Importance of Steric Effects in the Photochemical Ring Opening of Isochromenes

Richard E. Smith and Nigel G. J. Richards*

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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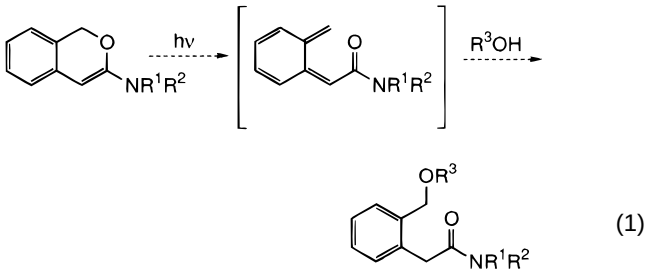
The use of time-resolved X-ray crystallography[1,2] is limited by the availability of suitably "caged" substrates that can be employed to initiate simultaneous reaction in a sufficient number of complexes in the crystal.[3] Compounds which can be transformed into appropriate substrates by photochemical activation, usually termed photosubstrates, have been successfully used to observe enzyme−substrate complexes.[4] The detailed characterization of the photochemical and photophysical behavior of heterocycles[5] represents an intriguing approach to developing novel photocaged enzyme substrates. We recently proposed that photoinitiated ring opening of 3-aminoisochromenes might allow generation of an amide bond within the active site of an aspartic proteinase, via solvent trapping of the reactive ring-opened intermediate (eq 1).



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The photochemical ring opening of substituted isochromenes has been previously investigated using experimental[6] and theoretical methods.[7] Thus, broadband irradiation of 3-phenylisochromenes **1**−**3** (Figure 1) was

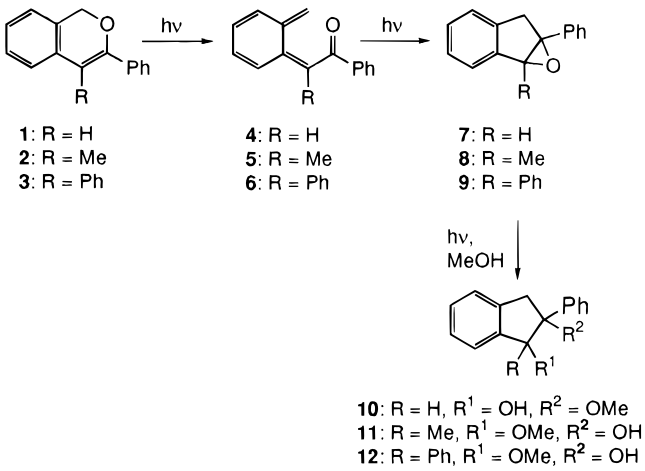
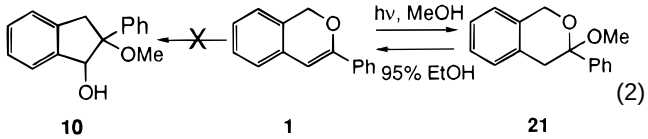


Figure 1. Results of previous broadband irradiation studies on 3-phenylisochromene (**1**) and 4-substituted derivatives **2** and **3**. Structures **4**−**7** are proposed intermediates. Epoxides **8** and **9** were identified using direct methods.

reported to give products **10**−**12**, in what was postulated to be a two-photon process.[6a] Absorption of the first photon was presumed to yield ring-opened intermediates **4**−**6** which subsequently underwent an intramolecular [4 + 2] cycloaddition after activation by a second photon. Surprisingly, while intermediate epoxides **8** and **9** were observed and characterized, no direct evidence for the intermediacy of **7** could be obtained in these experiments.[6a]

We now report, contrary to previous studies, that we do not obtain indan **10** when 3-phenylisochromene (**1**) is irradiated with either monochromatic or broadband radiation in dry methanol. Instead, the reaction consistently yields **21** through photochemically induced solvent addition to the C3−C4 double bond (eq 2). Our observations explain the failure to isolate **7** and may suggest some role for excited state steric interactions in controlling photoinduced isochromene ring-opening.



