Photocycloaddition and *ortho*-hydrogen abstraction reactions of methyl arylglyoxylates: structure dependent reactivities†

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In photocycloaddition reactions between methyl arylglyoxylates and certain cyclo-1,3-dienes, the diastereochemical outcome of the photoproducts is shown to depend on the steric demand of the aryl group in the glyoxylate. Exclusive *endo*-aryloxetanes were produced with bulky arylglyoxylates while no significant stereoselectivity was observed with glyoxylates containing less demanding aryl groups. This observation is rationalized by considering the stability of possible conformers of the intermediate 1,4-biradical at the instance of intersystem crossing. When these *ortho*-substituted phenylglyoxylates were irradiated in benzene, different reaction patterns were observed with different substituents on the aryl rings. The rates of *ortho*-hydrogen abstractions vary significantly among the individual compounds. Photoproducts thus resulting are dependent on the substrate structures.

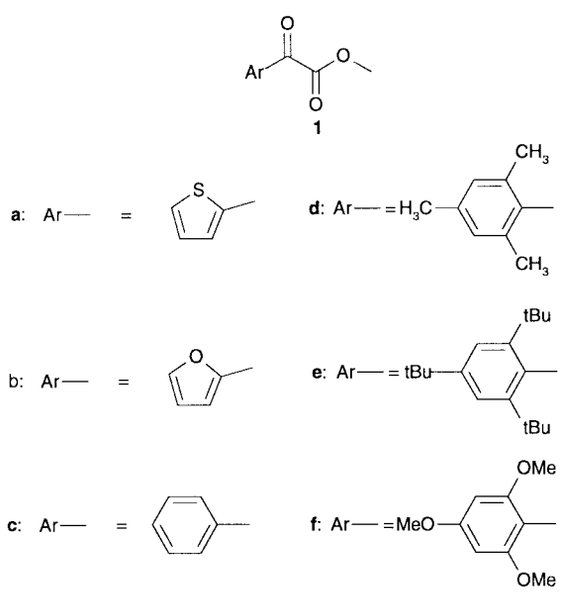
Introduction

Intermolecular photocycloaddition reactions between triplet excited carbonyl compounds and alkenes are of recent research interest from both mechanistic and synthetic points of view.[2] In a series of studies, Griesbeck *et al.* demonstrated that the diastereoselectivity in the resulting oxetane products depends on both the size of the α-substituent of the carbonyl compound and the substituent pattern as well as the flexibility of the alkene molecules.[3] The diastereoselectivity in the photoproducts was traced to the relative stability of the possible conformers adopted by the triplet 1,4-biradical intermediate at the point of intersystem crossing.[3] The cycloaddition reaction between alkyl phenylglyoxylates and various alkenes had been previously studied.[4,5] Different alkyl esters of phenylglyoxylic acid were shown to react with certain alkenes and the diastereochemistry of the photoproducts depended on the size of the ester alkyl group of the α-keto ester.[5,6] Herein, we report that the reaction outcome from the cycloaddition reactions between methyl arylglyoxylates and some cyclo-1,3-dienes is strongly dependent on the aryl group in the ester molecules, *i.e.* the diastereochemistry of the resulting bicyclic oxetanes is determined by the steric demand of the aryl group in the glyoxylate. Similar reactions between other triplet carbonyl compounds and furan were recently reported by Griesbeck's group.[7] We also reveal herein significantly different photoreaction patterns when these *ortho*-substituted arylglyoxylates are irradiated in benzene. This results from the difference in the rates of hydrogen abstraction by the excited carbonyl group from the *ortho*-substituents.

Results and discussion

Photocycloaddition

Arylglyoxylates **1** (Scheme 1) were synthesized and characterized as described in the Experimental section. The bulkiness of the aryl group in **1** was systematically altered. Since it was known that ^{13}C NMR chemical shifts of carbonyl groups in aryl carbonyl compounds are sensitive to the degree of coplanarity of the carbonyl group with the aryl section of the molecule,[8] the ground state geometry of these molecules can be inferred from their NMR spectra. Twisting the carbonyl group out of the plane of the aryl ring increases the chemical shift (δ) of the carbonyl carbon signal. The signals of the ester carbonyl carbons do not vary significantly among these compounds whereas those of the keto carbons change with different aryl groups. The δ values of the keto carbonyl group in **1a** and **1b** are significantly lower than that of the unsubstituted phenyl compound **1c**, indicating that the keto groups in **1a** and **1b** are more coplanar with the adjacent aryl rings than their counterpart in **1c**. It has been shown that most of the excited state energy in the lowest triplet excited states of the carbonyl chromophore in **1a** and **1b** is delocalized over the neighboring aryl rings, and that the lowest triplet states of **1a** and **1b** are π, π* in character as compared to the lowest n, π* triplet excited state of **1c**.[9] The keto carbonyl group of **1d** is forced out of planarity with the



Scheme 1

† ^{1}H and ^{13}C NMR (APT) spectra for all new compounds are available as supplementary data available from BLDSC (SUPPL. NO. 57569, pp. 19) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

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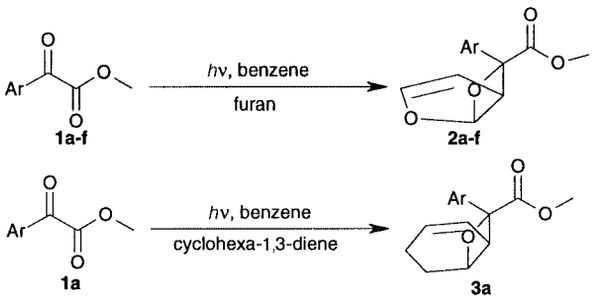
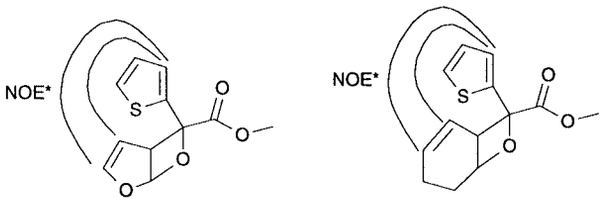
attached phenyl ring by the *o*-methyl groups as indicated by its high δ value.

