Photochemistry of the 9-Hydroxyxanthenyl Radical in the Laser-Jet: Evidence for Photochemically Induced, Regioselective Radical Coupling

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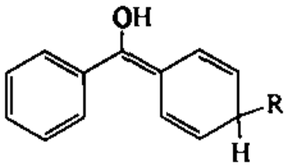
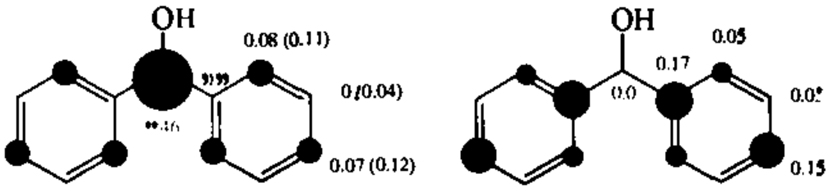
Abstract: The conventional irradiation (low intensity) of xanthone in ethanol was observed to produce pinacol **3** by photoreductive coupling and 9-hydroxy-9-(1-hydroxyethyl)-9*H*-xanthene (**4**) by *head-to-head* cross-coupling between the resultant 9-hydroxyxanthenyl (**2**) and 1-hydroxyethyl radicals. Under laser-jet conditions (high intensity), in addition to products **3** and **4**, 3-(1-hydroxyethyl)-9*H*-xanthen-9-one (**5d**) was obtained as the major *head-to-tail* cross-coupling product. The observed dependence of the product ratio of **4** and **5d** on the irradiation intensity is rationalized in terms of the higher spin density in the aryl rings, particularly at the 3-position (*para* to the hydroxy-substituted carbon atom), of the electronically excited 9-hydroxyxanthenyl radical (**2***). For the ground state radical **2**, as expected, the majority of spin density resides at the hydroxy-substituted carbon atom and, thus, constitutes the precursor to the *head-to-head* cross-coupling product **4**. The theoretical spin densities for the ground and excited state 9-hydroxyxanthenyl radicals **2**, calculated by semiempirical MO methods (PM3), indicate that upon photoexcitation the electron density in the SOMO shifts from the hydroxy-substituted radical center (ground state) to the aromatic π-system (first excited state) and is concentrated at the 1a- and 3-positions.

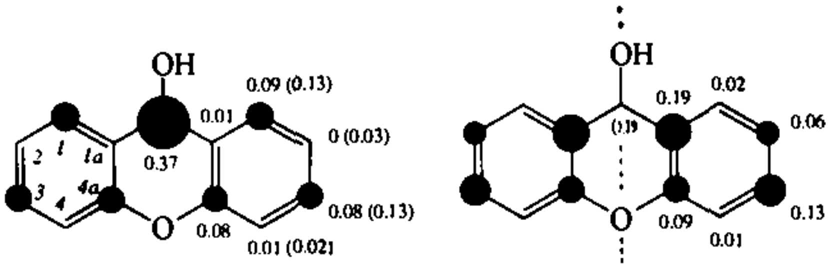
It was recently reported that the regioselectivity of the radical coupling between the hydroxydiphenylmethyl radical (**1**) and the 1-hydroxyethyl radical was strongly dependent upon the light intensity used during the irradiation.[1] Thus, under laser-jet[2] conditions (high intensity), irradiation of benzophenone in ethanol produced a significant amount of ring cross-coupling product (*head-to-tail* coupling), derived from the oxidation-sensitive *light-absorbing transient* (LAT). The latter has been of intense mechanistic interest in the photoreduction of aromatic ketones in H-donating solvents for more than three decades.[3] The observed dependence of the product distribution on the light intensity indicated that the *head-to-tail* product resulted mainly from the radical coupling reaction of the electronically excited hydroxydiphenylmethyl radical (**1***). Semiempirical MO calculations[4] of the spin density distributions in the SOMO of the ground state and the first excited state of the radical **1** seem to corroborate this observation (Figure 1).