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Results

The synthesis of isochromenes is well documented,[8] and 3-phenylisochromene **1** was efficiently prepared in three steps from dibromide **13** in 42% overall yield (Figure 2A).[9a] After quantitative formation of salt **14**, treatment with sodium benzoate gave **15** which yielded **1** via an intramolecular Wittig reaction. This route was easily extended to give analogs **18** and **19** (Figure 2A). Monochromatic irradiation of **1** at 325 nm, in deoxygenated methanol, using a helium−cadmium CW laser, gave acetal **21** as the only product. The photochemical reaction exhibited zero-order kinetics, becoming first order

* Address correspondence to this author at Department of Chemistry, P.O. Box 117200, University of Florida, Gainesville, FL 32611-7200. Phone: (352) 392-3601. Fax: (352) 846-2095. e-mail: richards@qtp.ufl.edu.

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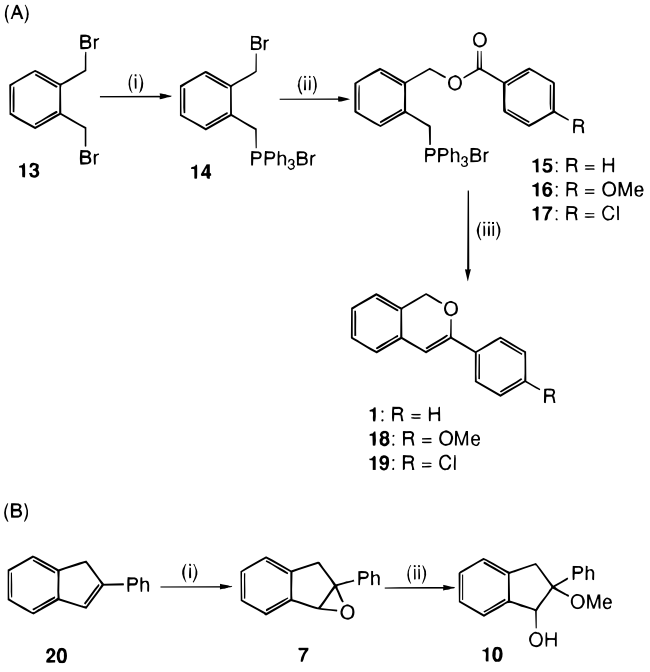


Figure 2. (A) Preparation of isochromenes **1**, **18**, and **19**. (i) PPh_3, toluene; (ii) RCO_2Na, acetone/H_2O, rt; iii) $CH_3CH_2C(ONa)(CH_3)CH_3$, toluene. (B) Synthesis of authentic **10**. (i) *m*-CPBA, CH_2Cl_2, rt; (ii) MeOH, TsOH.

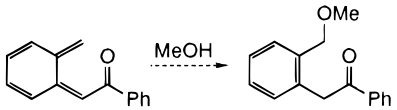
when **1** was present at concentrations less than 65 μM.[10] Since previous studies had reported that broadband irradiation of **1** gave the phenylindan derivative **10**, we confirmed that **21** was also obtained as the only product from **1** under these conditions. Finally, an authentic sample of **10** was prepared following literature procedures (Figure 2B),[6a,12] although the spectroscopic properties of the material synthesized in our laboratory were different from those reported for the product obtained in the previous photochemical studies of **1**.[6a]

Having established that irradiation of **1** under our conditions did not proceed as originally reported, we next examined the mechanism of formation of **21**. After ensuring that **21** was not obtained in the absence of light, we determined the primary quantum yield for photoinduced acetal formation from **1** to be 6.9×10^{-3} molecules/quantum, in reasonable agreement with that reported previously.[6a,11] Quantum yields for the phenyl-substituted analogs **18** and **19** were 7.5×10^{-3} and 2.9×10^{-3} molecules/quantum, respectively. For the photoaddition of methanol to an arylisochromene, the kinetic expression for the primary quantum yield Φ, under conditions of saturating arylisochromene and MeOH, can be written as $\Phi = \alpha k'/(k'+k_2)$ where $k' = k_1$[arylisochromene][MeOH] and is therefore the zero-order rate constant, k_2 is the net rate constant describing all other pathways by which the excited state can relax, and α is a proportionality constant. Rearranging gives $\alpha k'/k_2 = \Phi/(1-\Phi)$. In our experiments, the primary quantum yields for all compounds were significantly smaller than unity, and given the structural similarity of **1**, **18**, and **19**, it is likely that k_2 and α are approximately equal for all three arylisochromenes. Thus Φ was taken as approximating the rate of solvent addition to the excited state. Plotting $\log_{10}(\Phi/\Phi_H)$ against the Hammett σ values of the substituents on the phenyl ring gave a line of slope $\rho = -1.2 \pm 0.33$, consistent with the involvement of a carbocation intermediate in solvent addition.[11]