Irradiating a mixture of **1** and an equimolar quantity of furan in benzene (0.06 M) results in cycloaddition products **2**, Scheme 2. Reaction of **1a** with cyclohexa-1,3-diene under the



Scheme 2

same conditions results in **3a**. The structures of **2** and **3a** are established by complete spectroscopic characterizations. The *endo*-aryl stereochemistry is derived from the NOE experimental data such as those for compounds **2a** and **3a** shown in Scheme 3, and is further confirmed by comparing the ^{1}H NMR

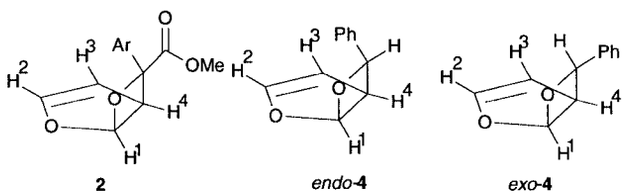


*Irradiating the protons on the residual C=C of the former cyclodiene selectively enhanced the 3-proton signal on the thiophene ring

Scheme 3

spectra (especially the chemical shifts of the protons on the former furan ring) of **2** with that of the known *endo*-phenyl compound **4**,[7] Table 1. The ^{1}H NMR spectra of **2**, in particular chemical shifts of H^3 and H^4, are in good agreement with those of *endo*-**4**.

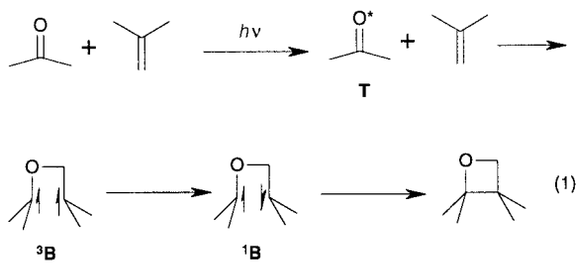
Table 1 ^{1}H NMR chemical shifts of selected protons on compounds **2** and **4**



δ/ppm	H^1	H^2	H^3	H^4
exo-**4**	6.54	6.71	5.47	3.65
endo-**4**	6.36	6.52	4.68	4.21
2a	6.36	6.53	4.86	4.38
2c	6.40	6.37	4.80	4.47
2d	6.38	6.39	4.88	4.61
2e	6.39	6.37	4.77	4.48

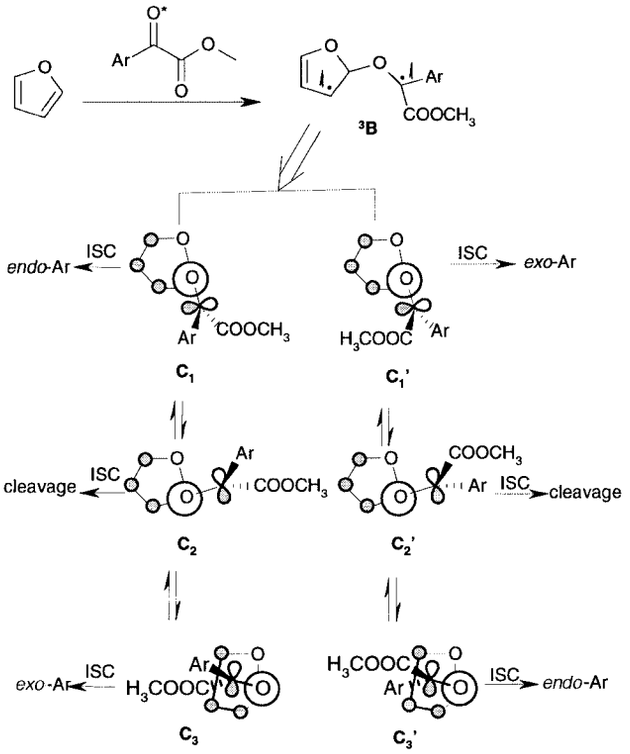
Compound **2a** was isolated in 92% yield from the reaction of **1a** and furan. The starting materials were consumed completely and the only other observed product as revealed by GC and GC/MS analyses of the photosylate is an isomer of **2a**, presumably the *exo*-aryl compound. Reaction between **1b** and furan results in four adducts in almost equal yields based on GC and GC/MS analyses of the reaction mixtures. We could not isolate **2b** from this mixture. Oxetane **2c** was isolated in 65% yield from the reaction of **1c**. The *exo*-phenyl product was also observed and the ratio of **2c**/*exo*-phenyl product is determined to be 90 : 10 determined from GC measurements. Compound **2d** was isolated in 33% yield in addition to **5** from reactions of **1d** with furan. No other isomers of **2d** can be detected by GC or GC/MS analyses of the reaction mixtures. Oxetane **2e** is the only product from the reaction of **1e** in quantitative yield. Compound **1f** is photostable under identical reaction conditions and the starting materials were recovered after extended irradiation.

It seems that the yield of **2** and the diastereoselectivity of the photoproduct depend on the steric demand of the aryl rings in **1**. Bulky aryl groups favor the *endo*-aryl geometry in the product and increase the yield of **2**. The *endo*-aryl selectivity follows the order **2e** ≈ **2d** > **2a** > **2c** > **2b**. This observation is rationalized as being analogous to that of other excited carbonyl compounds.[7]

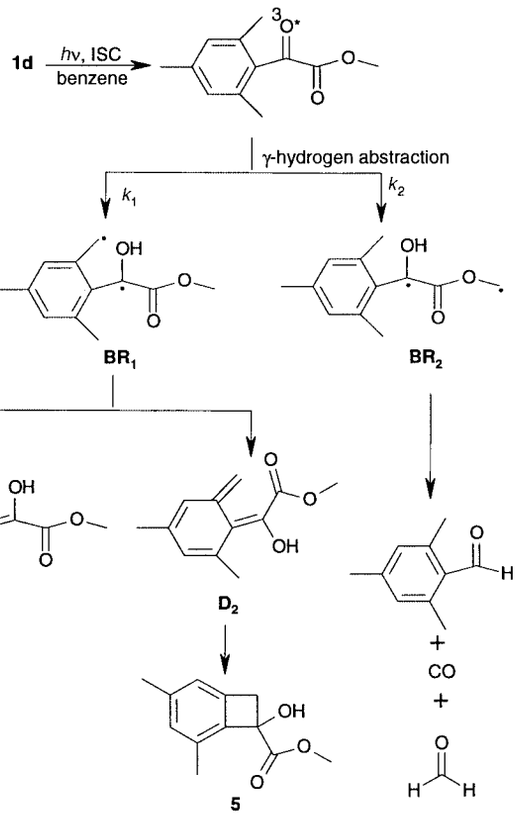


A general mechanistic picture for the cycloaddition reaction between an excited carbonyl compound and an alkene is displayed in eqn. (1). The initial formation of a C–O bond between the excited carbonyl compound (**T**) and the ground state alkene leads to the triplet biradical, ^{3}**B**. The rate restriction due to spin-forbidden intersystem crossing (ISC) has to be overcome before the transition to the singlet potential energy surface can occur from ^{3}**B**. This is followed immediately by the formation of a C–C bond in ^{1}**B** leading to the oxetane product. Spin-orbit coupling (SOC) has been recognized to control the rate of ISC. Factors influencing the magnitude of SOC have also been included in the Salem–Rowland rules.[10] Recent work by Michl[11] as well as Adam *et al.*[12] reveals that the spatial orientation of two singly occupied orbitals in ^{3}**B** is highly important while the through-space distance between the two radical centers plays a subordinate role in determining the rate of ISC. Intersystem crossing from ^{3}**B** to ^{1}**B** is expected to be concerted with the formation of a new C–C bond leading to a product whose stereochemical outcome is associated with the conformation adopted by the biradical at this instant. ISC may also occur with concurrent cleavage of the initially formed C–O bond to restore the starting carbonyl compound and alkene.

