

Migratory Aptitude Studies in the Photochemical Rearrangement of 2(5H)-Furanones¹

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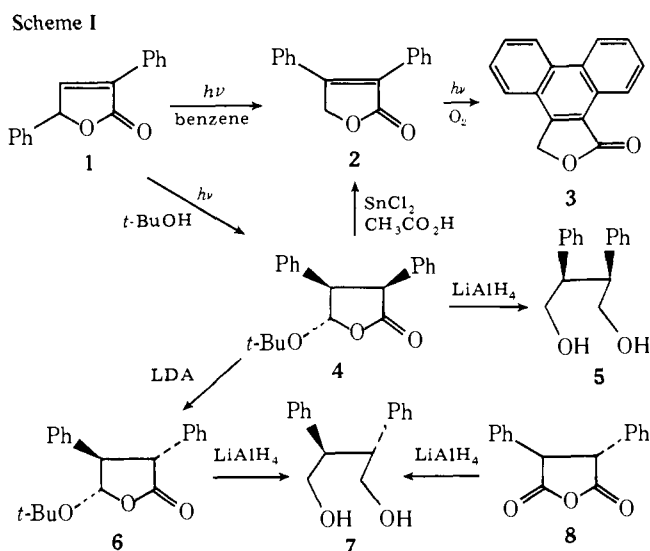
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Abstract: Irradiation of 3,5-diphenyl-5-aryl-2(5H)-furanones in benzene results in a novel rearrangement and affords a mixture of 3,4-diphenyl-5-aryl- and 3,5-diphenyl-4-aryl-2(5H)-furanones. Phosphorescence, sensitization, and quenching studies confirm the involvement of a $\pi-\pi^*$ triplet state in these reactions. The rate constants of aryl group migration were determined from quenching studies using piperylene as a quencher. These were found to be 0.18×10^{10} , 1.3×10^{10} , and $0.9 \times 10^{10} \text{ s}^{-1}$ for migration of phenyl, *p*-anisyl, and *p*-cyanophenyl, respectively. Thus, *p*-An and *p*-CNPh are more reactive migrating groups than phenyl by factors of 7.2 and 5.0 in benzene. The preferential migration of *p*-anisyl over phenyl (16/1) and *p*-cyanophenyl over phenyl (3.5/1) suggests that the excited state involved in benzene has significant odd-electron character on the β carbon of the α,β -unsaturated lactone moiety. A striking feature of these rearrangements is that a substantial crossover in migratory aptitude occurs upon changing the solvent from benzene to methanol. A nonmigrating *p*-anisyl group was found to significantly accelerate the rate of phenyl migration in methanol. Whereas the migration of *p*-anisyl in preference to phenyl in benzene is attributable to stabilization of the radical like free valence by the migrating group, the slight preference for migration of phenyl over *p*-anisyl in methanol may be attributed to stabilization of the electron deficiency which develops at C₅ by the nonmigrating *p*-anisyl group. The above results serve to emphasize the important role that electron distribution plays in photochemical migratory processes.

Light-induced transformations of five-membered enol lactones have been the subject of recent intensive study.²⁻⁷ These compounds undergo a facile decarbonylation when subjected to ultraviolet excitation and produce α,β -unsaturated ketones as primary photoproducts. Chapman and McIntosh have previously noted that a critical requirement for clean photochemical cleavage of the acyl-oxygen bond is the presence of a double bond adjacent to the ether oxygen.³ Stabilization of the incipient oxy radical was considered to be a determining factor in the photocleavage of this bond. In sharp contrast to the extensive studies concerned with the photochemistry of enol lactones, only scattered reports have appeared concerning the photochemical behavior of the related α,β -unsaturated γ -lactone system.⁷⁻⁹ As part of a continuing program dealing with the photochemical transformations of unsaturated lactones,¹⁰ we found that 5,5-diaryl-2(5H)-furanones undergo aryl group migration when subjected to ultraviolet excitation.¹¹ During the course of our studies with this system, we uncovered a striking crossover in the competitive migratory aptitudes of aryl groups which arises from a solvent alteration.¹² As there are relatively few examples of excited state migratory aptitudes being controlled by solvent variation,¹³ we decided to examine the photochemistry of this system in greater detail. We report here the results of this study which show that, in certain instances, excited-state migratory aptitudes can be controlled by stabilization of the nonmigrating aryl group.

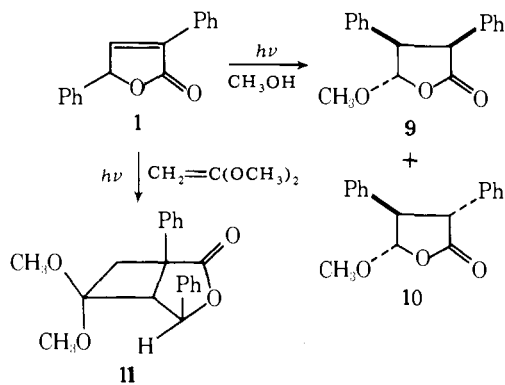
Results

Isolation and Identification of Photoproducts. As our first model we chose to investigate the photochemistry of 3,5-diphenyl-2(5H)-furanone (**1**).¹⁴ Irradiation of **1** in benzene under an argon atmosphere with Corex-filtered light for 1.5 h gave 3,4-diphenyl-2(5H)-furanone¹⁵ (**2**) in high yield. If molecular oxygen is present, **2** reacts further by the well-known stilbene-phenanthrene cyclization route to produce phenanthro[9,10-*c*]furanone (**3**), mp 253–254 °C.¹⁶ Studies on the photochemical behavior of **1** were also carried out using *tert*-butyl alcohol as the solvent (Scheme I). In this case, the only product isolated (87%) was *cis*-3,4-diphenyl-*trans*-5-*tert*-butoxy- γ -lactone (**4**). An alternative structure in which *tert*-butyl alcohol had added across the C-C double bond in a Michael fashion was ruled out on the basis of chemical degradation studies. Treatment of **4** with stannous chloride in refluxing

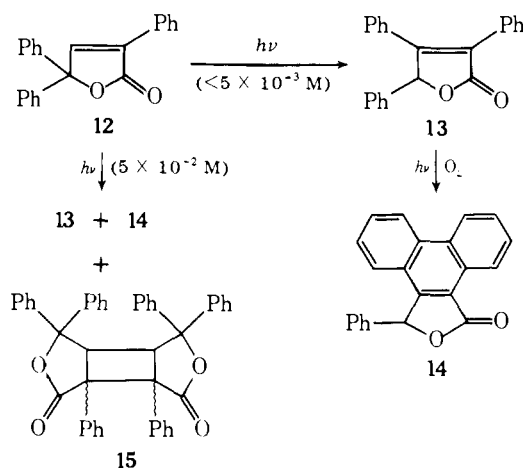


acetic acid gave **2**, while reduction of **4** with lithium aluminum hydride gave the known *meso*-2,3-diphenyl-1,4-butanediol (**5**).¹⁷ Further evidence which supports the stereochemical assignment was obtained by the observation that **4** was cleanly epimerized to *trans*-3,4-diphenyl-*trans*-5-*tert*-butoxy- γ -lactone (**6**) on treatment with lithium diisopropylamide in tetrahydrofuran. Subsequent reduction of **6** with lithium aluminum hydride produced *dl*-2,3-diphenyl-1,4-butanediol (**7**) which was identical with an authentic sample prepared by the lithium aluminum hydride reduction of *trans*-2,3-diphenylsuccinic anhydride (**8**). When the irradiation of **1** was carried out in methanol, a mixture of methoxy- γ -lactones **9** (30%) and **10** (45%) was obtained in good yield. The structural assignments were based on the characteristic NMR data of the lactones and by lithium aluminum hydride reduction to *meso*- and *dl*-2,3-butanediol.

