High-intensity, laser-jet photochemistry: photodecarboxylation of 3,3-diphenyl-1*H*,3*H*-naphtho[*cd*][2]pyran-1-one

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The novel photodecarboxylation of an aryl δ-lactone from an upper triplet state is described.

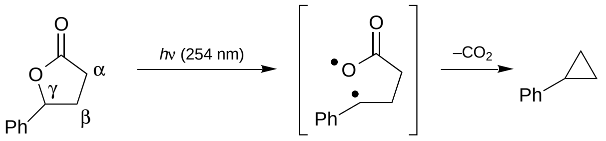
Although the photodecarboxylation of esters is a widely known process, loss of carbon dioxide from lactones is ordinarily a minor pathway in solution phase photochemistry.[1] The majority of cases reported indicate efficient photodecarboxylation requires that an excited aromatic chromophore cleave a benzyl ester bond to form a carboxy radical (Scheme 1).[2] Herein we report the novel high-intensity laser-jet photodecarboxylation of 3,3-diphenyl-1*H*,3*H*-naphtho[*cd*][2]pyran-1-one **1**.

The preparation of **1** in nearly quantitative yield involves the reaction of the ketone **2** with DBAHA [tris(2,4-dibromophenyl)ammonium hexachloroantimonate; Scheme 2] in an unprecedented SET Baeyer–Villiger lactonization.†

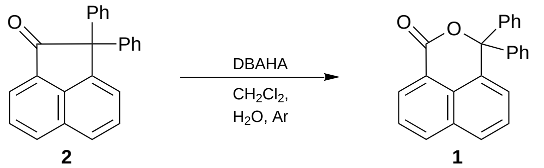
When **1** was irradiated under low-intensity conditions (356 nm, Rayonet Photochemical Reactor, C_6H_6, Ar, 7 days), no products were observed. However, under high-intensity, laser-jet conditions,[3] two new products were isolated: the carboxylic acid **3**, and the cycloheptatriene **4** (Scheme 3).‡

The mechanism for the formation of photoproducts **3** and **4** might be accounted for by either of two possible pathways [(*a*) and (*b*) in Scheme 3]. Pathway (*a*) involves absorption of a photon by **1** to form ^{3}**1**, which upon absorption of a second photon could result in homolytic C–O bond scission to produce **5**, which in turn might lose CO_2 thermally to form the novel triarylmethyl biradical **6**. Alternatively, **5** may undergo a most unusual addition to benzene to produce **3**. A second possible pathway (*b*) requires that absorption of the first photon by **1** results in homolytic bond scission to form biradical **5**, which upon the absorption of a second photon produces a biradical excited state that might either react with solvent to form **3** or undergo decarboxylation to produce **6**. In either case, the triarylmethyl biradical **6** apparently cyclizes at the *ipso* position of a phenyl group to form the norcaradiene **7**. The thermally labile **7** undergoes ring opening followed by a photochemically allowed 1,7-phenyl migration to produce the observed cycloheptatriene **4**.[4] Related 1,7-phenyl shifts have been found to be so facile that only the phenyl-shifted final product could be isolated under some conditions.[4b]

