Photochemical reactions of alkoxy-containing-alkyl phenylglyoxylates: remote hydrogen abstraction

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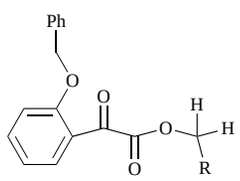
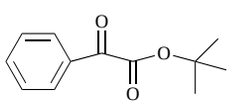
A series of alkoxy-containing-alkyl phenylglyoxylates have been synthesized and their photochemical reactions studied. The intention was to probe structural requirements for remote hydrogen abstraction. Products resulting from 1,10- and 1,11-hydrogen abstraction were isolated from the photochemical reactions of 4′-methoxybutyl phenylglyoxylate 3d and 5′-benzyloxypentyl phenylglyoxylate 3h respectively. Products resulting from Norrish Type II and intermolecular hydrogen abstraction reactions were also isolated. Triplet lifetimes of representative compounds were measured by laser flash photolysis.

Intramolecular γ-hydrogen abstractions of alkyl phenylglyoxylates have been thoroughly studied by us as well as by others.[1–3] We have measured the rate constants for the Norrish Type II reaction and found them to be relatively low (6.43×10^5 s^{-1}).[1b] This we attributed, based on AM1 semiempirical calculations[2b] and single-crystal X-ray diffraction,[4] to the unfavorable conformation for γ-hydrogen abstraction adopted by these α-keto esters. For example, *o*-benzyloxyphenylglyoxylate **1** undergoes



1a R = H
b R = Ph



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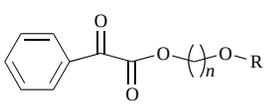
δ-hydrogen abstraction from the *o*-benzyloxy group rather than normal γ-hydrogen abstraction from the alkyl moiety of the ester.[5] On the other hand, *tert*-butyl phenylglyoxylate **2** is photoinert in benzene[1b] suggesting that the δ-hydrogens of the alkyl function are out of reach of the excited carbonyl group. There are scattered reports of medium range (1,9- and 1,12-) hydrogen abstractions from the ester alkyl moiety of phenylglyoxylates,[6] one of which is an oxidizable alkene incorporated in the ester alkyl group, even though electron transfer may play a role in most of these examples.[2f] We predicted that if the alkyl ester group were made longer and more flexible, remote hydrogens would become more readily abstracted in competition with the γ-hydrogen atoms because of the inherently low rates of the γ-hydrogen abstraction process. In contrast to earlier studies,[6] where conformational rigidity was imposed by incorporating a cyclopropyl ring, an alkene group or phenyl group in the ester function, we believed remote hydrogen atom abstraction from the flexible alkyl chain should be possible with proper activation. Indeed, products derived from 1,10-hydrogen abstraction (**8**) and 1,11-hydrogen abstraction (**9**) were obtained in competition with Norrish Type II γ-hydrogen abstraction and intermolecular hydrogen abstraction reactions in compounds **3d** and **3h** respectively.

Results and discussion

Two groups of alkyl phenylglyoxylates in which alkoxy functions were placed at varying distances from the to-be-excited



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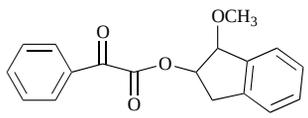
a, *n* = 2, R = CH_3
b, *n* = 2, R = CH_2CH_3
c, *n* = 3, R = CH_2CH_3
d, *n* = 4, R = CH_3
e, *n* = 5, R = CH_3
f, *n* = 6, R = CH_3
g, *n* = 3, R = Bn
h, *n* = 5, R = Bn



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carbonyl group were synthesized and their photochemistry studied. Ester **4** is of interest because the hydrogen atoms susceptible to remote oxidation by the excited carbonyl moiety are of differing reactivity.

