

# Photochemistry of Diaryl Vicinal Tetraketones and Chemistry of Intermediate (Aroyloxy)arylketenes<sup>1</sup>

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Photolysis of diaryl vic-tetraketones results in formation of tricyclic- $\gamma$ -lactones **3** and **4** with low quantum but high chemical yield. (Aroyloxy)arylketenes and carbon monoxide are the initial photochemical products of these photolyses. Subsequent reaction of ketene with ground-state tetraketone results in formation of the observed photoproducts via intermediate  $\beta$ -lactones. The latter are formed with a high degree of stereoselectivity. The failure of a cyclic tetraketone to react is attributed to its inability to undergo the cyclic mechanism proposed for formation of ketenes from tetraketones. Dimesityl and di-*tert*-butyl tetraketones react by a competing intramolecular hydrogen atom transfer mechanism. Dimerization of (benzoyloxy)phenylketene and its reactions with a number of tetraketones are described.

## Introduction

$\alpha$ -Diketones have a rich photochemistry which has been studied extensively.<sup>2</sup> Very different photochemistry of vic-triketones which is characterized by extremely low quantum yields and formation of complex product mixtures has recently been reported.<sup>3,4</sup> Although open-chain vic-tetraketones were first prepared,<sup>5,6</sup> in 1891, their photochemical reactions have not been reported. The present paper describes the delightful photochemistry (Scheme 1) of some such compounds (**1a–c**) involving reasonable reactivity and high chemical yields.

Absorption spectra of vic-tetraketones have been studied in detail by Horner and co-workers.<sup>7</sup> Typical is diphenyl tetraketone (**1a**, 1,4-diphenylbutane-1,2,3,4-tetrone) with UV-vis maxima at 262 (18000), 385 (160), and 515 (200) nm; long wavelength maxima for related tetraketones (**1a–e**, **5a**) lie in the range 510–525 nm. Our attempts and those of others<sup>8</sup> to observe light emission from tetraketones failed to detect either fluorescence or phosphorescence. Structures of **1a** and **1d** have been determined by X-ray crystallography.<sup>9</sup>

It should be emphasized that most vic-tetraketones undergo hydration extremely rapidly.<sup>10</sup> Simple standing

in air results in rapid replacement of the red color of tetraketone by the pale yellow of the hydrate. Tetraketones containing bulky end groups such as mesityl or *tert*-butyl or cyclic tetraketone **2**<sup>11</sup> are hydrated to a much lesser extent. Traces of hydrate are not a major problem in preparative photochemical experiments since appropriate filters can ensure that only the free tetrone absorbs light, but extreme dryness is a must for quantum yield or other quantitative measurements. The special drying techniques developed for working with these compounds in solution are described in the Experimental Section. The use of protic solvents such as alcohols is precluded for most tetraketones.

## Photolysis Results

Preparative scale irradiations of tetraketones were performed in *dry* benzene solutions under nitrogen or argon using a sodium chromate solution filter to ensure irradiation above 500 nm so that reaction product(s) would not undergo further photochemistry. Steady evolution of bubbles was observed during irradiation; the evolved gas was shown to be carbon monoxide by examination of the headspace after the reaction. Bubble formation ceased and the red solution became yellow when the reaction was complete. Dimesityl (**1d**) and di-*tert*-butyl (**1e**) tetraketones, and cyclic tetraketone<sup>12</sup> **2** were recovered unchanged under these irradiation conditions.

TLC analysis of crude products from **1a–c** showed one major spot and indications of a second, minor, spot of very similar  $R_f$  value. Crude reaction products were washed

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(1) A preliminary report of part of this work has appeared. Rubin, M. B.; Krochmal, E. C., Jr.; Kaftory, M. *Rec. Trav. Chim.* **1979**, *98*, 85. Taken in part from the M.Sc. thesis of M. Etinger, Technion, 1995.

(2) For reviews see Rubin, M. B. *Top. Curr. Chem.* **1969**, *13*, 251. Monroe, B. M. *Adv. in Photochem.* **1971**, *8*, 77. Rubin, M. B. *Top. Curr. Chem.* **1985**, *129*, 1.

(3) Netto-Ferreira, J. C.; Scaiano, J. C. *Photochem. Photobiol.* **1991**, *54*, 17.

(4) Rubin, M. B.; Heller, M.; Monisov, R.; Gleiter, R.; Dörner, T. *J. Photochem. Photobiol. A: Chem.* **1995**, *87*, 7.

(5) Abenius, P. W.; Soderbaum, H. G. *Ber.* **1891**, *24*, 3033.

(6) For a general review of the chemistry of vicinal polyketones see Rubin, M. B. *Chem. Rev.* **1975**, *75*, 177.

(7) Horner, L.; Maurer, F. *Ann.* **1970**, *736*, 145. *Idem. Chem. Ber.* **1968**, *101*, 1783.

(8) Fischer, E. (deceased), Weizmann Institute, personal communication.

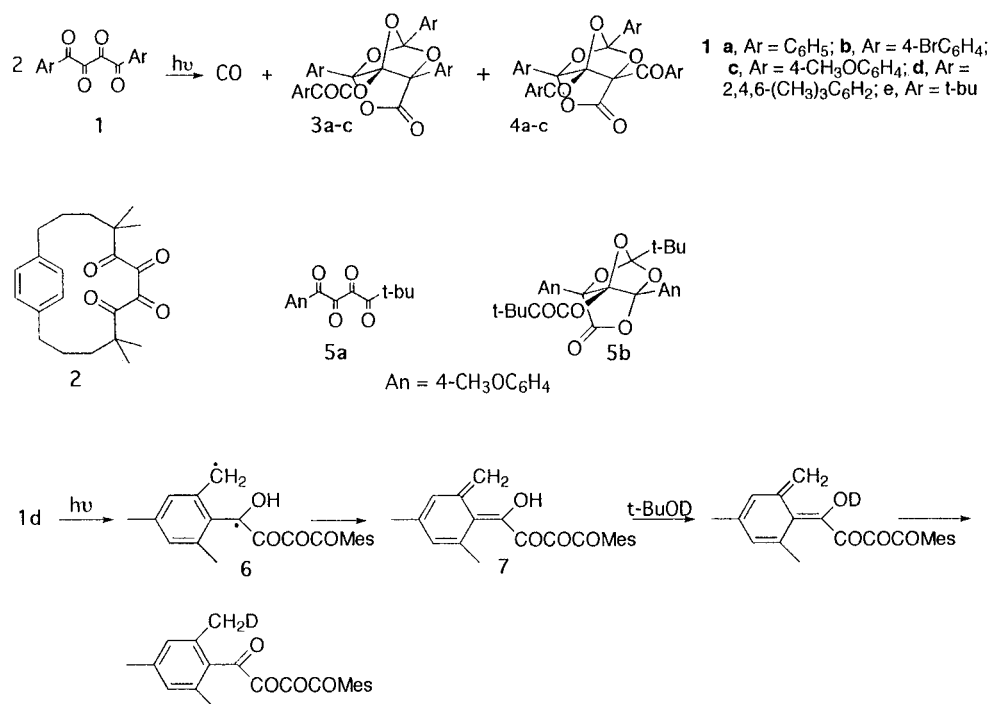
(9) Diphenyl tetraketone: Beddoes, R. L.; Cannon, J. R.; Heller M.; Mills, O. S.; Patrick, V. A.; Rubin, M. B.; White, A. H. *Aust. J. Chem.* **1982**, *35*, 543. Dimesityl tetraketone: Kaftory, M.; Rubin, M. B. *J. Chem. Soc., Perkin Trans. 2* **1983**, 149.

(10) The equilibrium constant for hydration of **1a** to its monohydrate in dioxane containing traces of water at 25 °C has been determined to be on the order of 1000, M. Heller, M. Sc. thesis, Technion.

(11) Gleiter, R.; Kramer, R.; Irngartinger, H.; Bissinger, C. *J. Org. Chem.* **1992**, *57*, 252.

(12) Kramer, R., Technion, unpublished results.

## Scheme 1



rapidly through short columns of neutral alumina or chromatographed carefully on silica gel columns. Slow decomposition occurred on both types of columns as indicated by loss of material. Crystallization of alumina washings from di-*p*-bromo (**1b**) and di-*p*-anisyl (**1c**) tetraketones gave pure, yellow crystalline products (**3b** 74%, **3c** 82%). The product from **1b** was shown to be the tricyclic lactone **3b**, a very unexpected result, by X-ray crystallographic analysis.<sup>13</sup> The structure includes  $\alpha$ -diketone,  $\gamma$ -lactone, and ortho ester moieties in a rigid molecule derived from two flexible open-chain tetraketones with loss of one molecule of carbon monoxide. Prior to the X-ray structure determination, we had explored a number of reductive degradation procedures with no success, a result which is not surprising in view of the sensitive functional groups present. Considerable spectroscopic data (see Experimental Section) in the UV-vis, IR, <sup>1</sup>H and <sup>13</sup>C NMR were diagnostic of the tricyclic system present and served to establish the structures of compounds of this type. The product from **1c** exhibited four *O*-methyl resonances in the <sup>1</sup>H NMR spectrum, consistent with the presence of four different aryl groups. We note the  $\gamma$ -lactone band in the IR at 1810–1820 cm<sup>-1</sup> in all cases. Electron impact mass spectra generally did not show the molecular ion; the most intense *m/z* peak corresponded to loss of carbon monoxide or carbon dioxide.

