

# Photochemical reactivities of alkyl thiopheneglyoxylates and alkyl furanylglyoxylates<sup>1</sup>

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## Abstract

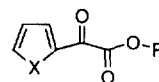
The photochemical reactions of alkyl thiopheneglyoxylates (**1a**, **2a**, **3a**) and alkyl furanylglyoxylates (**1b**, **2b**, **3b**) were studied, and reactivities were shown to be determined by the character of their lowest triplet states. Photodecompositions in an aprotic solvent such as benzene were inefficient ( $\Phi < 0.001$ ) and traces of Norrish type II product detected after prolonged irradiation. Based on the results of emission spectroscopy, laser flash photolysis experiments and reactivities in intermolecular hydrogen abstraction reactions, we conclude that the lowest triplet states of compounds **1**, **2** and **3** are  $\pi$ ,  $\pi^*$  in character. When **1** was irradiated in the presence of the electron-rich olefin, 2,3-dimethyl-2-butene (**6**), a Paternò–Büchi reaction from the upper  $n$ ,  $\pi^*$  triplet state proceeded exclusively. The expected 2 + 2 cycloaddition reaction between **6** and the thiophene or furan ring of the  $\pi$ ,  $\pi^*$  triplet state was not observed. The  $\pi$ ,  $\pi^*$  triplet states of alkyl thiopheneglyoxylates and alkyl furanylglyoxylates are, in general, unreactive. The limited reactivity observed derives from upper  $n$ ,  $\pi^*$  triplet states of the thienyl and furyl carbonyl groups. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Photochemical reactivities; Triplet state; Paternò–Büchi reaction; Alkyl thiopheneglyoxylates; Photochemical reactions

## 1. Introduction


We have previously studied the photochemical reactions of phenylglyoxylates and generally found that  $n$ ,  $\pi^*$  triplet states of the excited molecules underwent different, structure dependent reactions [1,2]. Our motive for the present study was to discover if new reaction pathways of the glyoxylate chromophore resulted from changing the triplet state from  $n$ ,  $\pi^*$  to  $\pi$ ,  $\pi^*$  in character. In earlier studies, cycloaddition products from the benzene ring of  $\pi$ ,  $\pi^*$  triplet phenylketones or benzonitriles and an olefin were observed [3–8]. Thienyl and furyl ketones have been shown to have  $\pi$ ,  $\pi^*$  lowest triplet states, while other thiophenes and furans have been shown to undergo cycloadditions to the thiophene and furan ring with alkenes [9] or alkynes [10].<sup>2</sup> We therefore synthesized a series of alkyl thiopheneglyoxylates (**1a**, **2a**, **3a**) and alkyl furanylglyoxylates (**1b**, **2b**, **3b**), hoping that by conjugating the keto ester chromophore with a heteroatomic aromatic ring, the lowest excited state of these ketone carbonyl groups would become more  $\pi$ ,  $\pi^*$  in character.


Indeed, the lowest triplet states of **1**, **2**, and **3** were characterized as  $\pi$ ,  $\pi^*$  by emission spectroscopy and from laser flash photolysis techniques. Photolyses of **1** and **2** in benzene were dominated by Norrish type II reactions and were deemed inefficient as evidenced by the kinetic parameters for the intramolecular  $\gamma$ -hydrogen abstraction. Irradiating **1** in the presence of 2,3-dimethyl-2-butene (**6**) produced oxetane (**7**) in high chemical yield. The absence of any reaction between the alkene and either the thiophene or furan ring of **1** implicates the relative reactivities of the lowest  $\pi$ ,  $\pi^*$  triplet states and the upper  $n$ ,  $\pi^*$  triplet states.



**1a:** X = S, R = CH<sub>3</sub>

**1b:** X = O, R = CH<sub>3</sub>

**2a:** X = S, R = 

**2b:** X = O, R = 

**3a:** X = S, R = C(CH<sub>3</sub>)<sub>3</sub>

**3b:** X = O, R = C(CH<sub>3</sub>)<sub>3</sub>

## 2. Experimental

### 2.1. General

Benzene was distilled from sodium benzophenone ketyl under argon immediately prior to use. Other chemicals were

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<sup>2</sup> Later the authors expressed doubts concerning the accuracy of the structures of the products [11].

the highest grade obtainable from commercial sources and used as received. Aldrich silica gel 60 Å (60–200 mesh) was used in column chromatography. NMR spectra were taken with a Varian Gemini 200 NMR or a Unity Plus 400 NMR spectrometer with chemical shifts in ppm and TMS as the internal standard. GC/MS measurements 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). Irradiation in solution was carried out in a Rayonet RPR-100 photoreactor equipped with 16 350 nm GE F8T5.BLB UV lamps as previously described [1,2]. High resolution mass spectra were obtained from the University of Illinois at Urbana-Champaign.

## 2.2. Steady state spectroscopy

UV-visible spectra were recorded on a Hewlett Packard 8452 diode array spectrophotometer. Fluorescence and phosphorescence spectra were measured using a SPEX Fluorolog spectrophotometer. The samples in EPA (ether:isopentane:ethanol = 5:5:2) were contained in sealed 5-mm NMR tubes. All phosphorescence spectra were recorded at 77 K after bubbling argon for 20 min. Phosphorescence lifetimes were determined from the 0,0 band on a SPEX 1934D Phosphorimeter.

