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Reaction Control

Product Selection through Photon Flux: Laser-Specific Lactone Synthesis[**]

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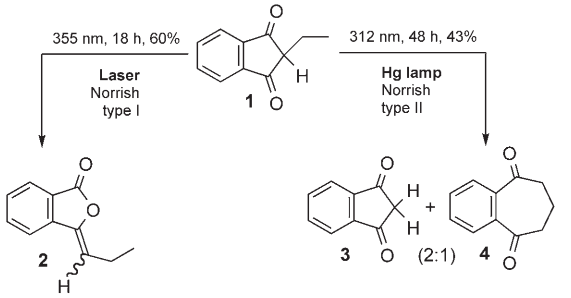
In ground-state chemistry, such as metal-catalyzed processes, exquisite levels of reaction control can often be achieved by subtle changes to the catalyst or reaction conditions. In photochemistry the situation is much more complex, as fates of excited states are governed by competing pathways for reaction, coupling to other electronic states, possible further photoexcitation, and relaxation to the ground state; thus, the outcomes of such processes are difficult to control once initiated. Some useful selectivity through singlet or triplet states can be achieved by a number of means, including use of triplet quenchers or sensitizers,[1–3] irradiation at user-selected wavelengths,[4] through higher exited states from multiphoton absorption,[5,6] and feedback-based optical control using evolutionary algorithms and pulse shapers.[7]

Herein, we describe how photon flux[8] can be used to switch cleanly between Norrish type I and type II pathways[1,5,6f–l,9] in the photochemical rearrangement of 1,3-indandiones.[10] In particular, the study demonstrates that photon flux, not average power or wavelength, is the controlling factor in product selection.

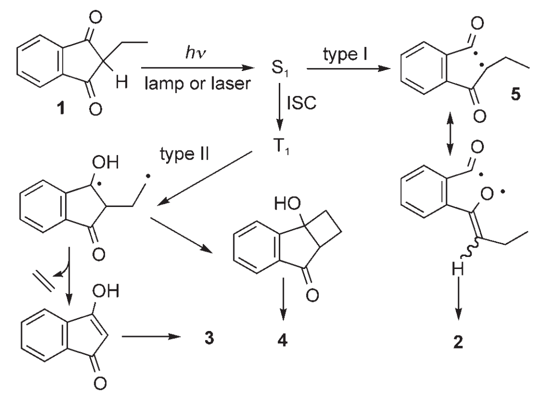
As part of an ongoing study of the [5+2] photocycloaddition of maleimides,[11,12] we investigated the photochemistry of 2-ethyl-1,3-indandione **1** (Scheme 1). Unfocused[13] Nd:YAG laser irradiation of **1** at 266 nm[14] gave rise to the volatile γ-alkylidinephthalide lactones **2** as an *E*/*Z* mixture (18 %). Using the higher power output of the laser at 355 nm (350 mW), a yield of 60 % of isolated **2** was obtained after 18 h. Addition of isoprene as a triplet quencher had no effect, suggesting a singlet mechanism. Quantum-yield (Φ) measurements using tunable lasers at five specific wavelengths between 222 and 355 nm indicated an inefficient photochemical reaction ($\Phi = 0.5$–$3.3\,\%$).

At this point we attempted to scale up the formation of **2** by irradiating **1** with higher (average) power UV lamps. To our surprise, however, irradiation of **1** with a low-pressure phosphor-coated mercury lamp (312 nm) gave only the diones **3** and **4** (43 %, 2:1). Similar results were obtained using medium-pressure lamps (125–600 W). Irradiation of **1** in CD_3CN and direct analysis of the photosylate by ^{1}H NMR spectroscopy showed greater than 99 % of **3** and **4** and a trace of **2** (less than 1 %). These results indicate that the pathway leading to **2** is effectively closed for lamp irradiation. Significantly, addition of isoprene (one equivalent) resulted in quenching of the reaction and recovery of **1**, thus indicating that **3** and **4** are formed from a different (triplet) pathway on lamp irradiation.