LAT



ground state of radical 1 excited state of radical 1*



ground state of radical 2 excited state of radical 2*

Figure 1. Spin density distributions calculated by semiempirical MO methods for radical 1 (AM1, torsion angle of the phenyl groups $\theta = 50°$) and radical 2 (PM3). Values in parentheses represent the spin densities extrapolated from EPR hyperfine coupling constants.[5]

To confirm the hypothesis that enhanced *head-to-tail* coupling under high-intensity conditions (laser-jet) is derived from the higher spin density at the *para* position in the electronically excited radical, the 9-hydroxyxanthenyl radical (**2**) was chosen as a test case. Compared to the hydroxydiphenylmethyl radical (**1**), the structurally related xanthenyl radical **2** is planar. In view of the high symmetry, a better correspondence between the semiem-

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[2] (a) Wilson, R. M.; Schnapp, K. A.; Hannemann, K.; Ho, D. M.; Memarian, H. R.; Azadnia, A.; Pinhas, A. R.; Figley, T. M. *Spectrochim. Acta, Part A* 1990, *46A*, 551–558. (b) Wilson, R. M.; Adam, W.; Schulte Oestrich, R. *Spectrum* **1991**, *4*, 8–17. (c) Wilson, R. M.; Schnapp, K. A. *Chem. Rev.* 1993, *93*, 223–249.

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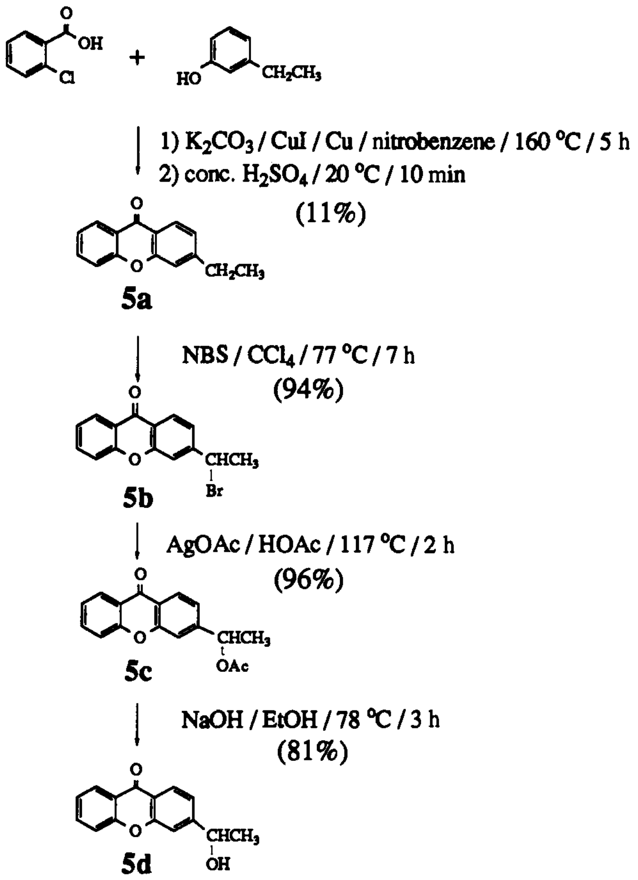
pirically calculated spin densities[4] and those assessed from EPR hyperfine coupling constants (a_i)[5a] according to the McConnell equation[6] is anticipated (Figure 1); nevertheless, the correspondence between the calculated and experimental spin densities for both radicals is quite satisfactory. Moreover, the first excited state of the radical **2*** possesses a nodal plane through the hydroxy-bearing carbon atom and the xanthene oxygen atom, so that the spin density in the excited state must be localized on the conjugated aromatic rings, especially at the 3-position. The absorption spectrum of the transient radical **2**, obtained through time-resolved laser-flash spectroscopy, indicates that radical **2** exhibits absorption in the UV region ($\lambda < 400$ nm; $\epsilon > 1 \times 10^3$ M^{-1} cm^{-1}),[7] which is accessible by the output of the argon ion laser (333, 351, 363 nm), and thus the photochemistry of the 9-hydroxyxanthenyl radical (**2**) is in principle observable.

Presently we report our results on the chemistry of the electronically excited 9-hydroxyxanthenyl radical (**2***), which has been generated by hydrogen abstraction by the triplet state of xanthone from the solvent and subsequent excitation under laser-jet conditions. The advantage of the laser-jet technique for multiple-photon chemistry is the fact that such irradiations can be conducted in the liquid phase under high photon densities in the continuous operating mode so that photoproducts can be obtained in sufficient amounts for identification and/or characterization.

Results and Discussion

The synthesis of authentic samples was performed according to the sequence illustrated in Scheme 1. The xanthone derivative **5a** was obtained through an Ullmann coupling between 2-chlorobenzoic acid and 3-ethylphenol, followed by Friedel–Crafts acylation. Bromination with *N*-bromosuccinimide, followed by acetylation and hydrolysis, afforded the target molecule **5d**.