The target α-keto esters were synthesized by dicyclohexylcarbodiimide (DCC) esterification of benzoylformic acid with the corresponding alcohols. ^{1}H NMR spectra of **3a** and **3b** show multiple peaks rather than the predicted simple triplet for the two methylene (C^{γ} and C^{δ}) groups located between the ester oxygen and the ether oxygen. This phenomenon is found to be common for 2′-alkoxy ethyl esters and is attributed to a non-bonding interaction[7] between the two oxygens which limits rotation along the C^{γ}–C^{δ} bond.

Benzene solutions (0.01–00.04 M) of the α-keto esters were irradiated with a medium-pressure mercury lamp through a Pyrex filter. Products were isolated by column chromatography on silica gel. In most of the cases, products derived both from the Norrish Type II and intermolecular hydrogen abstractions (Scheme 1)[1b] were observed. The results are summarized in Table 1. The isolation of aldehyde **6** was not successful because it is likely that it was oxidized to the corresponding acid during work-up and this would not have been eluted from the column. However, the formation of aldehyde **6** has been convincingly documented,[1–3] and, in the present study, analyses of the reaction mixtures by GC and GC–MS showed the representative signals of **6**. Retention times and MS patterns were compared with those of the authentic samples whenever necessary. The reductive dimers, dialkyl 2,3-dihydroxy-2,3-diphenylsuccinates **7**, were isolated but were not stable to mass spectral analyses.‡ The formation of products **5**, **6** and **7** is in agreement with the earlier study[1b] except that the yield of **7** is slightly higher in the reactions of **3** than the yield of dimer from non-alkoxy-containing-alkyl phenylglyoxylates. This results because alkoxy

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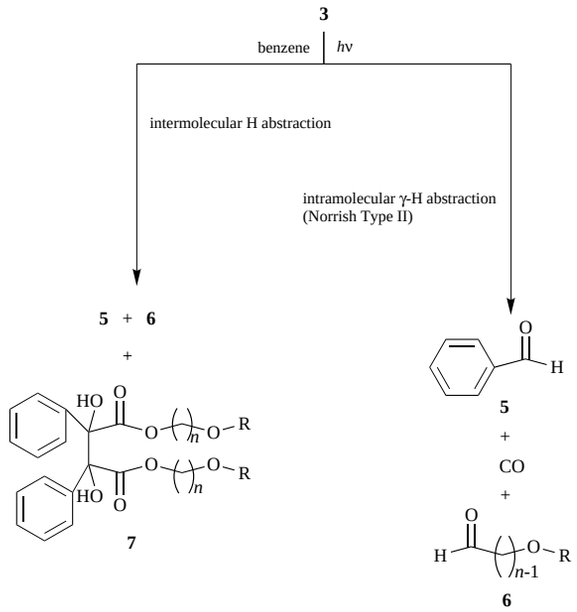
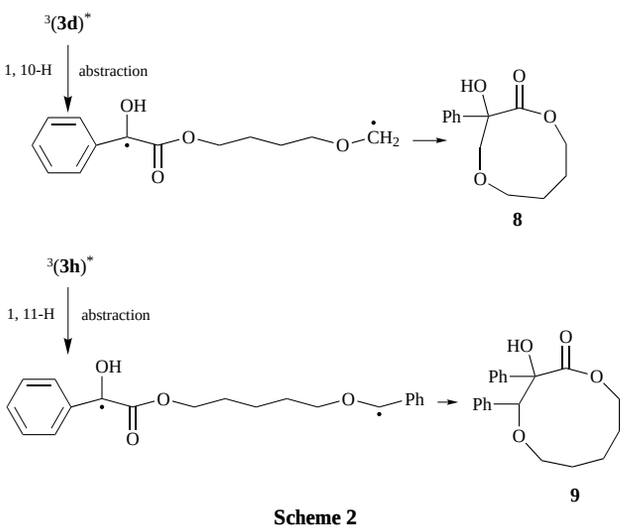
‡ Dimers **7** are characterized by NMR only in this study. Their formation and instabilities have been studied, see ref. 1(*b*).



Scheme 1

substitution activates additional hydrogens for intermolecular hydrogen abstraction processes.

