HETEROCYCLES, Vol. 60, No. 7, 2003, pp. 1615 - 1623
Received, 12th March, 2003, Accepted, 6th May, 2003, Published online, 12th May, 2003

PHOTOCHEMISTRY OF 2-INDOLYL ARYL ETHERS: AN UNEXPECTED REARRANGEMENT LEADING TO C-C BOND FORMATION

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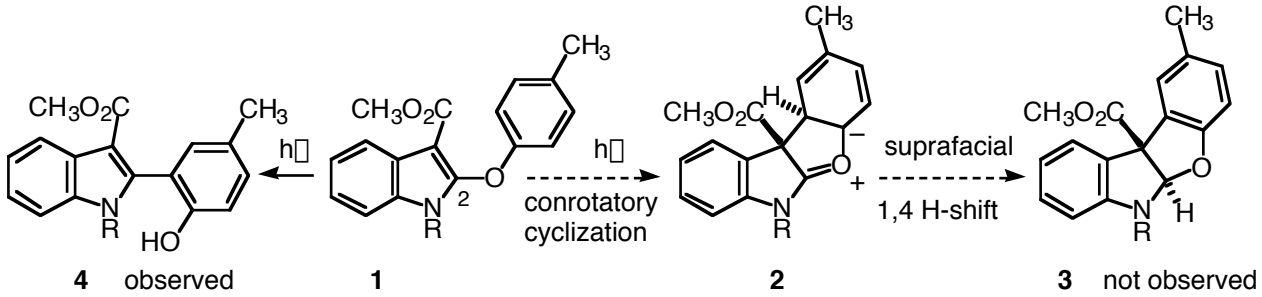
Abstract – Two types of 2-(*p*-tolyloxy)indole were prepared and their reactivity was studied under photochemical conditions. The expected electrocyclization was not observed. Instead, unprecedented rearrangement products were obtained. The reaction outcome was found to depend on the viscosity of the media.

Irradiation of aryl systems bearing pendant unsaturated functionality can lead to diverse modes of cyclization/rearrangement. In particular, six-electron systems containing a heteroatom are suitable substrates for photochemical promotion of electrocyclization, a process that leads to heterocycle formation in favorable cases.[1] For example, this type of reaction with diaryl or aryl vinyl ether substrates affords dihydrobenzofurans, a transformation of some value in the synthesis of cognate naturally occurring materials.[2]

The possibility that 2-indolyl aryl ethers (**1**) (Scheme 1) might participate in similar electrocyclizations prompted the investigations described below. Successful electrocyclization of this species might yield a tetracycle of the general type (**3**), a product that could further an ongoing project in natural products synthesis. Enthusiasm for the prospects for success in this transformation was tempered by the fact that (1) most high-yielding aryl vinyl ether electrocyclizations utilize substrates bearing an electron-stabilizing substituent at C(2) (cf. **1**), and (2) a highly strained trans bicyclo[3.3.0]octane skeleton (**3**) would result. Nevertheless, these points can only be settled by experiment, and so the photochemical reaction chemistry of **1** was explored. As it transpired, products of the type (**3**) were not observed. Rather, a completely different skeletal reorganization occurred, leading to 2-arylindole products (**4**) in a process reminiscent of

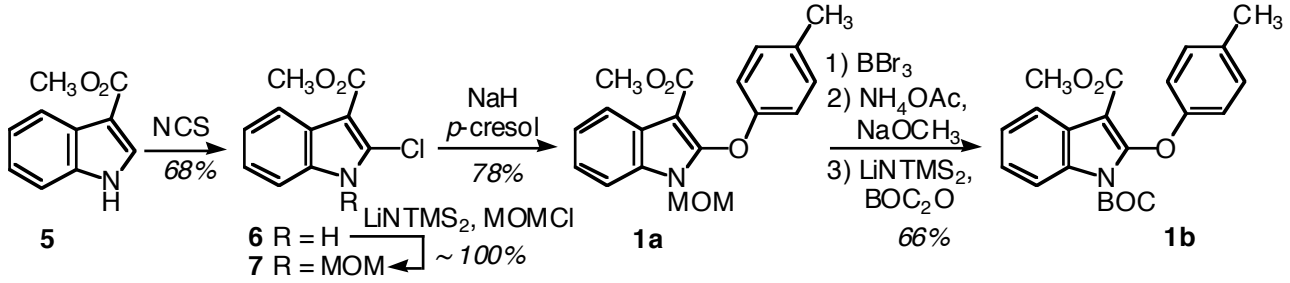
a formal photo-Fries rearrangement.[3] A description of this process, along with a discussion of the experimental evidence that addresses possible mechanistic pathways for the reaction, follows.