According to the Salem–Rowland rules,[10–12] strong SOC occurs when the p orbitals at the spin-bearing atoms are orthogonal to each other. The possible conformers (**C**) of the triplet biradical (^{3}**B**) are represented by the Newman projections $\mathbf{C_1}$–$\mathbf{C_3}$ and $\mathbf{C_1}'$–$\mathbf{C_3}'$ in Scheme 4. Bulky aryl groups prefer to stay away from the former furan ring so that conformers $\mathbf{C_1}$–$\mathbf{C_3}$ are favored over $\mathbf{C_1}'$–$\mathbf{C_3}'$. Among $\mathbf{C_1}$–$\mathbf{C_3}$, $\mathbf{C_1}$ and $\mathbf{C_2}$ are expected to be similarly populated whereas $\mathbf{C_3}$ is higher in energy. ISC from $\mathbf{C_1}$ leads to immediate C–C bond formation that rotates the aryl group over the former furan ring plane resulting in the *endo*-Ar product. ISC from $\mathbf{C_2}$ leads to cleavage of the initially formed C–O bond restoring the starting materials. Similarly, ISC from $\mathbf{C_3}$ furnishes the *exo*-Ar product. It was demonstrated that the relative stabilities of $\mathbf{C_1}$ and $\mathbf{C_3}$ depend on the size of the α-substituent of the aryl carbonyl compound.[7] When the α-substituent is small (such as H) compared to the aryl ring, $\mathbf{C_3}$ is the conformer responsible for



Scheme 4



Scheme 5

product formation and the *exo*-Ar product is selectively produced.[7] When the α-substituent is large as in the case of the $COOCH_3$ group in compound **1**, $\mathbf{C_1}$ is the dominating conformer and furnishes primarily the *endo*-Ar compound as the product.[7,13] If only conformers $\mathbf{C_1}$–$\mathbf{C_3}$ are responsible for product formation, the *endo*-/*exo*-Ar selectivity in producing **2** should not alter significantly with the change of the aryl group of **1** because the same α-substituent ($COOCH_3$) is involved in all these compounds, and therefore the energy differences between $\mathbf{C_1}$ and $\mathbf{C_3}$ are expected to be similar with different Ar groups. However, we observed significant changes in the product stereochemistry with alteration of the aryl groups, indicating that the other set of conformers, $\mathbf{C_1}'$–$\mathbf{C_3}'$, also plays a role in the product formation process. Analogously to the situation in $\mathbf{C_1}$–$\mathbf{C_3}$, $\mathbf{C_1}'$ leads to the *exo*-Ar product, $\mathbf{C_3}'$ leads to the *endo*-Ar products and $\mathbf{C_2}'$ restores the starting materials after ISC. Conformer $\mathbf{C_3}'$ is highly congested and probably does not contribute significantly to the formation of the *endo*-Ar product. However, $\mathbf{C_1}'$ may become populated to some degree when the steric demand of the aryl group is low. Therefore, when the aryl group is small enough to populate conformer $\mathbf{C_1}'$ as in the case of **1a**, *exo*-Ar product results in competition with the *endo*-Ar **2**. Bulky aryl groups in **1** favor only conformer $\mathbf{C_1}$ and this leads to exclusive formation of *endo*-Ar oxetanes.

Photolysis of *ortho*-substituted methyl phenylglyoxylates

We further studied the photolysis of *ortho*-substituted methyl phenylglyoxylates (**1d**, **1e**, **1f**). Irradiation of a benzene solution of **1d** (0.02 M) resulted in the formation of benzocyclobutenol **5** as the only product with low efficiency (*ca.* 50% conversion achieved after 7 days of irradiation). Compound **5** is proposed to derive from a triplet γ-hydrogen abstraction from the *o*-methyl groups, Scheme 5. Triplet biradical $\mathbf{BR_1}$ is produced after hydrogen abstraction and decays to ground state isomers of the *o*-xylylenol (*o*-xylylene = *o*-quinodimethane) with both *Z* ($\mathbf{D_1}$) and *E* ($\mathbf{D_2}$) configurations at the enol carbon.[14,15] Based on earlier reports on similar compounds,[16] the *E* isomer, $\mathbf{D_2}$, is expected to react with various dienophiles,[17,18] cyclize to benzocyclobutenol,[19] or revert to starting material.[20] The *Z* isomer, $\mathbf{D_1}$, usually undergoes an efficient 1,5-sigmatropic hydrogen shift to regenerate **1d**, accounting for, among other things, the inefficient reaction of **1d**. Compound **5** presumably results from cyclization of diene $\mathbf{D_2}$. However, attempts to trap this reaction intermediate ($\mathbf{D_2}$) with maleic anhydride are unsuccessful in this study. Irradiating **1d** in the presence of an equimolar amount of maleic anhydride in benzene solution led to rapid consumption of **1d**. The expected Diels–Alder adduct of $\mathbf{D_2}$ to the anhydride could not be observed.

Normal Norrish type II γ-hydrogen abstraction from the ester methyl group leading to 1,4-biradical $\mathbf{BR_2}$ was suppressed when **1d** was irradiated in benzene. The products (benzaldehyde, CO, and formaldehyde) expected from the cleavage of $\mathbf{BR_2}$[21] were not observed. The rate constant for the normal Norrish type II hydrogen abstraction in a typical alkyl phenylglyoxylate, k_2, is estimated to be $\approx 10^6$ s^{-1}.[21] Absence of Norrish type II products implies that the rate constant for hydrogen abstraction from the *o*-methyl group, k_1, is higher than 10^6 s^{-1}. This conclusion is further supported by the transient spectroscopy of **1d**.