The products resulting from remote hydrogen abstraction are the cyclic derivatives **8** isolated in the reaction of **3d**, and **9** from **3h** (Scheme 2). The structures of **8** and **9** are elucidated based



Scheme 2

on their spectroscopic data. Even though the molecular weights of cyclols are the same as those of the phenylglyoxylates from which they derived, the mass spectral fragmentation patterns of such cyclic compounds are very different from those of the corresponding α-keto esters. The NMR data are revealing. In ^{1}H NMR spectra, the methyl group in **3d** is shown as a singlet at 3.33 ppm. This signal is not observed in **8**. Instead, a singlet (OH) at 3.98 ppm and a set of multiple peaks at 3.91–4.00 ppm (2H) appears. This set of multiple peaks is assigned to the methylene group between the ether oxygen and the quaternary chiral carbon in **8**. The coupling patterns of other methylene proton signals in **8** are also influenced by this chiral center and appear different from their normal patterns. Attached proton tests (APT) clearly indicate that the methyl group in **3d** is converted to a methylene group in **8** and the ketone carbonyl in **3d** becomes the quaternary carbon in **8**. The existence of a hydroxy group in **8** is further confirmed by an IR signal at 3424 cm^{-1}. The structure of **9** is deduced from similar analyses of its spectroscopic data in comparison with those of **3h**.

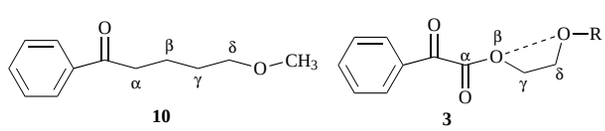
Formation of **8** is rationalized by a 1,10-hydrogen abstraction by the excited carbonyl group on the α-carbon of the ether oxygen on the farthest, or more remote side, followed by subsequent closure of the resulting biradical. The α-hydrogen on the opposite side of the oxygen is also activated. However, no products derived from abstraction of this hydrogen were observed. Abstraction of the 1,10 or more remote hydrogen must be favored conformationally, such that the longer chain allows better access of the carbonyl group. Compound **9** is proposed to be the result of 1,11-hydrogen abstraction by the excited carbonyl group in **3h**. Only one stereoisomer of **9** is observed and the *trans*-relationship of the two phenyl rings is assumed. On the other hand, 1,11-hydrogen abstraction is absent in **3e**, indicating that the degree of activation directly affects the reactivity of a hydrogen since the abstracted hydrogen in **3h** is activated by both an alkoxy and a phenyl group while only an alkoxy activation is available in **3e**. Remote hydrogen abstraction is also not observed in **3g**, suggesting that the chain length connecting the carbonyl group and the hydrogen to be abstracted also influences the accessibility of the target hydrogen.

Table 1 Photolysis results in benzene

Reactant	Isolated yield of products (%)				
3	**5**	**6**	**7**	**8**	**9**
3a	37	*a*	31		
3b	35	*a*	28		
3c	38	*a*	32		
3d	15	*a*	20	25	
3e	40	*a*	37		
3f	39	*a*	41		
3g	42	*a*	38		
3h	20	*a*	18		20
4	33	*a*	30		

[a] Product observed but not isolated.

We were disappointed that no products from either δ- or ζ-hydrogen abstraction were observed from the reaction of **4** even though conformational rigidity is imposed by the benzene-fused five-membered ring system on the alkyl function of the ester. The absence of δ-hydrogen abstraction in **3a**, **3b** and **4** is in sharp contrast to the situation in phenyl ketones, where activation by a single methoxy group makes the abstraction of the δ-hydrogen comparable in rate to that of the abstraction of the γ-hydrogen.[8] For example, in δ-methoxyvalerolphenone **10**, the



δ-hydrogen and the γ-hydrogen have comparable reactivity toward carbonyl group hydrogen abstraction processes. This is rationalized by the fact that in the more stable *Z* conformation of ester **3**, the C$^{\alpha}$=O bond is nearly eclipsed by the O$^{\beta}$–C$^{\gamma}$ bond.[2b] Therefore, in this stable conformation of **3**, both the γ- or δ-hydrogens are held away from the half-filled n orbital on the excited carbonyl oxygen that is responsible for the abstraction process. Because of the non-bonding interaction of the two oxygen atoms (indicated by the dotted line in structure **3**), the δ-hydrogens are even further removed than the γ-hydrogens from the orbital by means of which the abstraction reaction is occurring.