Scheme 1. Exploratory photochemistry of 2-indoyl aryl ethers.

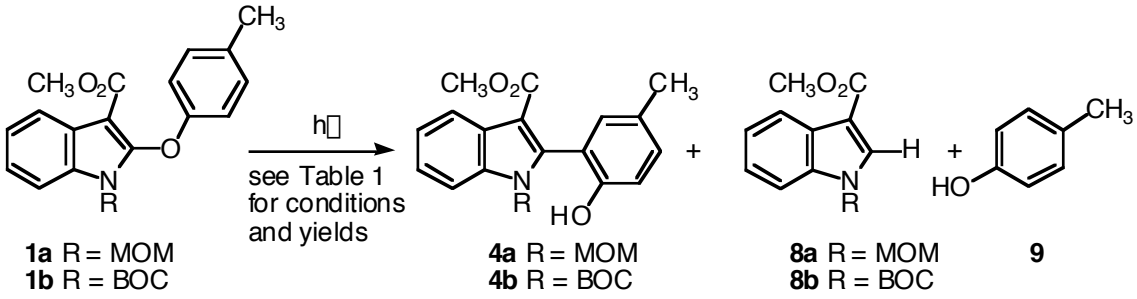
RESULTS AND DISCUSSION

The syntheses of ether substrates (**1a**) and (**1b**) are outlined in Scheme 2. Commercially available methyl indole-3-carboxylate (**5**) was chlorinated at C(2) at slightly elevated temperatures (45 – 50 ºC).[4] The chloro derivative (**6**) was protected at the indole nitrogen as its methoxymethyl ether (**7**). Substitution of the chloride with a *p*-tolyloxy group *via* an addition-elimination mechanism was accomplished under basic conditions at 85 - 90 ºC in *N,N*-dimethylacetamide, leading to the formation of **1a** in good yield.[5] Substrate (**1b**) was synthesized from **1a** *via* MOM group removal and reprotection of the indole nitrogen as its BOC derivative.



Scheme 2. Synthesis of substrates (**1a**) and (**1b**).

Diaryl ethers (**1a**) and (**1b**), independently, were irradiated at various wavelengths (254 and 300 nm), through different media (pyrex glass (300 nm irradiations) or quartz (254 nm irradiations)), at different concentrations (0.005 M – 0.5 M) and in different solvents (acetonitrile, methanol, benzene, acetone, 1,2-dichloroethane and cyclohexane). However, no set of reaction conditions led to any detectable levels of electrocyclization products of the type (**3**). Rather, a mixture of compounds (**4a**/**b**), (**8a**/**b**) and (**9**) was obtained in all cases, although in widely varying yields depending upon conditions (Scheme 3 and Table 1).



Scheme 3. Irradiation of 2-indole aryl ethers (**1a**) and (**1b**).

trial	substrate	solvent viscosity (mPa•s)	conc. M	wavelength (nm)	**4** (%)	**8** (%)	**9** (%)
1	**1a**	acetone-d_6 (0.306)	0.05	300	29	25	25
2	**1a**	acetonitrile-d_3 (0.369)	0.03	300	30	25	25
3	**1a**	methanol-d_4 (0.544)	0.05	300	20[a]	12	12
4	**1a**	benzene-d_6 (0.604)	0.06	300	37	8	8
5	**1a**	methanol-d_4	0.005	300	19	19	19
6	**1a**	acetonitrile-d_3	0.07	254	37	10	10
7	**1a**	$Cl(CH_2)_2Cl$	0.07	254	43	22	22
8	**1a**	cyclohexane-d_{12}	0.07	254	26	12	12
9	**1a**	CH_3OD	0.06	300	35[a]	18	18
10	**1b**	acetone-d_6	0.06	300	20	20	20
11	**1b**	acetonitrile-d_3	0.50	300	21	15	15
12	**1b**	methanol-d_4	0.05	300	23	7	7
13	**1b**	benzene-d_6	0.03	300	30	10	10