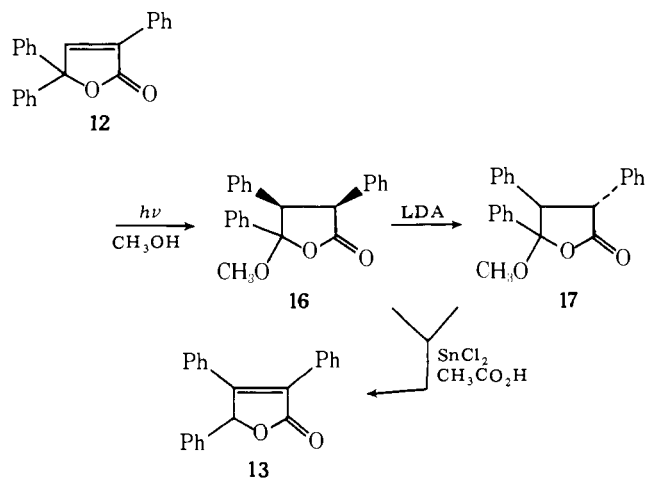
The photochemical reaction of **1** with an excess of 1,1-dimethoxyethylene in benzene was also studied. Irradiation of the mixture for 1 h gave a single product in nearly quantitative yield whose structure was assigned as cycloadduct **11** on the basis of its spectral properties. Under these conditions the photochemical rearrangement of **1** \rightarrow **2** was completely suppressed.



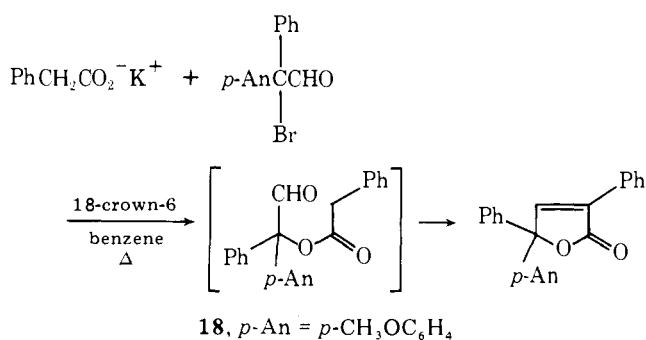
Attention was next turned to the photochemical behavior of 3,5,5-triphenyl-2(5*H*)-furanone (**12**). Irradiation of a dilute solution of this compound in benzene gave 3,4,5-triphenyl-2(5*H*)-furanone (**13**)¹⁶ as the initial photoproduct (78%); longer irradiation led to the formation of phenylphenanthro[9,10-*c*]furanone¹⁶ (**14**) in high yield. The structure of **13** was established by comparison with an independently synthesized sample. Irradiation of a concentrated solution (5×10^{-2} M) of **12** was found to produce a [2 + 2] dimer, tentatively assigned as **15**, in addition to **13** and **14**. The formation of this dimer could be totally suppressed by carrying out the irradiation on dilute solutions ($<5 \times 10^{-3}$ M) of **12**.



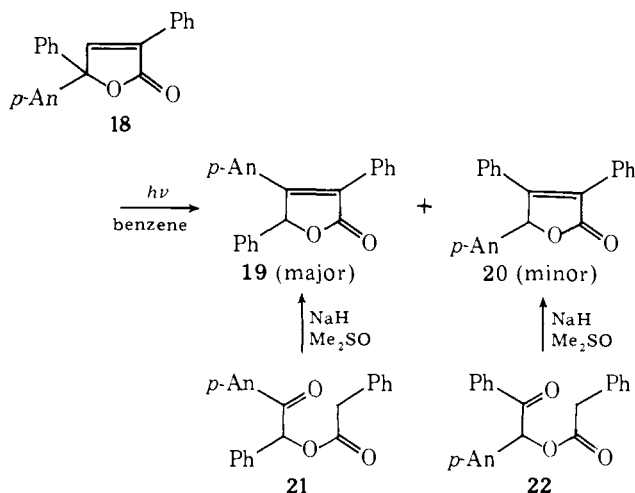
Studies on the photochemical behavior of **12** were also carried out in methanol. In this case, the only product isolated was *cis*-3,4,5-triphenyl-5-methoxy- γ -lactone (**16**). The structure of **16** was established by treatment with stannous chloride in refluxing acetic acid to give 2(5*H*)-furanone **13**. The stereochemical assignment of structure **16** was supported by the observation that **16** was cleanly epimerized to the



Scheme II



Scheme III

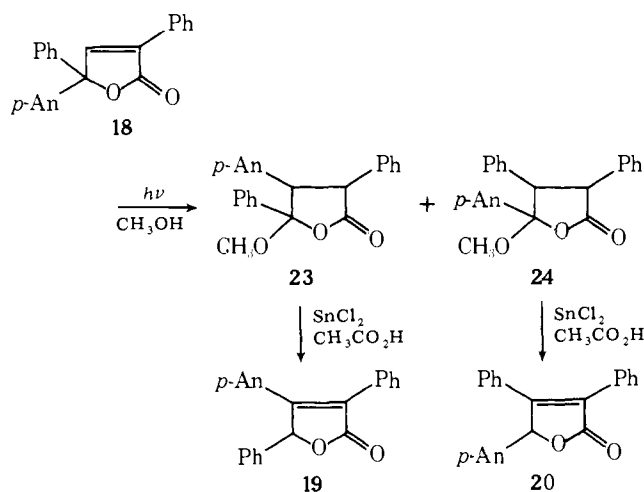


thermodynamically more stable *trans*-methoxy- γ -lactone **17** on treatment with base.

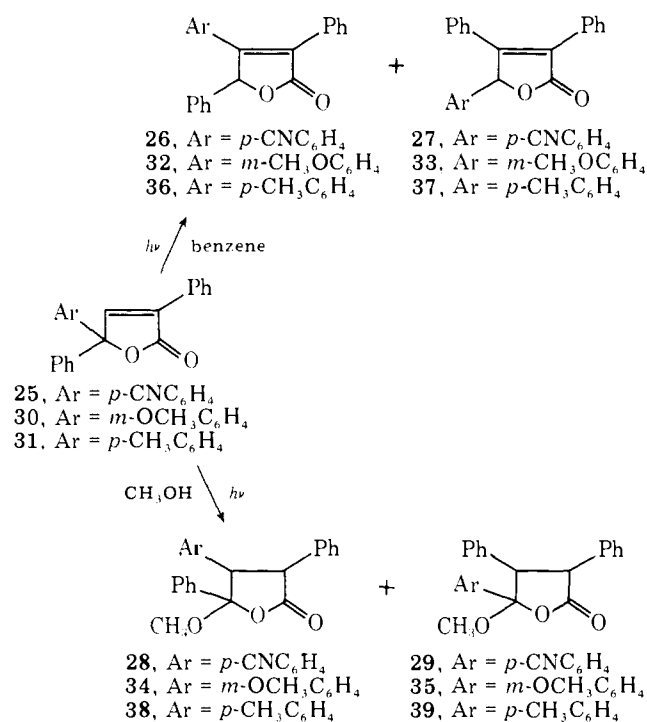
In order to gain insight into the nature of the rearranging excited state, the photolysis of a series of 3-phenyl-5,5-diaryl-2(5*H*)-furanones was investigated with the view that migratory aptitudes could be used as a probe for excited-state electronic makeup and reactivity.¹⁸ A survey of the literature revealed that there were no convenient methods to synthesize lactones of this type.¹⁹ An attractive route to the desired compounds was suggested by some recent work of Liotta²⁰ and Durst.²¹ These authors showed that when the potassium salt of an acid is solubilized by complexation with crown ethers,^{22,23} the anionic portion becomes sufficiently nucleophilic to react smoothly and quantitatively with a wide variety of organic substrates. For example, carboxylate salts were found to undergo phase transfer reaction with α -bromoacetophenone in nonpolar solvents to give phenacyl esters by an S_N2 process in quantitative yield.²⁰ By using a modification of the Durst procedure,²⁰ we have been able to convert a variety of diaryl acetaldehydes into 3-phenyl-5,5-diaryl-2(5*H*)-furanones in high yield. For example, 3,5-diphenyl-5-(*p*-anisyl)-2(5*H*)-furanone (**18**) was synthesized in 80% yield via the route depicted in Scheme II.

Irradiation of **18** in benzene gave two primary photoproducts, **19** and **20**, in a ratio of 16:1. The NMR, IR, and UV spectra (see Experimental Section) suggested that these products were 3-phenyl-4,5-diaryl-substituted 2(5*H*)-furanones. The photoproducts were unequivocally identified by comparison with authentic samples prepared by the routes outlined in Scheme III. It was especially important to have authentic **20** available, since only then would reference material be available to allow one to look effectively for this product in the crude photolysis mixture and place an upper limit on the amount formed. We found that high-speed liquid partition chromatography could be used as a fast, precise

Scheme IV



Scheme V



method for determining the ratio of photoproducts, giving base line separation between structures **19** and **20**.