Nanosecond laser flash photolyses of benzene solutions of **3** reveal a transient absorption which has a maximum around 440 nm attributed to the triplet excited state of the alkyl phenylglyoxylate. This is in agreement with earlier studies.[1b,9] A typical decay trace is displayed for **3d** in Fig. 1 and the triplet state lifetimes for the compounds studied are collected in Table 2.

As the chain length connecting the excited carbonyl group

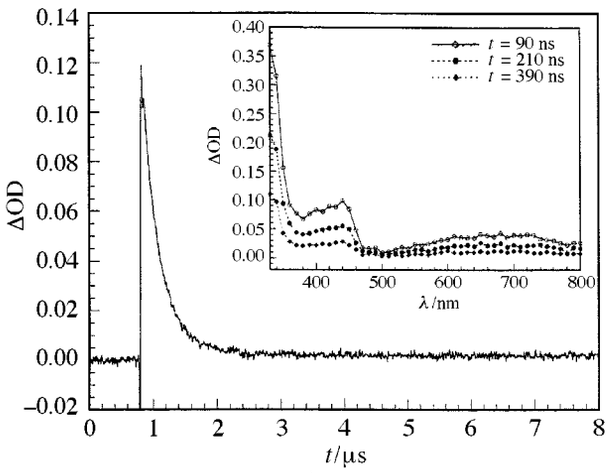


Fig. 1 Transient decay trace of **3d** in benzene (0.023 M) monitored at 440 nm. The transient absorption spectra at different delay times are in the insert.

and the methoxy group increases, the triplet lifetime increases (compare **3a**, **3d** and **3e**). The same is true for the lifetimes of **3g** and **3h**. The triplet lifetime of **3d** is significantly shortened due to the 1,10-hydrogen abstraction reaction thus indicating its rate in **3d** is high (about 10^6 s^{-1}). The triplet lifetime of **3h** is not perturbed to a significant degree by 1,11-hydrogen abstraction indicating the rate for 1,11-hydrogen abstraction is low.

In conclusion, we have studied a series of alkoxy-containing-alkyl phenylglyoxylates and established the existence of remote hydrogen abstraction in flexible chain alkyl phenylglyoxylates.

Experimental

Materials

Benzene (Aldrich) was dried over sodium under N_2. Other compounds were used as received. NMR spectra were recorded with either a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer in $CDCl_3$. Chemical shifts are in ppm with tetramethylsilane as the internal standard, and *J* values are given in Hz. GC measurements were carried out on a Hewlett-Packard (HP) 5890 Gas Chromatograph. GC–MS were obtained on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC, interfaced to a HP 2623A data processor. Infrared spectra were recorded with a Galaxy™ series 6020 FTIR Spectrometer. Thin layer chromatography was performed with Whatman® silica gel coated TLC plates. Silica gel 60 Å (60–200 mesh) used in column chromatography was from J. T. Baker Chemical Co. High resolution mass spectra were obtained from the University of Illinois at Urbana-Champaign.

General procedure for the DCC esterification

To the appropriate hydroxy-containing compound, benzoylformic acid and 4-*N*,*N*-dimethylaminopyridine (molar ratio: 1.0:1.1:0.1] in a round-bottomed flask, dry dichloromethane was added to make a *ca.* 0.2 M solution. The solution was then placed over ice and cooled to 0 °C. Equimolar amounts of 1,3-dicyclohexylcarbodiimide (DCC) in dry dichloromethane were added dropwise to the solution as it was being stirred. Generally a white precipitate formed instantly. The mixture was then allowed to warm to room temperature and stirring continued overnight. The precipitate was filtered and the solvent evaporated *in vacuo*. Purification by flash column chromatography with indicated eluents produced **3** or **4** in a yield of >85%.