Silica gel chromatography of the photoproduct from **1a** afforded the expected yellow **3a** (63%) and a second, colorless product **4a** (6%). The structure **3a** was assigned on the basis of spectroscopic properties as discussed above. Isomeric **4a** was a colorless compound lacking the second carbonyl group of an  $\alpha$ -diketone moiety, but showing the appropriate spectroscopic data for  $\gamma$ -lactone and ortho ester moieties. The presence of two benzoyl groups was inferred from the enhanced extinction coefficient (20000) at 260 nm and from the <sup>13</sup>C NMR. As

Table 1. Quantum Yields for Disappearance of Tetraketones at 546 nm in Toluene Solution

TK (1)	concn (M × 10 <sup>3</sup> )	anthracene (M × 10 <sup>2</sup> )	$\Phi_{546}$
a	3.4	—	0.016
a	3.6	1.8	0.015
a	3.4	3.4	0.015
a	2.7	5.3	0.014
b	2.1	—	0.022
b	1.8	1.8	0.021
c	3.1	—	0.013

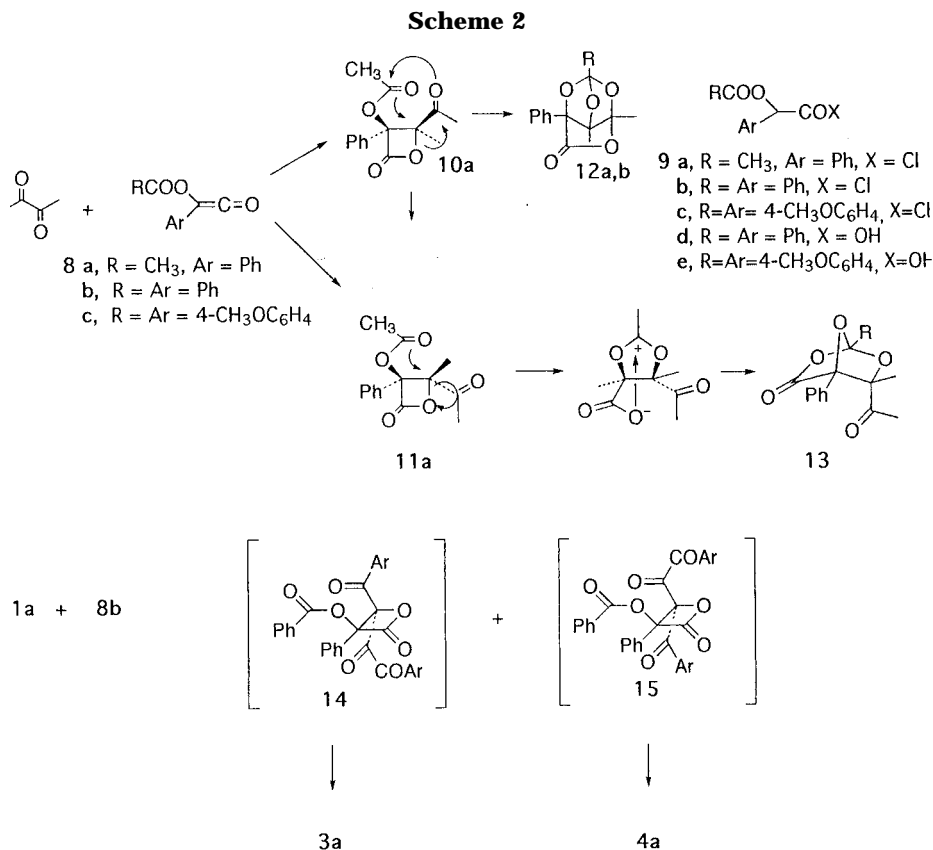
noted above, TLC analysis of crude reaction products showed major and minor spots of very similar *R<sub>f</sub>* value, and these were assigned to **3a** and **4a**, respectively. Products analogous to **4a** may be formed to a minor extent in photolyses of other tetraketones.

Photolysis of the unsymmetrical compound, *p*-anisyl *tert*-butyl tetraketone (**5a**), was also investigated. A priori, four different tricyclic lactones analogous to compounds **3** and four of type **4** could be formed in this reaction. In the event, we were able to isolate only one pure product in 20% yield. This yellow compound **5b** exhibited the expected diketone and  $\gamma$ -lactone absorptions but no anisoyl absorption. It is tentatively assigned structure **5b** on the basis of its spectroscopic properties. Since 80% of the reaction remains unknown, it is not possible to draw any conclusions regarding preferred modes of reaction from this result.

Quantum yield data for disappearance of tetraketones upon irradiation at 546 nm, calculated from the decrease in the long wavelength maximum, are summarized in Table 1. We note that the values for the three compounds measured are nearly identical even for bromine-containing **1b**. Quantum yields for reaction of **1a** were independent of light intensity over the range 1.7–5.4 × 10<sup>-6</sup> einstein/min<sup>14</sup> and of tetraketone concentration over the range 1.2–5.2 × 10<sup>-3</sup> M. The quantum yield for disap-

(13) Kaftory, M. *Acta Crystallogr.* **1979**, B35, 1717.

(14) Total light intensity on a 0.9 × 2.7 cm area of the cell.



pearance of **1a** at 366 nm was 0.08. The results obtained in the presence of added anthracene ( $E_T$  42 kcal/mol<sup>15</sup>) show that this potential triplet quencher has no effect on quantum yield, suggesting that reaction proceeds from the first excited singlet state of **1a**. In the absence of information on the triplet energy of tetraketones, this conclusion must be regarded as tentative. It is, however, supported by the observation that quantum yields were identical in the presence or absence of oxygen.

The failure of **1d** to undergo photochemical change could be due to a competing reaction, intramolecular abstraction of a hydrogen atom from an *o*-methyl group. This process is well-known with *o*-alkyl-substituted benzophenones<sup>16</sup> and has also been shown to occur with analogous  $\alpha$ -diketones.<sup>17</sup> This behavior could be demonstrated by irradiation of a solution of **1d** in toluene containing *tert*-butyl-OD and recovery of the "unreacted" starting material. The recovered tetraketone had incorporated a significant amount of deuterium in an *o*-methyl group, as shown by NMR and MS analysis. This is suggested to occur via H-atom abstraction to form biradical **6**.<sup>18</sup> Exchange with *tert*-butyl-OD can occur with **6** or with the subsequently formed enol **7**; in either case, ketonization will regenerate tetraketone incorporating a deuterium atom. A similar explanation or steric effects of the *tert*-butyl groups could be possible for the failure of **1e** to undergo photochemical change.

### Mechanism

We have found a single example in the literature of the tricyclic lactone skeleton present in the tetraketone photoproducts. In 1982 Dominguez and Cava<sup>19</sup> (Scheme 2) reported that reaction of biacetyl with phenylacetoxycarbonyl chloride (**9a**), generated *in situ* by reaction of  $\alpha$ -phenyl- $\alpha$ -acetoxyacetyl chloride (**8a**) with triethylamine, gave crystalline  $\beta$ -lactone **10a** (1840  $\text{cm}^{-1}$ ) in 30% yield (not optimized). Heating **10a** above its melting point, or distillation of crude reaction product from the reaction of biacetyl with **8a**, afforded a single crystalline substance in high yield. This was assigned structure **12a** on the basis of analytical data and spectroscopic properties; it incorporates the lactone ortho ester features of our tetraketone photoproducts. The mechanism suggested by Cava (Scheme 2) involves initial cycloaddition between ketene and one of the carbonyl groups of biacetyl. Two isomeric  $\beta$ -lactones, **10a** and **11a**, are possible from such a cycloaddition. In **10a**, where acetyl and acetoxy groups are in a *cis*-relationship, rearrangement to  $\gamma$ -lactone **12a** can occur as illustrated. The preferential formation of **10a** having this required *cis* relationship was attributed to secondary orbital interactions. Isomeric **11a**, in which acetyl and acetoxy groups are *trans*, would rearrange without involvement of the acetyl group to bicyclic lactone **13** possessing an intact acetyl group; this was not observed. We had no difficulty in repeating Dominguez and Cava's results and also found that an analogous reaction of (benzoyloxy)phenylketene (**8b**), prepared from the corresponding acid chloride, with biacetyl gave tricyclic lactone **12b**, isolated in 54% yield after chromatography on silica gel.

(15) Evans, D. *J. Chem. Soc.* **1957**, 1351. Lewis, G. N.; Kasha, M. *J. Am. Chem. Soc.* **1944**, *66*, 2100.

(16) Sammes, P. G. *Tetrahedron*, **1976**, *32*, 405. For a recent reference see Hopf, H.; Laue, T.; Zander, M. *Angew. Chem., Intl. Ed. Engl.* **1991**, *30*, 432.

(17) For a summary see Rubin, M. B. *Top. Curr. Chem.* **1985**, *129*, 1.

(18) The initial H-atom abstraction need not be by the carbonyl group adjacent to the aromatic ring since there will be a rapid equilibrium between ketyl radicals.