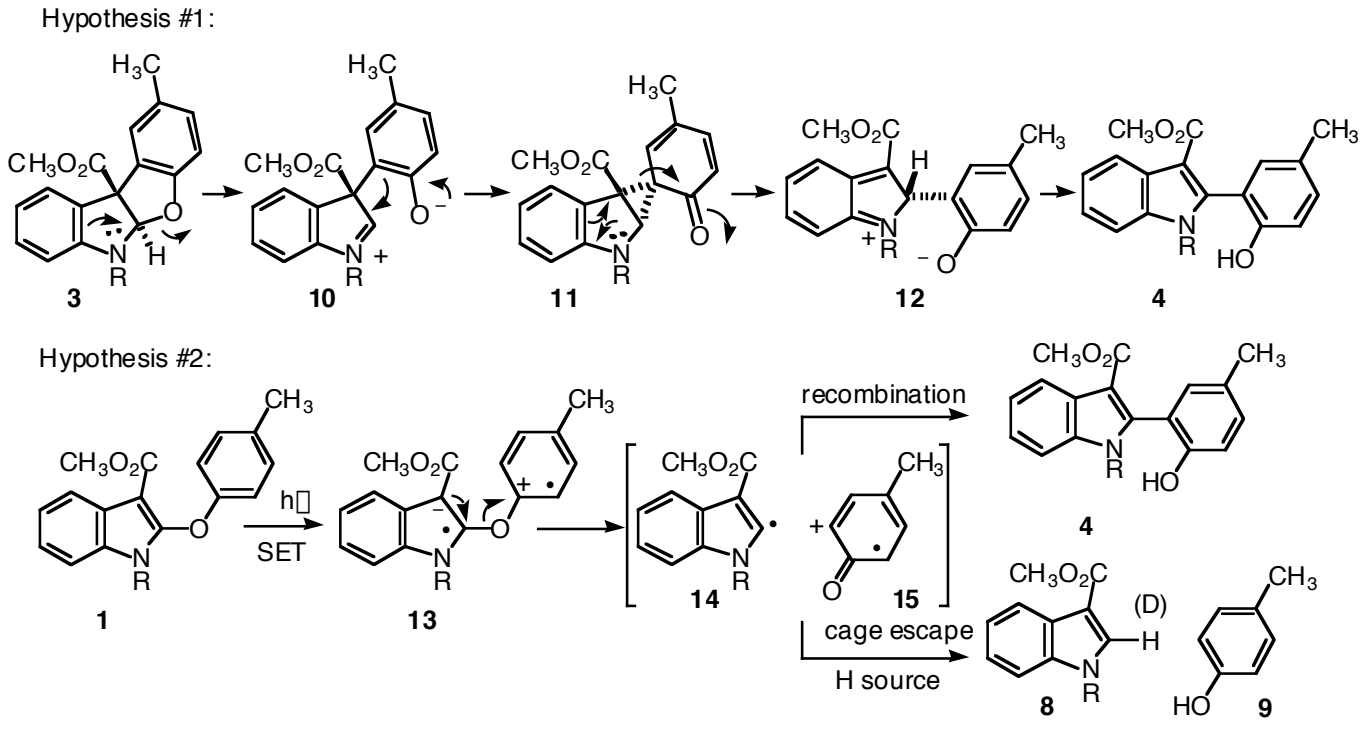
[a] mixture of **4a** and the corresponding lactone.

Table 1. Results of irradiation studies with diaryl ethers (**1a**) and (**1b**).