2′-Methoxyethyl phenylglyoxylate 3a. Eluent: hexanes–ethyl acetate, 20:1 to 8:1, yellowish oil, yield 93%; HRMS found: *m/z* 208.0735, $C_{11}H_{12}O_4$ requires: 208.0736; δ_H(400 MHz) 3.42 (s, 3H), 3.71–3.73 (m, 2H), 4.53–4.56 (m, 2H), 7.51–7.53 (m, 2H), 7.64–7.68 (m, 1H), 8.01–8.03 (m, 2H); δ_C(APT, 50 MHz) 59.20 (CH_3), 64.83 (CH_2), 70.02 (CH_2), 128.34 (CH), 130.06 (CH), 132.14 (C), 135.37 (CH), 163.88 (C), 186.14 (C); *m/z* 208 (M^+, 0.2%), 134 (0.7), 105 (100), 77 (27.4), 51 (6.9).

Table 2 Triplet lifetimes and maximum absorption wavelengths

Compd.	3a	3d	3e	3g	3h
τ/ns	415	249	493	385	505
λ_{max}/nm	440	440	450	430	450

2′-Ethoxyethyl phenylglyoxylate 3b. Eluent: hexanes–ethyl acetate, 20:1 to 8:1, yellowish oil, yield 90%; HRMS found: *m/z* 222.0893, $C_{12}H_{14}O_4$ requires: 222.0892; δ_H(400 MHz) 1.23 (t, *J* 6.8, 3H), 3.56 (q, *J* 6.8, 2H), 3.74–3.77 (m, 2H), 4.54–4.56 (m, 2H), 7.49–7.53 (m, 2H), 7.63–7.67 (m, 1H), 8.02–8.05 (m, 2H); δ_C(APT, 50 MHz) 14.98 (CH_3), 64.42 (CH_2), 66.23 (CH_2), 67.89 (CH_2), 128.14 (CH), 129.94 (CH), 132.01 (C), 134.12 (CH), 163.11 (C), 185.79 (C); *m/z* 194 ($M^+ - 28$, 0.05%), 178 (3.6), 117 (3.5), 105 (100), 77 (22.8), 51 (5.2).

3′Ethoxypropyl phenylglyoxylate 3c. Eluent: hexanes–ethyl acetate, 15:1, yellowish oil, yield 89%; HRMS found: *m/z* 236.1048, $C_{12}H_{14}O_4$ requires 236.1049; δ_H(200 MHz) 1.20 (t, *J* 7.0, 3H), 2.05 (quintet, *J* 6.0, 2H), 3.48 (q, *J* 7.0, 2H), 3.45 (q, *J* 6.0, 2H), 4.51 (t, *J* 6.0, 2H), 7.47–7.56 (m, 2H), 7.63–7.71 (m, 1H), 7.99–8.03 (m, 2H); δ_C(APT, 50 MHz) 15.09 (CH_3), 28.87 (CH_2), 63.55 (CH_2), 66.32 (CH_2), 66.41 (CH_2), 128.84 (CH), 129.97 (CH), 132.41 (C), 134.87 (CH), 163.84 (C), 186.33 (C); *m/z* 192 ($M^+ - 44$, 5.4%), 131 (1.8), 105 (100), 77 (25), 59 (9.1), 51 (5.2).