Scheme 1. Synthesis of *Head-to-Tail* Cross-Coupling Product **5d**



Photoreduction of xanthone in ethanol[8] generated the transient radical **2**, whereby triplet xanthone abstracted a hydrogen atom from the α carbon atom of ethanol solvent.[7,9] The photoproducts were identified and quantified by comparison of ^{1}H NMR spectra with those of authentic samples. The results are summarized in Table 1. The major product in all reactions was pinacol **3**. Under laser-jet conditions (high intensity) (cf. Table 1, entry 3), the ratio of the *head-to-head* and *head-to-tail* cross-coupling products **4** and **5d** is significantly lower than under low-intensity photolysis conditions (Table 1, entry 2), i.e. ca. 2.2:1 *versus* 22:1 or about 10-fold less.

Table 1. Product Studies of the Photolysis of Xanthone in Ethanol

entry	conc (10^{-3} M)	mode	irradiation time	conv[a] (%)	mb[a] (%)	product distribution[a,b] 3	4	5d
1	7.79	Rayonet[c,c]	55 min	71	93	87	13	
2	7.77	normal[c,e]	5 min	86	92	77	22	1
3	7.24	LJ[c,f]	ca. 50 μs	47	94	62	26	12

[a] Detected by ^{1}H NMR analysis, error ±5% of the stated value; mb stands for mass balance. [b] Normalized to 100%. [c] Irradiation under an argon atmosphere. [d] 300-nm lamps. [e] Direct irradiation with the widened beam of the argon ion laser, 2.5 W over all UV lines (333, 351, 363 nm), 4.10×10^{-3} M terephthalonitrile as the internal standard. [f] Laser-jet experiment, 4.4 W over all UV lines, 100-μm capillary, flow rate of 0.9 mL/min, photon irradiance ca. 10^{23} s^{-1} cm^{-2}, single pass through the focal region.

The lifetime of 370 ns[7c] for triplet xanthone in 2-propanol is quite long, and the generation of upper excited xanthone under high-intensity photolysis conditions is reasonable; however, it is difficult to rationalize how such a reaction channel can lead directly to photoproduct **5d**. We propose that in the cross-coupling process the increased yield of the *head-to-tail* product **5d** in the laser-jet irradiation derives from the electronically excited radical **2***, as exhibited in the mechanism of Scheme 2. Thus, the 9-hydroxyxanthenyl radical (**2**), generated in the photoreduction of xanthone in ethanol, either dimerizes to yield the symmetrical pinacol **3** or cross-couples with the 1-hydroxyethyl radical to form the *head-to-head* product **4**. Under high photon densities, the radical intermediate **2** absorbs another photon, producing the electronically excited **2***, which couples with a 1-hydroxyethyl radical at the 3-position of the aromatic ring to yield the LAT-type primary photoproduct, which after oxidation affords the *head-to-tail* product **5d**.

The observed product data are in good agreement with what is expected from the spin density distributions calculated by semiempirical methods. In its excited state, the radical **2*** possesses the highest spin density at the 1a-position ($\rho = 0.19$), but radical coupling at this carbon atom would generate a non-Kekulé diradical, which is energetically unfavorable. While similar reasoning applies to reactions at the 2- and 4-positions, cross-coupling at the 1-position to afford after oxidation 1-(1-hydroxyethyl)-9*H*-xanthen-9-one (**6**) is in principle possible. This regioisomer was not detected in the laser-jet photolysate, as established rigorously by spectral comparison with an authentic sample. The latter, which was prepared analogously to the regioisomer **5d**, was fully characterized but is not included in Scheme 1. The absence of regioisomer **6** is not surprising because of the small spin density at the 1-position ($\rho = 0.02$), but additional

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(5) (a) Wilson, R. *J. Chem. Soc . B* **1968**, 1581–1588. (b) Wilson, R. *J. Chem. Soc. B* **1968**, 84–90.

(6) (a) McConnell, H. M. *J. Chem. Phys.* **1956**, *24*, 764–766. (b) Colpa, J. P.; Bolton, J. R. *Mol. Phys.* **1963**, *6*, 273–282. $Q = 30$ G was employed.