Several conclusions emerge from consideration of these data. First, the nature of the indole nitrogen protecting group (electron donating as in **1a** or electron withdrawing as in **1b**) does not have a large impact on the course of the reaction. Second, irradiation of substrate (**1a**) at the shorter wavelength led to modest improvements in yield of **4a** when compared to the 300 nm run (e.g., trial 2 vs. trial 6). Variations in the concentration of substrate (within the range explored) did not lead to dramatic changes in the product yields or ratios. The most noticeable change in product yield accompanied the solvent studies. There appears to be a correlation between solvent viscosity (trials 1-4) and the ratio of Ar-Ar bonded product (**4a**) to Ar-H reduction product (**8a**). A similar trend is observed with the N-BOC substrate (**1b**) (trials 10-13). For both of these substrates, as the solvent viscosity increases, the ratio of **4** to **8** increases as well. These results, taken together, suggest that there are evident limitations to

developing this C–O-to-C–C bond shift as a useful method for 2-arylindole synthesis. However, they do provide some insight into the possible mechanistic course of the transformation.

Two mechanistic hypotheses for the formation of **4** were considered (Scheme 4). One hypothesis (#1) invokes a pathway proceeding through the intermediacy of the desired benzofuran derivative (**3**) en route to **4**. In this scenario, the inherent strain of the trans bicyclo[3.3.0]octane framework induces a fragmentation/recyclization to furnish **11**, which then suffers retro-Mannich cleavage to deliver **4**. This mechanistic model does not directly address the formation of reduction products (**8**) and (**9**), but variable yields of **8**/**9** formation (cf. Table 1) raised the possibility that these species resulted from alternative competitive processes whose occurrence were condition dependent. A second mechanistic hypothesis (#2) explicitly acknowledges a route for **8**/**9** production within the context of a radical-based pathway to **4** from **1**. In this scheme, an initial light-induced single electron transfer reaction within **1** would provide a diradical species (**13**) susceptible to cleavage of the scissile C-O bond. The resulting diradical pair could partition in one of several ways. Recombination within the solvent cage might afford **4**, whereas cage escape might provide opportunities for radical reduction to provide **8** and **9**.



Scheme 4. Two mechanistic hypothesis for the rearrangement of **1** into **4**.

A series of experiments designed to probe this mechanistic dichotomy were conducted. Irradiation of **1a** in the presence of a cation trap (Et_3Si-H) might, in principle, divert some of the intermediate (**10**) if mechanism #1 was operational. However, the results of this experiment did not lend any support to a proposal that required cationic intermediates. More telling was the outcome of the series of experiments that used solvents of varying viscosities (Table 1).[6] The observed trend that higher solvent viscosity

scaled with greater yield of the internal trapping product (**4**) is consistent with a cage recombination/cage escape mechanism such as that described in hypothesis #2 of Scheme 4. Finally, the results of a set of deuterium labeling experiments provide further insight into this mechanistic puzzle. When CD_3OD was used as solvent, deuterium incorporation at C(2) in **8** was detected to the extent of 75% (by MS and ^1H NMR spectroscopy). However, when the reaction was run in CH_3OD, no deuterium incorporation was detected. These results are again completely consistent with a radical mediated mechanism featuring the radical pair (**14**)/(**15**) as the key branch point.

In summary, an unprecedented photochemical rearrangement of 2-(*p*-tolyloxy)indoles has been observed. The products are 2-(indol-2-yl)-4-methylphenol and methyl indol-3-carboxylate. The product distribution was dependent on the solvent viscosity. These results, in conjunction with deuterium labeling studies, support a mechanistic hypothesis that features SET-induced bond cleavage/recombination as the primary source of the 2-arylindole products.

ACKNOWLEDGMENTS

We thank the National Institutes of Health (GM 35727) for support of this work.

EXPERIMENTAL

THF was distilled from sodium/benzophenone under Ar immediately before use. CH_2Cl_2 and MeOH were dried by CaH_2 and Mg, respectively, and distilled under Ar immediately before use. Oxygen- and moisture-sensitive reactions were performed in flame-dried glassware under an Ar atmosphere. Flash chromatography[7] was carried out using 32 – 63 μm silica gel and the indicated solvent system. The chromatography solvents hexanes, Et_2O and CH_2Cl_2 were distilled from CaH_2, whereas benzene was used without further purification (EM Science). ESI-MS, APCI-MS and HRMS spectra were obtained from the Mass Spectroscopy Laboratory at The Pennsylvania State University. All melting points are uncorrected. Combustion analyses were performed by Midwest Microlab, Indianapolis, IN.