## 2.3. Laser flash photolysis

Nanosecond laser flash photolyses were carried out on a set-up described by Ford and Rodgers [12]. The third harmonics (355 nm) of a Q-switch Nd:YAG laser with power of approximately 60 mJ/pulse and pulse width of 7 ns was used for excitation. Sample solutions were contained in 3 cm<sup>3</sup> quartz cuvettes and deaerated by continuous purging argon during the experiment. Temperature effects on triplet lifetimes were measured using this system and a temperature controller (Brinkmann MGW LAUDA RC6 and RCS).

## 2.4. Syntheses of 1, 2 and 3

A general esterification method [1,2] starting with the  $\alpha$ -keto acids and the corresponding diols and employing 1,3-dicyclohexylcarbodiimide (DCC) produced 1, 2 or 3 in better than 85% yields after column chromatography using the indicated solvents.

### Methyl thiopheneglyoxylate (1a)

Slightly yellowish oil, eluents: hexanes (H)/ethyl acetate (EA) = 10/1.  $R_f$  in H/EA (5/1) = 0.25. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.90 (s, 3H), 7.20 (dd,  $J_1 = 4.8$  Hz,  $J_2 = 4.0$  Hz, 1H), 7.85 (dd,  $J_1 = 1.2$  Hz,  $J_2 = 4.8$  Hz, 1H), 8.14 (dd,  $J_1 = 1.2$  Hz,  $J_2 = 4.0$  Hz, 1H). <sup>13</sup>C NMR (50 MHz, APT, CDCl<sub>3</sub>)  $\delta$  53.0, 128.6, 137.3, 137.6, 138.7, 161.7, 175.8. MS (EI, 70 eV): 39 (35), 57 (9.4), 83 (10), 111 (100), 142

(1.8), 170 (M<sup>+</sup>, 6.6). HRMS calculated for C<sub>7</sub>H<sub>6</sub>SO<sub>3</sub>: 170.0038, measured: 170.0038.

### Cyclohexyl thiopheneglyoxylate (2a)

Slightly yellowish oil, eluents: H:EA = 10/1.  $R_f$  in H/EA (5/1) = 0.49. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.25–1.47 (m, 3H), 1.56–1.66 (m, 3H), 1.79–1.83 (m, 2H), 1.97–2.04 (m, 2H), 5.04 (heptet, 1H), 7.18–7.21 (m, 1H), 7.81–7.83 (m, 1H), 8.08–8.10 (m, 1H). <sup>13</sup>C NMR (50 MHz, APT, CDCl<sub>3</sub>)  $\delta$  23.6, 25.0, 31.2, 75.8, 128.5, 136.9, 137.2, 139.1, 161.2, 176.8. MS (EI, 70 eV): 39 (33), 55 (100), 83 (92), 111 (83), 194 (2.3), 194 (2.3), 238 (M<sup>+</sup>, 0.4). HRMS calculated for C<sub>12</sub>H<sub>14</sub>SO<sub>3</sub>: 238.0664, measured: 238.0663.

### Tert-butyl thiopheneglyoxylate (3a)

Slightly yellowish oil, eluents: H/EA = 10/1.  $R_f$  in H/EA (5/1) = 0.37. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.63 (s, 9H), 7.19 (dd,  $J_1 = 4.8$  Hz,  $J_2 = 4.0$  Hz, 1H), 7.81 (dd,  $J_1 = 1.2$  Hz,  $J_2 = 4.8$  Hz, 1H), 8.04 (dd,  $J_1 = 1.2$  Hz,  $J_2 = 4.0$  Hz, 1H). <sup>13</sup>C NMR (50 MHz, APT, CDCl<sub>3</sub>)  $\delta$  27.8, 84.7, 128.4, 136.6, 136.9, 139.0, 161.1, 177.5. MS (EI, 70 eV): 41 (11), 57 (61), 83 (5.6), 111 (100), 156 (1.1), 169 (M<sup>+</sup> - 43, 0.5). HRMS calculated for C<sub>8</sub>H<sub>6</sub>O<sub>3</sub>: 169.0323, measured: 169.0323.

### Methyl furanylglyoxylate (1b)

Slightly yellowish oil, eluents: H/EA = 5/1 to 2/1.  $R_f$  in H/EA (1/1) = 0.67. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.97 (s, 3H), 6.66 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.76 (d,  $J = 3.6$  Hz, 1H), 7.81 (m, 1H). <sup>13</sup>C NMR (50 MHz, APT, CDCl<sub>3</sub>)  $\delta$  53.0, 113.0, 124.9, 149.5, 149.6, 161.2, 170.5. MS (EI, 70 eV): 39 (11), 67 (3.7), 95 (100), 154 (M<sup>+</sup>, 11). HRMS calculated for C<sub>7</sub>H<sub>6</sub>O<sub>4</sub>: 154.0266, measured: 154.0267.