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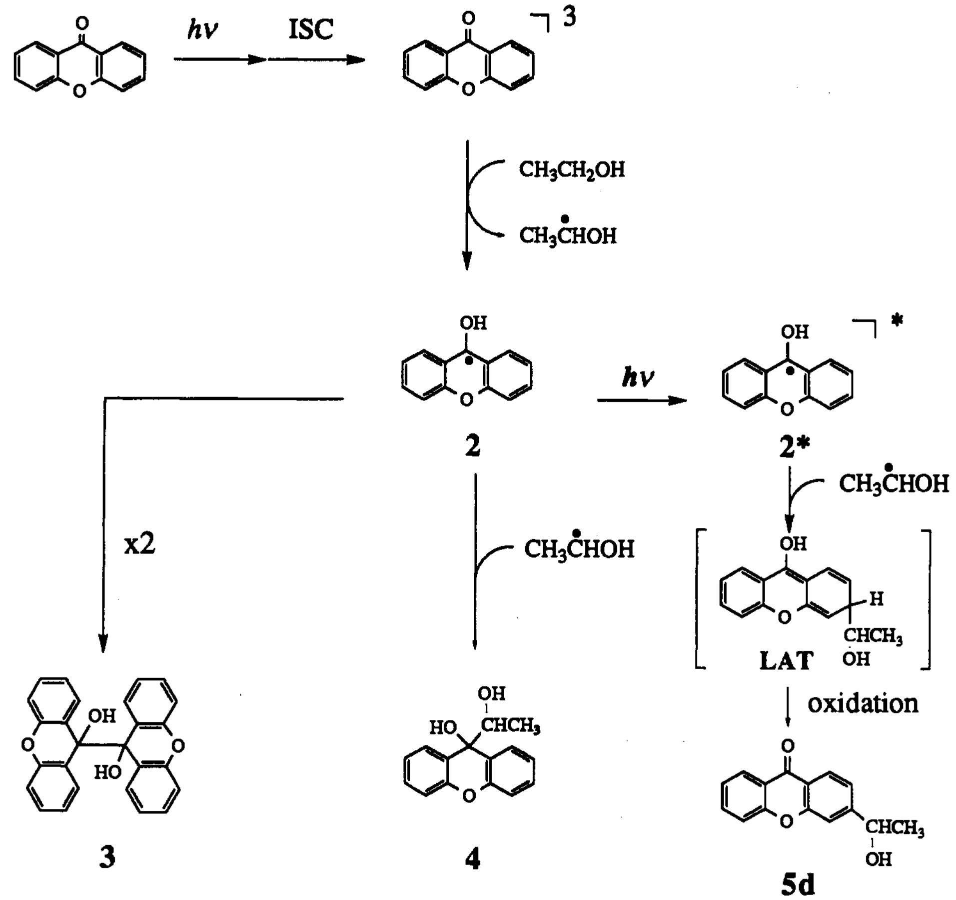
(8) Zanker, V.; Erhardt, E. *Bull. Chem. Soc. Jpn.* **1966**, *39*. 1694–1700. This paper describes the photochemistry of xanthone in deoxygenated ethanol by monitoring the UV spectra of the photolysate, while in our work, photoproducts were isolated (cf. Table 1).

(9) Jeandrau, J. P.; Gramain, J. C.; Lemaire, J. *J. Chem. Res., Synop.* **1979**, *6*, 186.

Scheme 2. Photochemical Generation and Transformations of the 9-Hydroxyxanthenyl Radical (**2**)



steric hindrance through *peri* interactions encumbers the coupling with the 1-hydroxyethyl radical. Consequently, for the electronically excited xanthenyl radical **2***, cross-coupling at the 3-position is guided by its relatively high spin density ($\rho = 0.13$) to produce preferentially product **5d**. In ground state xanthenyl radical **2**, the spin density at the 3-position is small but not zero, so that small amounts of product **5d** can derive also from the ground state radical **2**.

The major product in the laser-jet experiment is the *head-to-head* dimer, namely the pinacol **3** (Table 1). Thus, the LAT-type *head-to-tail* dimer, which would result from coupling of the ground state xanthenyl radical **2** at the *para*-position (3-position) of the electronically excited xanthenyl radical **2***, is not formed in sufficient amounts for detection. This is expected in view of the fact that such LAT coupling products have not been observed in the photoreduction of benzophenone in isopropyl alcohol and even in the presence of benzhydrol. Besides, like the labile *head-to-tail* dimers of the benzyl radicals, the so-called semibenzenes,[10] such LAT-type dimers would not be expected to persist under the laser-jet conditions and would be expected to rearrange thermally and/or photochemically to the more stable *head-to-head* dimers.[3e,h,l,m,n]

In conclusion, the major new observation in the laser-jet photochemistry of the 9-hydroxyxanthenyl radical (**2**), analogous to the hydroxydiphenyl radical (**1**),[1c] is the increased cross-coupling at its *para*-position (3-position) with the partner 1-hydroxyethyl radical. This regioselectivity appears to be controlled by accumulation of spin density in the aromatic ring of the excited state xanthenyl radical **2***.