Methyl 2-Chloro-1*H*-indole-3-carboxylate (**6**).[8]

N-Chlorosuccinimide (1.15 g, 8.63 mmol) was added in one portion to a solution of 1*H*-indole-3-carboxylic acid methyl ester (**5**) (1.16 g, 6.64 mmol) in 40 mL of CCl_4 and 40 mL of THF. The mixture was heated to 45 °C for 10 h. After cooling to rt, the reaction solution was poured into saturated $NaHCO_3$ solution and extracted with Et_2O (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to give an off-white solid. Purification of this residue by flash column chromatography using 100% CH_2Cl_2 as eluent gave 0.94 g (68%) of indole (**6**) as transparent crystals, mp 183 °C (recrystallized from EtOAc/hexane). IR (CCl_4) 3462 (NH), 1710 (C=O) cm^{-1}. ^1H-NMR (360

MHz, CD_3COCD_3) δ: 11.86 (br s, 1H); 8.07 (m, 1H); 7.43 (dddd, *J*=7.1, 3.5, 1.5, 0.7 Hz, 1H); 7.23 (m, 2H); 3.90 (s, 3H). ^{13}C-NMR (90 MHz, CD_3COCD_3) δ: 164.5, 135.4, 130.8, 127.3, 124.1, 122.9, 121.9, 112.1, 104.5, 51.2. MS *m/z* (relative intensity) 210 (MH^+, 100). HRMS Calcd for $C_{10}H_8NO_2Cl$ 209.0244, found 209.0263. *Anal.* Calcd for $C_{10}H_8NO_2Cl$: C, 57.30; H, 3.85; N, 6.68; Cl, 16.91. Found: C, 57.18; H, 3.84; N, 6.54; Cl, 16.86.

Methyl 2-Chloro-1-methoxymethyl-1*H*-indole-3-carboxylate (**7**).

Lithium hexamethyldisilazide (1.0 M in THF, 1.17 mL, 1.17 mmol) was added slowly to a solution of **6** (245 mg, 1.17 mmol) in 12 mL of THF at 0 °C. The reaction solution was stirred at 0 °C for 30 min and then chloromethyl methyl ether (108 μL, 1.42 mmol) was added dropwise. The solution was allowed to warm to rt, stirred for 3 h, and then poured into 15 mL of H_2O. The aqueous layer was neutralized with 1 mL 1 M H_3PO_4 and extracted with Et_2O (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo to give an orange oil. Purification of the residue by flash column chromatography using 20% Et_2O in hexanes as eluent gave 293 mg (99%) of **7** as a white amorphous solid, mp 36 - 37 °C. IR (thin film) 1712 (C=O) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.13 (ddd, *J*=5.0, 2.6, 0.7 Hz, 1H); 7.47 (ddd, *J*=5.0, 2.6, 0.7 Hz, 1H); 7.30 (m, 2H); 5.60 (s, 2H); 3.97 (s, 3H); 3.31 (s, 3H). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 164.4, 135.5, 132.2, 125.9, 123.9, 123.1, 121.7, 110.3, 105.2, 74.2, 56.5, 51.4. MS *m/z* (relative intensity) 254 (MH^+, 100). HRMS Calcd for $C_{12}H_{12}NO_3Cl$ 253.0506, found 253.0521. *Anal.* Calcd for $C_{12}H_{12}NO_3Cl$: C, 56.81; H, 4.77; N, 5.52; Cl, 13.98. Found: C, 56.72; H, 4.59; N, 5.48; Cl, 14.09.

Methyl 1-Methoxymethyl-2-(4-methylphenoxy)-1*H*-indole-3-carboxylate (**1a**).