In our last set of experiments, we irradiated **1** in dry, degassed methanol containing various concentrations of benzophenone using monochromatic light. A plot of $\Phi°/\Phi$ against the concentration of benzophenone yielded a straight line of zero slope (data not shown), where $\Phi°$ and Φ are the primary quantum yields for the formation of **21** in the presence, and absence, of benzophenone, respectively. In light of this result and our computational studies on the excited states of **1** after excitation at 325 nm,[7] the photochemical reaction probably proceeds from the singlet state.[11]

Discussion

Irradiation of **1** with monochromatic light at 325 nm, the absorption maximum most likely to yield the ring-opened product after electronic excitation,[6,7a] was anticipated to give **22** after solvent addition to **4** to restore the aromatic π-system (eq 3).



4 22 (3)

Calculations had also shown that the ring-opened intermediate **4** does not possess an appropriate absorption band at this wavelength,[7a] making the occurrence of multiple photon reaction pathways, as reported for broadband irradiation, unlikely. The formation of **21** in our irradiation experiments was therefore unanticipated given the previous work on the photochemistry of isochromenes **1**−**3**.[6a] In order to rule out the possibility that we were forming, but failing to isolate, **10** in our experiments, we prepared an authentic sample starting from 2-phenylindene using literature procedures.[6a,12] Comparison of the spectroscopic properties of **10** prepared in our laboratory, however, with those reported in the original broadband irradiation studies revealed a number of differences. First, a broad absorbance centered at 3325 cm^{-1} in the IR spectrum of authentic **10**, presumably associated with the hydroxyl group, was not reported for the photoproduct formed by broadband irradiation of **1** in the original study.[13] The IR data for the photoproduct obtained in the original work are strikingly similar to that observed for **1** (see Experimental Section). We have observed that addition of 95% EtOH (a recrystallization solvent in the earlier study) to **21** precipitates **1** as a white solid. Second, in the original characterization of the putative photoproduct, the resonance arising from the C1 protons was assigned a chemical shift of δ 4.93.[6a] In contrast, the cognate protons in **11** were reported to possess a chemical shift of δ 3.38,[6a] which is a striking difference given the structural similarity of **10** and **11**. Examination of the ^{1}H-NMR spectrum of authentic **10**, however, shows that a resonance at δ 3.58 can be

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(13) In the original experiments,[6a] the IR data for the compound produced on broadband irradiation of **1** was reported as IR (KBr) ν 1618, 1492, 1451, 1389, 1264, 1208, 1063 cm^{-1}.

assigned to the C1 protons, in agreement with the assignments previously reported for **11** and **12**.[6a,14] Furthermore, on addition of D_2O, the resonance at δ 1.53 was lost due to exchange of the hydroxyl proton and the δ 3.38 doublet collapsed to a singlet indicating that the hydroxyl group was attached to C-3 in **10**. These observations are further support for the proposal that the structure of the photoproduct originally obtained from broadband irradiation of **1** should be reassigned to that of **21**. On the other hand, the authors of the original study reported that mixing their photoproduct with an authentic sample of **10** (prepared by the independent route employed in our studies) did not depress the melting point. In light of the differences in spectroscopic data reported here, it is possible that the workup and purification conditions used in the original study might have transformed **21**, the actual photoproduct, and authentic **10** into a third compound via acid-catalyzed rearrangement. The validity of such a hypothesis remains to be investigated.