Experimental Section

Materials and General Aspects. Xanthone was recrystallized from ethanol before use. All solutions were degassed with a slow stream of dry argon gas for 20 min before irradiation. For column chromatography, silica gel (34–63-μm mesh) was used in a substrate:adsorbent ratio of 1:100. NMR spectra were recorded on a Bruker AC 200 or a Bruker AC 250 spectrometer. Mass balances were determined from the peak areas of the identified products by ^{1}H NMR analysis directly on the product mixtures. The IR spectra were recorded on a Perkin-Elmer 1420, the UV spectra on a Hitachi U-3200 spectrophotometer.

Rayonet Irradiations. The irradiation was carried out by placing the reaction mixture contained in a Schlenk tube into a Rayonet Photochemical Reactor [RPR (75 W, 110 V)] from the Southern New England Ultraviolet Co. The 50-mL sample was irradiated for 55 min under an argon atmosphere.

Normal Laser Irradiations. The irradiations were carried out in a Schlenk tube at the 333-, 351-, and 363-nm lines of the Coherent INNOVA 100 argon ion laser (2.5 W over all UV lines) supplied with UV optics. The beam was widened with a quartz lens ($f = 50$ mm) to the size of ca. 1 cm in diameter, and the 20-mL sample was irradiated for 5 min under an argon atmosphere.

Laser-Jet Irradiations. The experimental setup, as described in detail in two recent publications,[2a,b] was employed. The beam of the argon ion laser (4.4 W over all UV lines) was focused by means of a quartz lens ($f = 80$ mm) onto a free-falling liquid jet of the photolysis solution. The free-falling liquid jet was maintained by means of a Bischoff 2200 HPLC pump while it was passed through a 100-μm capillary. The irradiation chamber was kept under a positive argon gas pressure, and the substrate solution was passed once through the focal region of the laser beam.

Rayonet Photolysis of Xanthone in Ethanol: Isolation of [9,9′-Bi-9*H*-xanthene]-9,9′-diol (3) and 9-Hydroxy-9-(1-hydroxyethyl)-9*H*-xanthene (4). A sample of 1.42 g (7.24 mmol) of xanthone, dissolved in 400 mL of ethanol and degassed as described above, was irradiated for 16 h under a nitrogen atmosphere in a Rayonet Photochemical Reactor [RPR (800 W, 110 V)] equipped with 300-nm lamps. After completion of the irradiation, the solvent was removed under reduced pressure (ca. 20 °C, 18 Torr). To the residue were added methylene chloride (10 mL) and ethyl acetate (10 mL), and the soluble fraction of the photoproducts was purified by column chromatography (9:1 pentane:ethyl acetate as the eluent, $R_f = 0.06$). After removal of the solvent under reduced pressure (ca. 20 °C, 18 Torr), 123 mg (7%) of cross-coupling product **4** was obtained

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(10) Langhals, H.: Fischer, H. *Chem. Ber.* **1978**, *111*, 543–553.

as colorless oil: IR (CCl_4) 3590–3530 (OH), 3560–3490 (OH), 3035, 2960, 1585, 1460, 1435, 1300, 1230, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.69 (d, $J_{11,12}$ = 6.4 Hz, 3 H, 12-H), 2.49 (d, $J_{11,11\text{–}OH}$ = 4.3 Hz, 1 H, 11-OH), 3.14 (s, 1 H, 9-OH), 3.95 (qd, $J_{11,12}$ = 6.4 Hz, $J_{11,11\text{–}OH}$ = 4.3 Hz, 1 H, 11-H), 7.10–7.71 (m$_c$, 8 H, arom.-H); ^{13}C NMR ($CDCl_3$, 63.4 MHz) δ 16.5 (q, C-12), 71.7 (s, C-9), 76.2 (d, C-11), 116.0 (d), 116.0 (d), 122.7 (s), 123.2 (d), 123.3 (d), 125.1 (s), 126.4 (d), 127.5 (d), 129.2 (d), 129.2 (d), 150.7 (s), 150.8 (s). Anal. Calcd for $C_{15}H_{14}O_3$ (242.3): C, 74.36; H, 5.82. Found: C, 74.27; H, 6.10. The other photoproduct was recrystallized from toluene to afford 1.29 g (90%) of pinacol **3** as colorless needles, mp 185–186 °C. The ^{1}H NMR and ^{13}C NMR spectra match those in the literature.[11]