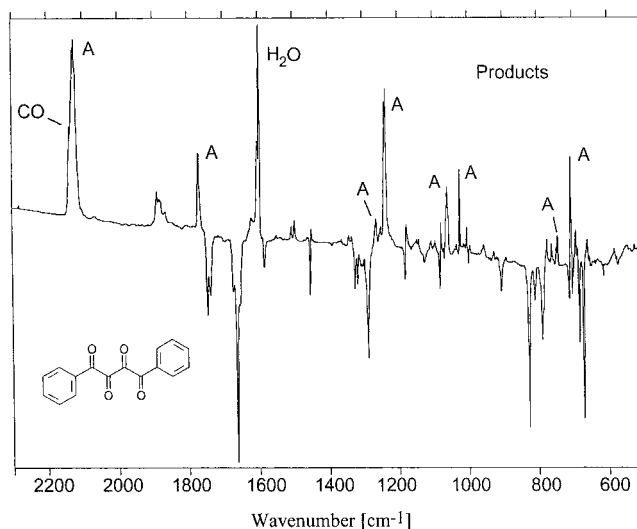
(19) Dominguez, F.; Cava, M. P. *Tetrahedron Lett.* **1982**, 5513.

The Cava mechanism described above can also apply to the reaction of ketenes with tetraketones. Addition of **8b** to tetraketone would be expected to occur at one of the more reactive<sup>6</sup> central carbonyl groups of **1** and could produce two stereoisomeric  $\beta$ -lactones **14** and **15**. In **14**, benzoyl and benzoyloxy groups are in the cis relationship; the product of rearrangement to  $\gamma$ -lactone should be identical with the major product **3a** of photolysis of tetraketones. Isomeric **15** has a phenylglyoxyl moiety cis to benzoyloxy; the product of its rearrangement would then have the structure of the minor photoproduct **4a**. Gratifyingly, reaction of **8b** with **1a** indeed produced two products identical with **3a** and **4a** in yields similar to those obtained in the photolysis reaction; the ratio **3a**:**4a** was 10:1. Similar reaction of (anisoyloxy)anisylketene (**8c**) with tetraketone **1c** gave photoproduct **3c** in 85% yield, and no isomeric product was isolated in this case. Further reactions of **8b** are described later in this report.

These results clearly establish that reactions of appropriate ketenes with tetraketones yield the same products as do photoreactions of tetraketones. They do not prove that ketenes are formed photochemically from tetraketones and are intermediates in the photoreactions, only that if ketenes were formed, they would react thermally to give the observed products. Attempted trapping of a ketene intermediate by irradiation of solutions of **1a** containing added cyclopentene, benzhydrol, diphenyl triketone, or biacetyl resulted in formation of **3a** and **4a** alone. Preliminary evidence supporting the intermediacy of ketenes was obtained when the reaction of **1a** was performed at low temperatures in toluene solution in a UV cell. In a narrow range of temperature, approximately  $-80$  to  $-100$  °C, a new absorption ( $\lambda_{\text{max}} \sim 510$  nm) appeared. At lower temperatures, the photoreaction was very slow and at higher temperatures the new absorption disappeared rapidly and was difficult to observe. Unfortunately, it was not possible to achieve a high degree of conversion because spectra of **1a** and the new intermediate overlapped, and the new intermediate underwent further photochemical reaction. Similar spectroscopic behavior with a maximum at the same wavelength was observed when triethylamine was added to a solution of ketene precursor in toluene at  $-80$  °C.

Definitive results were obtained in Braunschweig by irradiation of **1a** in an argon matrix at 10 K. The difference IR spectrum from irradiation at  $\lambda \geq 360$  nm is shown in Figure 1. It exhibits a shoulder at  $2135$   $\text{cm}^{-1}$ , assigned to CO, and strong absorptions at  $2128$  (100, rel intensity),  $1771$  (45),  $1266$  (35),  $1240$  (90),  $1237$  (56),  $1026$ , and  $709$  ( $64$ )  $\text{cm}^{-1}$ , assigned to ketene **8b** formed by photochemical reaction of tetraketone. On irradiation at shorter wavelengths ( $\lambda \geq 330$  nm), the bands for **8b** disappeared and new absorptions at  $1678$ ,  $1311$ ,  $1214$ ,  $1178$ ,  $944$ ,  $922$ ,  $702$ ,  $647$ , and  $640$   $\text{cm}^{-1}$  grew in, consistent with the results observed in toluene solution at  $-80$  °C. Simultaneously with the decay of **8b**, larger amounts of CO and  $\text{CO}_2$  were formed.

If the photochemical reaction of tetraketones proceeds from a singlet state as suggested earlier, the formation of (benzoyloxy)phenylketene from such a singlet could be a concerted, cyclic process as illustrated (Scheme 3). Alternative stepwise mechanisms involving biradical **16** or zwitterionic intermediates such as **17** are also possible and would be required from the triplet state. The failure of cyclic tetraketone **2** to react photochemically is presumably due to the fact that a cyclic mechanism is not



**Figure 1.** Argon matrix IR difference spectrum (product bands upward) showing the photochemistry of **1a** upon irradiation at 10 K with  $\lambda \geq 360$  nm. Bands labeled A are assigned to ketene **8b**.

feasible. It is interesting to compare the formation of **8b** from **1a** with the photochemical reaction of *cis*-dibenzoyl ethylene (**18**) which also has terminal benzoyl groups as part of a four-carbon chain. In this case, phenyl migration from the singlet state is observed to give a ketene<sup>20</sup> as illustrated. However, if a similar phenyl migration occurred in the case of tetraketones (cf. Scheme 3), the products would be two molecules of CO or the elusive ethylenedione<sup>21</sup> and phenoxyphenylketene. The latter is not consistent with the observed results; the difference in behavior could be due to differing geometries of excited states.

An alternative mechanism for photochemical formation of **8b** involves initial  $\alpha$ -cleavage of tetraketone (Scheme 3). This would produce either a pair of phenylglyoxyl radicals **19** or a benzoyl radical plus triketo radical **20**. Facile decarbonylation of **19** or **20** would produce<sup>22</sup> benzoyl and phenylglyoxyl radicals, possibly still in the original solvent cage. Subsequent coupling of these two radicals could lead to **8b**. However, it seems likely that such a coupling should also produce photochemically inert<sup>3</sup> diphenyl triketone (**21**). Triketones have not been observed in any tetraketone photolysis. Further, benzil might be expected to be formed by coupling of benzoyl radicals, but none could be detected even though benzil does not react (v.i.) with **8b**. We note that analogous  $\alpha$ -cleavage is not observed<sup>2</sup> with vic-di- or triketones.

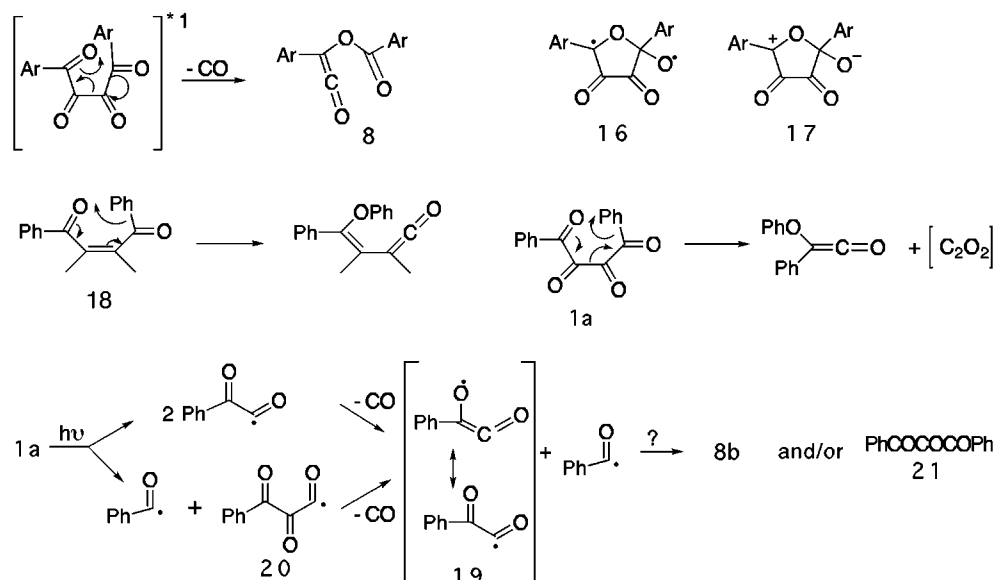
The failure to obtain products analogous to **4a** in other photolyses and in some of the thermal reactions of **8b** with tetraketones may be the result of failure of chromatographic separation, particularly in view of the lability of the tricyclic lactones on silica gel or alumina columns. The only other case in which a significant amount of product analogous to **4** was formed was the reaction of **8b** with **1d** where steric factors may be involved. The ratio **3d**:**4d** was unity in this case.

(20) Griffin, G. W.; O'Connell, E. J. *J. Am. Chem. Soc.* **1962**, *84*, 4148. Zimmerman, H. E.; Durr, H. G. C.; Lewis, R. G.; Bram, S. *Ibid.* **1962**, *84*, 4149. Barik, R.; Bhattacharya, K.; Das, P. K.; George, M. V. *J. Org. Chem.* **1986**, *51*, 3420 and references therein.

(21) Rubin, M. B.; Patyk, A.; Sander, W. *Tetrahedron Lett.* **1988**, *29*, 6641.

(22) These radicals might be close to one another in a solvent cage.