There is no doubt that compounds **2** and **3** undergo photoconversion to **11** and **12**, respectively, via the postulated ring-opening pathway (Figure 1). For example, epoxides **8** and **9** have been isolated and demonstrated to give **11** and **12**, respectively, upon further broadband irradiation in methanol.[6a] We note, however, that the intermediacy of epoxide **7** was only inferred in previous irradiation experiments involving 3-phenylisochromene (**1**) on the basis of the photoproduct identification.

In further experiments, we obtained an approximate linear free energy relationship for the addition of methanol to **1**, under conditions of monochromatic irradiation, using a series of analogs of **1**.[15] While the number of derivatives possessing absorption maxima close to 325 nm was limited, the ρ-value obtained from our experiments was consistent with the intermediacy of a transition state possessing cationic character. This raised the possibility that acetal **21** was being produced by acid-catalyzed solvent addition due to the photochemical oxidation of methanol.[16] We determined, however, that 3-phenylisochromene (**1**) is recovered unchanged after being stirred at room temperature for up to 18 h in 0.2 M HCO_2H/MeOH. It is therefore likely that **21** is formed by photochemical addition of methanol to the C3−C4 double bond of **1**[17] and that the reaction does not involve ring-opened compound **4** as an intermediate. While it is possible that addition of methanol to the carbonyl group of **4** followed by 6-endo-trig ring closure could yield **21**, the second step corresponds to a disfavored cyclization.[18] In addition, we have been unable to detect the formation of adduct **22** under our standard reaction conditions.

Photochemical excitation of cyclic olefins, at least for cyclohexenes[19a,b] and larger ring systems,[17] gives products from the singlet excited state via double-bond isomerization. In protic solvents, protonation of this highly strained species gives a carbocation which can then react with the solvent. It is clear from our experiments that the formation of **21** proceeds via such a mechanism, raising questions concerning the molecular reasons underlying our observation that the photochemical reaction of **1** differs from that of **2** and **3**. In our computational investigations of the ring opening of isochromenes **1**−**3**,[7a] we determined that the absorption at 323 nm corresponds to a $\pi-\pi^*$ transition principally associated with the C3−C4 bond. As a result, there is a localized distortion of the molecular geometry in the excited state, analogous to that observed for ethylene upon $\pi-\pi^*$ electronic excitation. Our calculations also indicate that the cyclic system must become substantially distorted before the σ^* antibonding MO associated with the C1−O2 bond becomes the dominant contribution in the S_1 excited state.[7a] Given the fusion of the cyclohexene and benzene rings, however, molecular distortion is likely to be difficult, consistent with the low quantum yield for the conversion of **1** into **21**, unless steric interactions between substituents, other than hydrogen, at C3 and C4 can be relieved by the twisting motion. Hence, in **1**, as the C4 substituent is a hydrogen, it is possible that the amount of C3−C4 double-bond twisting might be lower compared to that in the excited states of **2** and **3**. With the ring-opening pathway disfavored, the excited state would then return to the ground state by the usual mechanisms or undergo subsequent reaction with methanol. Alternatively, the additional sp^2 centers in **1** might prevent cis−trans isomerization and give rise to a zwitterionic intermediate via electronic polarization,[20] unless steric interactions between the C3 and C4 substituents, other than hydrogen, could be relieved. Trapping of the carbocation formed by protonation of the zwitterion would then yield **21**. While this pathway is less plausible, the effect of fused aromatic rings on the isomerization of cyclohexenes does not appear to have been investigated by direct spectroscopic measurement. In any case, such models suggest that the steric interactions between the C3 and C4 substituents are an important factor in modulating the photoinitated ring opening of 3-arylisochromenes. The general applicability of this observation to a number of related heterocyclic compounds is under investigation.