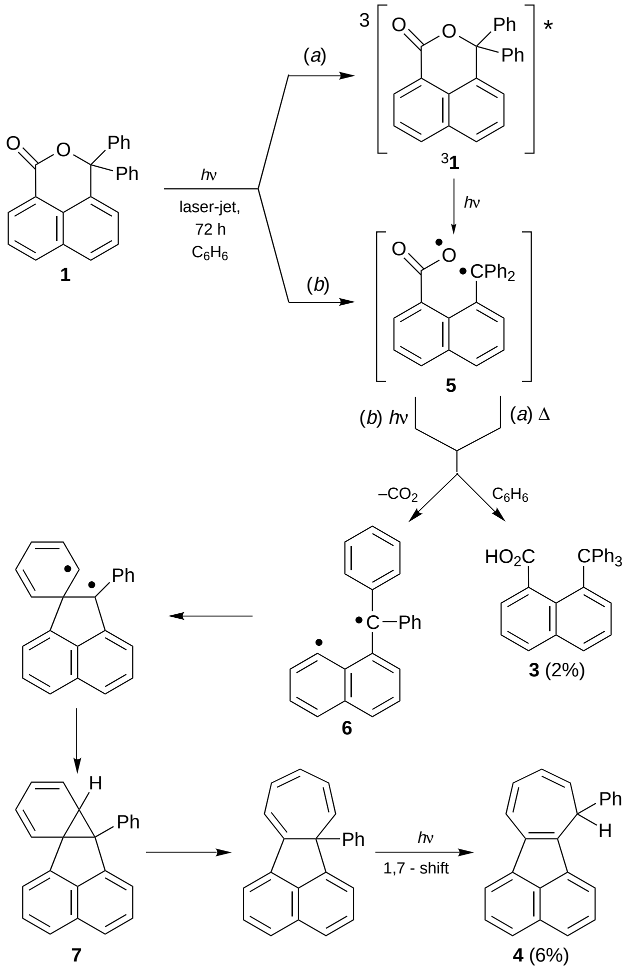
The transient absorption spectroscopy of pyranone **1** was examined in order to gain further insight into the mechanism of decarboxylation. Excitation of **1** produced a transient signal (λ_{max} = 460 nm, $\tau \geqslant 10$ μs)§ which was independent of solvent (benzene, acetonitrile or cyclohexane). The transient spectrum for **1** was similar to the spectrum determined independently for triplet 1-acetonaphthone, which is expected to be the chromophore with lowest energy in **1**. The transient for **1** was quenched with similar efficiency by O_2 and cyclohexa-1,3-diene (1–3 × 10^9 dm^3 mol^{-1} s^{-1}). These results are consistent with an assignment of the transient of **1** to its triplet state. The biradicals can be ruled out as the transient, since these species would be expected to have shortened lifetimes in cyclohexane due to



Scheme 1



Scheme 2



Scheme 3

hydrogen abstraction from the solvent and probably would not be effciently quenched by cyclohexa-1,3-diene.

Two-laser experiments were performed in order to address the question of whether C–O bond scission occurs from an upper triplet state of **1**.[5][¶] Reactive upper triplet states have been observed for benzil[6] and 1,3-bis(1-naphthyl)propan-2-one.[7] In both of these instances, the first excited triplet state was unreactive, and 'reluctant' reactivity was observed only from upper triplet states. When the triplet of **1** in benzene was further excited at 355 nm, a small but detectable, amount of bleaching was observed within 10 ns following the YAG laser pulse (Fig. 1). The actual amount of bleaching is somewhat larger than shown in Fig. 1, since some triplet was formed by the irradiation of **1** with the 355 nm laser only. The same transient spectra were recorded before and after the irradiation of the triplet by the second laser pulse. This bleaching indicates that **1**^{3} is photoreactive and this observation is consistent with pathway (*a*). It is worth noting that the energy of the photolysis (second) laser pulse corresponds to the energy employed in the high-intensity argon laser-jet experiments. When this energy was decreased by irradiating the triplet at 532 nm no bleaching was observed, suggesting that the bleaching quantum yield is dependent on the energy of excitation of the triplet.

Thus, the formation of the high intensity photoproducts **3** and **4** is probably initiated *via* pathway (*a*) (Scheme 3) involving a β-scission[3] in which an excited aromatic ring cleaves the benzyl C–O bond. In previous work,[2a,b] this type of bond was β to an excited phenyl group rather than to an excited naphthyl group. Apparently the higher energy triplet state of a phenyl group (82.5 kcal mol^{-1} for toluene; 1 cal = 4.184 J)[8] leads to direct cleavage of the benzyl C–O bond, while the much lower energy naphthyl triplet state (59.6 kcal mol^{-1} for 1-methyl naphthalene)[8] requires an additional photon to promote it to a higher energy triplet state, from which the benzyl C–O cleavage becomes energetically favourable. Once the decarboxylation has occurred, formation of the cycloheptatriene *via* collapse of **6** to the norcaradiene **7** has precedent in several reactions studied earlier.[4] Finally, it is interesting to note that while high intensity irradiation of the parent ketone **2** might also be expected to form the biradical **6** *via* photodecarbonylation, **2** was found to be photochemically unreactive.