Nanosecond laser flash photolysis of a 0.006 M benzene solution of **1d** results in transient absorptions being displayed (insert Fig. 1). The absorption spectrum is significantly different from that of the triplet absorption of a typical alkyl phenylglyoxylate.[21] It is suspected that the triplet excited state of **1d** is deactivated rapidly by *o*-hydrogen abstraction and escapes detection on the nanosecond time scale, *i.e.* k_1 is close to 10^8–10^9 s^{-1}. Therefore the Norrish type II process ($k_2 \approx 10^6$ s^{-1}) cannot compete. The transient decay monitored at 440 nm (Fig. 1, upper) is best fitted by a biexponential decay with lifetimes of 25 μs and 96 μs. The quality of this fitting is indicated by the residual plot (Fig. 1, lower) representing the difference between the experimental data and the fitted curve. The biradical intermediate $\mathbf{BR_1}$ is also expected to be short-lived,[16,22] and may also absorb in the same region (420–440 nm) as the transients detected in Fig. 1. This further prevents its direct observation. Based on the similarities between the absorption spectra as well as the lifetimes of the transients detected herein

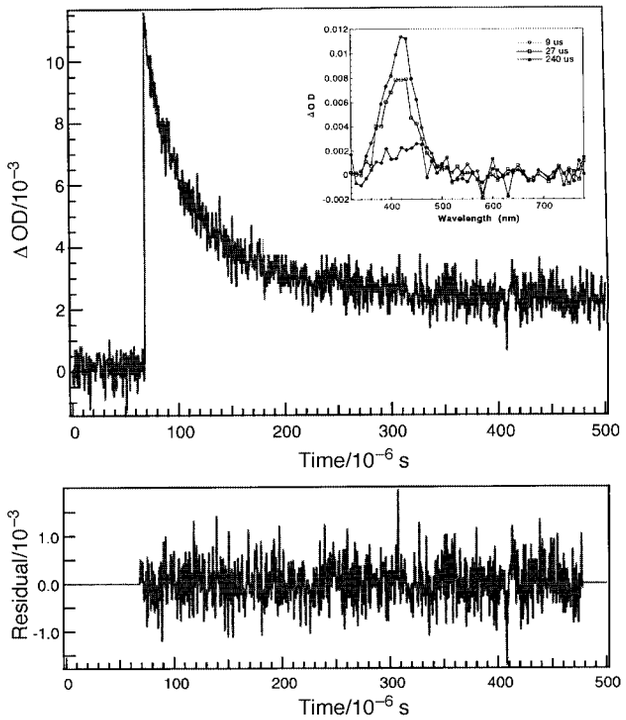
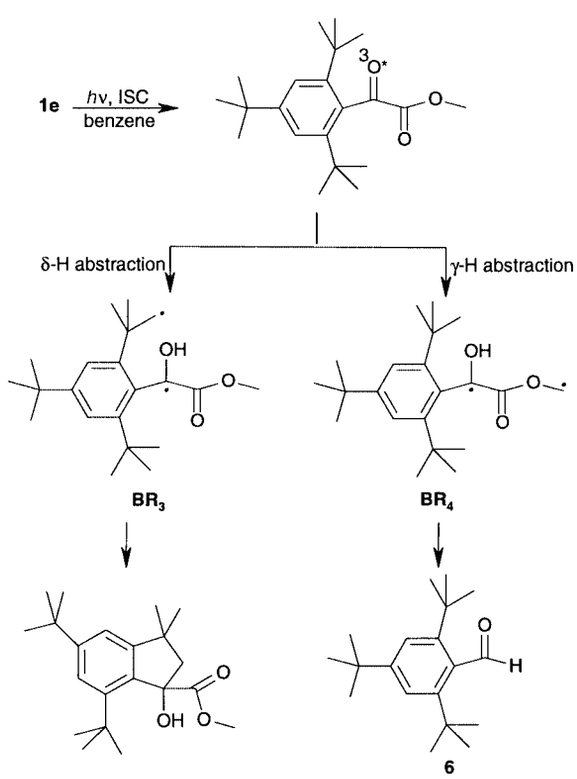


Fig. 1 Transient decays monitored at 440 nm when a 0.006 M benzene solution of **1d** was flashed (upper). The insert is the transient absorption spectra at different delay times after the laser pulse. The residual plot (lower) reveals the quality of the biexponential fitting of the decay trace.

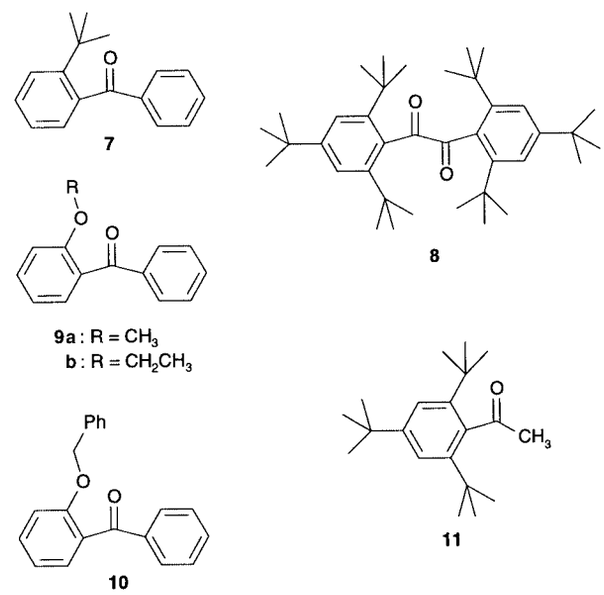
(Fig. 1) and those of other *o*-xylylenols reported in the literature,[16,22] we assign the longer lived transient (96 μs) to $\mathbf{D_2}$ and the short lived species ($\tau = 25$ μs) to $\mathbf{D_1}$ due to the allowed 1,5-hydrogen shift causing reformation of the ketone.

