. Conclusion

The photochemical rearrangement of (coumarin-4-yl)methyl phenyl ethers described here is a new tool for the selective formation of carbon-carbon bonds and is a simple method for the synthesis of otherwise difficulty accessible hydroxylated 4-benzylcoumarins such as compound **4**. 4-Substituted coumarin derivatives are known for their wide range of biological properties. The introduction of an OH group in the benzyl moiety provides an effective handle for further modification of the benzyl part of the molecule. Furthermore, the experimental protocol presented in this article should be of general utility for the preparation of hydroxylated 4-hetarylcoumarins.

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