Scheme 1. Lamp versus laser irradiation of 1,3-indandiones.

This stark, source-dependent difference in behavior can be explained by the mechanisms in Scheme 2. Initial excitation of **1** with either source leads to the singlet state (S_1), from which two separate pathways can evolve. With the laser, S_1 undergoes α cleavage to the diradical **5** and subsequent recombination to the lactones **2** through a Norrish type I pathway. A singlet manifold is supported by the lack of quenching observed on the addition of isoprene. In the case of Hg-lamp irradiation, intersystem crossing (ISC) from S_1 to T_1



Scheme 2. Competing Norrish type I and type II mechanistic pathways.

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and subsequent 1,5-hydrogen abstraction in a Norrish type II sequence leads to **3** and **4** by two distinct and well-documented pathways.

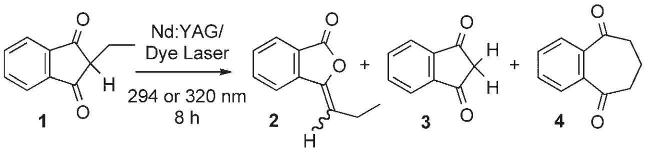
A key question arises: Why does **1** react so differently when two different UV sources are employed? Clearly it is not a simple issue of monochromaticity, as only type I products were obtained on laser irradiation at 222, 266, 280, 300, 320, 355, and 370 nm.

Initially we investigated if other physical parameters could influence the reaction pathway. In particular, it was important to establish if the enol form of **1** was involved (it was not observed by ^{1}H NMR spectroscopy).[10d,15] Changes to temperature, pH value, solvent, and concentration did not change the product distribution between the two different sources, ruling out a reactive contribution from the enol tautomer. Previous work with 2-aryl-substituted indandiones indicated photoreversibility in lactone formation.[10a–d] Irradiation of **2** formed neither starting material **1** nor type II products, thus ruling out **2** as an intermediate in the lamp experiments.

In the lamp experiments much higher average powers (6–600 W) are available compared to the lasers used (ca. 350 mW). However, this picture is too simplistic, and power delivery needs to be considered. Without taking scattering and reflection losses into account, a 600-W lamp can deliver a maximum of 370 mW cm^{-2} in the 270–390 nm region.[16] The laser beam at 355 nm has a cross-sectional area of 0.50 cm^2, and a figure of 700 mW cm^{-2} can be accurately calculated at the target cuvette. Moreover, the entire beam is delivered to the sample with very small fractional losses in power. When the laser power was decreased to 50 mW, no change in reaction profile was observed, and only lactones **2** were formed. With a pulsed laser beam, however, the photons are delivered in short, higher intensity bursts[17] than for a continuous lamp source operating at comparable average power, and type I products could potentially arise from a two-photon process (TPP) through a higher excited state.

At this stage we placed a quartz diffuser directly in front of the target cuvette. This served to scatter the laser radiation into a larger incident area on the sample and to destroy the mode structure of the laser beam without greatly affecting pulse duration. This arrangement allowed experiments to be carried out in which both collimated and scattered beams of equal power were delivered to the sample, thus allowing the effects of photon flux to be investigated (Table 1).

Table 1: Laser irradiation (8 h) of **1** (0.02 M, MeCN) at 294 and 320 nm with and without diffuser.