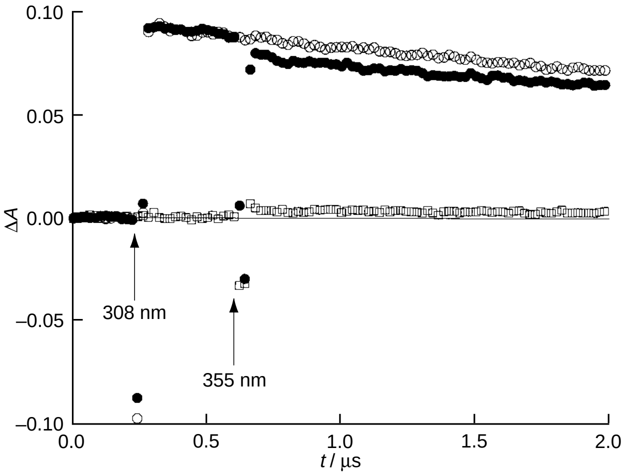


Fig. 1 Transient signals at 460 nm for the excitation of **1** at (○) 308 nm only, (□) 355 nm only and (●) 308 nm followed by 355 nm

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Footnotes

† The details and further examples of this type of reaction will be reported shortly.

‡ *Selected data* for **1**: mp 208–209 °C (lit.,[9] 204 °C); ^{1}H NMR (250 MHz; CDCl$_3$) δ 8.39 (d, *J* 7.2 Hz, 1 H), 8.15 (d, *J* 8.2 Hz, 1 H), 7.92 (d, *J* 8.3 Hz, 1 H), 7.63 (t, *J* 7.7 Hz, 1 H), 7.52 (t, *J* 7.5 Hz, 1 H), 7.31–7.18 (m, 10 H), 7.11 (d, *J* 7.2 Hz, 1 H); ν_{max} (CH$_2$Cl$_2$)/cm^{-1} 3067, 3038, 1723 (vs), 1623, 1586, 1493, 1402, 1353; HRMS (EI) calc. for $C_{24}H_{16}O_2$ (M$^+$), 336.1172. Observed, 336.1175. For **3**: ^{1}H NMR (250 MHz; CDCl$_3$) δ 9.05 (d, *J* 8.0 Hz, 1 H), 8.79 (d, *J* 8.3 Hz, 1 H), 8.71 (d, *J* 7.5 Hz, 1 H), 7.94 (dd, *J* 8.0, 8.0 Hz, 1 H), 7.76 (dd, *J* 6.7, 6.7 Hz, 1 H), 7.63–7.51 (m, 9H), 7.41 (brs, 3 H), 7.30–7.07 (m, 3 H), 6.64 (d, *J* 10.0 Hz, 1 H); ν_{max}(CH$_2$Cl$_2$)/cm^{-1} 3400 (br), 1720, 1595; GC–MS *m/z* 414.45. For **4**: ^{1}H NMR (250 MHz; CDCl$_3$) δ 7.79–7.71 (m, 3 H), 7.56 (d, *J* 7.1 Hz, 1 H), 7.50 (d, *J* 4.3 Hz, 2 H), 7.32 (d, *J* 7.0 Hz, 2 H), 7.23–7.12 (m, 4 H), 6.52 (dd, *J* 11.0, 6.2 Hz, 1 H), 6.40 (dd, *J* 10.3, 6.6 Hz, 1 H), 6.10 (dd, *J* 9.2, 9.2 Hz, 1 H), 5.10 (d, *J* 8.3 Hz, 1 H); ν_{max} (CH$_2$Cl$_2$)/cm^{-1} 3066, 3027, 1599, 1482; HRMS (EI) calc. for $C_{23}H_{16}$ (M$^+$), 292.1252. Observed 292.1239.

§ The basic laser flash photolysis system is described in Y. Liao and C. Bohne, *J. Phys. Chem.*, 1996, **100**, 734. Since some destruction of **1** was observed, most experiments were performed with a flow cell or the sample was subjected to less than 50 laser shots. The transient lifetime is limited by residual oxygen in the flow cell.

¶ The triplet state was formed by the excitation of **1** with an excimer laser (Lumonics EX-510) at 308 nm. The triplet was monitored at 460 nm, and was irradiated after a suitable delay (Stanford Research Delay Generator, model DG535) by a YAG laser (Spectra Physics GCR-12) at 355 or 532 nm. The excimer laser irradiated the sample at 90° to the monitoring beam, whereas the Yag laser beam irradiated the sample from the front at a small angle with respect to the monitoring beam. The negative Δ*A* values in Fig. 1 correspond to fluorescence of **1** and scattered light.

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