Dimethylacetamide (DMA) (2 mL) was added to sodium hydride (89 mg, 2.24mmol, 60% in oil) previously washed with 2 x 1 mL hexanes. After the suspension was stirred for 5 min, *p*-cresol (260 μL, 2.48 mmol) was added one portion. The mixture was stirred until no evolution of gas was observable. A solution of **7** (272.0 mg, 1.07mmol) in 10 mL of DMA was added dropwise at rt and the reaction was heated at 85 °C overnight. The solvent was removed in vacuo and the residual brown oil was partitioned between water and CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, concentrated, and the residue was purified by flash column chromatography, eluting with 20% Et_2O in hexanes. The pure product (**1a**) was recovered as a clear oil (272 mg, 78%) which solidified upon standing, mp 50 - 54 °C. IR (CCl_4) 1709 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, CD_3CN) δ: 8.10 (ddd, *J*=5.9, 1.8, 0.7 Hz, 1H); 7.54 (ddd, *J*=5.8, 1.7, 0.7 Hz, 1H); 7.31 (m, 2H); 7.13 (dd, *J*=8.8, 0.7 Hz, 2H); 6.87 (br d, *J*=8.7 Hz, 2H); 5.41 (s, 2H); 3.64 (s, 3H); 3.22 (s, 3H); 2.29 (s, 3H). ^{13}C-NMR (90 MHz, CD_3CN) δ: 164.4, 156.9, 151.6, 134.0, 133.0, 131.1, 126.0, 124.1, 123.7, 122.2, 116.2, 111.6, 95.0, 73.9, 56.9, 51.2, 20.6. MS *m/z*

(relative intensity) 326 (MH^+, 100). HRMS Calcd for $C_{19}H_{19}NO_4$ 325.1314, found 325.1299. *Anal.* Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 69.77; H, 5.93; N, 4.46.

Methyl 2-(4-Methylphenoxy)-1-*tert*-butyloxycarbonyl-1-*H*-indole-3-carboxylate (**1b**).

Boron tribromide (1.0 M in CH_2Cl_2, 2.85 mL, 2.85 mmol) was added dropwise to a –75 °C solution of **1a** (459 mg, 1.41 mmol) in 14.2 mL of CH_2Cl_2. The reaction mixture was stirred for 30 min, warmed to rt, and then poured into ice cold water. The two layers were separated, and the organic phase was dried over Na_2SO_4 and concentrated in vacuo. The recovered off-white solids were dissolved in 28.2 mL CH_2Cl_2 and NH_4OAc (446 mg, 578 mmol) was added in one portion. The mixture was stirred for 3 h and then the solvent was removed in vacuo. MeOH (28.2 mL) was added followed by NaOMe (541 mg, 10.0 mmol). The reaction mixture was stirred for 2 h and then poured into ice cold water. The aqueous layer was acidified with 1 M H_3PO_4 and extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$ and concentrated. Purification of the residue *via* flash column chromatography using 100% CH_2Cl_2 as eluent gave 321 mg (81%) of the free N-H indole as a white solid, mp 167 °C (recrystallized from Et_2O/hexane). IR (thin film) 3228 (NH), 1681 (C=O) cm^{-1}. ^{1}H-NMR (360 MHz, CD_3CN) δ: 9.72 (br s, 1H); 8.01 (dddd, *J*=8.2, 5.9, 2.7, 0.8 Hz, 1H); 7.30 (dddd, *J*=8.1, 5.9, 2.6, 0.7 Hz, 1H); 7.20 (m, 4H); 6.98 (dd, *J*=6.5, 2.1 Hz, 2H); 3.74 (s, 3H); 2.33 (s, 3H). ^{13}C-NMR (90 MHz, $CDCl_3$) δ: 164.6, 153.7, 152.4, 134.4, 130.5, 129.9, 125.9, 122.4, 122.2, 121.2, 117.7, 110.7, 92.0, 50.9, 20.7. MS *m/z* (relative intensity) 282 (MH^+, 100) 250 (M - CH_3O, 55). HRMS Calcd for $C_{17}H_{15}NO_3$ 281.1052, found 281.1074. *Anal.* Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.36; H, 5.41; N, 4.95.