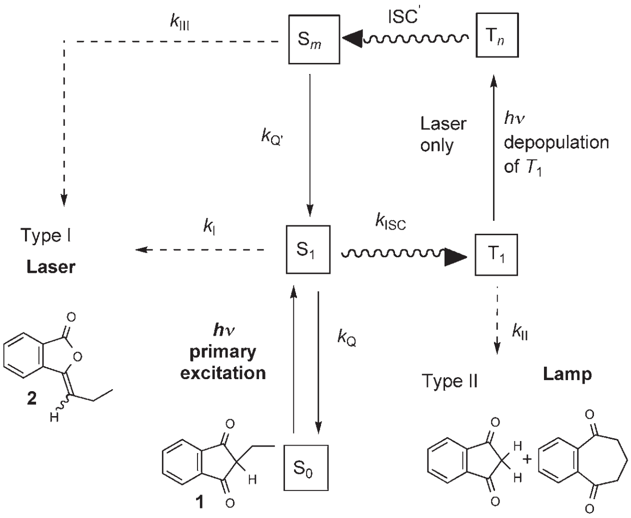


Entry	Diffuser	Power [mW][a]	λ [nm]	Isoprene 1 equiv	Product ratio[b] **1**:**2**:(**3**+**4**)
1	No	100	294	No	31:69:0
2	Yes	100[c]	294	No	61:25:14
3	No	100	294	Yes	28:72:0
4	Yes	100[c]	294	Yes	78:22:0
5	No	100	320	No	75:25:0
6	Yes	100[c]	320	No	75:0:25

[a] All laser powers were measured immediately before and after irradiation of samples using a Molectron 500-A power meter. Any UV radiation transmitted by the irradiated samples was continually monitored. [b] Calculated from ^{1}H NMR spectroscopy. [c] Measured value after scattering.

On carrying out these experiments with a scattered beam with **1** at 294 nm we observed, for the first time, the formation of type II products **3** and **4** upon laser irradiation (Table 1, entry 2). As the power delivered to the samples with and without the diffuser was the same in each case, this change of mechanism can be attributed to the effects of photon flux. Significantly, when scattered laser light was used in the presence of quencher (entry 4), the formation of type II products (**3** and **4**) reduced to zero. Added quencher did not affect the formation of **2** under normal laser irradiation conditions (entry 3). Similar behavior was observed at 320 nm (entries 5 and 6). Although the formation of **2** is less efficient at this wavelength, the use of a diffuser resulted in a complete shift of the reaction pathway from type I to type II. The scattered-laser experiment at 320 nm reproduces the results obtained with the medium-pressure mercury lamps, which have strong emissions in the 320-nm region.[18]

In order to explain this divergent behavior we propose the following sequence involving triplet depopulation by secondary $T_1 \rightarrow T_n$ excitation (Scheme 3): 1) Once S_1 is formed, it may undergo inefficient type I reaction (k_I) or follow the competitive intersystem crossing (k_{ISC}) to T_1 or quenching[19] (k_Q)—the latter is likely to be the most competitive pathway. 2) In lamp experiments when T_1 is populated, it undergoes classic type II product formation (k_{II}) and thus competes effectively with the much less efficient type I reaction. Addition of isoprene quenches T_1 back to S_0 and thus shuts down the type II pathway. Although type I products should still be formed inefficiently, under the conditions of lamp



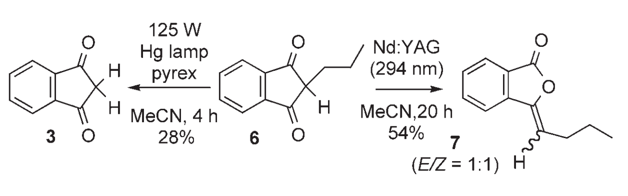
Scheme 3. Type I versus type II: depopulation of the T_1 state (relative energies of excited states not illustrated). Rate constants for various processes denoted by k.

irradiation we were unable to detect **2**. 3) In the laser experiments, with a much higher photon flux, the longer lifetime of T_1 may allow it to absorb a second photon, thus resulting in a higher-energy triplet state T_n. The second photon most likely comes from the same laser pulse as the first because of fast ISC. There are no stringent wavelength restrictions, because at the two-photon energy, the density of T_n states will be high. This constant depopulation means that the effective lifetime of T_1 is too short to allow formation of type II products. 4) T_n then likely undergoes ISC′ back to S_m and then to S_1 by quenching ($k_{Q'}$). This repopulated S_1 state can then react to type I products (k_I), although it mainly undergoes quenching (k_Q) to S_0 and ISC (k_{ISC}) back to T_1 as before. This provides another channel for type I products in the laser experiments. The low quantum yield associated with k_I ($\Phi = 0.5$–3.3%) is consistent with the inefficiency of this type I process.