Experimental Section

Melting points were recorded using a Fisher−Johns melting point apparatus and are uncorrected. Chemical shifts are reported in ppm (δ) downfield of tetramethylsilane as an internal reference (δ 0.0). Splitting patterns are abbreviated as follows: s, singlet, d, doublet, t, triplet, q, quartet, and, m, multiplet. Combustion analyses for C, H, and N were determined in the Microanalysis Facility in the Department of Chemistry, University of Florida. Ammonia or isobutane was used in the CI measurements. Analytical thin layer chromatography (TLC)

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was performed on silica gel 60F-245 plates, unless otherwise stated. Flash chromatography was performed by standard methods[21] on Davisil grade 633 type 60A silica gel (200−425 mesh). Laser (monochromatic) irradiation experiments were performed using a Liconix He/Cd CW laser at 325 nm, nominally rated at 10 mW. Laser power determinations employed a Phir Model 10A thermopile power meter. A 450 W Hanovia mercury-vapor arc lamp, fitted with a Pyrex water-cooling jacket, was used in all broadband irradiation experiments. Diethyl ether was distilled from sodium metal/benzophenone ketyl. Toluene and CH_2Cl_2 were distilled from CaH_2 before use while MeOH was purified by distillation from magnesium. *m*-Chloroperbenzoic acid (*m*-CPBA) was purified by being washed with $NaHCO_3$ before being dried *in vacuo*. All other compounds were purchased from Aldrich and used without further purification. Reactions requiring anhydrous conditions were performed under a positive pressure of N_2.

General Procedure for the Preparation of 3-Arylisochromenes. Solutions of the appropriate carboxylate salts (1 equiv) in either water or 1:1 aqueous acetone were added to a slurry of the known triphenylphosphonium salt **14** (1 equiv) (prepared by reaction of triphenylphosphine and dibromide **13**)[9] and stirred at rt for 8−12 h. After removal of acetone *in vacuo*, an equal volume of water was added and the resulting solution was extracted with CH_2Cl_2. The organic extracts were then dried (Na_2SO_4), and removal of the solvent under reduced pressure gave the esters **15**−**17** in isolated yields of greater than 94%. Conversion of these esters into the corresponding isochromenes was accomplished by the dropwise addition of 1 equiv of sodium amylate (0.11 M solution in anhydrous toluene) to a stirred slurry of the appropriate ester in boiling toluene (0.1 M concentration). After being refluxed for a further 4−8 h, the solution was allowed to cool and the solvent was removed under reduced pressure to give a solid residue that was washed with 95% aqueous EtOH. Purification was then effected by recrystalization.

3-Phenylisochromene (1). Sodium benzoate (1.59 g, 11 mmol) was reacted with triphenylphosphonium salt **14** (5.25 g, 10 mmol), according to the general procedure, to give ester **15** (5.56 g, 98%) of sufficient purity for use in the subsequent cyclization reaction. Treatment of **15** (1.42 g, 2.5 mmol) with sodium amylate in toluene and subsequent workup gave a solid residue. Recrystallization from aqueous EtOH produced isochromene **1** as a white solid: 226 mg, 41%; mp 122−124 °C [lit.[6a] mp 122−124 °C]; IR (KBr) ν 1618, 1489, 1451, 1388, 1275, 1264, 1203, 1075, 1063 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 5.23 (2 H, s), 6.46 (1 H, s), 7.00−7.75 (9 H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 69.0 (t), 101.1 (d), 123.4 (d), 123.7 (d), 125.0 (d), 126.4 (d), 128.0 (s), 128.2 (d), 128.3 (d), 128.8 (d), 132.0 (s), 134.3 (s), 154.1 (s); UV (MeOH) λ (ϵ) 323 (15 600), 235 nm (15 200); MS (FAB/NBA) *m*/*e* (relative intensity) 208 (M^+, 100), 136 (68), 91 (48); exact mass calcd for M^+ $C_{15}H_{12}O$ requires 208.0994, found 208.0888 (FAB/NBA).