When a benzene solution (0.02 M) of **1e** was irradiated, the starting material was rapidly consumed and 2,4,6-tri(*tert*-butyl)benzaldehyde (**6**) was isolated, Scheme 6. Aldehyde **6**,



Scheme 6

together with CO and formaldehyde (not studied herein) are the only products from the photolysis of **1e** and are proposed to result from the decomposition of $\mathbf{BR_4}$ following a Norrish type II γ-hydrogen abstraction in the triplet excited state.[21] Abstraction of a *δ*-hydrogen from the *o*-*tert*-butyl group by the excited carbonyl chromophore producing $\mathbf{BR_3}$ which subsequently cyclizes to an indanol (Scheme 6) is expected from **1e** considering that the analogous reaction occurred at a rate constant of $\geq 1 \times 10^9$ s^{-1} in the triplet state of *o*-*tert*-butylbenzophenone **7**, (Scheme 7).[23] The total absence of

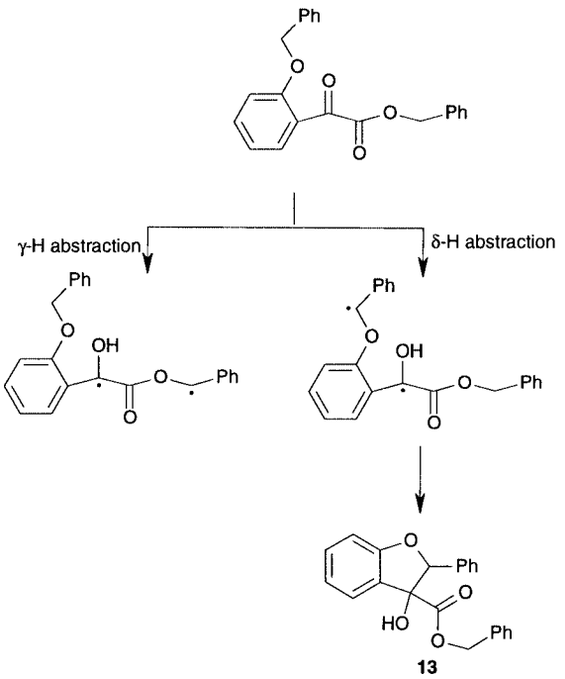


Scheme 7

δ-hydrogen abstraction products from **1e** is initially surprising. Laser flash photolysis (*vide infra*) further indicates that the lack of indanol product from **1e** is due to the absence of a significant δ-hydrogen abstraction process (rate constant smaller than 10^6 s^{-1}). Such a low rate constant for the δ-hydrogen abstraction was also observed in 2,2′,4,4′,6,6′-hexa(*tert*-butyl)benzil (**8**) though it was not satisfactorily accounted for.[24] It is also noted that the δ-hydrogen abstraction process in 2,4,6-tri(*tert*-butyl)acetophenone (**11**) resulted in a cyclization product from the resulting 1,5-biradical. The rate of this hydrogen abstraction process was supposedly low due to the observed inefficient reaction.[25]

On the other hand, δ-hydrogen abstraction from *ortho*-substituents is not as atypical for α-keto esters as it is for α-diketones. The slower *δ*-hydrogen abstraction in the case of **1e** cannot be, even in part, attributed to the influence of the α-keto group on the excited carbonyl chromophore as it was in the case of **8**.[24] Pappas *et al.* have discovered that δ-hydrogen abstraction dominates the photoreaction of benzylglyoxylate **12** furnishing **13** as the only product, Scheme 8,[26] indicating that the Norrish type II γ-hydrogen abstraction reaction in **12** could not compete with the δ-hydrogen abstraction. It is also noted that δ-hydrogen abstraction in **12** proceeded at a rate comparable with that of the phenyl ketone **10**,[19] probably indicating that replacing an ester functionality ($COOCH_3$) with a phenyl group does not significantly alter the δ-hydrogen abstraction rate from the *ortho*-groups. Therefore, the difference in the rate constants of the δ-hydrogen abstraction between glyoxylate **1e** (and to a lesser degree, diketone **8**) and ketone **7** is probably due to the steric hinderance introduced by three *tert*-butyl groups on the phenyl ring of the former.[27]

To exclude the possibility that the absence of an indanol product from **1e** is due to reformation of the ketone from $\mathbf{BR_3}$ following a δ-hydrogen abstraction, **1e** was subjected to laser flash photolysis. Transient absorptions attributable to the



Scheme 8

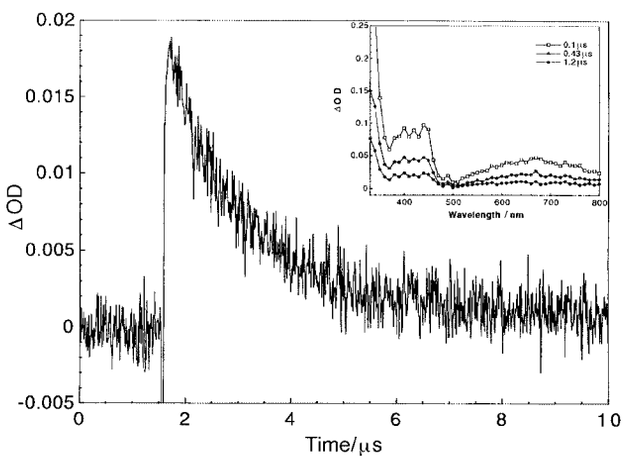
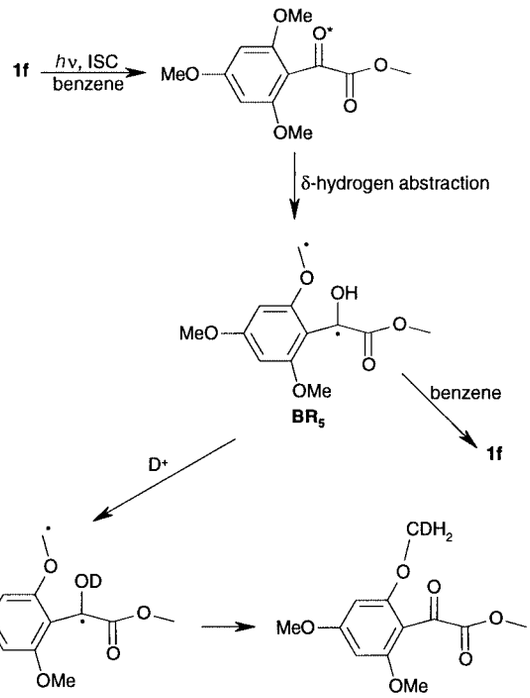


Fig. 2 Transient decay trace monitored at 440 nm after laser flash photolysis of a benzene solution (0.006 M) of **1e**. Insert: the transient absorption spectra.

excited triplet state of the alkyl phenylglyoxylates[21] are detected and the trace monitored at 440 nm decays exponentially (Fig. 2) with a lifetime of 1.6 μs. This is typical for a phenylglyoxylate ester undergoing only the Norrish type II γ-hydrogen abstraction.[21] Had δ-hydrogen abstraction occurred at a rate constant comparable to or larger than that of the Norrish type II process (≈10^6 s^{-1}), a shortening of the triplet lifetime would be expected.