3-Ethyl-9*H*-xanthen-9-one (5a). **5a** was prepared according to the Goldberg and Walker modification[12] of the Ullmann coupling reaction.[13] By starting with 4.00 g (25.5 mmol) of *o*-chlorobenzoic acid dissolved in 20 mL of nitrobenzene, the catalyst was prepared by mixing slowly 4.60 g (33.3 mmol) of potassium carbonate, 400 mg of copper,[14] and 400 mg of cuprous iodide at 80 °C. Then 3.15 g (25.8 mmol) of *p*-ethylphenol was added and the reaction mixture was stirred at 160 °C for 5 h. The solvent was removed under reduced pressure (ca. 20 °C, 18 Torr), and 50 mL of concentrated H_2SO_4 was added slowly. After 10 min of stirring at room temperature, 400 mL of distilled water was added, and the aqueous solution was extracted with methyl *tert*-butyl ether (3 × 100 mL). The organic phase was washed with 100 mL of aqueous (10%) Na_2CO_3 solution and with 100 mL of water. The organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure (ca. 20 °C, 18 Torr) to afford 1.28 g of a 1:1 mixture of the desired product **5a** and 1-ethyl-9*H*-xanthen-9-one. Regioisomer **5a** was isolated by column chromatography (14:1 pentane:ethyl acetate as the eluent, R_f = 0.19) to yield 608 mg (11%) of product **5a** as colorless oil: IR (CCl_4) 3050, 2940, 1640 (CO), 1600, 1590, 1450, 1415, 1320, 1310, 1135 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.32 (t, $J_{11,12}$ = 7.6 Hz, 3 H, 12-H), 2.80 (q, $J_{11,12}$ = 7.6 Hz, 2 H, 11-H), 7.21 (dd, $J_{1,2}$ = 8.2 Hz, $J_{2,4}$ = 1.5 Hz, 1 H, 2-H), 7.29 (d, $J_{2,4}$ = 1.5 Hz, 1 H, 4-H), 7.36 (ddd, $J_{7,8}$ = 8.0 Hz, $J_{6,7}$ = 7.2 Hz, $J_{5,7}$ = 0.9 Hz, 1 H, 7-H), 7.46 (dd, $J_{5,6}$ = 8.6 Hz, $J_{5,7}$ = 0.9 Hz, 1 H, 5-H), 7.70 (ddd, $J_{5,6}$ = 8.6 Hz, $J_{6,7}$ = 7.2 Hz, $J_{6,8}$ = 1.7 Hz, 1 H, 6-H), 8.24 (d, $J_{1,2}$ = 8.2 Hz, 1 H, 1-H), 8.34 (dd, $J_{7,8}$ = 8.0 Hz, $J_{6,8}$ = 1.7 Hz, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 63.4 MHz) δ 14.8 (q, C-12), 29.1 (t, C-11), 116.4 (d), 117.8 (d), 119.7 (s), 121.8 (s), 123.7 (d), 124.3 (d), 126.5 (d), 126.6 (d), 134.5 (d), 152.4 (s), 156.1 (s), 156.3 (s), 170.0 (s, C-9). Anal. Calcd for $C_{15}H_{12}O_2$ (224.3): C, 80.34; H, 5.39. Found: C, 80.65; H, 5.32.

3-(1-Bromoethyl)-9*H*-xanthen-9-one (5b). A solution of 330 mg (1.47 mmol) of **5a**, 260 mg (1.46 mmol) of *N*-bromosuccinimide, and catalytic amounts of dibenzoyl peroxide in 30 mL of CCl_4 was stirred for 7 h at 77 °C. The solid matter was removed by filtration and the solvent removed under reduced pressure (ca. 20 °C, 18 Torr). After recrystallization from methanol, 419 mg (94%) of product **5b** was obtained as colorless needles, mp 122–123 °C: IR (CCl_4) 3050, 2960, 1650 (CO), 1607, 1595, 1450, 1420, 1330, 1170, 1130, 670 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.10 (d, $J_{11,12}$ = 6.9 Hz, 3 H, 12-H), 5.25 (q, $J_{11,12}$ = 6.9 Hz, 1 H, 11-H), 7.39 (ddd, $J_{7,8}$ = 8.0, $J_{6,7}$ = 7.2 Hz, $J_{5,7}$ = 1.1 Hz, 1 H, 7-H), 7.45 (dd, $J_{1,2}$ = 8.3 Hz, $J_{2,4}$ = 1.7 Hz, 1 H, 2-H), 7.48 (dd, $J_{5,6}$ = 8.7 Hz, $J_{5,7}$ = 1.1 Hz, 1 H, 5-H), 7.56 (d, $J_{2,4}$ = 1.7 Hz, 1 H, 4-H), 7.73 (ddd, $J_{5,6}$ = 8.7 Hz, $J_{6,7}$ = 7.2 Hz, $J_{6,8}$ = 1.6 Hz, 1 H, 6-H), 8.31 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 8.33 (dd, $J_{7,8}$ = 8.0 Hz, $J_{6,8}$ = 1.6 Hz, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 63.4 MHz) δ = 26.4 (q, C-12), 47.2 (d, C-11), 116,1 (d), 117.9 (d), 121.5 (s), 121.9 (s), 122.8 (d), 124.1 (d), 126.7 (d), 127.4 (d), 134.9 (d), 150.3 (s), 156.1 (s), 156.2 (s), 176.6 (s, C-9). Anal. Calcd for $C_{15}H_{11}BrO_2$ (303.2): C, 59.43; H, 3.66. Found: C, 59.08; H, 3.77.