3-(4′-Methoxyphenyl)isochromene (18). Sodium *p*-methoxybenzoate (2.61 g, 15 mmol) was reacted with triphenylphosphonium salt **14** (7.88 g, 15 mmol), according to the general procedure, to give ester **16** (8.6 g, 96%) of sufficient purity for use in the subsequent cyclization reaction. Treatment of **16** (2.99 g, 5 mmol) with sodium amylate in toluene and subsequent workup gave a solid residue. Recrystallization from aqueous EtOH yielded isochromene **18** as white plates: 480 mg, 38%; mp 126−128 °C; IR (KBr) ν 1602, 1502, 1443, 1249, 1172, 1114, 1055, 1026 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 3.83 (3 H, s), 5.20 (2 H, s), 6.43 (1 H, s), 6.85−7.28 (8 H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 55.3 (q), 69.0 (t), 99.5 (d), 113.8 (d), 123.1 (d), 123.7 (d), 126.0 (d), 126.6 (d), 127.0 (s), 127.8 (d), 128.1 (d), 132.3 (s), 154.1 (s), 160.3 (s); UV (MeOH) λ (ϵ) 330 (22 300), 240 nm (14 600); MS (FAB/TD) *m*/*e* (relative intensity) 239 (MH^+, 32), 238 (M^+, 100), 237 (15), 209 (8), 135 (15), 105 (10), 91 (8); exact mass calcd for M^+ $C_{16}H_{14}O_2$ requires 238.0994, found 238.0974 (FAB/TD).

3-(4′-Chlorophenyl)isochromene (19). Sodium *p*-chlorobenzoate (3.57 g, 20 mmol) was reacted with triphenylphosphonium salt **14** (10.53 g, 20 mmol), according to the general procedure, to give ester **17** (11.42 g, 95%) of sufficient purity for use in the subsequent cyclization reaction. Treatment of **17** (6.02 g, 10 mmol) with sodium amylate in toluene and subsequent workup gave a solid residue. Recrystallization from aqueous EtOH yielded isochromene **19** as white plates: 816 mg, 32%; mp 109−110 °C; IR (KBr) ν 1614, 1484, 1449, 1402, 1273, 1091, 1055, 1002 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 5.20 (2 H, s), 6.43 (1 H, s), 7.00−7.40 (8 H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 69.0 (t), 101.5 (d), 123.6 (d), 123.8 (d), 126.3 (d), 126.7 (d), 128.0 (d), 128.3 (d), 128.5 (d), 131.7 (s), 132.8 (s), 134.6 (s), 152.9 (s); UV (MeOH) λ (ϵ) 328 (18 300), 240 nm (17 100); MS (FAB/TD) *m*/*e* (relative intensity) 244 ($(M + 2)^+$, 29), 242 (M^+, 94), 155 (22), 89 (15); exact mass calcd for M^+ $C_{15}H_{11}ClO$ requires 242.0498, found 242.0473 (FAB/TD). Anal. Calcd for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57. Found: C, 74.62; H, 4.81.

3-Hydroxy-2-methoxy-2-phenylindan (10). A solution of phenylindene **20** (300 mg, 1.56 mmol)[12] and freshly purified *m*-CPBA (673 mg, 3.90 mmol) in CH_2Cl_2 (20 mL) was stirred at rt for 14 h. The reaction mixture was then washed sequentially with 10% aqueous $NaHCO_3$ (20 mL) and water (20 mL) before the organic phase was dried ($MgSO_4$). Removal of the solvent under reduced pressure yielded 2,3-epoxyphenylindan (**7**) as a colorless oil: 242 mg, 74%; ^1H NMR ($CDCl_3$, 300 MHz) 3.41 (1 H, d, J = 18.0 Hz), 3.57 (1 H, d, J = 18.0 Hz), 4.33 (1 H, s), 7.20−7.70 (9 H, m). The epoxide **7** (233 mg, 1.12 mmol) was then dissolved in MeOH (5 mL) together with TsOH (4 mg, 0.02 mmol) and the solution stirred at rt for 1 h. After removal of the solvent under reduced pressure, flash chromatography (alumina; eluant 50% EtOAc/petroleum ether; R_f = 0.8) yielded **10** as a pale yellow oil: 113 mg, 42%; IR ($CHCl_3$) ν 3330, 1518, 1496, 1407, 1248, 1233, 1202, 1170, 1028 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) 1.53 (1 H, exchangeable d, J = 8.0 Hz), 3.10 (3 H, s), 3.33 (1 H, d, J = 16.0 Hz), 3.58 (1 H, d, J = 16.0 Hz), 5.19 (1 H, d, J = 8.0 Hz), 7.10−7.60 (9 H, m); MS (FAB/NBA) *m*/*e* (relative intensity) 240 (M^+, 5), 239 (M^+ − H, 9), 223 (M^+ − OH), 184 (24), 137 (100); exact mass calcd for M^+ − OH $C_{16}H_{15}O$ requires 223.1123, found 223.1229 (FAB/NBA).