When **1f** was irradiated in benzene, no product was formed even after extended illumination, and the starting ester was recovered unchanged. When irradiated in methanol-d_4, however, a H/D exchange of the *o*-methyl proton occurs, Scheme 9. Laser flash photolysis of a benzene solution of **1f** (0.006 M) gives no detectable transient absorption on the nanosecond time scale. We surmise that *δ*-hydrogen abstraction from the *o*-methoxy group of **1f** occurs with a high rate constant furnishing biradical $\mathbf{BR_5}$ and shortens the triplet lifetime of **1f** to less than nanoseconds. The hydrogen shift in $\mathbf{BR_5}$ regenerating **1f** is also efficient so that no observable photoproduct can be formed. It is suggested that hydrogen bonding between the hydroxy group in $\mathbf{BR_5}$ and methanol slows the hydrogen shift (leading to **1f**) and allows a proton exchange process between

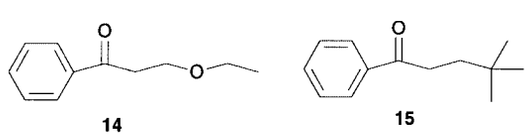


Scheme 9

$\mathbf{BR_5}$ and solvent molecules to proceed. The efficient regeneration of **1f** from $\mathbf{BR_5}$ also explains the lack of cycloaddition products between **1f** and furan when they were irradiated in benzene (*vide supra*). The fact that no triplet of **1f** is detected on the nanosecond time scale and no photoproduct is observed from the steady state photolysis indicates that the rates of δ-hydrogen abstraction in triplet **1f** and that of the hydrogen shift in $\mathbf{BR_5}$ are close to, or higher than, 10^9 s^{-1}. These processes rapidly deactivate the triplet regenerating ground state **1f** such that the addition of furan to the excited carbonyl chromophore cannot compete.

It is interesting to note that while attaching three *tert*-butyl groups to the phenyl ring of **1e** significantly lowers the rate constant for δ-hydrogen abstraction when compared to that of a phenyl ketone with only one *o*-*tert*-butyl substitutent (**7**),[23] having three *o*-methoxy groups in **1f** seems to greatly increase its δ-hydrogen abstraction rate as compared to that of the similar compounds containing only one *o*-alkoxy group (phenyl ketones **9a** or **9b**, $k_\delta \approx 5 \times 10^6$ s^{-1}, **10**, $k_\delta \approx 10^7$ s^{-1}; phenylglyoxylate **12**, $k_\delta \approx 10^7$ s^{-1}). The reason for the different effects exerted by additional *tert*-butyl *vs*. alkoxy substituents on the rate of *ortho*-δ-hydrogen abstraction is not clear.

It is known that alkoxyl radicals[28] and triplet ketones[29] attack the secondary α-C–H bond of an ether about 40 times faster than they do an unactivated methyl C–H bond. This selectivity was revealed in the δ-hydrogen abstraction rate constants of conformationally flexible acyclic ketones. For example, triplet state δ-hydrogen abstraction rate constants in β-ethoxypropiophenone (**14**)[30] and γ,γ-dimethylvalerophenone (**15**)[31] were reported as 2×10^7 $s^{-1}$and 5×10^5 s^{-1} respectively, Scheme 10. However, the roughly four orders of magnitude



Scheme 10

difference between the δ-hydrogen abstraction rate constants of **1e** and **1f** cannot be fully accounted for by this electronic effect. On the other hand, in conformationally restricted

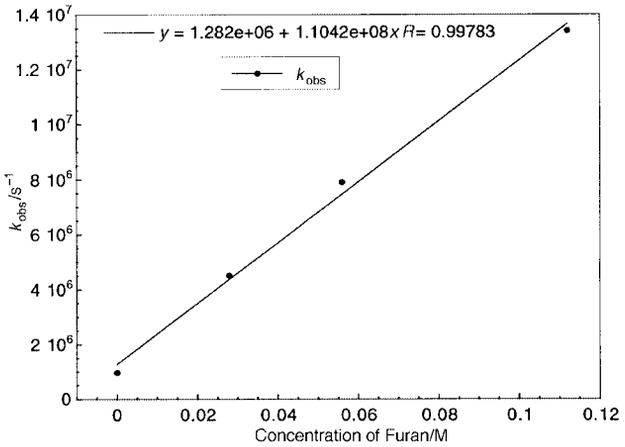


Fig. 3 Observed decay rate constants of **1c** (0.006 M in benzene) triplet at different furan concentrations.

systems with only one *ortho*-substituent, triplet **9b** abstracts δ-hydrogens only 1/200 as rapidly as does the triplet of **7**,[32] revealing that conformational effects, not electronic effects, play a primary role in the δ-hydrogen abstraction process of such restricted systems. Analogous conformational effects predict a faster δ-hydrogen abstraction for triplet **1e** than that of **1f**, which is opposite to the experimental observations. It seems likely that the conformational effects responsible for facilitating δ-hydrogen abstraction in the tri-substituted system are different from those in the mono-*ortho*-substituted systems, and that the electronic effects are also different in these two systems.

In summary, the photolysis of *ortho*-substituted methyl phenylglyoxylates **1d**, **1e**, **1f**, presents a picture where the rate constant of hydrogen abstraction from *ortho*-substituents strongly depends on the structures of the starting materials. The Norrish type II γ-hydrogen abstraction from the ester methyl group serves as a 'clock reaction' competing with other possible processes available to the excited carbonyl chromophore.

Competition between cycloaddition and photolysis

Of the *ortho*-substituted phenylglyoxylates (**1d**, **1e**, **1f**), only **1e** undergoes exclusive cycloaddition when irradiated with furan (0.06 M in benzene). With furan **1e** yielded **2e**. Benzocyclobutenol **5** and oxetane **2d** result from **1d** while **1f** gives no cycloaddition product. We have demonstrated that the rates of *o*-hydrogen abstraction reactions vary significantly among these compounds. To quantify the competition between the hydrogen abstraction processes and the cycloaddition reaction with furan, the quenching rate constant of triplet phenylglyoxylate by furan was measured. Thus, the triplet lifetimes of **1c** are derived from laser flash photolysis experiments in the presence of various amounts of furan. The quenching rate constant of 1.1×10^8 M^{-1} s^{-1} is obtained from plotting the observed triplet decay rate constants against the concentrations of furan, Fig. 3.

It is clear that at a furan concentration of 0.06 M, the rate at which **1e** reacted with the triplet carbonyl chromophore (7×10^6 s^{-1}) is higher than the rate of γ-hydrogen abstraction so that the cycloaddition reaction is the only reaction observed. Cycloaddition apparently competes with the *ortho*-γ-hydrogen abstraction in **1d** but does not compete with the rapid *ortho*-δ-hydrogen abstraction in **1f** ($k \approx 10^9$ s^{-1}).