Lithium hexamethyldisilazide (1.0 M in THF, 44 μL, 0.44 mmol) was added slowly to a 0 °C solution of the indole from above (124 mg, 0.44 mmol) in 4.5 mL of THF. The mixture was stirred for 30 min and then BOC_2O (100 mg, 0.46 mmol) was added in one portion. The reaction mixture was allowed to warm slowly to rt while stirred for 6 h. The solution was washed with water and the aqueous phase was further extracted with EtOAc. The combined organic layers were dried over Na_2SO_4, concentrated in vacuo, and the residue was purified by flash column chromatography using 10% Et_2O in hexanes as eluent. The product (**1b**) was recovered as a colorless oil (136 mg, 81%) which solidified upon standing, mp 64 °C. IR (thin film) 1743 (C=O), 1708 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.16 (m, 2H); 7.36 (m, 2H); 7.08 (dt, *J*=11.6, 2.9 Hz, 2H); 6.79 (dt, *J*=11.6, 3.0 Hz, 2H); 3.76 (s, 3H); 2.30 (s, 3H); 1.40 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 163.7, 156.3, 149.6, 148.5, 132.3, 131.9, 130.1, 125.0, 124.9, 124.3, 121.5, 115.0, 114.8, 99.6, 85.4, 51.5, 27.9, 20.9. MS *m/z* (relative intensity) 382 (MH^+, 30) 326 (MH^+ - iC_4H_8, 60) 294.1 (MH^+ - iC_4H_8 - CH_3OH, 5) 282.1 (MH^+ - iC_4H_8 - CO_2, 100) 250.0 (MH^+ - iC_4H_8 - CH_3OH - CO_2, 47). HRMS Calcd for $C_{22}H_{23}NO_5$ 381.1576, found 381.1590. *Anal.* Calcd for $C_{22}H_{23}NO_5$: C, 69.28; H, 6.08; N, 3.67. Found: C, 68.97; H, 6.30; N, 3.68.

General Procedure for Photochemistry.

In a typical procedure, the starting ether (**1a**) or (**1b**) was dissolved in the indicated solvent at the indicated concentration and transferred into either a pyrex or quartz NMR-tube. The solution was degassed either by three freeze-pump-thaw cycles or by bubbling Ar through for 30 min (both methods led to equivalent results). The sample was placed into a Rayonet photochemical reactor equipped with either 254-nm or 300-nm bulbs. The mixture was irradiated until no further conversion of the starting material was detected by ^{1}H-NMR monitoring. The reaction mixture was concentrated in vacuo and purified by preparative TLC eluting with the indicated solvent system.

Methyl 2-(2-Hydroxy-5-methyl-phenyl)-1-methoxymethyl-1*H*-indole-3-carboxylate (**4a**).

Following the general procedure and using the indicated solvent/concentration/wavelength, **1a** was converted to **4a**, **8a**, and **9**, which were separated by preparative TLC eluting with 10% Et_2O in benzene. Crystallization was induced by scratching the wall of the glass vessel containing the initially formed oil, and then cooling at 4 ºC overnight. Compound (**4a**) was isolated as transparent crystals, mp 217 °C. IR (CCl_4) 3551, 3258 (OH), 1709 (C=O), 1682 (C=O) cm^{-1}. ^{1}H-NMR (400 MHz, CD_3CN) □: 8.15 (m, 1H); 7.61 (m, 1H), 7.32 (m, 2H); 7.19 (ddd, *J*=8.3, 2.2, 0.5 Hz, 1H); 7.08 (dd, *J*=2.2, 0.5 Hz, 1H); 6.87 (d, *J*=8.3, 1H); 6.74 (br s, 1H); 5.39 (d, *J*=11.0 Hz, 1H); 5.19 (d, *J*=11.0 Hz, 1H); 3.71 (s, 3H); 3.05 (s, 3H); 2.29 (s, 3H). ^{13}C-NMR (90 MHz, CD_3CN) □: 166.2, 154.0, 144.3, 137.8, 133.4, 132.5, 129.9, 128.0, 124.2, 123.3, 122.6, 119.1, 117.0, 112.1, 108.0, 75.8, 56.5, 51.4, 20.5. MS *m/z* (relative intensity) 326 (MH^+, 15%) 294 (M - CH_3O, 100). HRMS Calcd for $C_{19}H_{19}NO_4$ 325.1314, found 325.1249.