Scheme 3



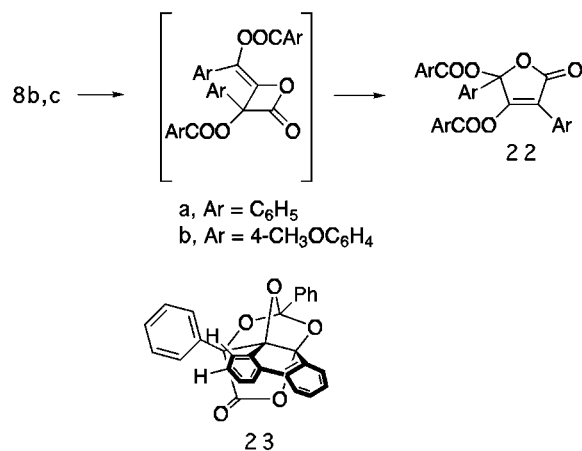
We have previously reported<sup>3</sup> single electron transfer (SET) when diphenyl triketone was irradiated in the presence of DABCO or *p*-dimethoxybenzene. Rates of photolysis were enhanced in the presence of these electron donors and exclusive formation of benzil was observed. Attempts to observe similar SET with **1a** were not successful. The photochemical reaction in the presence of dimethoxybenzene produced the same products as observed in its absence. A similar experiment with DABCO was precluded by the observation of decomposition of **1a** in the presence of DABCO, and no identifiable products were obtained.

#### Additional Reactions of Ketene **8b**

It appeared of interest to examine additional reactions of the novel type of ketene<sup>23</sup> obtained in the present work. To our knowledge, such compounds have not been described previously except for the preliminary report of Dominguez and Cava describing acetoxyphenylketene. In all cases, **8b** or **8c** was generated by reaction of equimolar amounts of the appropriate acid chloride with triethylamine in benzene solution at room temperature.

**A. Dimerization.** Generation of **8b** in benzene or toluene at room-temperature resulted in appearance of a red color ( $\lambda_{\text{max}}$  510 nm) and separation of crystalline amine hydrochloride. After 3 h at room temperature, the color had faded to pale yellow, and workup provided a white solid, mp 116–117 °C, in 74% yield. A higher melting form (mp 144–145 °C) was obtained upon recrystallization. Both products had identical solution spectra. The structure of the higher melting form was established as **22a**, a dimer of starting ketene (Scheme 4), by X-ray crystallographic analysis; the ORTEP diagram of **22a** together with selected bond lengths and angles are shown in Figure 2, and details of the structure analysis are provided in the Experimental Section and

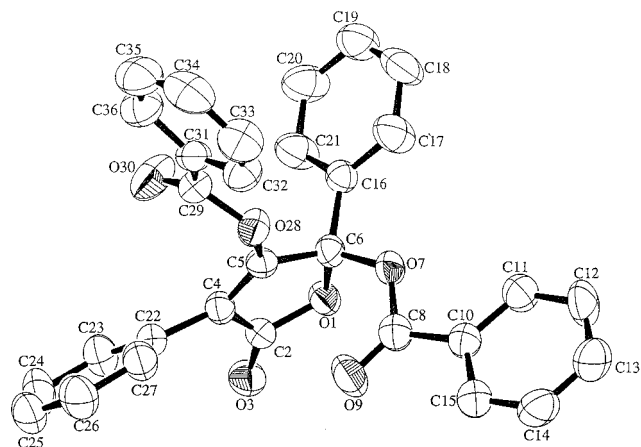
Scheme 4



the Supporting Information.<sup>24</sup> This product may have resulted from rearrangement of an initially formed  $\beta$ -lactone such as that illustrated (or a stereoisomer). Intermediacy of 1,3-cyclobutanediones, often formed in dimerization of disubstituted ketenes, does not seem reasonable. A noncrystalline dimer, **22b**, was obtained from **8c**, and spectroscopic properties suggest that its structure is analogous to that of **22a**. We note that Dominguez and Cava obtained an intractable gum from attempted dimerization of acetoxyphenylketene under similar conditions. The dimerization of **8b** limits the possibility of observing its products of reaction in some cases and provides an internal “clock” which allows qualitative comparison of rates of reaction of various compounds with the ketene. The much greater reactivity of tetraketones is evidenced by the fact that dimeric products were not observed in any of the reactions with tetraketones in contrast to the results with other compounds as discussed below. Also, tetraketone photolyses in the presence of added di- or triketones yielded only the tetraketone photoproducts.

(23) For summaries of ketene chemistry see: Borrmann, D. *Methoden der Organischen Chemie (Houben-Weyl)*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1968; vol VII/4. Tidwell, T. *Ketenes*; Wiley: Chichester, 1995.

(24) M. Kapon has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

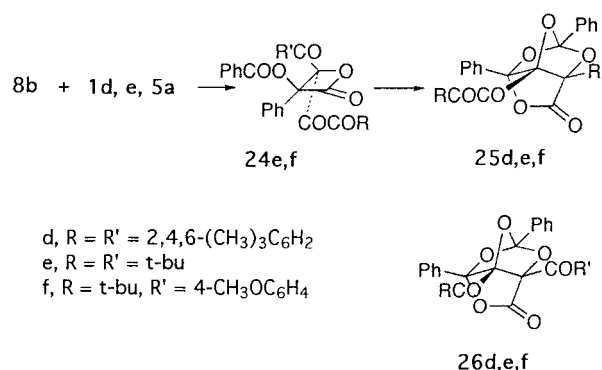


**Figure 2.** ORTEP diagram of **22a**, the dimer of ketene **8b**. Hydrogen atoms are omitted for clarity. Bond lengths (Å): O(1)–C(2) 1.379(3), O(1)–C(6) 1.437(3), C(2)–O(3) 1.202(3), C(2)–C(4) 1.469(4), C(4)–C(5) 1.317(4), C(5)–O(28) 1.376(3), C(5)–C(6) 1.501(4), C(6)–O(7) 1.423(3). Selected bond angles (deg): C(2)–O(1)–C(6) 109.0(2), O(3)–C(2)–O(1) 119.5, O(3)–C(2)–C(4) 130.6(3), O(1)–C(2)–C(4) 109.9(3), C(5)–C(4)–C(2) 105.5, C(4)–C(5)–O(28) 131.2(3), C(4)–C(5)–C(6) 112.8(3), O(28)–C(5)–C(6) 116.0(2), O(7)–C(6)–O(1) 109.1(2), O(7)–C(6)–C(5) 114.3(2), C(5)–C(6)–O(1) 102.6(2).

**B. Reaction of **8b** with Monoketones and  $\alpha$ -Diketones.** Only dimer formation was observed when **8b** was generated in the presence of excess acetone or acetophenone. As noted earlier, **8b** reacted readily with biacetyl to give the tricyclic lactone **12b**. However, in contrast to the reaction of **8a** with biacetyl, where intermediate  $\beta$ -lactone could be isolated by trituration of crude reaction product, no crystalline  $\beta$ -lactone could be obtained from reaction of **8b**. Benzil, in contrast to biacetyl, was unreactive with **8b** affording recovered benzil, a trace of benzoin benzoate, and the dimer **22a**. Dominguez and Cava reported a failure to observe a product from reaction of benzil with acetoxyphenylketene. These results support the view that reaction of ketenes with tetraketones occurs at a central, more reactive carbonyl group. Reaction with 9,10-phenanthrenequinone (PQ) was also investigated. A labile, crystalline product was obtained in crude yield of 81%. It is tentatively assigned structure **23** on the basis of its spectroscopic properties.

**C. Reaction with Tetraketones.** In addition to the reactions of **8b** with **1a** and of **8c** with **1c** described earlier in connection with the mechanism of photolysis, reactions of **8b** with **1d–f** were also investigated. In two cases (**1e,f**), trituration of the crude reaction product afforded a crystalline yellow solid in about 50% yield (Scheme 5). Both of these products (**24e,f**) showed infrared maxima at about  $1840\text{ cm}^{-1}$  characteristic of  $\beta$ -lactones. Each  $\beta$ -lactone rearranged in chloroform solution at room temperature to a single, yellow  $\gamma$ -lactone (**25e,f**) whose structure was assigned as shown on the basis of spectroscopic properties and mechanism. The results observed with anisyl *tert*-butyl tetraketone (**1f**) suggest that initial addition of ketone occurs at the central carbonyl group furthest from the *tert*-butyl group. In addition, a low yield of an isomeric product having two monoketone functions instead of the  $\alpha$ -diketone group was obtained. The stereochemistry of the  $\beta$ -lactones is assigned as shown on mechanistic grounds as discussed above. Minor products in these reactions were the isomeric  $\gamma$ -lactones **26e** and **26f**. In contrast, no

### Scheme 5



$\beta$ -lactone could be observed in the reaction of **1d** with **8b**. The crude reaction product had infrared absorption at  $1820\text{ cm}^{-1}$  and consisted of a 1:1 mixture of  $\gamma$ -lactones **25d** and **26d** which could be separated by crystallization.