### Cyclohexyl furanylglyoxylate (2b)

Slightly yellowish oil, eluents: H:EA = 10/1 to 2/1.  $R_f$  in H/EA (2/1) = 0.50. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.26–1.32 (m, 1H), 1.38–1.45 (m, 2H), 1.57–1.66 (m, 3H), 1.79–1.83 (m, 2H), 1.97–2.00 (m, 2H), 5.02 (heptet, 1H), 6.64 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.67 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.77–7.79 (m, 1H). <sup>13</sup>C NMR (50 MHz, APT, CDCl<sub>3</sub>)  $\delta$  23.5, 25.0, 31.1, 75.7, 112.8, 124.2, 149.2, 149.3, 160.5, 173.6. MS (EI, 70 eV): 41 (19), 55 (69), 83 (100), 95 (56), 110 (16), 222 (M<sup>+</sup>, 0.2). HRMS calculated for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: 222.0892, measured: 222.0893.

### Tert-butyl furanylglyoxylate (3b)

Slightly yellowish oil, eluents: H/EA = 8/1 to 2/1.  $R_f$  in H/EA (2/1) = 0.57. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.62 (s, 9H), 6.63 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 1.2$  Hz, 1H), 7.61 (d,  $J = 3.6$  Hz, 1H), 7.75–7.77 (m, 1H). <sup>13</sup>C NMR (50 MHz, APT, CDCl<sub>3</sub>)  $\delta$  27.8, 84.6, 112.8, 123.9, 149.1, 149.7, 160.5, 172.4. MS (EI, 70 eV): 41 (24), 57 (91), 95 (100), 140 (1.1), 153 (M<sup>+</sup> - 43, 0.8). HRMS calculated for C<sub>8</sub>H<sub>6</sub>O<sub>3</sub>: 153.0552, measured: 153.0552.

2-(Methoxycarbonyl)-2-thiophene-3,3,4,4-tetramethyl-oxetane (**7a**)

Yellow oil, eluents: H/EA = 10/1.  $R_f$  in H/EA (5/1) = 0.38.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.93 (s, 3H), 1.24 (s, 3H), 1.38 (s, 3H), 1.44 (s, 3H), 3.80 (s, 3H), 7.00 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 1.6$  Hz, 1H), 7.20–7.22 (m, 1H), 7.27–7.29 (m, 1H).  $^{13}\text{C NMR}$  (50 MHz, APT,  $\text{CDCl}_3$ )  $\delta$  21.4, 21.9, 25.6, 25.8, 47.3, 52.0, 85.7, 88.0, 125.0, 125.4, 126.8, 143.2, 172.2. MS (EI, 70 eV): 41 (13), 69 (58), 84 (100), 111 (49), 164 (1.4), 195 ( $\text{M}^+$  -59, 0.8). HRMS calculated for  $\text{C}_{11}\text{H}_{15}\text{SO}$ : 195.0844, measured: 195.0847.

2-(Methoxycarbonyl)-2-furanyl-3,3,4,4-tetramethyloxetane (**7b**)

Yellow oil, eluents: H/EA = 10/1 to 2/1.  $R_f$  in H/EA (1/1) = 0.50.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.98 (s, 3H), 1.24 (s, 3H), 1.39 (s, 3H), 1.42 (s, 3H), 3.82 (s, 3H), 6.36–6.38 (m, 1H), 6.53 (d,  $J = 3.2$  Hz, 1H), 7.45–7.47 (m, 1H).  $^{13}\text{C NMR}$  (50 MHz, APT,  $\text{CDCl}_3$ )  $\delta$  20.8, 21.8, 25.6, 47.6, 52.0, 68.9, 86.0, 125.4, 125.6, 126.8, 151.9, 170.7. MS (EI, 70 eV): 41 (9.5), 69 (50), 84 (92), 95 (100), 148 (5.0), 179 (5.3), 238 ( $\text{M}^+$ , 0.2). HRMS calculated for  $\text{C}_{13}\text{H}_{18}\text{O}_4$ : 238.1205, measured: 238.1206.

### 3. Results

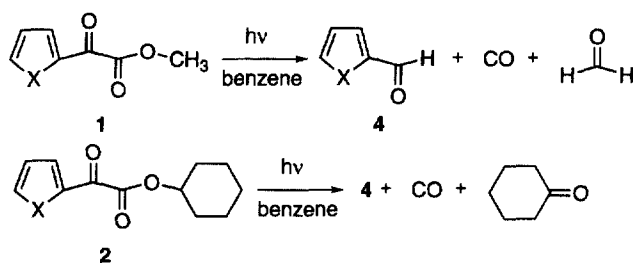
#### 3.1. Photolyses in benzene

Benzene solutions (0.01 M) of **1**, **2** and **3** were irradiated ( $\lambda_{\text{max}} = 350$  nm) and the ensuing reaction monitored by GC and GC/MS. Photodecompositions were observed in the cases of **1a**, **1b**, **2a** and **2b** with quantum yields of starting material disappearance below the limits of detection (estimated to be 0.001). The products identified by co-injection with authentic compounds are shown in Scheme 1.<sup>3</sup> Compounds **3a** and **3b** proved to be stable under identical irradiation conditions likely because they contain no  $\gamma$ -hydrogens. Most of **1**, **2** and all of **3** were recovered after prolonged irradiation and characterized by NMR after purification by column chromatography. In all the cases, the starting materials were recovered unchanged indicating no rearrangement of the thiophene or furan ring.