4′-Methoxybutyl phenylglyoxylate 3d. To a solution of butane-1,4-diol (4.5 g, 50 mmol) in hexanes placed in an ice bath was added tetrabutylammonium hydrogen sulfate (85 mg) and a 50% aqueous NaOH solution (from 2.6 g of NaOH and 2.6 g of H_2O). The mixture was stirred vigorously for 30 min. An equimolar amount of dimethyl sulfate (6.3 g, 50 mmol) was then added dropwise and the mixture was stirred for another 6 h. The resulting mixture was then poured into water and extracted with dichloromethane three times. The combined organic layer was washed with water until the washings were neutral. Evaporation of solvent *in vacuo* left 4-methoxybutan-1-ol in 80% yield. The crude alcohol was used without further purification in DCC esterification and **3d** was obtained in 89% yield as a yellowish oil, eluent: hexanes–ethyl acetate, 10:1; HRMS found: *m/z* 236.1048, $C_{13}H_{16}O_4$ requires 236.1049; δ_H(400 MHz) 1.66–1.73 (m, 2H), 1.83–1.91 (m, 2H), 3.33 (s, 3H), 3.42 (t, *J* 6.4, 2H), 4.42 (t, *J* 6.4, 2H), 7.49–7.54 (m, 2H), 7.64–7.68 (m, 1H), 7.99–8.02 (m, 2H); δ_C(APT, 50 MHz) 25.32 (CH_2), 25.90 (CH_2), 58.49 (CH_3), 66.01 (CH_2), 71.83 (CH_2), 128.81 (CH), 129.90 (CH), 132.36 (C), 134.83 (CH), 163.86 (C), 186.33 (C); *m/z* 208 ($M^+ - 28$, 0.1%), 148 (1.0), 105 (100), 87 (9.9), 77 (26), 45 (19).

5′-Methoxypentyl phenylglyoxylate 3e. Compound **3e** was obtained by a similar procedure as outlined for **3d**; eluent: hexanes–ethyl acetate, 10:1, yellowish oil, yield 90%; HRMS found: *m/z* 250.1204, $C_{14}H_{18}O_4$ requires 250.1205; ν_{max}/cm^{-1} ($CDCl_3$), 2940, 2871, 1736, 1690, 911; δ_H(400 MHz) 1.46–1.52 (m, 2H), 1.59–1.65 (m, 2H), 1.76–1.83 (m, 2H), 3.32 (s, 3H), 3.38 (t, *J* 6.8, 2H), 4.40 (t, *J* 6.8, 2H), 7.49–7.53 (m, 2H), 7.64–7.67 (m, 1H), 7.99–8.01 (m, 2H); δ_C(APT, 50 MHz) 22.41 (CH_2), 28.16 (CH_2), 29.01 (CH_2), 58.41 (CH_3), 66.05 (CH_2), 72.25 (CH_2), 128.77 (CH), 129.85 (CH), 132.32 (C), 134.78 (CH), 163.82 (C), 186.29 (C); *m/z* 222 ($M^+ - 28$, 0.03%), 162 (1.2), 105 (100), 77 (22), 45 (15).

6′-Methoxyhexyl phenylglyoxylate 3f. Compound **3f** was obtained by a similar procedure as outlined for **3d**; eluent: hexanes–ethyl acetate, 10:1, yellowish oil, yield 93%; HRMS found: *m/z* 264.1362, $C_{14}H_{18}O_4$ requires 264.1362; ν_{max}/cm^{-1} ($CDCl_3$), 2937, 2867, 1736, 1690, 1200; δ_H(400 MHz) 1.42–1.44 (m, 4H), 1.56–1.60 (m, 2H), 1.77–1.80 (m, 2H), 3.32 (s, 3H), 3.37 (t, *J* 6.4, 2H), 4.39 (t, *J* 6.8, 2H), 7.49–7.53 (m, 2H),

7.64–7.66 (m, 1H), 7.99–8.01 (m, 2H); δ_C(APT, 50 MHz) 25.54 (CH_2), 25.65 (CH_2), 28.38 (CH_2), 29.36 (CH_2), 58.42 (CH_3), 66.12 (CH_2), 72.49 (CH_2), 128.79 (CH), 129.86 (CH), 132.36 (C), 134.78 (CH), 163.86 (C), 186.33 (C); *m/z* 264 (M^+, 0.1%), 220 (0.6), 176 (0.6), 131 (1.2), 105 (100), 77 (20), 45 (14).