The irradiation of 2(5H)-furanone **18** was also carried out in methanol. With this solvent, the photolysis afforded a mixture of 3,5-diphenyl-4-(*p*-anisyl)-5-methoxy- γ -lactone (**23**, 42%) and 3,4-diphenyl-5-(*p*-anisyl)-5-methoxy- γ -lactone (**24**, 58%) (ratio **23/24** = 0.72). The structures of **23** and **24** were established by treatment with stannous chloride in refluxing acetic acid to give furanones **19** and **20** (Scheme IV). The effect of solvent on the migratory aptitude was further evaluated by performing the irradiation of **18** in a mixed solvent system. When a 5% methanol-benzene mixture was employed, methoxy- γ -lactones **23** and **24** were the only products produced. Under these conditions, *p*-anisyl was found to migrate in strong preference to phenyl (ratio **23/24** = 16/1). This result clearly establishes that the products of migration are markedly dependent on the nature of the solvent system employed.

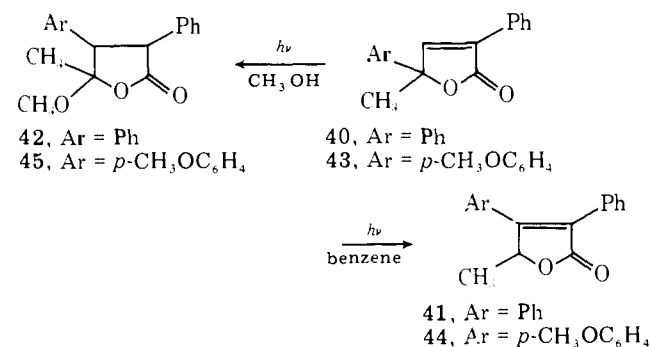
The irradiation of 3,5-diphenyl-5-(*p*-cyanophenyl)-2(5H)-furanone (**25**) in benzene proceeded quite similarly to the case of **18**. Two rearranged 2(5H)-furanones (**26** and **27**, ratio **26/27** = 3.5/1) were obtained whose structures were established by comparison with independently synthesized

Table I. Migratory Aptitudes in the Photolysis of 3,5,5-Triaryl-2(5H)-furanones

2(5H)-furanone derivative	solvent	Ar/Ph
3,5-diphenyl-5- <i>p</i> -anisyl (18)	benzene	16
	methanol	0.72
	5% methanol-benzene	16
3,5-diphenyl-5- <i>p</i> -cyanophenyl (25)	benzene	3.5
	methanol	4.5
3,5-diphenyl-5- <i>m</i> -anisylphenyl (30)	benzene	1.5
	methanol	0.95
3,5-diphenyl-5- <i>p</i> -toluyl (31)	benzene	3.5
	methanol	0.81

samples. When methanol was used as the solvent, methoxy- γ -lactones **28** and **29** were obtained (ratio **28/29** = 4.5/1) in high yield. Photorearrangement of the 5-substituted *m*-anisyl- and *p*-toluyl-2(5H)-furanones **20** and **31** was also studied in benzene and methanol. Products were isolated by crystallization and chromatography and were identified by comparison with authentic material using the general method described for the synthesis of 3,4,5-triaryl-2(5H)-furanones.²⁴ Rearrangement of furanone **30** in benzene indicated that the *m*-anisyl group had migrated with slight preference over phenyl (ratio **32/33** = 1.5/1). When methanol was used as the solvent, both groups had migrated with the same ease (i.e., ratio **34/35** = 0.95). With *p*-toluyl furanone **31**, irradiation in benzene afforded lactones **36** and **37** (ratio 3.5/1), whereas photolysis in methanol resulted in preferential phenyl migration (ratio **38/39** = 0.81). Table I lists the migratory aptitudes found for the 3-phenyl-5,5-diaryl-2(5H)-furanones in both benzene and methanol.

The photochemical behavior of the closely related 5-methyl-3,5-diaryl-2(5H)-furanone system was also studied in order to assess the generality of the rearrangement. Irradiation of **40** in benzene afforded 5-methyl-3,4-diphenyl-2(5H)-furanone (**41**) in 85% yield as the only detectable photoproduct. When the irradiation was carried out in methanol, methoxy- γ -lactone **42** was obtained as the exclusive photoproduct. Similar results were encountered on irradiation of the analogous *p*-anisyl furanone system **43**.



In order to determine whether the photorearrangement of a 2(5H)-furanone devoid of an aryl group in the 5 position would occur, we subjected furanone **46** to ultraviolet irradiation. We found that this system was perfectly stable to prolonged photolysis in both benzene and methanol. This observation would tend to indicate that the rearrangement of the 3,5,5-triaryl-furanone system proceeds via a di- π -methane mechanism.²⁵

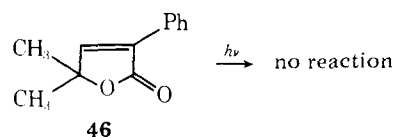
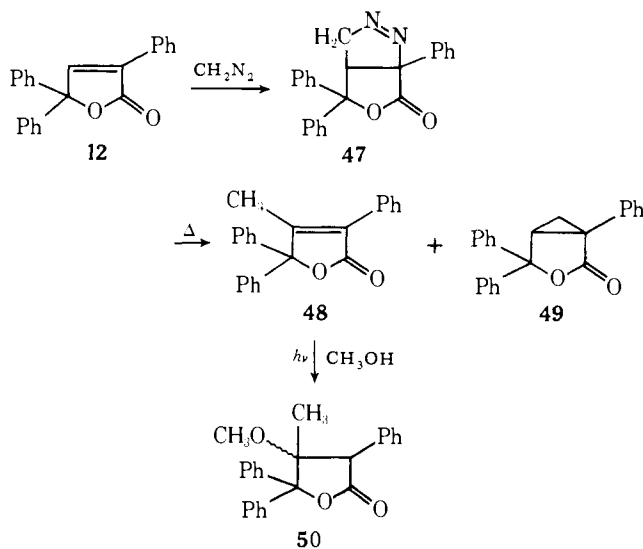


Table II. Rate Constants for Reaction and Decay from the Triplet States of 3,5,5-Triaryl-2(5H)-furanones

2(5H)-furanone derivative	solvent	$\Phi_{\text{direct}}^{a,i}$	τk_q^b	$10^{-10}k_d^c$ s ⁻¹	$k_r^{Ar}/k_r^{\text{Ph}}^d$	$10^{-10}k_r(\text{net})^e$ s ⁻¹	$10^{-10}k_r(\text{Ar})^f$ s ⁻¹	$10^{-10}k_r(\text{Ph})^g$ s ⁻¹
3,5,5-triphenyl (12)	benzene	0.37	0.52	0.6		0.36		0.18
3,5-diphenyl-5- <i>p</i> -anisyl (18)	benzene	0.36	0.12	2.75	16	1.5	1.3	0.09
3,5-diphenyl-5- <i>p</i> -cyanophenyl (25)	benzene	0.48	0.21	1.25	3.5	1.15	0.9	0.25
3,5,5-triphenyl (12)	methanol	0.37	0.53	0.6		0.35		0.17
3,5-diphenyl-5- <i>p</i> -anisyl (18)	methanol	0.06	0.056 ^h	5.4	0.72	3.6 ^j	1.5	2.1
3,5-diphenyl-5- <i>p</i> -cyanophenyl (25)	methanol	0.43	0.55	0.51	4.5	0.39	0.32	0.07

^a Sum of both products. ^b Slope of Stern-Volmer plot. ^c $(1 - \Phi)/\tau$. ^d From product ratios. ^e Φ/τ . ^f $(\Phi_{Ar}/\Phi_{\text{total}})k_r(\text{net})$. ^g $(\Phi_{\text{Ph}}/\Phi_{\text{total}})k_r(\text{net})$. ^h $\pm 40\%$ as a consequence of the low magnitude of the slope. ⁱ $\pm 10\%$ experimental error. ^j Φ_a/τ ; in this case the efficiency of intersystem crossing (a) of **18** in methanol is only 15% (refer to discussion in text).