The likelihood that $k_Q > k_{ISC} \gg k_I$ provides an explanation for why only trace amounts (less than 1%)[20] of the type I products can form upon lamp irradiation. Furthermore, as the photon flux in the lamp is low, $T_1 \rightarrow T_n$ excitation is unlikely. The reduced photon flux in the scattered laser beam experiments accounts for the observed reaction of **1** by mixed type I and II pathways.

It is also possible that type I products are formed from direct reaction (k_{III}) of S_m, but this would be a non-Kasha process. With a pulsed nanosecond Nd:YAG laser, however, it is improbable that S_m could be populated directly from S_1, as the lifetime of the latter is short. A second photon absorption would be more favorable for the photon fluxes provided by an ultrafast laser source.[6a] As discussed above, S_m could be accessed by ISC′ from T_n, but this pathway should be quenched by isoprene. Triplet–triplet annihilation ($T_1 + T_1 \rightarrow S_1 + S_0$) can also be considered as a possible explanation.[1,3,6c] S_1 could then follow the same pathway as discussed above. If it were to proceed by this mode, however, some type II products would be expected on laser irradiation of **1** as the T_1 concentration falls to a point where bimolecular annihilation would be much less likely.

Finally, we explored the application of these finding to the synthesis of alkylidenephthalide natural products.[21] Both *E* and *Z* isomers of 3-butylidinephthalide **7** can be isolated as volatile components from the fragrant oils of a number of plant sources.[22] We were intrigued to see if these lactones could be synthesized from 2-propyl-1,3-indandione **6**. Irradiation of **6** under lamp conditions gave the indandione **3** only, by way of a diverted type II pathway. Irradiation of **6** at 294 nm with a Nd:YAG laser gave the lactones **7** as an *E*/*Z* mixture (Scheme 4).



Scheme 4. Laser-specific synthesis of the naturally occurring *E*/*Z* 3-butylidinephthalides **7**.

In summary, we have shown that Norrish type I and type II reactions of a dione substrate can be controlled by appropriate choice of UV light source. It has been found that the different mechanistic pathways are controlled by photon flux. Specifically, in the laser experiments it is suggested that the triplet state leading to type II products is depopulated by further excitation.[23] This effectively shuts down the type II pathway and favors reaction by the type I route. These findings offer intriguing opportunities for reaction control in synthetic organic photochemistry using high-power monochromatic laser sources. For example, this study clearly demonstrates that the formation of the lactone natural products **7** by photochemical means would not be possible using conventional lamp techniques; yet such products are directly accessible by laser irradiation of readily available diones.

Experimental Section

7 (*E*/*Z*): A solution of **6** in acetonitrile (0.04 M, 25 mL) was placed in a quartz cell and irradiated at 294 nm for 20 h using the output from a Nd:YAG pumped dye laser system (400 mW). Concentration in vacuo and purification by flash chromatography (8% Et_2O in hexane) gave **7** as a fragrant volatile liquid (68 mg, 54% based on recovered starting material).

(*Z*)-**7**: IR (film): $\tilde{\nu} = 2959$ (w), 2929 (w), 1770 (s), 1686 (w), 1473 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.99$ (t, ^3J(H,H) = 7.3 Hz, 3H), 1.56 (dq, ^3J(H,H) = 7.3, 7.6 Hz, 2H), 2.46 (q, ^3J(H,H) = 7.6 Hz, 2H), 5.65 (t, ^3J(H,H) = 7.9 Hz, 1H), 7.49–7.53 (m, 1H), 7.63–7.70 (m, 2H), 7.89–7.92 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 13.9$ (CH_3), 22.6 (CH_2), 27.9 (CH_2), 109.6 (CH), 119.7 (CH), 124.5 (C=C), 125.3 (CH), 129.4 (CH), 134.3 (CH), 139.6 (C=C), 145.8 (C=C), 167.3 ppm (C=O); MS (70 eV): *m*/*z* (%) = 189 (100), 159 (15).