3′-Benzyloxypropyl phenylglyoxylate 3g. Eluent: hexanes–ethyl acetate, 10:1, yellowish oil, yield 96%; HRMS found: *m/z* 298.1196, $C_{18}H_{18}O_4$ requires 298.1192; ν_{max}/cm^{-1} ($CHCl_3$), 3068, 2964, 2867, 1737, 1690, 1200; δ_H(400 MHz) 2.07 (quintet, *J* 6.4, 2H), 3.59 (t, *J* 6.4, 2H), 4.50 (s, 2H), 4.52 (t, *J* 6.4, 2H), 7.24–7.31 (m, 1H), 7.31–7.33 (m, 4H), 7.45–7.49 (m, 2H), 7.60–7.65 (m, 1H), 7.97–8.00 (m, 2H); δ_C(APT, 50 MHz) 28.76 (CH_2), 63.39 (CH_2), 66.12 (CH_2), 72.94 (CH_2), 127.48 (CH), 127.52 (CH), 128.29 (CH), 128.77 (CH), 129.86 (CH), 132.36 (C), 134.79 (CH), 138.03 (C), 163.75 (C), 186.22 (C); *m/z* 259 ($M^+ - 39$, 0.3%), 192 (34), 146 (2.6), 105 (100), 91 (40), 77 (28), 51 (7.3).

5′-Benzyloxypentyl phenylglyoxylate 3h. Eluent: hexanes–ethyl acetate, 10:1, yellowish oil, yield 90%; HRMS found: *m/z* 326.1519, $C_{20}H_{22}O_4$ requires 326.1518; ν_{max}/cm^{-1} ($CDCl_3$), 3033, 2914, 2803, 1736, 1690, 1200; δ_H(400 MHz) 1.48–1.53 (m, 2H), 1.64–1.68 (m, 2H), 1.76–1.80 (m, 2H), 3.46 (t, 6.4, 2H), 4.37 (t, *J* 6.4, 2H), 4.48 (s, 2H), 7.23–7.27 (m, 1H), 7.31–7.32 (m, 4H), 7.44–7.48 (m, 2H), 7.59–7.63 (m, 1H), 7.97–8.00 (m, 2H); δ_C(APT, 50 MHz), 22.43 (CH_2), 28.10 (CH_2), 29.11 (CH_2), 65.99 (CH_2), 69.76 (CH_2), 72.71 (CH_2), 127.33 (CH), 127.41 (CH), 128.17 (CH), 128.72 (CH), 129.77 (CH), 132.27 (C), 134.70 (CH), 138.36 (C), 163.78 (C), 186.26 (C); *m/z* 326 (M^+, 0.3%), 220 (4.8), 152 (6.6), 105 (100), 91 (69), 77 (26).

2-Benzoylcarboxy-1-methoxyindan 4. Eluent: hexanes–ethyl acetate, 10:1, yellow oil, yield 90%; HRMS found: *m/z* 296.1048, $C_{18}H_{16}O_4$ requires 296.1049; ν_{max}/cm^{-1} ($CDCl_3$), 3072, 3033, 2936, 2832.37, 1737, 1690, 1598, 1200; δ_H(400 MHz) 2.98 (dd, *J* 16.8, 4.4, 1H), 3.55 (s, 3H), 2.63 (dd, *J* 16.8, 6.8, 1H), 4.94 (d, *J* 3.2, 1H), 5.67–5.70 (m, 1H), 7.20–7.28 (m, 3H), 7.38–7.40 (m, 1H), 7.44–7.48 (m, 2H), 7.58–7.62 (m, 1H), 7.97–8.00 (m, 2H); δ_C(APT, 50 MHz) 36.46 (CH_2), 57.15 (CH_3), 80.79 (CH), 87.52 (CH), 124.79 (CH), 125.15 (CH), 128.75 (CH), 129.08 (CH), 129.72 (CH), 132.07 (C), 134.81 (CH), 139.00 (C), 139.29 (C), 163.27 (C), 185.69 (C); *m/z* 191 ($M^+ - 105$, 0.1%), 163 (7.7), 146 (76), 131 (16), 115 (14), 105 (100), 91 (7.6), 77 (33), 51 (10).