One additional system which was also studied involved the photochemistry of 3,5,5-triphenyl-4-methyl-2(5H)-furanone (**48**). This material was conveniently prepared by treating 2(5H)-furanone **12** with diazomethane and thermolyzing the initially produced diazabicyclooctenone **47**. Furanone **48** could readily be separated from structure **49** by fractional crystallization. Irradiation of **48** in benzene did not produce a rearranged furanone, and it therefore seems that the incorporation of an additional methyl group in the 4 position of the furanone ring retards the di- π -methane rearrangement. Irradiation of



48 in methanol, however, afforded a mixture of the *cis* and *trans* isomers of 4-methoxy-4-methyl-3,5,5-triphenyl- γ -lactone (**50**). Simple Michael addition of methanol to the excited state of **48** best rationalizes the formation of **50**. The 1,4-addition of hydroxylic solvents to α,β -unsaturated cyclic ketones to yield β -alkoxy ethers is a well-known reaction²⁶ and provides reasonable analogy for this transformation. It is interesting to note, however, that the parent 2(5H)-furanone system undergoes solvent addition to yield α and β solvent adducts.²⁷⁻²⁹ This reaction has been postulated to involve hydrogen abstraction both by the carbonyl group to yield β solvent adducts and by the β carbon atom to yield α adducts. Thus, the pathway for photochemical solvent addition with **48** is decidedly different from that which occurs with the parent system. This may well be related to the presence of the phenyl group in the 3 position of the 2(5H)-furanone ring which either suppresses hydrogen atom abstraction from the solvent or enhances the 1,4-addition reaction.

Determination of Reaction Efficiency, Multiplicity, and Reaction Rates. In order to derive additional mechanistic information concerning the photorearrangement, a more quantitative investigation of these reactions was undertaken. Quantum yields for product formation were determined using benzophenone-benzhydrol as the chemical actinometer.³⁰

Degassed and sealed quartz tubes containing solutions of the 2(5H)-furanones were irradiated along with actinometer tubes in a rotating photochemical assembly. Reactions were carried out to low conversions to prevent appreciable light absorption by the products, and yields of products were determined by analytical high-pressure liquid chromatography using internal standards. The results of these determinations are listed in Table II. Further details are described in the Experimental Section. In general, the photochemical rearrangements were highly efficient, with quantum yields varying from 0.36 to 0.48.

It was next necessary to determine the multiplicity of the species leading to the photoproducts. To determine if a triplet excited state could give rise to the observed photoproducts, acetophenone or *m*-methoxyacetophenone sensitization was employed under conditions where only the sensitizer absorbed light. In these runs, concentrations were adjusted so that sensitizer singlets would decay to triplets before collision with the acceptor, but triplet energy transfer would be efficient.³¹ The results obtained showed that triplet sensitization led to the same quantum yield, within experimental error, as obtained in direct irradiation runs. Additionally, the product "fingerprint",³² as determined by quantum yields of the two photoproducts, was the same in the direct irradiation runs as in the sensitized runs where the triplet excited state of the reactant was artificially generated. The equivalence of the direct and sensitized irradiations provides strong evidence for a triplet state in the direct photolysis experiments. That the rearrangement is readily quenched by piperylene furnishes additional confirmation for the triplet state assignment. Moreover, the ratio of the photoproducts with all the 2(5H)-furanones was insensitive to the extent of triplet quenching. If more than one excited state were involved in these reactions (e.g., one being the lowest energy triplet), then one would expect that the product distribution would change with increasing concentration of the quencher. This was not the case and thus we can conclude that the photochemical rearrangement encountered with the 3,5,5-triaryl-2(5H)-furanone system proceeds via a single triplet excited state.

We expected that the lowest lying triplet state of the 3,5,5-triaryl-2(5H)-furanone system would correspond closely to the relatively low-lying $^3(\pi,\pi^*)$ state of styrene with little perturbation by the lactone carbonyl group. Since twisting around the double bond will be limited in the five-membered ring, radiationless triplet deactivation should be restrained in favor of emission at low temperature, and the lowest triplet energy of this system should approximate the spectroscopic $S_0 \rightarrow T_1$ transition energy measured for styrene by absorption under high pressure of oxygen (61.7 kcal/mol).³³ These expectations were met. Thus, furanones **12**, **18**, **25**, **30**, and **31** show phosphorescence spectra (MCIP or methanol-ethanol, 77 K, 0-0 band at 483 nm = 59 kcal, τ_p 170 ms) which correspond closely to the low-lying $^3\pi-\pi^*$ state of 1-phenylcyclopentene.³⁴ The excitation spectra were in good agreement with the corresponding absorption spectra. We assume from these

measurements that the lowest lying styrene-type π,π^* triplet of the 2(5H)-furanone system is the excited state responsible for the rearrangement.

In order to obtain the rate constants for aryl group rearrangement, the reciprocals of both individual quantum yields, as well as the total quantum yield, were plotted against piperylene concentration. The Stern–Volmer plots obtained were linear over the quenching range studied. The slope of this plot gives k_q/k_r , the bimolecular quenching rate divided by the rate of triplet rearrangement.

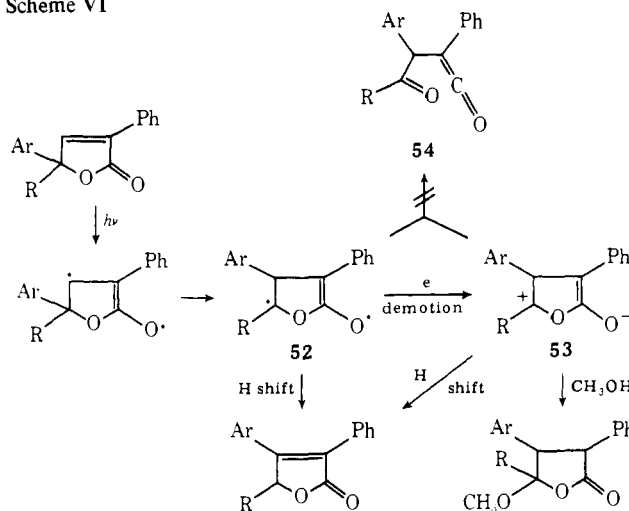
$$\frac{1}{\Phi} = \frac{k_r^{\text{tot}} + k_d}{ak_r} + \frac{k_q[Q]}{ak_r}$$

In this expression, k_r^{tot} represents the sum of all reaction rates of triplet. It is assumed that a , the efficiency of intersystem crossing, is unity (note discussion below). Thus one can calculate k_r if k_q is known. The values of k_r calculated in both benzene and methanol are listed in Table II together with the quantum yields for rearrangement. These values were used together with the intercept of each Stern–Volmer plot to solve for k_d , the rate of excited-state decay to reactant ground state. It should be noted that k_r^{tot} in the numerator of the intercept is the sum of all the individual reaction constants and thus k_d will include all modes of decay whether radiative, nonradiative, or involving incipient reaction. The rate constants listed in Table II are based on a common k_q value of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in benzene and methanol.³⁵ Since the 3,5,5-triaryl-2(5H)-furanone system possesses a low triplet energy (ca. 58 kcal), energy transfer to piperylene may not be diffusion controlled and consequently the rate values listed may be somewhat high. It should also be noted that the k_r 's measured are net k_r 's which are equal to the rates of formation of any intermediate species multiplied by the fractions of the intermediates which continue on toward product. Thus, the values listed are minimum values for k_r , although it is conceivable that there is no triplet decay and that $k_r = 1/\tau$. The relative k_r values listed in Table II are based on the assumption that there is either no return of an intermediate to ground state or else that all of the lactones undergo the same fraction of such return. One additional point worth mentioning is that since we are interested in the rate of migration of a single aryl group, for statistical reasons the rate constant for the 3,5,5-triphenyl-2(5H)-furanone system (**12**) is halved.