Broadband Irradiation of 3-Phenylisochromene (1). A solution of **1** (25 mg, 0.12 mmol) in anhydrous MeOH (75 mL), purged with dry N_2, was irradiated at rt in a sealed Pyrex flask for 22 h, using a mercury-vapor arc lamp fitted with a Pyrex water-cooling jacket. Removal of the solvent under reduced pressure gave 3-methoxy-3-phenylbenzo-2*H*-pyran (**21**) as a yellow oil: 28 mg, 97%; IR ($CHCl_3$) ν 1151, 1105, 1047 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.01 (1 H, d, J = 17.5 Hz), 3.11 (3 H, s), 3.16 (1 H, d, J = 17.5 Hz), 4.94 (1 H, d, J = 19.0 Hz), 4.97 (1 H, d, J = 19.0 Hz), 7.03−7.75 (9 H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 40.8 (t), 49.6 (q), 62.8 (t), 99.6 (s), 124.1 (d), 125.6 (d), 126.0 (d), 127.1 (d), 127.3 (d), 127.5 (d), 131.9 (d), 134.0 (s), 135.8 (s), 141.8 (s); MS (FAB MAGIC/TFA) *m*/*e* (relative intensity) 279 (MK^+, 47), 223 (12), 103 (67), 85 (100); exact mass calcd for M^+ $C_{16}H_{16}O_2K$ requires 279.0787, found 279.0915 (FAB MAGIC/TFA).

Monochromatic Irradiation of 3-Phenylisochromene (1). A solution of **1** (4.3 mg, 21 μmol) in dry MeOH (3 mL), purged thoroughly with dry N_2, was irradiated using a laser source at 325 nm for 86 h in a sealed quartz cell. Removal of the solvent under reduced pressure yielded a 3:2 mixture of starting material **1** and the acetal **21**, upon ^1H NMR analysis. No other compounds were evident in the NMR spectrum of the crude reaction products or by TLC analysis.

Primary Quantum Yield Determinations. Primary quantum yields for the conversion of **1**, **18**, and **19** into their respective methanol adducts were obtained by monitoring the decrease in their associated UV absorption spectra at 325, 330, and 328 nm, respectively. Samples containing a single isochromene (3 mL aliquots) were subject to monochromatic irradiation at 325 nm, and the absorbance was measured at 10 min intervals. The photon dose rate I (nmol photons/s) was calculated from

$$I = (\lambda/hcf_m A)\mathrm{R} = 1.135R$$

where h is Planck's constant, λ is the wavelength of the photons, c is the velocity of light, A is Avogadro's constant, f_m is the power meter calibration factor (W mV^{-1}), and R is the mean of ten power meter determinations (mV). Primary quantum yields (Φ) were obtained from the linear portion of the plot describing the decrease in concentration of isochromene *versus* photon dose.[10]

(21) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923−2925.

Separate experiments to determine the effects of varying concentrations of benzophenone upon the primary quantum yields for the conversion of **1** to **21** were carried out in dry, N_2-purged MeOH. Thus, the concentration of benzophenone was varied from 0.15 to 1.5 mM, while that of **1** was fixed at 0.15 mM. A linear calibration curve, constructed using a 1.5 mM solution of benzophenone in MeOH, was employed to correct the number of photons absorbed by **1** in solutions containing benzophenone, as the latter compound has a small absorbance, relative to that of **1** at the irradiation wavelength.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **1**, **18**, **19**, **20**, and **21** and ^{1}H spectra for **10** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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