#### 3.2. Steady state spectroscopy

The absorption spectra of **1a** were measured in benzene ( $\lambda_{\text{max}} = 302$  nm) and in 2-propanol ( $\lambda_{\text{max}} = 297$  nm), Fig. 1. The absorption coefficient of **1a** in benzene at 302 nm ( $\epsilon_{\text{max}} = 6400 \text{ M}^{-1} \text{ cm}^{-1}$ ) is approximately the same as that

<sup>3</sup> As reported earlier with alkyl phenylglyoxylates, [1,2] intermolecular hydrogen abstractions also occur in **1** and **2** producing their reductive dimers among other products shown in Scheme 1. As for the dimers of alkyl phenylglyoxylates, [1,2] the dimers of **1** and **2** were unstable under GC analysis conditions and their characterizations were not attempted in this study.



Scheme 1.

of thiophene at its absorption maximum wavelength in cyclohexane ( $232$  nm,  $\epsilon_{\text{max}} = 6100 \text{ M}^{-1} \text{ cm}^{-1}$ ), which corresponds to the promotion of the ground state to  $\pi$ ,  $\pi^*$  singlet state. Long wavelength absorption ( $>330$  nm) is also observed indicating the lowest energy absorption for **1a** is the carbonyl  $n \rightarrow \pi^*$  transition.

The phosphorescence spectra of **1a** and **1b** were recorded in EPA (ether:isopentane:ethanol = 5:5:2) at 77 K along with that of a representative alkyl phenylglyoxylate (**1c**). The spectra (Fig. 2) show good vibrational resolution. Triplet energies ( $E_T$ ) determined from the 0,0 phosphorescence bands and the lifetimes of phosphorescence emission ( $\tau_p$ ) are reported in Table 1. For comparison, data for benzophenone and 2-benzoylthiophene are included [13].

The emission spectra of **1b** and **1c** are very similar in gross features. However, the lifetime of **1b** is more than 25 times longer than that of **1c**. The shape of emission spectrum of **1a** differs from those of **1b** and **1c** with a lifetime longer than that of **1b** or **1c**. That the phosphorescence emission lifetimes of **1a** and **1b** are substantially longer than that of **1c** is evidence that the lowest triplet states of **1a** and **1b** have  $\pi$ ,  $\pi^*$  character. The triplet energies of **1a** and **1b** are lower than that of the  $n$ ,  $\pi^*$  triplet of **1c** suggesting again that the triplet of **1a** and **1b** are  $\pi$ ,  $\pi^*$  in character. The  $n$ ,  $\pi^*$  triplet energy of the  $\alpha$ -keto ester **1c** is lower than that of a typical ketone (e.g., benzophenone). In line with this difference, the  $\pi$ ,  $\pi^*$  triplet energy of esters **1a** and **1b** is lower than that of the  $\pi$ ,  $\pi^*$  for 2-benzoylthiophene.

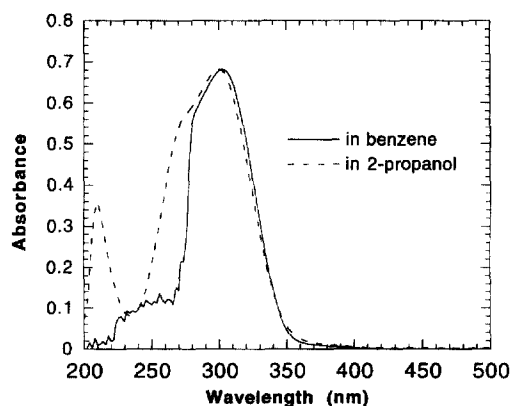


Fig. 1. Absorption spectra of **1a** in benzene and 2-propanol.

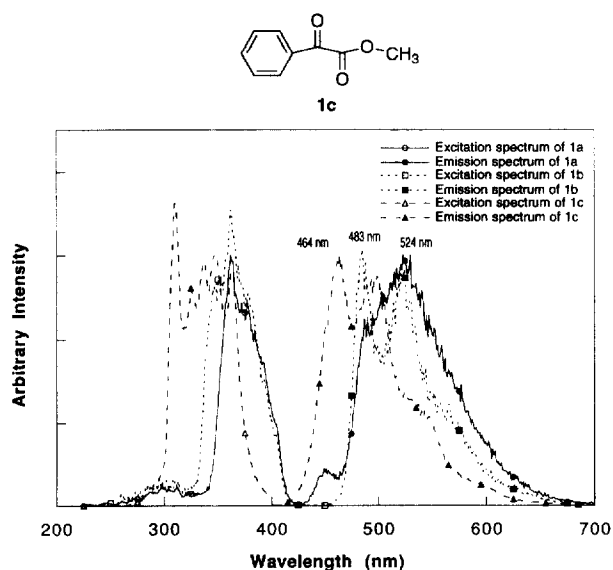
Fig. 2. Phosphorescence excitation and emission spectra of **1a**, **1b** and **1c**.