Discussion

The photochemical rearrangement of the 3,5,5-triaryl-2(5H)-furanone system is most readily accounted for by the pathway outlined in Scheme VI in which the bridging step and the subsequent cleavage leading to **52** are simply the first two formal steps of a di- π -methane rearrangement.²⁵ Electron demotion through the divalent oxygen atom proceeds to give a zwitterion (**53**) which is trapped by the alcoholic solvent. The stereochemistry of the 5-alkoxy- γ -lactone obtained corresponds to kinetic protonation of the enolate anion (or enol) from the least hindered side. In the absence of a hydroxylic solvent the diradical or zwitterion undergoes either a hydrogen shift or proton loss to give the rearranged 2(5H)-furanone. A ketene intermediate (**54**) could not be detected by low-temperature infrared studies,³⁶ thus ruling out a fragmentation of **52** or **53**. Agosta³⁷ and Zimmerman³⁸ had previously reported that irradiation of the closely related 4,4-diarylcyclopentenone system proceeds by a mechanism which involves ring opening to a transient ketene. This process and the photochemical ring openings reported for the β,γ -unsaturated lactones²⁻⁶ do not appear to occur in the 2(5H)-furanone system. The contrast in behavior with the 4,4-diarylcyclopentenone system probably results from the ability of the oxygen to stabilize the adjacent positive charge in the zwitterion **53** (or the radical center in **52**).

Scheme VI

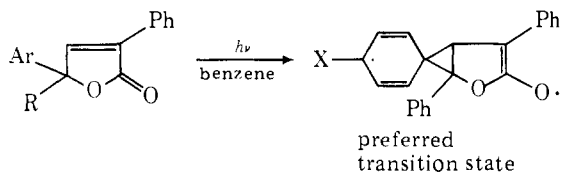


An additional point to be noted is the occurrence of only aryl group migration in the rearrangement of furanones **40** and **43**, as would be expected for a di- π -methane rearrangement. In fact, furanone **46** is perfectly stable toward irradiation. Another observation which may be made pertains to the multiplicity of the reacting excited species. Zimmerman and co-workers²⁵ have shown that di- π -methane systems having nonconstrained or free π moieties usually give an efficient rearrangement from the excited singlet state, because of an energy dissipation process available in the triplet state, i.e., rotation about the excited π bond. The deactivation process was termed the "free rotor effect". In the case of compounds having constrained π moieties, the di- π -methane rearrangement usually proceeds efficiently from the triplet and inefficiently from the singlet state. The triaryl-2(5H)-furanone system, being made up of constrained nonfree π moieties, would be expected to proceed from the excited triplet state. This is indeed the case as shown by both the sensitization and quenching studies. The fact that the triplet state of **1** can be intercepted with dimethoxyethylene to give a [2 + 2] cycloadduct (i.e., **11**) and that **12** undergoes [2 + 2] dimerization at high furanone concentrations provides additional support for the involvement of the triplet state. Related [2 + 2] cycloadditions of the triplet states of α,β -unsaturated lactones have been reported in the literature³⁹⁻⁴¹ and provide good analogy for the above reactions.

Migratory aptitudes of substituted aryl groups have been used by Zimmerman and co-workers for understanding the excited state electronic makeup and reactivity of 4,4-diarylcyclohexenones.⁴² Zimmerman found that phenyl groups having *p*-methoxy or cyano substituents migrated in preference to an unsubstituted phenyl group.⁴² This effect was attributed to the lower free energy of the bridged transition state in which the free valence is delocalized by the para substituent of the migrating aryl group. It was assumed that, in analogy to ground-state aryl migrations, greater stabilization results from substitution of a resonance stabilizing group on the migrating aryl group than on the nonmigrating aryl group.

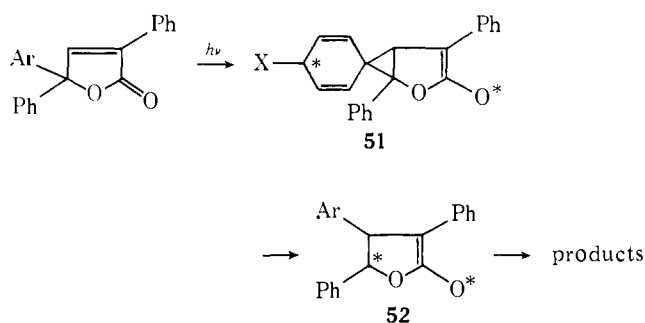
We have also used this approach to gain insight into the nature of the rearranging excited state of the 2(5H)-furanone system. When benzene was used as the solvent, it was observed that *p*-anisyl migrated in strong preference to phenyl (ratio *p*-An/Ph = 16/1) and that *p*-cyanophenyl migrated in preference to phenyl (ratio *p*-CNPh/Ph = 3.5/1). Rearrangement of furanones **30** and **31** in benzene indicated that both *m*-anisyl and *p*-toluyl had also migrated with preference over phenyl (see Table I). The migratory aptitudes in benzene agree generally with the results of Zimmerman for the 4,4-diarylcyclo-

clohexenone system (p -An vs. Ph = 12.5/1 and p -CNPh vs. Ph = 14/1) except that the p -CNPh:Ph preference in the furanone system is somewhat lower (3.5:1) than that found in the enone case. The rate constants of aryl group migration with phenyl remaining at C-5 were obtained from quenching studies using piperylene as a quencher. These were found to be 0.18×10^{10} , 1.3×10^{10} , and $0.9 \times 10^{10} \text{ s}^{-1}$ for migration of phenyl, p -anisyl, and p -cyanophenyl in benzene (Table II). Thus, p -An and p -CNPh are more reactive migrating groups than phenyl by factors of 7.2 and 5.0, respectively. This is consistent with the expected radical character of the migration termini for the reactive electronic state in this solvent system. Zimmerman



and Lewin¹⁸ found that a nonmigrating p -CNPh group increased the rate constant for phenyl migration by a factor of 1.3. We find that, relative to phenyl migration with nonmigrating phenyl, the rate of phenyl migration is accelerated 1.4-fold by nonmigrating p -CNPh and decreased 2.0-fold by a nonmigrating p -An group when benzene is used as the solvent. We conclude that the nonmigrating group has a small influence on the rate of rearrangement in benzene, with an electron-donating group decreasing the rate and an electron-withdrawing group increasing the rate.

Regarding the differences in the 2(*5H*)-furanones and the diarylcyclohexenones,⁴³ the furanones react faster by factors of about 10^2 , and they show somewhat greater influences of substituents on the rate constants for decay. That the 2(*5H*)-furanones in the ground state are virtually planar⁴⁴ whereas the cyclohexenones are puckered may be related to the rate differential. Moreover, the migrations in the cyclohexenones appear to be accompanied by puckering of the ring and synchronous 1,3-bonding leading directly to a bridged product. This interaction does not appear to be involved in the furanone system. Thus it appears that the furanone rearrangement involves formation of a discrete intermediate **52** from the half-migrated species **51**. Intermediate **52** would have



a half-vacant orbital at C-5 (stabilized by the adjacent oxygen orbitals); the corresponding intermediate in the cyclohexenone rearrangement is either bypassed or less fully formed.

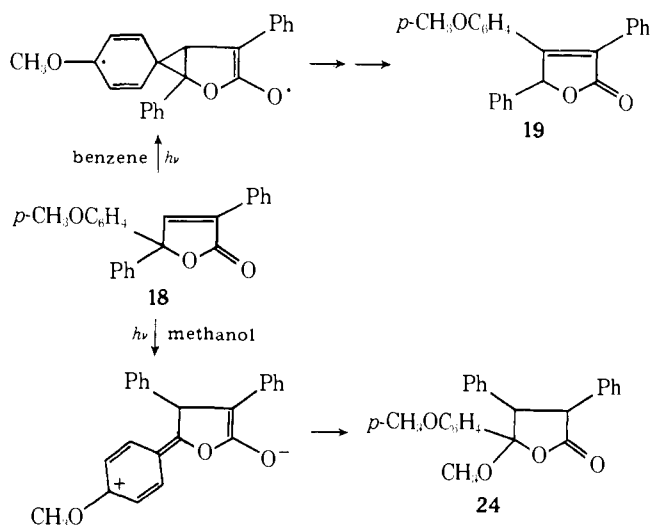
Two conclusions may be drawn on the basis of this mechanistic difference. According to the principle of least motion,⁴⁵ those elementary reactions will be favored which involve the least change in atomic positions and electronic configuration. Since the first step (k_r) in the furanone rearrangement is simple bridging from aryl to the β carbon whereas that in the cyclohexenone involves, in addition, puckering of the ring and C_2 - C_4 bonding, the simpler reaction of the furanones would be expected to occur more rapidly. Secondly, unlike the cyclohexenone pathway, the conversion from **51** to **52** may involve a significant energy barrier permitting the decay pathway to

intervene and compete with the rearrangement pathway. The observed parallelism between k_d and k_r is reasonable if the principal decay process is initiated by the same step which leads to chemical reaction.