General procedures for irradiation of samples and isolating products

Samples were dissolved in benzene and sealed with a rubber septum bound by sticky parafilm. Degassing was achieved by bubbling dry argon gas through the solution for 10–15 min. Irradiation was carried out in a Rayonet RPR-100 photoreactor equipped with 16 350 nm GE® F8T5-BLB UV lamps. After irradiation, solvent was evaporated on a rotary evaporator and the resulting mixture was chromatographed under pressure using hexanes–ethyl acetate as eluting solvent.

3-Hydroxy-3-phenyl-1,5-dioxacyclonoan-2-one 8. Eluent: hexanes–ethyl acetate, 8:1 to 1:1, clear oil, yield 25%; HRMS found: *m/z* 236.1048, $C_{18}H_{16}O_4$ requires: 236.1049; ν_{max}/cm^{-1} ($CDCl_3$), 3424, 2944, 2832, 1721, 1092; δ_H(400 MHz) 1.65–1.81 (m, 2H), 1.89–1.95 (m, 1H), 2.02–2.09 (m, 1H), 3.24–3.31 (m, 2H), 3.57 (ddd, *J* 15.6, 4.8, 3.6, 1H), 3.91–4.00 (m, 2H), 3.98 (s, 1H), 4.99 (dt, *J* 10.8, 4.8, 1H), 7.32–7.39 (m, 3H), 7.62–7.64 (m, 2H); δ_C(APT, 50 MHz) 26.67 (CH_2), 25.94 (CH_2), 67.83 (CH_2), 73.51 (CH_2), 78.07 (CH_2), 80.97 (C), 125.95 (CH), 128.28 (CH), 128.37 (CH), 137.18 (C), 174.81 (C); *m/z* 236 (M^+, 1.5%), 192 (2.6), 136 (8.9), 120 (25), 105 (100), 77 (40), 40 (35).

3-Hydroxy-3,4-diphenyl-1,5-dioxacyclodecan-2-one 9. Eluent: hexanes–ethyl acetate, 10:1 to 1:1, clear oil, yield 20%; HRMS found: *m/z* 326.1519, $C_{20}H_{22}O_4$ requires 326.1518; ν_{max}/cm^{-1} ($CDCl_3$), 3423, 2944, 2832, 1721, 1455, 1092; δ_H(400 MHz) 1.61–1.73 (m, 2H), 1.76–1.93 (m, 4H), 2.45 (td, *J* 7.2, 2.0 Hz, 1H), 3.45–3.50 (m, 1H), 3.80 (m, 1H), 4.32–4.50 (m, 1H), 4.49 (s, 1H), 4.79 (s, 1H), 7.07–7.09 (m, 1H), 7.12–7.17 (m, 4H), 7.28–7.34 (m, 3H), 7.51–7.53 (m, 2H); δ_C(APT, 50 MHz) 21.55 (CH_2), 24.87 (CH_2), 27.16 (CH_2), 66.79 (CH_2), 69.45 (CH_2), 80.66 (C), 87.35 (CH), 126.88 (CH), 127.19 (CH), 127.32 (CH), 127.48 (CH), 127.57 (CH), 128.33 (CH), 136.32 (C), 137.09 (C), 174.14 (C); *m/z* 326 (M^+, 1.5), 220 (6.6), 152 (13), 105 (100), 77 (38), 69 (28), 40 (36).

Time resolved laser flash photolysis

Nanosecond laser flash photolysis was carried out on a setup described by Ford and Rodgers[10] using the third harmonic of a Q-switched ND:YAG laser as excitation source. The sample solution in a quartz cuvette was purged by argon for 5 min before and during the experiment. The samples were excited with 355 nm pulses (pulse width *ca.* 7 ns).

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