3-(1-(Acetyloxy)ethyl)-9*H*-xanthen-9-one (5c). To a solution of 211 mg (0.696 mmol) of **5b** in 5 mL of acetic acid was added 114 mg (0.683 mmol) of silver acetate, and the mixture was stirred for 2 h at 117 °C. The solid matter was removed by filtration and the solvent by distillation (ca. 20 °C, 18 Torr). The product was purified by column chromatography (9:1 pentane:ethyl acetate as the eluent, R_f = 0.19) to yield 189 mg of (96%) **5c** as colorless needles, mp 88–89 °C: IR (CCl_4) 3050, 2910, 1730 (CO), 1650 (CO), 1612, 1598, 1453, 1420, 1225, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.60 (d, $J_{11,12}$ = 6.7 Hz, 3 H, 12-H), 2.15 (s, 3 H, 14-H), 5.98 (qd, $J_{11,12}$ = 6.7 Hz, $J_{2,11}$ = 0.5 Hz, 1 H, 11-H), 7.36 (ddd, $J_{1,2}$ = 8.2 Hz, $J_{2,4}$ = 1.6 Hz, $J_{2,11}$ = 0.5 Hz, 1 H, 2-H), 7.40 (ddd, $J_{7,8}$ = 8.0 Hz, $J_{6,7}$ = 7.1 Hz, $J_{5,7}$ = 1.1 Hz, 1 H, 7-H), 7.49 (d, $J_{2,4}$ = 1.6 Hz, 1 H, 4-H), 7.50 (ddd, $J_{5,6}$ = 8.5 Hz, $J_{5,7}$ = 1.1 Hz, $J_{5,8}$ = 0.5 Hz, 1 H, 5-H), 7.75 (ddd, $J_{5,6}$ = 8.5 Hz, $J_{6,7}$ = 7.1 Hz, $J_{6,8}$ = 1.8 Hz, 1 H, 6-H), 8.33 (d, $J_{1,2}$ = 8.2 Hz, 1H, 1-H), 8.35 (ddd, $J_{7,8}$ = 8.0 Hz, $J_{6,8}$ = 1.8 Hz, $J_{5,8}$ = 0.5 Hz, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 21.3 (q, C-12 or C-14), 22.3 (q, C-12 or C-14), 71.5 (d, C-11), 115.1 (d), 117.9 (d), 121.2 (s), 121.6 (d), 121.9 (s), 124.0 (d), 126.7 (d), 127.2 (d), 134.9 (d), 149.4 (s), 156.2 (s), 156.2 (s), 170.2 (s, C-13), 176.9 (s, C-9). Anal. Calcd for $C_{17}H_{14}O_4$ (282.3): C, 72.33; H, 5.00. Found: C 72.16; H, 5.12.