The most striking feature of these rearrangements is that a substantial crossover in migratory aptitude occurs upon changing the solvent from benzene to methanol. The reversal of the migratory aptitude of p -anisyl vs. phenyl when the reaction of **18** is carried out in methanol is of special interest. The quantum yield for the reaction of **18** in methanol ($\Phi = 0.06$) is much lower than for the reaction in benzene ($\Phi = 0.36$). The triplet-sensitized reaction in methanol, however, is quite efficient ($\Phi = 0.40$). The product distribution for the sensitized reaction was found to be virtually identical with that for the direct irradiation. These results indicate either that the product distribution for rearrangement in the singlet manifold is identical with that for the triplet, or, more plausibly, that rearrangement occurs only in the triplet manifold. Assuming the latter, the efficiency of intersystem crossing of **18** in methanol based on $\Phi_{\text{sens}} = 0.40$ is estimated to be only 15%. Intersystem crossing by each of the furanones, including **18**, in benzene occurs with an efficiency indistinguishable from unity by sensitization studies. The marked decrease in intersystem crossing in methanol occurs only for **18** and not for **12** or **25**. We presently consider the possibility that radiationless deactivation modes of the excited singlet state of the electron-rich p -anisyl furanone **18** in methanol are substantially larger than those of furanones **12** and **25**, thereby suppressing the intersystem crossing of this compound to the triplet state. It should be pointed out that a similar effect of solvent on the efficiency of intersystem crossing has been noted by others in the p -aminobenzophenone system.^{46,47} Apparently, some sort of intramolecular charge transfer interaction is common to both systems. A similar but less dramatic crossover in migratory aptitude was also noted with p -toluyl furanone **31**.

The foregoing results suggest that the photochemistry of the p -anisyl furanone system (**18**) proceeds from a diradical state in benzene while in methanol the rearrangement occurs from a zwitterionic state. Salem has pointed out that an increase in solvent polarity will stabilize zwitterionic states relative to diradical states^{48,49} thereby providing some justification for this contention. Whereas the migration of p -anisyl in preference to phenyl in benzene is attributable to stabilization of the radical-like free valence by the *migrating* group, the slight preference for migration of phenyl over p -anisyl in methanol may be attributed to stabilization of the electron deficiency which develops at C-5 by the *nonmigrating* p -anisyl group.

According to the above rationale, the migratory aptitude of furanone **18** in methanol will be controlled by the reluctance



of the phenyl group to "remain behind" rather than from an inherent tendency of the *p*-anisyl group to migrate. This contention was reached by consideration of the data outlined in Table II. As noted in the table, the rate constant in methanol for phenyl migration with *p*-anisyl nonmigrating is $2.1 \times 10^{10} \text{ s}^{-1}$. This contrasts with the rate of $0.17 \times 10^{10} \text{ s}^{-1}$ of a single phenyl with phenyl nonmigrating (i.e., **12**). Thus a nonmigrating *p*-anisyl group has significantly accelerated (12 times) the rate of phenyl migration in methanol. In contrast, the rate constant for *p*-anisyl migration in triplet **18** is little affected by solvent (i.e., $1.3 \times 10^{10} \text{ s}^{-1}$ in benzene vs. $1.5 \times 10^{10} \text{ s}^{-1}$ in methanol). Additionally, it is of interest to inspect the effect of a nonmigrating *p*-cyanophenyl group. It was found that both *p*-cyanophenyl and phenyl migration occur less readily in methanol than in benzene. The nonmigrating *p*-cyanophenyl retards phenyl migration by a factor of 3.5 in methanol whereas it aids it in benzene.

These results tell us that in the excited-state rearrangement of **18** in methanol, stabilization by the nonmigrating *p*-anisyl group of the electron deficiency which develops at C-5 during phenyl migration is the major factor responsible for the observed migratory aptitudes.⁵⁰ The diminution of the rate of phenyl migration by the nonmigrating *p*-cyanophenyl group in methanol is also in accord with this picture. Our results clearly show that in certain cases, excited-state migratory aptitudes can be controlled by stabilization of the nonmigrating aryl group. This is clearly different from the situation which usually prevails in the ground state.⁵¹⁻⁵⁸

Finally, one also has to consider the competitive decay of the excited state to reactant as another factor in determining the migratory aptitude ratio. Thus, in the *p*-anisyl vs. phenyl comparison, one finds that the rate of decay of **18** in methanol is ten times larger than that of **12**. This would tend to suggest that the excited-state species in which *p*-anisyl begins to migrate undergoes rapid decay back to ground-state reactant. The loss of electronic excitation, either by an electronic transition or by intersection of the excited- and ground-state potential energy curves, precedes the rate-limiting and irreversible stage of the reaction. Consequently, the product distribution (*p*-An vs. phenyl) will not be controlled by the ease of aryl group migration but rather will be dominated by the relative rates of decay of the two partially rearranged species. The above results serve to emphasize the important role that electron distribution plays in photochemical migratory processes.

Experimental Section⁵⁹

Irradiation of 3,5-Diphenyl-2(5H)-furanone (1) in Benzene. A solution containing 100 mg of 3,5-diphenyl-2(5H)-furanone (**1**)¹⁴ in 475 mL of benzene under an argon atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 1 h. Removal of the solvent under reduced pressure left a yellow solid which was recrystallized from 95% ethanol to give 78 mg (82%) of 3,4-diphenyl-2(5H)-furanone (**2**): mp 110–111 °C (lit.¹⁵ 112–113 °C); IR (KBr) 1760 cm^{-1} ; UV (methanol) 283 nm (ϵ 12 700); NMR (CDCl_3 , 100 MHz) δ 5.01 (s, 2 H), 7.30 (s, 10 H); m/e 236 (M^+). The structure of this material was further verified by comparison with an authentic sample. To a stirred solution containing 3.90 g of phenacyl phenylacetate in 50 mL of dry dimethyl sulfoxide was added 368 mg of sodium hydride. The slightly exothermic reaction mixture was stirred at room temperature for 2 h, then warmed quickly to 60–70 °C for 5 min. The cooled reaction mixture was poured into cold water and extracted with ether. The ether layer was washed with a 2% hydrochloric acid solution and water and dried over magnesium sulfate. Removal of the solvent gave 3.15 g (87%) of 3,4-diphenyl-2(5H)-furanone (**2**) which was identical in every detail with the material obtained from the photolysis of **1**.

When the irradiation of **1** was carried out in the presence of oxygen for 4 h, the major product isolated (40 mg) was identified as phenanthro[9,10-*c*]furanone¹⁶ (**3**): mp 253–254 °C; IR (KBr) 1755 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 5.40 (s, 2 H), 7.0–7.8 (m, 8 H); m/e 234 (M^+).

Anal. Calcd for $\text{C}_{16}\text{H}_{10}\text{O}_2$: C, 82.04; H, 4.30. Found: C, 81.74; H, 4.39.

Irradiation of 3,5-Diphenyl-2(5H)-furanone (1) in *tert*-Butyl Alcohol. A solution containing 200 mg of **1** in 500 mL of *tert*-butyl alcohol was irradiated with a 450-W Hanovia lamp through a Corex filter sleeve under an argon atmosphere for 3 h. Removal of the solvent left a yellow-white solid which was recrystallized from ether-hexane to give 230 mg of *cis*-3,4-diphenyl-5-*tert*-butoxy- γ -lactone (**4**): mp 113–114 °C; IR (CHCl_3) 1776 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 1.30 (s, 9 H), 3.68 (dd, 1 H, $J = 9.0$ and 2.0 Hz), 4.48 (d, 1 H, $J = 9.0$ Hz), 5.88 (d, 1 H, $J = 2.0$ Hz), 6.7–7.10 (m, 10 H); m/e 266 ($\text{M}^+ - \text{CO}_2$).

Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3$: C, 77.39; H, 7.14. Found: C, 77.14; H, 7.09.