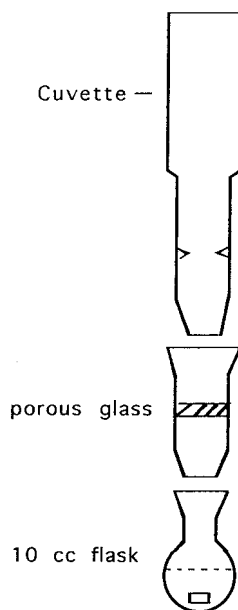
### Experimental Section

Melting points are uncorrected. Combustion analyses were performed by the Microanalytical Laboratory, Hebrew University, Jerusalem. <sup>1</sup>H NMR spectra were determined at 200 MHz in CDCl<sub>3</sub> and <sup>13</sup>C spectra at 100 MHz in CDCl<sub>3</sub> unless specified otherwise and are expressed in ppm from tetramethylsilane. Infrared spectra were determined with a Nicolet Impact 400 FT spectrometer using KBr pellets for solids and neat or in chloroform solution for noncrystalline materials. A Hewlett-Packard diode array instrument was used for UV-vis spectra. High-resolution mass spectra were measured with a Varian MAT-711 at 70 eV unless noted otherwise and low resolution spectra with a Finnigan TSQ 70.

**Irradiations.** Irradiations were performed in Pyrex vessels using a 200 W high-pressure mercury lamp (Osram HBO 200) in a Wild housing or a 900 W xenon lamp (Osram XBO-900) in a Schoeffel housing. A Schott interference filter was used to isolate the 546 nm mercury line. For preparative irradiations, analytical grade benzene was boiled briefly before use to ensure dryness, and solutions were bubbled with argon or nitrogen for 30 min before closing and starting irradiation. An 18 mm layer of 10% aqueous potassium chromate between the light source and the sample eliminated light of wavelength shorter than 500 nm. Quantum yields at 546 nm were determined in square Pyrex cells (light path 10 mm). Dry solutions of tetraketone in toluene were prepared by the procedure described below. Light intensities incident on a 9 × 27 mm area of the cell were on the order of  $1 \times 10^{-6}$  einstein/min. The actinometer was the colored form of Aberchrom 540.<sup>25</sup>

**Sample Preparation.** The extremely anhydrous conditions required for quantitative measurements with tetraketones were achieved by the use of the apparatus shown in Figure 3, consisting of a 10 mm square Pyrex cell fused to a length of tubing with a constriction (for sealing off) and a standard taper joint. This was connected to a tube with a coarse fritted disk which in turn connected via a standard taper joint to a 10 mL round-bottomed flask containing a magnetic stirring bar. The appropriate amount of tetraketone, carefully dried solvent, and phosphorus pentoxide (10–15 mg) were introduced into the flask, the apparatus was connected, and the flask was stirred for about 15 min. The flask was then inverted and the cell cooled in dry ice–acetone mixture so that the liquid flowed through the frit into the cell. The absorption spectrum was measured after warming to room temp, the apparatus inverted, and the round-bottom flask cooled so that the liquid flowed into it. The process was then

(25) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **1989**, *61*, 198. Cf also Wintgens, V.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 511.



**Figure 3.** Apparatus for obtaining dry solutions of tetraketones.

repeated until the spectrum of the filtered solution remained unchanged after further contact with phosphorus pentoxide. The apparatus was rapidly disassembled and the cell immediately closed or connected to a vacuum line, cooled, and sealed off. Freeze-pump-thaw degassing could be performed at this stage. The absorption spectrum of cells stored in the dark was measured at 1 day intervals, and only cells whose absorption spectrum remained unchanged were used for further work.

**Photolysis of Diphenyl Tetraketone (1a).** A degassed solution of **1a** (0.69 g, 0.0023 mol) in benzene (10 mL) was irradiated for 48 h with light from the 200 W mercury lamp filtered through an 18 mm layer of 10% aqueous potassium chromate. Bubbles of gas evolved during this time, and the red color faded to pale yellow. A commercial carbon monoxide detector gave a positive test in the headspace of the cell. After removal of solvent, the residue was chromatographed on silica gel (35 g), eluting with hexanes-ethyl acetate (50:1) to give two crystalline products: **3a** (0.37 g, 63%) and **4a** (0.034 g, 6%).

The major product, **3a**, was a yellow solid, mp 93–95 °C. IR, 1820, 1733, 1662  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR, 83.19, 99.60, 106.48, 122.19, 126.92, 126.98, 127.87, 128.02, 128.41, 128.56, 128.69, 129.32; 129.84, 130.39, 130.53, 131.05, 131.66, 135.21, 168.23, 187.70 ppm. UV ( $\text{CH}_3\text{CN}$ ), 268 (6800), 280 (6600), 398 (50) nm. MS,  $m/z$  460.1311; calcd for  $\text{C}_{30}\text{H}_{20}\text{O}_5$  ( $\text{M} - \text{CO}_2$ ) 460.1314. Anal. Calcd for  $\text{C}_{31}\text{H}_{20}\text{O}_7$ : C, 73.80, H, 4.00. Found: C, 73.65; H, 4.21.

The minor product, **4a**, was a white solid, mp 172–174 °C. IR, 1824, 1686, 1667  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR 83.70, 97.96, 108.61; 123.53; 126.99, 127.66, 127.90, 128.19, 128.44, 128.72, 129.20, 129.75, 130.78, 131.48, 131.81, 133.75, 135.03, 135.54, 167.99; 185.44, 191.23 ppm. UV ( $\text{CH}_3\text{CN}$ ), 260 (22000) nm. MS,  $m/z$  476.1266, calcd for  $\text{C}_{30}\text{H}_{20}\text{O}_6$  ( $\text{M} - \text{CO}$ ) 476.1259. Anal. Calcd for  $\text{C}_{31}\text{H}_{20}\text{O}_7$ : C, 73.80, H, 4.00. Found: C, 73.40, H, 4.06.

**Photolysis of Di-*p*-bromophenyl Tetraketone (1b).** Dry benzene (ca 50 mL) was distilled on the vacuum line into a cylindrical vessel containing tetraketone (7.0 g) and the solution irradiated with the 900 W lamp until gas evolution ceased and the color faded to pale yellow. Evaporation of solvent gave crude product (6.90 g) which afforded **3b** (5.26 g, 82%) after washing rapidly through neutral alumina (20 g) with methylene chloride. A sample was crystallized from methylene chloride-cyclohexane and then from ether to give the pale yellow analytical sample of **3b**, mp 161–163 °C. IR, 1817, 1729, 1664  $\text{cm}^{-1}$ .  $^{13}\text{C}$  NMR, 82.90, 99.73, 106.22, 122.18,

125.22, 126.06, 126.63, 126.93, 128.24, 128.70, 128.81, 129.04, 129.88, 129.96, 131.27, 132.12, 132.28, 132.42, 132.61, 167.37, 187.02 ppm. UV ( $\text{CH}_3\text{CN}$ ) 230 (42800), 302 (7100) nm. MS, CI (isobutane), 872, 874, 876, 878, 880 (relative intensities 1:4:6:4:1). Anal. Calcd for  $\text{C}_{31}\text{H}_{16}\text{O}_7\text{Br}_4$ : C, 45.40, H, 1.97, Br, 38.97. Found: C, 45.18, H, 2.23, Br, 38.77.

**Photolysis of Di-*p*-anisyl Tetraketone (1c).** A solution of **1c** (20 g) in dry benzene (300 mL) was irradiated under nitrogen with the 900 W lamp for 70 h when the characteristic red color of starting material had disappeared. Evolution of bubbles of gas occurred throughout the irradiation. The yellow solution was concentrated in vacuo, a small sample withdrawn for spectroscopic analysis, and the remainder washed through neutral alumina (48 g) with methylene chloride (350 mL). Removal of solvent gave material (13.4 g, 74%) which crystallized on standing; crystallization from methylene chloride-hexane gave pure **3c** (11.3 g), mp 145.5–146.5 °C. Spectra (IR, NMR) of crude product and pure **3c** were very similar. The analytical sample of **3c** was prepared by further crystallization from methylene chloride-hexane, mp 146–7 °C. IR, 1811, 1728, 1648, 1616, 1592  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR, 3.66 (s, 3H), 3.74 (s, 3H), 3.80 (s, 3H), 3.86 (s, 3H), 6.66 (d,  $J = 6.4$  Hz, 2H), 6.72 (d,  $J = 6.4$  Hz, 2H), 6.84 (d,  $J = 8$  Hz, 2H), 7.02 (d,  $J = 8$  Hz, 2H), 7.28 (d,  $J = 8$  Hz, 2H), 7.45 (d,  $J = 8$  Hz, 2H), 7.65 (d,  $J = 8$  Hz, 2H), 7.88 (d,  $J = 8$  Hz) ppm.  $^{13}\text{C}$  NMR, 55.13, 55.39, 55.55, 82.82, 99.51, 106.21, 113.70, 113.90, 120.13, 121.55, 121.89, 123.17, 123.50, 128.31, 128.50, 129.46, 132.53, 160.47, 161.03, 161.93, 165.17, 168.66, 186.04, 186.86 ppm. UV ( $\text{CH}_3\text{CN}$ ) 328 nm (10000) nm. Anal. Calcd for  $\text{C}_{35}\text{H}_{28}\text{O}_{11}$ : C, 67.30, H, 4.26. Found: C, 67.50, H, 4.32.