Table 1

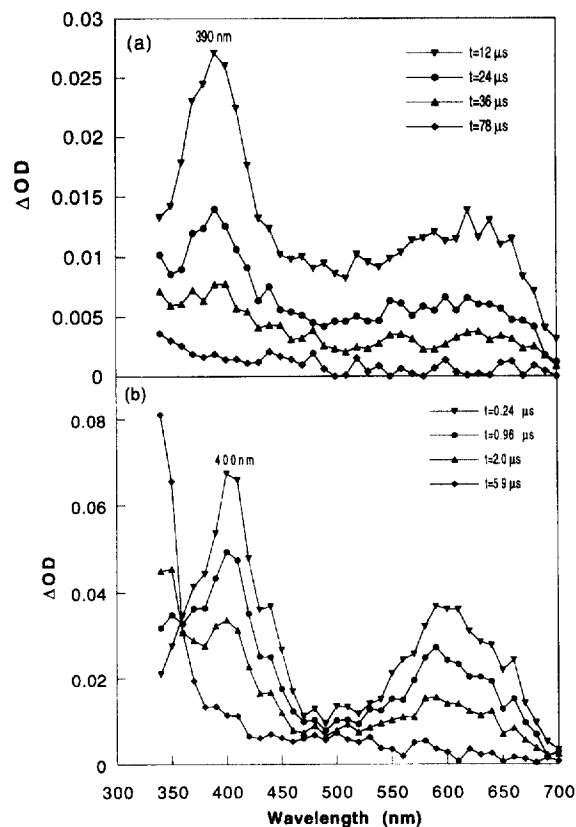
Triplet energies and phosphorescence emission lifetimes

Triplet of	$E_T$ (kcal/mol)	$\tau_T$ (s)
<b>1a</b>	54.6	1.11
<b>1b</b>	56.8	0.11
<b>1c</b>	61.6	0.00399
2-Benzoylthiophene	63.4 <sup>a</sup>	—
Benzophenone	69.1 <sup>a</sup>	—

### 3.3. Transient spectroscopy

The time resolved transient absorption spectrum of **1a** in benzene (0.001 M) at room temperature excited at 355 nm was recorded and is shown in Fig. 3a. A maximum at 390 nm and a broad band around 600 nm were observed in the absorption after laser irradiation. The two absorption decay with the same lifetime of 24.8  $\mu\text{s}$  ( $\pm 3\%$ ) as deduced from a first order kinetics was assigned to the triplet state of **1a**. When irradiated in 2-propanol (0.001 M), the transient absorption of triplet **1a** (Fig. 3b) evidences a maximum at 400 nm and a broad band at around 600 nm with the same lifetime (2.39  $\mu\text{s}$ ). The absorption maximum of the triplet state in the polar solvents showed a red shift from that in benzene which is a characteristic of  $\pi$ ,  $\pi^*$  triplets. The triplet lifetime of **1a** in benzene (24.8  $\mu\text{s}$ ) is significantly longer than that of both **1c** (1.3  $\mu\text{s}$ ) and the photoinert (in benzene) *tert*-butyl phenylglyoxylate (12.7  $\mu\text{s}$ ) under the same conditions, providing additional evidence that the triplet of **1a** is of different electronic character than that of **1c** or *tert*-butyl phenylglyoxylate.

It is reasonable to assume that the difference between the lifetime of **1a** in benzene from that in 2-propanol is solely the result of the reaction of the triplet with 2-propanol. The reaction rate at which **1a** reacts with 2-propanol can be calculated from the difference in the triplet lifetime in the two solvents and is  $3.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . Such a low reactivity with 2-

Fig. 3. Triplet absorption spectra of **1a** in benzene (a) and 2-propanol (b).

propanol is also an evidence for the  $\pi$ ,  $\pi^*$  character of the **1a** triplet [14]. A typical  $n$ ,  $\pi^*$  triplet reacts with 2-propanol with a rate constant of about  $10^6 \text{ M}^{-1} \text{ s}^{-1}$  [15]. The rate constant of triplet **1c** reacting with 2-propanol is  $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  [1].

The transient absorption spectrum of the stable compound **3a** was also recorded in benzene and found to be similar to that of **1a** under similar conditions, though the lifetime is slightly longer (25.2  $\mu\text{s}$ ,  $\pm 1\%$ ). The maximum absorption of the triplet of **2a** is at a shorter wavelength (380 nm) and decays with a lifetime of 4.38  $\mu\text{s}$  ( $\pm 5\%$ ) at a concentration of 0.001 M. Furthermore, the lifetime is dependent on the concentration of **2a** as shown in Fig. 4. The triplet lifetime of **2a** extrapolated to zero concentration is 7.6  $\mu\text{s}$ . A self-quenching rate constant ( $k_q$ ) of  $7.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  can be calculated (Fig. 4). Intermolecular hydrogen abstraction has been observed in **1c** and results in a self-quenching rate constant of  $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  [1]. To some degree, the same hydrogen abstraction process is also expected in **2a** and is accounted for by the self-quenching phenomenon. The rate of intermolecular hydrogen abstraction in **2a** is not expected to be faster than that of **1c** due to the lower reactivity in hydrogen abstraction for the  $\pi$ ,  $\pi^*$  triplet [14]. However, the  $k_q$  of **2a** is more than 30 times faster than that of **1c**. Other processes such as intermolecular electron transfer are often responsible for high self-quenching constants of  $\pi$ ,  $\pi^*$  triplets [16].