Conclusions

Photocycloaddition reactions between different methyl arylglyoxylates and furan are studied and the diastereoselectivity of the reaction is shown to depend on the steric demand of the aryl group in the glyoxylate molecule. The photochemistry of several *ortho*-substituted methyl phenylglyoxylates has been investigated. Competition between the different hydrogen abstraction processes and the cycloaddition reaction is observed. Kinetic data associated with these processes are also obtained. The modes of reaction and the resulting photoproducts of these processes are strongly dependent on the structures of the reactants.

Experimental

Materials

Benzene (Aldrich) was dried over sodium benzophenone ketyl under argon. Other chemicals obtained from commercial sources were used as received. NMR spectra were taken either on a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer using chloroform-*d* as solvent. Chemical shifts in ^{1}H NMR were in ppm with TMS as the internal standard (0 ppm) and those in ^{13}C NMR were referenced against the center peak of chloroform-*d* (77.0 ppm). Routine GC measurements were carried out on a Hewlett-Packard (HP) 5890 Gas Chromatograph with a 30 m × 0.253 mm ID × 0.25 μm film thickness DB-1 column (J & B Scientific) and a flame ionization detector. GC/MS were taken on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC with a 30 m × 0.25 mm ID × 0.25 μm film thickness DB-5 ms column (J & B Scientific), interfaced to an HP 2623A data processor. Infrared spectra were taken with a Galaxy™ series 6020 FTIR spectrometer. Thin layer chromatography was performed with Whatman® silica gel coating TLC plates. Silica gel (60 Å, 60–200 mesh) was used in column chromatography. Melting points were determined with a Thomas Hoover capillary melting point apparatus and were uncorrected. High resolution mass spectra were obtained from the University of Illinois at Urbana-Champaign.

Time resolved laser flash photolysis

Nanosecond laser flash photolysis was carried out on a setup described by Ford and Rodgers[33] using the third harmonic of a *Q*-switched Nd:YAG laser (Continuum, YG660) as the excitation source. The sample solution in a quartz cuvette was purged with argon for ten minutes before and continuously during the experiment. Samples were excited with 355 nm pulses (pulse width *ca.* 7 ns).

Synthesis of 1

Compounds **1a** and **1b** were available from an earlier study[9] while **1c** was purchased commercially. Compounds **1d**, **1e**, and **1f** were synthesized from the substituted aryl compounds and methyl oxalyl chloride following Friedel–Crafts reaction procedures.[21] The resulting products were purified through column chromatography using the indicated solvent mixtures.

Methyl 2,4,6-trimethylphenylglyoxylate (1d). Yield 84%; yellow oil; hexanes (H)–ethyl acetate (EA) = 10:1; R_f in H–EA (5/1) = 0.52; δ_H(400 MHz, $CDCl_3$) 2.23 (s, 6H), 2.27 (s, 3H), 3.86 (s, 3H), 6.85–6.86 (m, 2H); δ_C(50 MHz, APT§, $CDCl_3$) 19.4, 21.1, 52.9, 128.9, 132.8, 136.1, 140.9, 162.9, 191.3; *m*/*z* (EI, 70 eV) 206 (M^+, 0.8), 177 (0.05), 147 (100), 119 (35), 103 (4.6), 91 (15.4), 77 (9.4), 65 (4.1), 51 (4.6); HRMS calcd for $C_{12}H_{14}O_3$: 206.0943, found 206.0946.

Methyl 2,4,6-tri(*tert*-butyl)phenylglyoxylate (1e). Yield 56%; yellow oil; H–EA = 10:1; R_f in H–EA (5/1) = 0.62; δ_H(400 MHz, $CDCl_3$) 1.35 (s, 27H), 3.98 (s, 3H), 7.75-7.76 (m, 2H); δ_C(50 MHz, APT, $CDCl_3$) 31.2, 34.9, 52.6, 124.3, 129.5, 132.0, 151.6, 164.5, 186.8; *m*/*z* (EI, 70 eV) 276 ($M^+ - 56$, 0.5), 261

§ Attached proton test.

(2.6), 217 (100), 133 (11), 91 (6.6), 77 (3.3), 57 (25); HRMS calcd for $C_{17}H_{24}O_3$: 276.1725, found 276.1726.

Methyl 2,4,6-trimethoxyphenylglyoxylate (1f). Yield 86%; yellowish solid; melting point: 73–75 °C; H–EA = 1 : 1 to 2 : 1; R_f in H–EA (1/1) = 0.30; δ_H(400 MHz, $CDCl_3$) 3.78 (s, 6H), 3.815 (s, 3H), 3.820 (s, 3H), 6.07 (s, 2H); δ_C(50 MHz, APT, $CDCl_3$) 52.3, 55.5, 56.1, 90.8, 106.8, 162.5, 165.0, 165.7, 183.9; *m/z* (EI, 70 eV) 254 (M^+, 0.7), 195 (100), 180 (9.5), 152 (5.4), 137 (8.5), 69 (5.2), 59 (4.3); HRMS calcd for $C_{12}H_{14}O_6$: 254.0790, found 254.0795.

General procedures for irradiation of samples and isolating products

Starting materials dissolved in the proper solvent were placed in Pyrex test tubes which were then sealed with rubber septa and bound using sticky parafilm. Degassing was achieved by bubbling dry argon gas through the solution for 20–25 min. Irradiation was carried out in a Rayonet RPR-100 photoreactor equipped with sixteen 350 nm GE® F8T5·BLB UV lamps. After irradiation, the solvent was evaporated on a rotary evaporator and the resulting solution was chromatographed under pressure using hexanes (H)–ethyl acetate (EA) as eluting solvent.

6-Methoxycarbonyl-*endo*-6-(2-thienyl)-2,7-dioxabicyclo-[3.2.0]hept-3-ene (2a). Yellow oil; H–EA = 10 : 1; R_f in H–EA (5/1) = 0.23; δ_H(400 MHz, $CDCl_3$) 3.88 (s, 3H), 4.38 (td, J_1 = 2.8 Hz, J_2 = 1.2 Hz, 1H), 4.86 (t, J = 2.8 Hz, 1H), 6.36 (dd, J_1 = 0.8 Hz, J_2 = 4.0 Hz, 1H), 6.53 (ddd, J_1 = 1.2 Hz, J_2 = 0.8 Hz, J_3 = 4.0 Hz, 1H), 6.99 (dd, J_1 = 4.0 Hz, J_2 = 5.2 Hz, 1H), 7.11 (dd, J_1 = 4.0 Hz, J_2 = 1.6 Hz, 1H), 7.30 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1H); δ_C(50 MHz, APT, $CDCl_3$) 53.0, 55.7, 90.5, 100.6, 105.3, 138.7, 149.4, 171.6; *m/z* (EI, 70 eV) 238 (M^+, 2.5), 192 (4.5), 178 (14), 150 (9.6), 121 (17), 111 (100), 68 (58), 39 (27); HRMS calcd for $C_{11}H_{10}SO_4$: 238.0293, found 238.0292.