(*E*)-**7**: ^1H NMR ($CDCl_3$): $\delta = 1.03$ (t, ^3J(H,H) = 7.3 Hz, 3H), 1.63 (dq, ^3J(H,H) = 7.3, 7.6 Hz, 2H), 2.54 (q, ^3J(H,H) = 7.6 Hz, 2H), 5.86 (t, ^3J(H,H) = 8.3 Hz, 1H), 7.54–7.58 (m, 1H), 7.70–7.76 (m, 1H), 7.82–7.87 (m, 1H), 7.93–7.97 ppm (m, 1H). $\delta = 13.9$ (CH_3), 22.9 (CH_2), 28.1 (CH_2), 114.1 (CH), 123.4 (CH), 125.6 (CH), 126.2 (C=C), 129.6 (CH), 134.3 (CH), 138.4 (C=C), 145.8 (C=C), 166.8 ppm (C=O); MS (70 eV): *m*/*z* (%) = 189 (100), 159 (15).

3: A solution of **6** in acetonitrile (11 mM, 100 mL) was irradiated (4.5 h) using a 125-W medium-pressure mercury lamp in a pyrex immersion well. Purification by flash chromatography (Et_2O/Hex = 3:7 to 2:3) gave **3** (28%) as a purple solid. IR (neat): $\tilde{\nu} = 2918$ (w), 1744 (m), 1702 (s), 1585 (m), 1350 (m), 1254 (s), 766 (s) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 3.26$ (s, 2H), 7.83–7.87 (m, 2H), 7.97–8.00 ppm (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 45.1$ (CH_2), 123.1 (CH), 135.7 (CH), 143.3 (C=C), 197.4 ppm (C=O); MS (70 eV): *m*/*z* (%) = 147 (100), 146 (20).

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[13] From the direct output of the YAG laser at 266 and 355 nm the diameter of the beam was 0.6–0.8 cm (200–500 mW). The output from the dye laser was typically of smaller diameter, for example, 0.3 cm at 320 and 294 nm (100 mW).

[14] A Surelite Continuum Nd:YAG laser was used with an output power of 350 mW, approximately 10-ns pulse length, 20 Hz repetition rate.

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[17] A TPP from T_1 might typically be observed for photon fluxes of the order of 10^{23}–10^{28} photon cm^{-2} s^{-1}.[5] Such powers can be delivered by excimer lasers and a variety of pulsed pico- and femtosecond lasers. Although the time-averaged photon flux from the nanosecond laser used in this study was approximately 10^{18} photon cm^{-2} s^{-1}, TPPs cannot be ruled out, as the corresponding peak fluxes during single pulses are of the order of 10^{24} photon cm^{-2} s^{-1}. The photon flux (photon cm^{-2} s^{-1}) of a 350-mW pulsed (20 Hz rep. rate, 10 ns duration) laser at 355 nm can be calculated by the following: photons per pulse/(pulse duration [s] × beam area [cm^2]) $= 3.1\times10^{16}/(10^{-8}\times0.5) = 6\times10^{24}$ photon cm^{-2} s^{-1}.

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[19] Quenching in this case refers to decay of an excited state by processes such as fluorescence, internal conversion, and vibrational relaxation where appropriate. The competing ISC is generally known to be an efficient process with aromatic ketones (reference [1]).

[20] Under the conditions of the lamp/isoprene experiments, we were unable to detect any **2**. This finding is a consequence of the very low type I quantum yield and the short irradiation times used for product-ratio determinations. However, as one referee suggests, in the presence of a quencher, synthetically useful quantities of type I products may be produced on prolonged irradiation with very high power (excimer) lamps.

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[23] Further spectroscopic and kinetic studies are in progress to try to unravel further the excited states that are involved in the competing pathways for Norrish type I and II photochemistry in these indandiones.