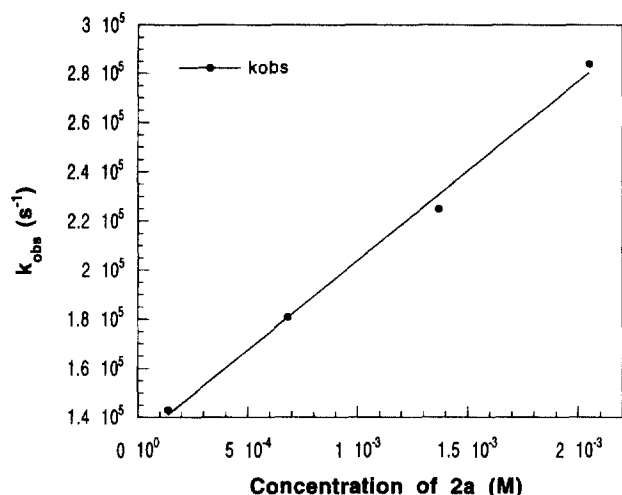


Fig. 4. Triplet decay rate constants at different concentrations of **2a** in benzene.

In the steady state experiments, the rate of the disappearance of **2a** was noticeably higher than that of **1a**. By assuming that the decay rate constant of the unreactive triplet **3a** represents all physical decay processes that alkyl thiophenylglyoxylates undergo, [1,17] the rate constants for Norrish type II reaction ( $k_N$ ) of **1a** and **2a** were calculated. Thus,  $1/\tau_1 = 1/\tau_3 + k_N$ . The  $k_N$  values calculated are  $6.4 \times 10^2 \text{ s}^{-1}$  for **1a** and  $9.1 \times 10^4 \text{ s}^{-1}$  for **2a**, both are substantially lower than that of the  $n, \pi^*$  triplet of **1c**. The higher  $k_N$  of **2a** in comparison to that calculated for **1a** is likely the result of the different reactivity of the  $\gamma$ -hydrogens. The  $\gamma$ -hydrogen of **2a** is tertiary while that of **1a** is primary. The conformation effects imposed by the cyclohexyl ring also contribute as has been described earlier [1].<sup>4</sup>

The triplet deactivation of **1a** and **2a** were measured in benzene at different temperatures. An Arrhenius plot was constructed for the rate constant of intramolecular  $\gamma$ -hydrogen abstraction (Fig. 5). The activation energy ( $E_a$ ) and the frequency factor ( $A$ ) in the Arrhenius equation [ $k = A \cdot \text{Exp}(-E_a/RT)$ ] were determined from the plot and are collected in Table 2 together with the data of **1c** [18]. The  $A$  factor of **1c** is substantially higher than that of **2a**, which is in turn higher than that of **1a**. This is in order with the rates of  $\gamma$ -hydrogen abstraction of these compounds. However, the activation energy of **1c** is higher than that of **1a** and **2a**, which is in apparent contradiction with the rate constants. This may be explained by considering that the hydrogen abstraction reaction of **1a** and **2a** takes place from the upper  $n, \pi^*$  ( $T_2$ ) state, which is in a thermal equilibrium with  $T_1$  ( $\pi, \pi^*$ ) as have been demonstrated for phenylketones [19,20]. As shown in Scheme 2, the actual activation energy measured for **1a** includes the value measured for  $T_2$  and the energy gap between  $T_1$  and  $T_2$ , the value of which is obtained from the phosphorescence spectrum of **1a** (7 kcal/mol). The

<sup>4</sup> Norrish type II reactivities of  $n, \pi^*$  triplet alkyl phenylglyoxylate was shown to be apparently insensitive to the reactivities of the  $\gamma$ -hydrogen [1].

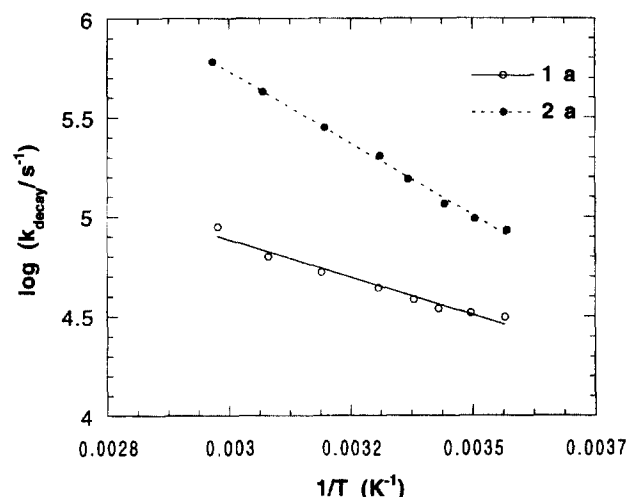
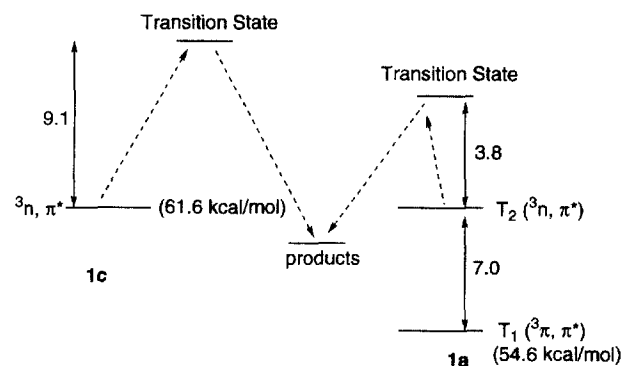