6-Methoxycarbonyl-*endo*-6-phenyl-2,7-dioxabicyclo[3.2.0]-hept-3-ene (2c). Yellow oil; H–EA = 10 : 1 to 5 : 1; δ_H(400 MHz, $CDCl_3$) 3.73 (s, 3H), 4.47 (td, J_1 = 2.8 Hz, J_2 = 1.2 Hz, 1H), 4.80 (t, J = 2.8 Hz, 1H), 6.37–6.38 (m, 1H), 6.39–6.40 (m, 1H), 7.28–7.42 (m, 5H); δ_C(50 MHz, APT, $CDCl_3$) 52.9, 54.1, 91.9, 101.3, 105.3, 125.1, 127.9, 128.0, 136.5, 148.4, 172.4; *m/z* (EI, 70 eV) 172 (M^+ − 60, 0.3), 115 (5.7), 105 (50), 77 (27), 68 (100), 51 (9.6); HRMS calcd for $C_{11}H_9O_2$: 173.0603, found 173.0604.

6-Methoxycarbonyl-*endo*-6-(2′,4′,6′-trimethylphenyl)-2,7-dioxabicyclo[3.2.0]hept-3-ene (2d). Yellow oil; H–EA = 10:1; R_f in H–EA (5/1) = 0.20; δ_H(400 MHz, $CDCl_3$) 2.28 (s, 9H), 3.75 (s, 3H), 4.60–4.62 (m, 1H), 4.88 (t, J = 3.2 Hz, 1H), 6.38–6.39 (m, 2H), 6.75–6.82 (m, 2H); δ_C(50 MHz, APT, $CDCl_3$) 22.2, 24.4, 56.9, 71.8, 97.5, 104.0, 107.6, 130.4, 133.1, 135.0, 150.6, 172.3; *m/z* (EI, 70 eV) 206 (M^+ − 68, 1.3), 159 (1.0), 147 (100), 119 (13), 91 (6.5), 77 (3.6), 68 (11); HRMS calcd for $C_{12}H_{14}O_3$: 206.0943, found 206.0945.

6-Methoxycarbonyl-*endo*-6-[2′,4′,6′-tri(*tert*-butyl)phenyl]-2,7-dioxabicyclo[3.2.0]hept-3-ene (2e). Yellow oil; H–EA = 10:1; R_f in H–EA (5/1) = 0.38; δ_H(400 MHz, $CDCl_3$) 1.32 (s, 27H), 3.80 (s, 3H), 4.48 (td, J_1 = 2.8 Hz, J_2 = 1.2 Hz, 1H), 4.77 (t, J = 2.8 Hz, 1H), 6.37 (ddd, J_1 = 1.2 Hz, J_2 = 0.8 Hz, J_3 = 4.0 Hz, 1H), 6.39 (dd, J_1 = 0.8 Hz, J_2 = 4.0 Hz, 1H), 7.22 (d, J = 2.0 Hz , 2H); δ_C(50 MHz, APT, $CDCl_3$) 31.3, 34.8, 52.9, 54.3, 92.5, 101.4, 105.2, 119.4, 121.7, 135.5, 148.2, 150.3, 172.8; *m/z* (EI, 70 eV) 276 (M^+ − 124, 1.4), 261 (1.8), 217 (100), 133 (7.4), 115 (3.4), 91 (4.6), 68 (18), 57 (25).

8-Methoxycarbonyl-*endo*-8-(2-thienyl)-7-oxabicyclo[4.2.0]-oct-2-ene (3a). Yellowish oil, solidified upon standing; δ_H(400 MHz, $CDCl_3$) 1.25–1.40 (m, 2H), 2.01–2.10 (m, 1H), 2.32–2.42 (m, 1H), 3.88 (s, 3H), 5.26 (dt, J_1 = 5.6 Hz, J_2 = 2.8 Hz, 1H), 5.47 (ddd, J_1 = 3.2 Hz, J_2 = 5.6 Hz, J_3 = 9.6 Hz, 1H), 5.98 (ddd, J_1 = 2.8 Hz, J_2 = 3.2 Hz, J_3 = 9.6 Hz, 1H), 6.96 (dd, J_1 = 1.2 Hz, J_2 = 3.6 Hz, 1H), 7.01 (dd, J_1 = 1.6 Hz, J_2 = 3.6 Hz, 1H), 7.24 (dd, J_1 = 1.6 Hz, J_2 = 3.6 Hz, 1H); δ_C(50 MHz, APT, $CDCl_3$) 19.7, 24.7, 42.6, 52.8, 76.2, 87.6, 122.1, 124.5, 125.5, 126.6, 132.5, 140.4, 173.2; *m/z* (EI, 70 eV) 250 (M^+, 0.7), 191 (2.2), 172 (17), 147 (4.9), 111(77), 80 (100). HRMS calcd for $C_{13}H_{14}SO_3$: 250.0664, found 250.0654.

3,5-Dimethyl-1-methoxycarbonylbenzocyclobutenol (5). Yellow oil; H–EA = 10:1; R_f in H–EA (5/1) = 0.24; δ_H(400 MHz, $CDCl_3$) 2.13 (s, 2H), 2.24 (s, 1H), 2.31 (s, 6H), 3.74 (s, 3H), 6.82–6.83 (m, 2H); δ_C(50 MHz, APT, $CDCl_3$) 19.8, 22.1, 44.8, 53.0, 77.4, 121.0, 129.4, 132.0, 140.1, 142.4, 175.0; *m/z* (EI, 70 eV) 190 (M^+ − 16, 27), 159 (11), 147 (100), 131 (4.0), 119 (12), 91 (9.2), 77 (3.7); ν_{max} (film)/cm^{-1} 3523.10, 2955.85, 2928.32, 2867.10, 1728.75, 1439.34; HRMS calcd for $C_{12}H_{14}O_2$: 190.0994, found 190.0996.

2,4,6-Tri(*tert*-butyl)benzaldehyde (6).[24] Yellowish liquid; H–EA = 10 : 1; R_f in H–EA (5/1) = 0.69; ^{1}H NMR (400 MHz) δ 1.30 (s, 9H), 1.37 (s, 18H), 7.73 (s, 2H), 10.01 (s, 1H).

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