3-(1-Hydroxyethyl)-9*H*-xanthen-9-one (5d). A solution of 164 mg (0.581 mmol) of **5c** and 40.0 mg (1.00 mmol) of NaOH in 25 mL of ethanol was stirred at 78 °C for 3 h. To the reaction mixture was added 75 mL of distilled water, and the aqueous phase was extracted with methyl *tert*-butyl ether (4 × 50 mL). The combined organic phases were dried over $MgSO_4$, and the solvent was removed under reduced pressure (ca. 20 °C, 18 Torr). The residue was submitted to column chromatography (3:1 pentane:ethyl acetate as the eluent, R_f = 0.10) to yield 113 mg (81%) of **5d** as colorless needles, mp 126–127 °C: IR (CCl_4) 3620–3550 (OH), 3050, 2900, 1645 (CO), 1608, 1593, 1450, 1415, 1330, 1138 cm^{-1}; UV (ethanol) λ_{max} (log ϵ) 263 nm (4.093), 286 (3.841), 291 (3.848), 335 (3.780); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.54 (d, $J_{11,12}$ = 6.5 Hz, 3 H, 12-H), 2.28 (b. s., 1 H, 11-OH), 5.01 (q, $J_{11,12}$ = 6.5 Hz, 1 H, 11-H), 7.31 (dd, $J_{1,2}$ = 8.3 Hz, $J_{2,4}$ = 1.4 Hz, 1 H, 2-H), 7.38 (ddd, $J_{7,8}$ = 8.0 Hz, $J_{6,7}$ = 7.1 Hz, $J_{5,7}$ = 1.0 Hz, 1 H, 7-H), 7.45 (dd, $J_{5,6}$ = 8.5, $J_{5,7}$ = 1.0 Hz, 1 H, 5-H), 7.46 (d, $J_{2,4}$ = 1.4 Hz, 1 H, 4-H), 7.72 (ddd, $J_{5,6}$ = 8.5 Hz, $J_{6,7}$ = 7.1 Hz, $J_{6,8}$ = 1.7 Hz, 1 H, 6-H), 8.22 (d, $J_{1,2}$ = 8.3 Hz, 1 H, 1-H), 8.32 (dd, $J_{7,8}$ = 8.0 Hz, $J_{6,8}$ = 1.7 Hz, 1 H, 8-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 25.3 (q, C-12), 69.7 (d, C-11), 114.3 (d), 117.9 (d), 120.8 (s), 121.3 (d), 121.8 (s), 123.9 (d), 126.7 (d), 126.9 (d), 134.8 (d), 153.8 (s), 156.2 (s), 156.3 (s), 177.1 (s, C-9). Anal. Calcd for $C_{15}H_{12}O_3$ (240.3): C, 74.99; H, 5.03. Found: C, 74.56; H, 5.18.

1-(1-Hydroxyethyl)-9*H*-xanthen-9-one (6). A solution of 118 mg (0.420 mmol) of 1-(1-(acetyloxy)ethyl)-9*H*-xanthen-9-one (prepared analogously to the regioisomer **5c**, cf. Scheme 1) and 30.3 mg (0.758 mmol) of NaOH in 5 mL of ethanol was stirred for 3 h at 78 °C, 15 mL of distilled water was added, and the aqueous phase was extracted with methyl *tert*-butyl ether (5 × 10 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure (ca. 20 °C, 18 Torr). The residue was submitted to column chromatography (19:1 methylene chloride:ethyl acetate as the eluent, R_f = 0.17) to afford 88.5 mg (88%) of **6** as colorless needles, mp 113–114 °C: IR (CCl_4) 3520–3260 (OH), 3050, 2960, 1630 (CO), 1603, 1585, 1460, 1423, 1340, 1102 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.66 (d, $J_{11,12}$ = 6.6 Hz, 3 H, 12-H), 5.25 (d, $J_{11,11\text{–}OH}$ = 7.2 Hz, 1 H, 11-OH), 5.52 (dq, $J_{11,11\text{–}OH}$ = 7.2 Hz, $J_{11,12}$ = 6.6 Hz, 1 H, 11-H), 7.41 (ddd, $J_{7,8}$ = 8.0 Hz, $J_{6,7}$ = 7.1 Hz, $J_{5,7}$ = 1.1 Hz, 1 H, 7-H), 7.48 (dd, $J_{3,4}$ = 8.7 Hz, $J_{2,4}$ = 2.0 Hz, 1 H, 4-H), 7.48 (dd, $J_{2,3}$ = 7.2 Hz, $J_{2,4}$ = 2.0 Hz, 1 H, 2-H), 7.51 (ddd, $J_{5,6}$ = 8.5 Hz, $J_{5,7}$ = 1.1 Hz, $J_{5,8}$ = 0.5 Hz, 1 H, 5-H), 7.71 (dd, $J_{3,4}$ = 8.7 Hz, $J_{2,3}$ = 7.2 Hz, 1 H, 3-H), 7.76 (ddd, $J_{5,6}$ = 8.5 Hz, $J_{6,7}$ = 7.1 Hz, $J_{6,8}$ = 1.7 Hz, 1 H , 6-H), 8.35 (ddd, $J_{7,8}$ = 8.0 Hz, $J_{6,8}$ = 1.7 Hz, $J_{5,8}$ = 0.5 Hz, 1H, 8-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 22.7 (q, C-12), 69.1 (d, C-11), 117.4 (d), 118.1 (d), 119.5 (s), 122.3 (s), 122.6 (d), 124.1 (d), 127.0 (d), 134.9 (d), 135.1(d), 148.0 (s), 155.2 (s), 158.2 (s), 179.6 (s, C-9). Anal. Calcd for $C_{15}H_{12}O_3$ (240.3): C, 74.99; H, 5.03. Found: C, 74.85; H, 5.40.

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