**Photolysis of *tert*-Butyl *p*-Anisyl Tetraketone (5a).** A solution of **5a** (0.011 mol) in benzene (80 mL) was irradiated with light from the 900 W lamp until complete disappearance of the long wavelength maximum at 518 nm. The oil obtained after evaporation of solvent was chromatographed on silica gel with hexanes-ethyl acetate (20:1) to give yellow crystalline **5b** (0.26 g, 20%), mp 165–167 °C. IR, 1810, 1740, 1715, 1700, 1615  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR, 0.66 (s, 9H), 1.38 (s, 9H), 3.75 (s, 3H), 3.76 (s, 3H), 6.84 (d,  $J = 8$  Hz,  $J = 8$  Hz, 4H), 7.34 (d,  $J = 8$  Hz, 2H), 7.46 (d,  $J = 8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR, 24.89, 24.98, 34.33, 42.07, 55.23, 55.35, 81.82, 99.32, 106.03, 113.58, 113.73, 113.91, 121.92, 123.74, 126.86, 128.11, 129.29, 160.32, 161.02, 169.11, 202.39 ppm. UV, 236 (25000), 268 (2000), 420 (24) nm. Anal. Calcd for  $\text{C}_{29}\text{H}_{32}\text{O}_9$ :  $m/z$  524.2046, C, 66.40; H, 6.15. Found: C, 66.77, H, 6.24,  $m/z$  524.2081.

**Irradiation of Dimesityl Tetraketone (1d).** A. **In Toluene Solution.** A solution of **1d** in approximately 3 mL of toluene in a cuvette was irradiated for 16 h with the 200 W lamp. The absorbance at 512 nm decreased from 1.30 to 1.28.

B. **In Toluene Solution Containing *t*-BuOD.** A solution of tetraketone (10.6 mg) in toluene (3.5 mL) was dried over  $\text{P}_2\text{O}_5$  in the standard manner in a Pyrex cell fitted with a standard taper joint. The cell was immediately connected to the vacuum line, *tert*-butyl alcohol-OD (0.37 g) distilled in, and the cell sealed off. The absorbance at 512 nm after sealing was 1.285. The solution was irradiated with the 200 W lamp for 16 h under the usual conditions. Final absorbance was 0.9 at 512 nm. The cell was opened, and solvents were evaporated. Determination of the proton-decoupled  $^{13}\text{C}$  NMR spectrum of a sample showed a triplet centered at 20.44 ppm with couplings of 27 and 32 Hz which is assigned to the  $\text{CH}_2\text{D}$  group replacing an *o*- $\text{CH}_3$  group (20.35 ppm) in the mesityl moiety. A second sample was subjected to mass spectroscopic analysis. The ratio of the mesityl peaks at  $m/z$  147 and 148 was 4.7:1 in the irradiated sample as compared to 8.5:1 in the starting material.

**2-Phenyl-2-(benzoyloxy)acetic Acid (9d).**<sup>26</sup> A solution of methyl 2-phenyl-2-(benzoyloxy)acetate<sup>27</sup> (methyl ester of the

(26) Angus, W. R.; Owen, R. P. *J. Chem. Soc.* **1943**, 227 reported isolation of a compound mp 115 °C from reaction of mandelic acid and benzoyl chloride to which they assigned the structure **9d**. Repetition of this procedure in our hands afforded a product of similar melting point which, however, could be shown by spectroscopic properties to be impure benzoic acid and could be purified by recrystallization to give pure benzoic acid, mp 122 °C, identical with an authentic sample.

benzoate of mandelic acid, 6 g, 0.022 mole) in dioxane (200 mL) in a three-necked flask maintained at water pump vacuum (ca. 15 mm) and a 1% solution (180 mL) of potassium hydroxide in water was added through an equalizing arm dropping funnel with magnetic stirring during 15 min. Stirring was continued for 40 min while maintaining the vacuum. The flask was disconnected from the vacuum, and ether (200 mL) was added. After cooling to 10 °C, 1% hydrochloric acid solution (125 mL) was added with stirring. The ether layer was separated, washed with water, and dried over sodium sulfate, and the ether was removed with a rotary evaporator. Hexane (50 mL) was added to the residual oil. After standing in the refrigerator, a white solid separated. Filtration and drying afforded 4.5 g (78%) of **9d**. Crystallization from ether-hexane yielded 4.2 g, mp 98–100 °C. IR, (CHCl<sub>3</sub>) 1600, 1720, 3000–3500 cm<sup>-1</sup>. <sup>1</sup>H NMR, 6.14 (1H), 7.39–7.56 (m, 8H), 8.09 (d, *J* = 8 Hz, 2H), 8.99 (1H) ppm. MS, *m/z* 256 (M<sup>+</sup>). Anal. Calcd for C<sub>15</sub>H<sub>12</sub>O<sub>4</sub>: C, 70.31; H, 4.72. Found: C, 70.63; H, 4.68.

**α-(Benzoyloxy)-α-phenylacetyl Chloride (9b).** The acid chloride was prepared by heating **9d** (4.49 g) with excess freshly distilled thionyl chloride (2.7 mL) for 1 h at 80 °C. Distillation gave 3.57 g (74%) of **9b**, bp (0.1 mm) 150–2 °C. The product crystallized on standing, mp 46–48 °C. IR<sub>max</sub> (CHCl<sub>3</sub>), 1725, 1800 cm<sup>-1</sup>. <sup>1</sup>H NMR, 6.31 (1H), 7.42–7.60 (m, 8H), 8.10 (d, *J* = 8 Hz, 2H) ppm.

**Methyl α-(*p*-Anisoyloxy)-α-*p*-anisylacetate.** A solution of *p*-anisoyl chloride (4.43 g, 0.026 mol) in dry ether (5 mL) was added dropwise with stirring at room temp to a solution of methyl *p*-methoxymandelate<sup>28</sup> (5.14 g, 0.026 mol) and pyridine (2.07 g, 0.026 mol) in dry ether (30 mL) over 30 min. The mixture was stirred for 24 h, precipitated pyridinium hydrochloride was filtered off, and the solvents were removed in vacuo. The crude product was crystallized from methanol to give diester (5 g, 60%), mp 95–96 °C. IR, 1610, 1710, 1745 cm<sup>-1</sup>. <sup>1</sup>H NMR, 3.72 (s, 3H), 3.79 (s, 3H), 3.82 (s, 3H), 6.89 (d, *J* = 8 Hz, 2H), 6.92 (d, *J* = 8 Hz, 2H), 7.47 (d, *J* = 8 Hz, 2H), 8.03 (d, *J* = 8 Hz, 2H) ppm. UV (CH<sub>3</sub>OH), 236 (13000), 260 (20000) nm. Anal. Calcd for C<sub>18</sub>H<sub>18</sub>O<sub>6</sub>: C, 65.45; H 5.49. Found: C, 65.81; H, 5.24.

**α-(*p*-Anisoyloxy)-α-*p*-anisylacetic Acid (9e).** The procedure described above for preparation of **9d** afforded acid **9e** in 70% yield, mp 109–110 °C. IR, 1710, 1725, 2700–3500 cm<sup>-1</sup>. <sup>1</sup>H NMR, 3.79 (s, 3H), 3.82 (s, 3H), 6.05 (s, 1H), 6.88 (d, *J* = 8 Hz, 2H), 6.91 (d, *J* = 10 Hz, 2H), 7.47 (d, *J* = 10 Hz, 2H), 8.02 (d, *J* = 8 Hz, 2H) ppm. UV (CH<sub>3</sub>OH), 232 (13000), 258 (19000) nm.

**α-(*p*-Anisoyloxy)-α-*p*-Anisylacetyl Chloride (9c).** Thionyl chloride (1.5 mL) in dry benzene (20 mL) was added dropwise to **9e** (3.94 g; 0.0125 mole) in benzene (30 mL). The mixture was refluxed for 40 min and cooled to room temp and solvent evaporated in vacuo. The oily residue crystallized slowly on standing. The crystals of **9c** (2 g, 50%) were separated and dried, mp 72–74 °C. Standing with methanol gave the methyl ester of **9e**, identical in all respects with the substance described above.

**Formation and Dimerization of (Benzoyloxy)phenylketene (8b).** Triethylamine (TEA) (0.5 mL, 3.6 mM) was added with a syringe to a solution of acid chloride **9b** (0.955 g) in dry benzene (10 mL). A deep red color appeared immediately, and a precipitate began to form. The mixture was left at room temp for 3 h when the color had completely disappeared. The precipitated triethylamine hydrochloride (TEA·HCl) (0.47 g, 100%) was filtered and washed with benzene (5 mL). The benzene solutions were concentrated to give an oil (0.8 g). Washing through silica gel (24 g) with 20:1 hexanes-ethyl acetate gave a white solid (**22a**, 0.55 g, 72%), mp 98–102 °C. Crystallization from 1:1 hexanes-ether (48 mL) gave 0.3 g of white solid, mp 116–117 °C. IR (KBr), 1672, 1740, 1726, 1795 cm<sup>-1</sup>. <sup>13</sup>C NMR, 101.36, 117.84, 125.32, 127.08, 127.32, 128.01, 128.61, 128.92, 129.20, 129.53, 129.99,

130.06, 130.50, 133.29, 134.69, 160.25, 160.87, 163.38, 167.60 ppm. UV (CH<sub>3</sub>OH), 276 (11500), 234 (30000) nm. Anal. Calcd for C<sub>30</sub>H<sub>20</sub>O<sub>6</sub>: C, 75.62; H, 4.23. Found: C, 75.23; H, 4.32.