Methyl 1-Methoxymethyl-1*H*-indole-3-carboxylate (**8a**).[9]

mp 58 - 60 °C (recrystallized from Et_2O/hexane). IR ($CHCl_3$) 1702 (C=O) cm^{-1}. ^{1}H-NMR (360 MHz, $CDCl_3$) □: 8.19 (ddd, *J*=4.4, 2.7, 0.7 Hz, 1H); 7.89 (s, 1H); 7.52 (ddd, *J*=4.5, 2.7, 0.7 Hz, 1H); 7.31 (m, 2H); 5.47 (s, 2H), 3.93 (s, 3H); 3.26 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) □: 165.5, 136.7, 134.5, 127.1, 123.6, 122.7, 122.0, 110.8, 108.5, 76.8, 56.4, 51.31. MS *m/z* (relative intensity) 220 (MH^+, 100). HRMS Calcd for $C_{12}H_{13}NO_3$ 219.0895, found 219.0911. *Anal.* Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.54; H, 6.00; N, 6.32.

Methyl 2-(2-Hydroxy-5-methyl-phenyl)-1-*tert*-butyloxycarbonyl-1-*H*-indole-3-carboxylate (**4b**).

Following the general procedure and using the indicated solvent/concentration/wavelength, **1b** was converted into **4b**, **8b**, and **9**, which were separated by preparative TLC eluting with 10% Et_2O in hexanes. Compound (**4b**) was isolated as colorless oil. IR (thin film) 1739 (C=O), 1720 (C=O) cm^{-1}. ^{1}H-

NMR (300 MHz, $CDCl_3$) □: 7.63 (d, *J*=7.6 Hz, 2H); 7.44 (dd, *J*=1.3, 0.6 Hz, 1H); 7.26 (dt, *J*=7.8, 1.4 Hz, 1H); 7.16 (br s, 1H); 7.04 (dt, *J*=7.6, 1.0 Hz, 1H); 6.98 (ddd, *J*=8.2, 2.0, 0.7 Hz, 1H); 6.76 (d, *J*=8.1 Hz, 1H); 3.85 (s, 3H); 2.32 (s, 3H); 1.66 (s, 9H). ^{13}C-NMR (90 MHz, $CDCl_3$) □: 169.9, 156.3, 152.4, 141.1, 131.2, 130.5, 129.6, 129.6, 126.6, 124.8, 124.6, 123.6, 115.5, 110.2, 110.0, 98.7, 82.3, 53.5, 28.6, 21.1. MS *m/z* (relative intensity) 382 (MH^+, 1) 326 (MH^+ - *i*C_4H_8, 15) 294 (MH^+ - *i*C_4H_8 - CH_3OH, 100) 282 (MH^+ - *i*C_4H_8 - CO_2, 90) 250 (MH^+ - *i*C_4H_8 - CH_3OH - CO_2, 95).

Methyl 1-*tert*-Butyloxycarbonyl-1-*H*-indole-3-carboxylate (**8b**). [9]

White crystals, mp 117 - 120 °C (recrystallized from hexane). IR (thin film) 1746 (C=O), 1716 (C=O) cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$) □: 8.27 (s, 1H); 8.17 (m, 2H); 7.36 (m, 2H); 3.94 (s, 3H); 1.69 (s, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) □: 164.83, 149.11, 135.72, 132.24, 127.67, 125.29, 124.11, 121.82, 115.34, 112.36, 85.21, 51.62, 28.26. MS *m/z* (relative intensity) 276 (MH^+, 10) 220 (MH^+ - *i*C_4H_8, 100) 176 (MH^+ - *i*C_4H_8 - CO_2, 35) 144 (MH^+ - *i*C_4H_8 - CO_2- CH_3OH, 15). *Anal.* Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.56; H, 6.32; N, 5.10.

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