Fig. 5. Decay rate constants of **1a** and **2a** as a function of temperature in benzene.

Table 2  
The activation energies and  $A$  factors

	$E_a$ (kcal/mol)	$A$ ( $\text{s}^{-1}$ )
<b>1a</b>	3.8	$2.58 \times 10^7$
<b>2a</b>	7.3	$3.98 \times 10^{10}$
<b>1c</b>	9.1 <sup>a</sup>	$2.51 \times 10^{12}$ <sup>a</sup>

<sup>a</sup>Data from Ref. [18].

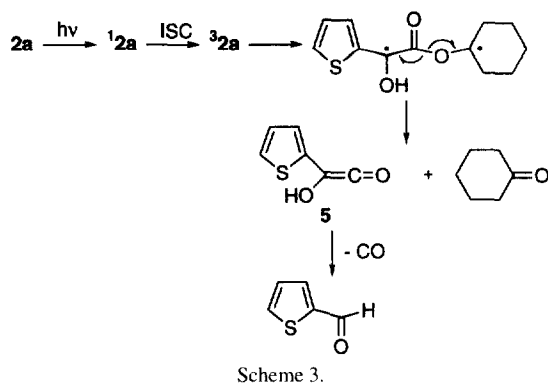


Scheme 2.

total activation energy for hydrogen abstraction from the lowest triplet state ( $T_1$ ) of **1a** is more than 12 kcal/mol higher than that of **1c**.

### 3.4. Reaction mechanism

A Norrish type II mechanism analogous to that observed in the case of the alkyl phenylglyoxylates is proposed to account for the photoproducts in benzene (Scheme 3). The 1,4-biradical produced by  $\gamma$ -hydrogen abstraction was trapped and proven to be relatively short-lived (1–10 ns) in the reactions of alkyl phenylglyoxylates [21,22]. The phenylhydroxyketene derived from  $\alpha, \beta$  cleavage of the 1,4-biradical was also trapped by various method in previous exper-



iments  $\{\}$ . In this study, thiophenehydroxyketene **5** was detected from the different absorption spectrum of a benzene solution of **2a** before and after 5 min continuous laser irradiation at 355 nm (Fig. 6). The disappearance of starting material is shown as the negative peak at around 300 nm while the positive peak at around 400 nm is attributed to the generation of **5**.<sup>5</sup> A yellow solution developed after irradiation. Unfortunately, the rate of formation of **5** can not be measured with our pulsed transient spectroscopy because the concentration of **5** generated under such conditions is low ( $\sim 10^{-3}$  M) and the absorption coefficients of ketenes are generally small ( $\epsilon = 10\text{--}310 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>5</sup>

### 3.5. Cycloaddition

When irradiated with an equal molar amount of 2,3-dimethyl-2-butene (**6**) in benzene, **1** disappeared rapidly with the formation of a single product **7** in about 90% yield (Scheme 4). The structure of **7** was confirmed by complete spectroscopic analyses.

No evidence was obtained for the addition of **6** to the thiophene or furan ring. In our earlier study, alkenes like **6** were found to undergo ring addition with thienyl and furyl carbonyl  $\pi, \pi^*$  triplets [9].<sup>2</sup> The validity of this report was challenged by systematic studies of benzoylthiophenes in which only oxetanes were obtained as products when irradiated with alkenes  $\{\}$ ,<sup>24</sup>. It was found that alkynes such as dimethyl acetylenedicarboxylate add to the ring rather than the carbonyl group of the benzoylthiophene when irradiated [10]. The tendency of dimethyl acetylenedicarboxylate and other electron poor alkynes and alkenes to add to the ring of benzo[*b*]thiophene, [25] as well as activated indoles, [26] has been demonstrated. However, irradiating **1** with either dimethyl acetylenedicarboxylate or tetrachloroethylene results in no products.

Presumably, cycloaddition of **7** is derived from the  $n, \pi^*$  triplet of **1** since cycloaddition in the  $\pi, \pi^*$  state would have occurred on the aromatic ring. The absence of ring addition products even in the case of reactive alkenes or alkynes demonstrates that the  $\pi, \pi^*$  triplet of **1** is unreactive.

<sup>5</sup> Diphenyl ketene has an absorption maximum at 390 nm in cyclohexane. For a review, see: Ref. [23].