The structure of the photoproduct was further verified by reduction to *meso*-2,3-diphenyl-1,4-butanediol (**5**). To a mixture containing 50 mg of lithium aluminum hydride in 30 mL of ether was added a solution containing 75 mg of **4** in 10 mL of ether. The solution was stirred at 25 °C for 12 h. After the usual workup the residue was recrystallized from benzene-ligroin to give 68 mg (87%) of *meso*-2,3-diphenyl-1,4-butanediol (**5**), mp 141–142 °C (lit.¹⁷ 142–143 °C), IR (KBr) 3400 cm^{-1} .

The stereochemistry of the photoproduct was further verified by a base-catalyzed epimerization. A 56-mg sample of *cis*-3,4-diphenyl-5-*tert*-butoxy- γ -lactone (**4**) in 10 mL of ether was added to a solution containing lithium cyclohexylisopropylamide at –78 °C. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The mixture was then poured into 75 mL of ether, washed with water and a 2% hydrochloric acid solution, and then dried over magnesium sulfate. Removal of the solvent left 51 mg (91%) of *trans*-3,4-diphenyl-5-*tert*-butoxy- γ -lactone (**6**): mp 86–87 °C; IR (KBr) 1770 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 1.10 (s, 9 H), 3.40 (dd, 1 H, $J = 12.0$ and 8.0 Hz), 3.80 (d, 1 H, $J = 12.0$ Hz), 5.40 (d, 1 H, $J = 8.0$ Hz), 6.95 (m, 10 H). Lithium aluminum hydride reduction of this material afforded a 63% yield of *trans*-2,3-diphenyl-1,4-butanediol (**7**) which was identical in every respect with the material obtained from the reduction of *trans*-2,3-diphenylsuccinic anhydride⁶⁰ (**8**).

Irradiation of 3,5-Diphenyl-2(5H)-furanone in Methanol. A solution containing 100 mg of **1** in 400 mL of methanol was irradiated with a 450-W Hanovia lamp through a Corex filter sleeve under an argon atmosphere for 4 h. Removal of the solvent under reduced pressure gave an oily residue which was dissolved in chloroform and separated into two components by chromatography using a thick layer silica gel plate with a 25% chloroform-hexane mixture as the eluent. The first component isolated from the plate (53 mg, 45%) was identified as *trans*-3,4-diphenyl-5-methoxy- γ -lactone (**10**): mp 89–90 °C; IR (KBr) 1760 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.60 (s, 3 H), 3.81 (d, 1 H, $J = 8.0$ Hz), 4.58 (d, 1 H, $J = 8.0$ Hz), 5.60 (s, 1 H), 6.79–7.21 (m, 10 H); m/e 224 ($\text{M}^+ - \text{CO}_2$).

Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$: C, 76.10; H, 6.01. Found: C, 75.83; H, 6.20.

The second compound isolated from the thick layer plate (36 mg, 30%) was identified as *cis*-3,4-diphenyl-5-methoxy- γ -lactone (**9**): mp 114–115 °C; IR (KBr) 1760 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.59 (s, 3 H), 3.62 (dd, 1 H, $J = 10.0$ and 5.0 Hz), 4.00 (d, 1 H, $J = 10.0$ Hz), 5.40 (d, 1 H, $J = 5.0$ Hz), 7.28 (m, 10 H); m/e 224 ($\text{M}^+ - \text{CO}_2$).

Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$: C, 76.10; H, 6.01. Found: C, 75.74; H, 6.09.

The structure assignments of **10** and **9** were made on the basis of the lithium aluminum hydride reduction of **10** to *dl*-2,3-diphenyl-1,4-butanediol and **9** to *meso*-2,3-diphenyl-1,4-butanediol.

Irradiation of 3,5-Diphenyl-2(5H)-furanone (1) in the Presence of Excess 1,1-Dimethoxyethylene. A solution containing 100 mg of **1** in 475 mL of dry benzene containing 1.0 g of 1,1-dimethoxyethylene was irradiated with a 450-W Hanovia lamp equipped with a Corex filter for 1 h. Removal of the solvent left a crystalline solid which was recrystallized from benzene-ligroin to give the [2 + 2] cycloadduct **11** (125 mg) in 91% yield: mp 181–182 °C; IR (KBr) 1760 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 2.30 (dd, 1 H, $J = 12.0$ and 1.5 Hz), 2.50 (d, 1 H, $J = 12.0$ Hz), 2.78 (s, 3 H), 3.30 (s, 3 H), 4.20 (s, 1 H), 4.80 (d, 1 H, $J = 1.5$ Hz), 7.0–7.8 (m, 10 H).

Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}_4$: C, 74.05; H, 6.22. Found: C, 74.13; H, 6.18.

Preparation of 3,5,5-Triphenyl-2(5H)-furanone (12). To a stirred solution of 2.32 g of diphenylacetaldehyde in 50 mL of carbon disulfide

was added a solution containing 1.35 g of bromine in 5 mL of carbon disulfide. After stirring for 1 h, the reaction mixture was quenched by the addition of 20 mL of a 1% aqueous sodium thiosulfate solution. The reaction mixture was washed with water and dried over sodium sulfate. Removal of the solvent gave α -bromodiphenylacetaldehyde in nearly quantitative yield; IR (neat) 1695 cm^{-1} ; NMR (CCl_4 , 100 MHz) δ 7.22 (m, 10 H) and 9.61 (s, 1 H). The crude bromo aldehyde was taken up in 125 mL of benzene and 1.50 g of potassium phenylacetate and 662 mg of 18-crown-6 were added to the solution. The mixture was heated at reflux for 24 h with an attached Dean-Stark tube. At the end of this time the solution was concentrated under reduced pressure to 20 mL and passed through a short silica gel column with benzene to remove the crown ether. Evaporation of the solvent and recrystallization of the solid from methanol gave 3,5,5-triphenyl-2(5H)-furanone (**12**) in 90% yield; mp 152–153 °C; IR (KBr) 1750 cm^{-1} ; NMR (CDCl_3) δ 7.31 (m, 15 H), 7.98 (s, 1 H); UV (95% ethanol) 267 nm (ϵ 13 000); m/e 312 (M^+), 207, 179, and 105 (base).

Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{O}_2$: C, 84.59; H, 5.16. Found: C, 84.28; H, 5.05.

Irradiation of 3,5,5-Triphenyl-2(5H)-furanone (12) in Benzene. A deaerated solution of 3,5,5-triphenyl-2(5H)-furanone (**12**, 100 mg) in 475 mL of dry benzene was irradiated with a 450-W Hanovia mercury arc lamp equipped with a Corex filter for 1 h. The progress of the reaction was monitored by high-pressure liquid chromatography. Evaporation of the solvent under reduced pressure gave a yellow-white solid which was purified by filtration through a short column of dry column silica gel eluting with benzene. Recrystallization from methanol gave 78 mg (78%) of 3,4,5-triphenyl-2(5H)-furanone (**13**); mp 125–126 °C (lit.¹⁶ 125–126 °C); IR (KBr) 1760 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 6.15 (s, 1 H), 6.9–7.5 (m, 15 H); UV (95% ethanol) 285 nm (ϵ 12 300); m/e 312 (M^+), 207, 179 (base), and 105.

Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{O}_2$: C, 84.59; H, 5.16. Found: C, 84.32; H, 5.18.

The structure of the above product was verified by comparison with an authentic sample. To a stirred solution containing 2.0 g of benzoin phenylacetate in 40 mL of dry dimethyl sulfoxide was added 145 mg of sodium hydride. The reaction mixture was stirred at room temperature for 2 h and was then warmed quickly to 60–70 °C for 10 min. The cooled reaction mixture was poured into cold water and extracted with ether. The ether layer was washed with a 2% hydrochloric acid solution and then repeatedly with water. Evaporation of the dried ethereal layer gave a crystalline solid which was recrystallized from methanol to give 1.76 g (93%) of 3,4,5-triphenyl-2(5H)-furanone (**13**) which was identical in every detail with the product obtained from the irradiation of **12**.

Further irradiation of 3,4,5-triphenyl-2(5H)-furanone (**13**) in the presence of oxygen led to the formation of 3-phenylphenanthro[9,10-*c*]furan-1(3H)-one (**14**) in 76% yield; mp 259–260 °C (lit.¹⁶ mp 262 °C); UV (95% ethanol) 355, 338, 306, 278, 261, 253, and 231 nm (ϵ 1450, 1700, 9800, 12 200, 43 000, 39 500, and 41 000).