Refluxing a sample (25 mg) in benzene for 1 h followed by evaporation gave a white solid, mp 144–145 °C. Crystallization from hexanes-ether gave white crystals of **22a**, mp 146–7 °C. IR (KBr), 1682, 1733, 1767, 1782 cm<sup>-1</sup>. UV (CH<sub>3</sub>OH), 276 (9000), 236 (22000) nm. The IR and <sup>1</sup>H NMR spectra in chloroform solution were identical with that of the material mp 116–117 °C described above.

When the reaction with TEA was performed in a UV cuvette, a maximum at 510 nm was observed.

**Crystal Data for 22a.** *T* 293 K, wavelength 0.71069 Å, crystal system monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 17.102(8), *b* = 12.086(6), *c* = 12.084(6) Å, β = 104.76°, *V* = 2415 Å<sup>3</sup> *Z* = 4, *D<sub>x</sub>* = 1.310 g cm<sup>-3</sup>, μ = 0.091 mm<sup>-1</sup>, *F*(000) 992, crystal size 0.15 × 0.22 × 0.35 mm, θ range for data collection 2.09–25.02°, index ranges -20 ≤ *h* ≤ 19, 0 ≤ *k* ≤ 14, 0 ≤ *l* ≤ 14, reflections collected 4459, independent reflections 4253 [*R*(int) = 0.0255], refinement method full-matrix least-squares on *F*<sup>2</sup>, number of parameters 405, goodness-of-fit on *F*<sup>2</sup> 1.078, final *R* indices [*I* > 2σ(*I*)] *R*1 = 0.061, *wR*2 = 0.099, *R* indices (all data) *R*1 = 0.126, *wR*2 = 0.125, largest diff peak and hole 0.153 and -0.170 eÅ<sup>-3</sup>.

**Reaction of Ketene 8b with Methanol.** Preparation of **8b** in toluene solution by reaction of acid chloride (0.325 g, 1.18 mM) with TEA (0.165 mL, 1.18 mM) at -80 °C afforded a deep red solution. After 4 h at -90 °C, methanol (5 mL) was added. The deep red color disappeared immediately. After warming to room temp, the solution was concentrated under reduced pressure, ether was added, and TEA·HCl (0.151 g, 98%) was removed by filtration. Evaporation gave a white solid which was washed through silica gel (10 g) with 8:1 hexanes-ether to give methyl α-phenyl-α-(benzoyloxy)acetate (0.256 g, 80%), mp 74–76 °C, identical with an authentic sample.

**Formation and Dimerization of *p*-Anisyl-*p*(anisoyloxy)ketene (8c).** TEA (0.26 mL, 0.0019 mol) was added with a syringe to a solution of acid chloride **9c** (0.63 g, 0.0019 mol) in dry toluene (5 mL) maintained at 0–3 °C. A deep violet color appeared immediately and a precipitate began to form. The mixture was stirred at 0–3 °C for 1 h when the color had disappeared completely. TEA·HCl was filtered (0.25 g, 100%) and washed with 5 mL of toluene. The filtrate and washings were concentrated at reduced pressure to give an oil (0.56 g). Washing through silica gel (17 g) with a mixture of hexanes-ethyl acetate (3:1) gave an oil (0.5 g, 76%). All attempts to crystallize failed. Prolonged drying of this oil in high vacuum resulted in a solid foam, **22b**. IR (CCl<sub>4</sub>), 1730, 1750 (sh), 1780 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>), 3.76 (s, 3H), 3.79 (s, 3H), 3.84 (s, 3H), 3.86 (s, 3H), 6.84 (d, *J* = 9 Hz, 2H), 6.92 (d, *J* = 8 Hz, 2H), 7.56 (d, *J* = 8 Hz, 2H), 7.68 (d, *J* = 8 Hz, 2H), 7.94 (d, *J* = 9 Hz, 2H), 8.01 (d, *J* = 8 Hz, 2H) ppm. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>), 3.00 (s, 3H), 3.07 (s, 6H), 3.14 (s, 3H), 6.36 (d, *J* = 10 Hz, 2H), 6.26 (d, *J* = 8 Hz, 2H), 6.59 (d, *J* = 8 Hz, 2H), 6.68 (d, *J* = 8 Hz, 2H), 7.75 (d, *J* = 8 Hz, 2H), 7.86 (d, *J* = 8 Hz, 2H), 7.99 (d, *J* = 8 Hz, 2H), 8.14 (d, *J* = 10 Hz, 2H) ppm. <sup>13</sup>C NMR, 55.20, 55.29, 55.48, 55.61, 101.37, 113.80, 114.04, 116.54, 119.42, 119.97, 121.71, 126.10, 126.75, 128.28, 129.43, 132.20, 132.81, 159.71, 160.04, 160.18, 160.57, 163.14, 163.89, 164.64, 168.21 ppm. Anal. Calcd for C<sub>34</sub>H<sub>28</sub>O<sub>16</sub>: C, 68.45, H, 4.73. Found: C, 68.22, H, 4.92.

**Reactions of Ketene 8b with Carbonyl Compounds.**

**General Procedure.** Equivalent amounts of carbonyl compound, triethylamine (TEA), and acid chloride in benzene (1 mL per 50 mg of carbonyl compound) were used. Triethylamine was added dropwise with a syringe at room temp to a stirred solution of carbonyl compound and 2-(benzoyloxy)phenylacetyl chloride in benzene. After 1 h, triethylamine hydrochloride was filtered off and washed with benzene, and the combined benzene solutions were evaporated to dryness.

**Ketene with Diphenyl Tetraketone (1a).** Reaction of 0.41 g of **1a** afforded a 54% yield of solidified foam after rapid chromatography on silica gel eluting with hexanes-ethyl acetate (50:1); IR, 1815, 1730, 1715, 1685, 1670 cm<sup>-1</sup>. Further

(27) Freudenberg, K.; Markert, L. *Chem. Ber.* **1925**, *58*, 1758.

(28) Barthel, W. F.; Leon, J.; Hall, S. A. *J. Org. Chem.* **1954**, *19*, 485.



careful chromatography with the same system afforded crystalline **3a** and **4a** in the ratio 10:1. These products were identical in all respects with the products of the photolysis of **1a**.

**Ketene with Dimesityl Tetraketone (1d).** The crude product from 0.24 g of **1d** was an oil, IR (neat), 1822, 1725, 1680  $\text{cm}^{-1}$ . Chromatography on silica gel eluting with hexanes–ethyl acetate (40:1) gave a yellow solid (45%), which contained **25d** and **26d** in the ratio approximately 1:1 (by spectroscopic analysis). Crystallization from hexane afforded **25d** as yellow crystals, mp 143–146 °C. IR, 1808, 1728, 1678  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz), 1.24 (s, 6H), 2.16 (s, 6H), 2.56 (broad s, 6H), 6.62 (s, 2H), 6.78 (s, 2H), 7.34–7.35 (m, 3H), 7.53–7.56 (m, 3H), 7.72 (broad peak, 2H), 7.95 (d,  $J = 8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR, 18.61, 20.46, 21.14, 23.95 (broad), 25.41 (broad), 81.40, 100.78, 109.94, 121.80, 124.80, 126.86, 127.26, 127.76, 128.00, 128.43; 128.65, 128.80, 129.10, 129.62, 129.81, 131.39, 132.82, 136.84, 139.35 (broad), 139.91, 141.53, 167.54, 193.38 ppm. UV ( $\text{CH}_3\text{CN}$ ), 262 (14000), 330 (10000), 458 (100) nm. MS,  $m/z$  544.2153, calcd for  $\text{C}_{36}\text{H}_{32}\text{O}_5$  ( $M - \text{CO}_2$ ) 544.2159.

The mother liquors, upon standing at  $-15$  °C in hexane, afforded **26d** as white crystals, mp 154–157 °C. IR, 1826, 1712 (w), 1657  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR, 1.92 (s, 6H), 2.21 (s, 6H), 2.27 (s, 6H), 6.74 (s, 2H), 6.87 (2H), 7.33–7.37 (m, 3H), 7.49–7.56 (m, 3H), 7.78 (d,  $J = 8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ), 1.92 (3H), 2.03 (3H), 2.17 (6H), 2.41 (s, 6H), 6.54 (s, 2H), 6.60 (2H), 6.98–7.07 (m, 6H), 7.74 (d,  $J = 8$  Hz, 2H), 7.81 (d,  $J = 8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR, 19.89, 20.92, 21.07, 21.13, 84.25, 99.06, 107.95, 122.83, 126.78, 127.93, 128.17, 128.61, 128.74, 129.45, 129.75, 129.92, 131.57, 133.11, 133.69, 135.15, 138.82, 139.90, 141.58, 168.30, 196.81, 196.90 ppm. UV ( $\text{CH}_3\text{CN}$ ), 282 (6500) nm. MS,  $m/z$  544.02243, calcd for  $\text{C}_{36}\text{H}_{32}\text{O}_5$  ( $M - \text{CO}_2$ ) 544.2159. Anal. Calcd for  $\text{C}_{37}\text{H}_{32}\text{O}_7$ : C, 75.49, H, 5.48. Found: C, 75.39, H, 5.48.