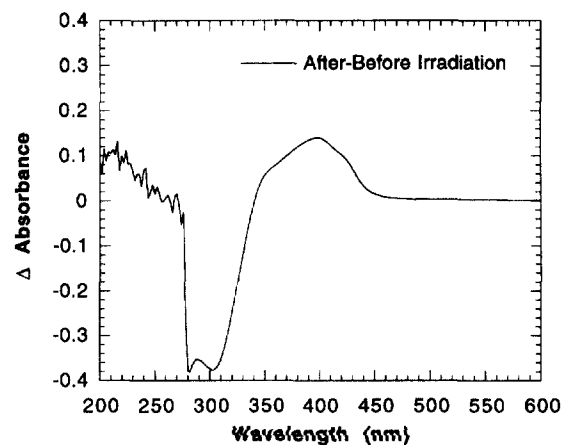


Fig. 6. Different absorption spectra of **2a** in benzene before and after laser irradiation.

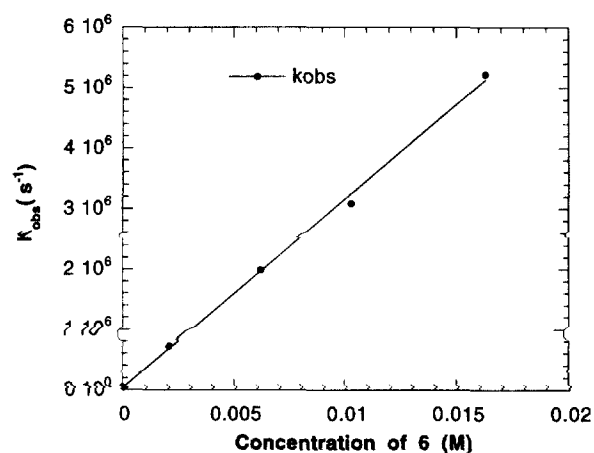
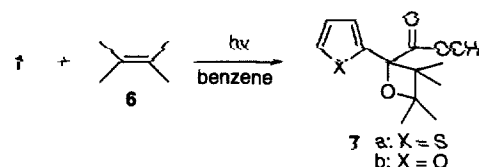
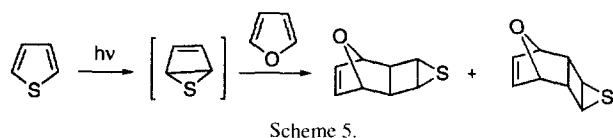


Fig. 7. Decay constants of **1a** (0.001 M) at different concentrations of **6**.

The rate at which the triplet of **1a** is quenched by **6** was measured by monitoring the decay constant of the triplet with respect to the quencher concentration in benzene (Fig. 7). The quenching rate constant obtained (Fig. 7) is  $3.13 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . This is less than 1/3 of the value for **1c** ( $9.39 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) [1]. Assuming **6** quenches the  $n, \pi^*$  triplet of **1a** at the same rate as it does the  $n, \pi^*$  state of **1c**, then one can conclude that less than 1/3 of all the triplets of **1a** are in the  $n, \pi^*$  state under this equilibrium condition.

## 4. Discussion

Excited states of both alkylthiophenes [27] and alkylfurans [28] have previously been found to undergo extensive



ring isomerizations. Initially, we suspected that the lack of reactivity of **1** and **2** might be due to similar rearrangements. Unreacted starting materials were recovered and purified before analysis by NMR. No isomerized products were observed from the reactions of **1**, **2** and **3**.

When thiophene was irradiated at 229 nm, a 2+2 cycloaddition within the same molecule of thiophene occurred via a Dewar thiophene intermediate. The latter was also trapped by furan or could be observed directly in a glassy matrix at low temperature (Scheme 5) [29,30]. The existence of an intramolecular cycloaddition in an isolated thiophene ring could explain the lack of ring addition products when benzylthiophenes [11,24] and thiopheneglyoxylates were irradiated with alkenes.

Compared with the  $\pi$ ,  $\pi^*$  triplet of phenylketones, the  $\pi$ ,  $\pi^*$  triplet of thienyl and furyl carbonyl compounds are less reactive. The triplet benzene ring in the former add successfully to an alkene and furnish products that are synthetically useful [3–8]. The upper  $n$ ,  $\pi^*$  triplet states of **1** and **2** were of limited reactivity. That their  $\pi$ ,  $\pi^*$  triplets are unreactive is likely due to other photochemical processes occurring with the excited heteroatomic aromatic rings. In this regard,  $\pi$ ,  $\pi^*$  triplet benzene rings of phenylglyoxylates are expected to be reactive and seem to be a worthwhile adventure.

## 5. Conclusion

The  $\pi$ ,  $\pi^*$  triplet states of alkyl thiopheneglyoxylates and alkyl furanylglyoxylates are unreactive. The products that are observed result from the upper  $n$ ,  $\pi^*$  triplet states. These results correspond well with the reactivities of other thienyl and furyl carbonyl compounds and are in comparison with those of the  $\pi$ ,  $\pi^*$  triplet states of phenylketones. Explanations are presented to account for the difference in reactivities between a  $\pi$ ,  $\pi^*$  triplet for an all carbon aromatic compound and that of a heteroatomic aromatic counterpart.

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