**Ketene with Di-*tert*-butyl Tetraketone (1e).** The crude product from 0.30 g of **1e** showed IR<sub>max</sub> (neat), 1840, 1790, 1720  $\text{cm}^{-1}$ . Trituration with ether gave yellow crystals of  $\beta$ -lactone **24e** (70%), mp 113–116 °C. IR, 1838, 1738, 1711  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) 0.73 (9H), 1.24 (9H), 6.93–7.18 (m, 6H), 7.97 (d, 2H,  $J = 8$  Hz), 8.12 (d, 2H,  $J = 8$  Hz) ppm.  $^{13}\text{C}$  ( $\text{C}_6\text{D}_6$ ) 25.81, 27.45, 42.69, 45.86, 90.69, 92.66, 121.81, 125.86, 127.18, 127.67, 127.75, 127.87, 128.58, 128.76, 128.84, 129.76, 130.01, 131.82, 165.49, 186.81, 203.22, 203.80 ppm. UV ( $\text{CH}_3\text{CN}$ ) 254 (14000), 444 (35) nm. MS,  $m/z$  436.1923, 420.1944; calcd for  $\text{C}_{26}\text{H}_{26}\text{O}_6$  ( $M - \text{CO}$ ) 436.1886, for  $\text{C}_{26}\text{H}_{28}\text{O}_5$  ( $M - \text{CO}_2$ ) 420.1937.

After standing for 1 h in chloroform at room temp, **24e** had rearranged in 90% yield to  $\gamma$ -lactone **25e** mp 128–131 °C. IR, 1807, 1734, 1719  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR, 0.81 (s, 9H), 1.02 (s, 9H), 7.29–7.33 (m, 3H), 7.47–7.60 (m, 5H), 7.83 (d,  $J = 8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR, 24.80, 24.98, 25.06, 36.93, 42.61, 97.99, 113.20, 120.46, 126.81, 128.26, 128.47, 128.72, 128.93, 129.14, 129.63, 130.38, 131.26, 168.51, 201.64 ppm. UV ( $\text{CH}_3\text{CN}$ ), 226 (2000), 256 (1500), 428 (25) nm. MS,  $m/z$  464.1821; calcd for  $\text{C}_{27}\text{H}_{28}\text{O}_7$  464.1835. Anal. Calcd for  $\text{C}_{27}\text{H}_{28}\text{O}_7$ : C, 69.81; H, 6.08. Found: C, 69.58; H, 6.01.

The mother liquors after separation of **24e** were concentrated and chromatographed on silica gel with hexanes–ethyl acetate (20:1) to give additional **25e** (2%) and **26e** (3%, mp 108–110 °C). IR, 1827, 1717, 1687  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR, 0.81 (s, 9H), 1.32 (s, 9H), 7.33–7.37 (m, 5H), 7.57–7.60 (m, 3H), 7.84 (d, 2H,  $J = 8$  Hz) ppm.  $^{13}\text{C}$  NMR, 24.57, 25.04, 25.26, 26.08, 26.25, 26.40, 44.06, 45.94, 83.67, 98.66, 108.42, 122.80, 126.99, 127.68, 127.89, 127.99, 128.26, 128.50, 129.04, 129.62, 130.17, 131.54, 168.51, 201.18, 205.32 ppm. MS,  $m/z$  436.1916, calcd for  $\text{C}_{26}\text{H}_{28}\text{O}_6$  ( $M - \text{CO}$ ) 436.1886.

**Ketene with *p*-Anisyl *tert*-Butyl Tetraketone.** The crude product from reaction of 0.30 g of tetraketone had IR<sub>max</sub> (neat), 1841, 1734, 1706, 1682  $\text{cm}^{-1}$ . Trituration with ether gave yellow crystals of **24f** (53%), mp 102–103 °C. IR, 1844, 1734, 1703, 1682  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ), 0.77 (s, 9H), 3.02 (s, 3H), 6.42 (d,  $J = 8$  Hz, 2H), 7.09–7.18 (m, 6H), 8.10–8.14 (m, 6H) ppm.  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ) 25.32, 42.56, 54.87, 90.21, 91.39, 114.26, 122.00, 164.19, 165.89, 187.30, 188.54, 201.80 ppm.

Compound **24f** rearranged rapidly in chloroform solution at room temp to give **25f**, mp 145–147 °C, in 85% yield. IR, 1815, 1733, 1692  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR, 0.68 (9H), 3.78 (3H), 6.68 (d,  $J =$

8 Hz, 2H), 7.32–7.58 (m, 10H), 7.94 (d,  $J = 8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR, 24.89, 42.15, 55.42, 114.03, 123.28, 126.96, 127.96, 128.11, 128.34, 128.65, 129.57, 129.79, 131.54, 161.29, 168.45, 202.36 ppm. UV ( $\text{CH}_3\text{CN}$ ), 230 (21000), 262 (1800); 424 (20) nm. MS,  $m/z$  514.1761, calcd for  $\text{C}_{30}\text{H}_{26}\text{O}_8$  514.1728. Anal. Calcd for  $\text{C}_{30}\text{H}_{26}\text{O}_8$ : C, 70.03, H, 5.09. Found: C, 69.87, H, 5.15.

The mother liquors after separation of **24f** were concentrated and passed through silica gel with hexanes–ethyl acetate (20:1) affording additional **25f** (7%), and white crystals of **26f** (9%), mp 152–153 °C. IR, 1813, 1718, 1651  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR, 1.34 (9H), 3.76 (3H), 6.73 (d, 2H,  $J = 8$  Hz), 7.22–7.26 (m, 3H), 7.37–7.40 (m, 2H), 7.53–7.60 (m, 3H), 7.85 (d, 2H,  $J = 8$  Hz), 7.89 (d, 2H,  $J = 8$  Hz) ppm.  $^{13}\text{C}$  NMR, 26.05, 44.12, 55.42, 83.46, 98.75, 108.06, 113.58, 123.15, 126.99, 127.50, 127.99, 128.14, 128.23, 128.69, 128.74, 129.60, 131.69, 132.01, 164.30, 168.39, 189.04, 201.58 ppm. UV ( $\text{CH}_3\text{CN}$ ), 298 (20000) nm. MS  $m/z$  514.1761, calcd for  $\text{C}_{30}\text{H}_{26}\text{O}_8$  514.1728.

**Reaction of *p*-(Anisoyloxy)-*p*-anisylketene (8c) with 1c.** The crude oil obtained from reaction of **1c** (0.34 g) with  $\alpha$ -(*p*-anisyl)- $\alpha$ -(*p*-anisoyloxy)acetyl chloride (**9c**) and triethylamine had IR maxima at 1810 and 1720  $\text{cm}^{-1}$ . Washing through silica gel gave 0.53 g (85%) of yellow solid identical in all respects with **3c** described above.

**Reaction of 8b with Biacetyl.** Reaction of **8b** (0.6 g) with biacetyl gave a crude oil, IR 1840 (sh), 1795  $\text{cm}^{-1}$ . Trituration with pentane–ether did not give crystalline material. Trituration with methanol resulted in decomposition of the substance. Washing through silica gel with hexanes–ethyl acetate (20:1) gave white crystals of **12b**, yield 54%, mp 114–115 °C. IR, 1795, 1605  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR 1.31 (s, 3H), 1.70 (s, 3H), 7.41–7.51 (m, 8H), 7.81 (d,  $J = 8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR 10.15, 17.82, 82.67, 91.56, 108.43, 121.28, 126.65, 127.02, 128.32, 128.48, 129.11, 129.29, 130.63, 131.06, 170.33 ppm. UV ( $\text{CH}_3\text{CN}$ ) 260 (600) nm. MS  $m/z$  (CI, isobutane) 325 ( $M + \text{H}$ )<sup>+</sup>. Anal. Calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_5$ : C, 70.36; H, 4.97. Found: C, 70.29; H, 5.03.

**Reaction of 8b with Benzil.** The crude oil obtained after standing of 0.64 g of benzil with **8b** for 3 h at room temp showed IR maxima at 1815, 1785, 1740, 1720  $\text{cm}^{-1}$ . Chromatography on silica gel gave 78% of unreacted benzil, 4% of benzoin benzoate, and 20% (based on acid chloride) of dimer **23a**.

**Reaction of Ketene with 9,10-Phenanthrenequinone (PQ).** The crude oil from reaction of 0.20 g of PQ was triturated with ether to give **23** as white crystals (0.34 g, 81%), mp 135–142 °C. The analytical sample of **23** was obtained by crystallization from hexanes–ethyl acetate, mp 148–150 °C. IR, 1805  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ), 6.32 (d, 1H,  $J = 8$  Hz), 6.60 (t, 1H,  $J = 8$  Hz), 6.96–7.24 (m, 10H), 7.49 (d, 1H,  $J = 8$  Hz), 7.57 (d, 1H,  $J = 8$  Hz), 7.84–7.93 (m, 4H) ppm. MS,  $m/z$  446.1180, calcd for  $\text{C}_{29}\text{H}_{18}\text{O}_5$  446.1162.

**Reaction of *p*-(Anisoyloxy)-*p*-anisylketene (8c) with Di-*p*-Anisyltetraketone (1c).** Reaction of **1c** (0.34 g) with **8c**, generated from acid chloride **9c**, followed by chromatography on silica gel gave a crystalline yellow product in 85% yield. It was identical in all respects with **3c** obtained from the photochemical reaction of tetraketone **1c**.

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**Supporting Information Available:** Details of X-ray structure analysis of **22a** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.