When a relatively concentrated solution (5×10^{-2} M) of 3,5,5-triphenyl-2(5H)-furanone (**12**) was irradiated in benzene, a [2 + 2] photodimer of starting material (**15**) was also obtained in 20% yield, mp 430 °C, IR (KBr) 1743 cm^{-1} .

Anal. Calcd for $\text{C}_{44}\text{H}_{32}\text{O}_4$: C, 84.59; H, 5.16. Found: C, 84.30; H, 5.18.

Irradiation of 3,5,5-Triphenyl-2(5H)-furanone (12) in Methanol. A solution containing 200 mg of **12** in 500 mL of methanol was irradiated with a 450-W Hanovia lamp under a argon atmosphere through Corex-filtered light for 1 h. Removal of the solvent left 202 mg (92%) of *cis*-3,4,5-triphenyl-5-methoxy- γ -lactone (**16**); mp 143–144 °C; IR (KBr) 1765 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.11 (s, 3 H), 4.20 (d, 1 H, $J = 8.0$ Hz), 4.98 (d, 1 H, $J = 8.0$ Hz), 6.4–7.4 (m, 15 H); m/e 312 ($\text{M}^+ - \text{CH}_3\text{OH}$), 207, 179 (base), and 105.

Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_3$: C, 80.21; H, 5.85. Found: C, 80.06; H, 5.87.

The initial photoadduct (**16**) could be epimerized when it was treated with base. To a stirred solution of cyclohexylisopropylamine in 10 mL of dry ether at –78 °C was added 0.2 mL of *n*-butyllithium under an argon atmosphere. After stirring for 30 min, the above photoproduct (35 mg in 5 mL of ether) was added dropwise over a 10-min interval. The reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was then poured into

75 mL of ether, washed with water and 2% hydrochloric acid solution, and then dried over magnesium sulfate. Evaporation of the ether gave a white solid which was recrystallized from ether–hexane to give 30 mg (86%) of *trans*-3,4,5-triphenyl-5-methoxy- γ -lactone (**17**); mp 159–160 °C; IR (KBr) 1770 cm^{-1} ; NMR (CDCl_3) δ 3.27 (s, 3 H), 4.14 (s, 2 H), 6.63–7.43 (m, 15 H).

A 60-mg sample of *cis*- (or *trans*-) 3,4,5-triphenyl-5-methoxy- γ -lactone was dissolved in 7 mL of glacial acetic acid which contained 140 mg of stannous chloride. The solution was heated at reflux for 48 h. At the end of this time the mixture was diluted with water and was extracted with ether. The ethereal layer was washed with a 5% sodium bicarbonate solution and was dried over magnesium sulfate. Removal of the solvent left 50 mg of a clear oil which solidified on standing to give pure 3,4,5-triphenyl-2(5H)-furanone (**12**), mp 125–126 °C.

Synthesis of 3,5-Diphenyl-5-(*p*-anisyl)-2(5H)-furanone (18). The above lactone was prepared by an identical procedure with that previously outlined for the synthesis of 3,5,5-triphenyl-2(5H)-furanone (**12**). The desired lactone (**18**) was a crystalline solid; mp 139–140 °C (80%); IR (KBr) 1756 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.95 (s, 3 H), 6.86–7.80 (m, 14 H), 7.91 (s, 1 H); m/e 342 (M^+), 252, 237, 209, 194, and 105; UV (95% ethanol) 268 nm (ϵ 13 500).

Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3$: C, 80.68; H, 5.30. Found: C, 80.63; H, 5.28.

Irradiation of 3,5-Diphenyl-5-(*p*-anisyl)-2(5H)-furanone (18) in Benzene. A deaerated solution of 3,5-diphenyl-5-(*p*-anisyl)-2(5H)-furanone (**18**, 100 mg) in 475 mL of dry benzene was irradiated with a 450-W Hanovia mercury arc lamp equipped with a Corex filter for 1 h. The progress of the reaction was monitored by high-pressure liquid chromatography. Evaporation of the solvent under reduced pressure left a yellow-white solid residue whose NMR spectrum indicated it to be a 16/1 mixture of 3,5-diphenyl-4-(*p*-anisyl)- (19) and 3,4-diphenyl-5-(*p*-anisyl)-2(5H)-furanone (**20**). The structures of the photoproducts were unambiguously established by comparison with independently synthesized samples.

Independent Synthesis of Diphenyl-4-(*p*-anisyl)-2(5H)-furanone (19). To a stirred solution containing 431 mg of 4'-methoxydeoxybenzoin (mp 69–70 °C) (lit.⁶¹ mp 77 °C) in 100 mL of ether was added a solution of 306 mg of bromine in 5 mL of ether. After stirring for 30 min, the ether was washed with 20 mL of a 1% aqueous solution of sodium thiosulfate to remove any excess bromine. After washing with water and drying over magnesium sulfate, the solvent was removed under reduced pressure leaving a solid residue; mp 67–68 °C; IR (KBr) 1690 cm^{-1} ; NMR (CDCl_3 , 60 MHz) δ 3.81 (s, 3 H), 6.38 (s, 1 H), 7.81–8.02 (complex m, 9 H). The α -bromo ketone was taken up in 30 mL of acetonitrile and 363 mg of potassium phenylacetate and 125 mg of 18-crown-6 were added to the solution. The mixture was heated at reflux for 1 h, the acetonitrile was removed under reduced pressure, and the oily residue was washed through a short column of silica gel with benzene. Evaporation of the solvent under reduced pressure gave an oil which crystallized on standing. Several recrystallizations from methanol gave 615 mg (89%) of 4'-methoxybenzoin phenylacetate (**21**); mp 107–108 °C; IR (KBr) 1730 and 1680 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.79 (s, 3 H), 3.80 (s, 2 H), 6.83–8.08 (complex m, 15 H).

Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_4$: C, 76.65; H, 5.59. Found: C, 76.62; H, 5.56.

To a stirred solution containing 1.0 g of 4'-methoxybenzoin phenylacetate (**21**) in 25 mL of dry dimethyl sulfoxide was added 70 mg (1 equiv) of sodium hydride. The reaction mixture was stirred at room temperature for 2 h and was allowed to warm to 60–70 °C for 10 min. The cooled reaction mixture was poured into cold water and extracted several times with ether. The ether layer was washed with a 2% hydrochloric acid solution and then repeatedly with water. Evaporation of the dried ethereal layer gave a white solid which was recrystallized several times from methanol to give 735 mg (77%) of 3,5-diphenyl-4-(*p*-anisyl)-2(5H)-furanone (**19**); mp 120–121 °C; IR (KBr) 1755 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.62 (s, 3 H), 6.18 (s, 1 H), 6.58 (d, 1 H, $J = 8.0$ Hz), 6.98 (d, 1 H, $J = 8.0$ Hz), 7.41 (m, 10 H); UV (95% ethanol) 314 nm (ϵ 16 100); m/e 342 (M^+), 311, 206, 179 (base), 156, and 105.

Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3$: C, 80.68; H, 5.30. Found: C, 80.39; H, 5.40.

Independent Synthesis of 3,4-Diphenyl-5-(*p*-anisyl)-2(5H)-furanone (20). To a stirred solution of 4-methoxydeoxybenzoin⁶² (2.26 g) in 125 mL of ether was added a solution of 1.60 g of bromine in 10 mL of ether. After stirring for 30 min, the ether was washed with 20 mL of

a 1% aqueous solution of sodium thiosulfate to remove any excess bromine. After drying over magnesium sulfate, the solvent was removed under reduced pressure leaving behind an oily residue. The crude α -bromo ketone was taken up in 75 mL of acetonitrile and 2.0 g of potassium phenylacetate and 350 mg of 18-crown-6 were added to the solution. The mixture was heated at reflux for 1 h. The acetonitrile was removed under reduced pressure and the oily residue was washed through a short column of silica gel with benzene. Evaporation of the benzene under reduced pressure gave an oil which crystallized on standing. Several recrystallizations from methanol gave 2.96 g (82%) of 4-methoxybenzoin phenylacetate (**22**): mp 106–107 °C; IR (KBr) 1740 and 1680 cm^{-1} ; NMR (CDCl_3 , 60 MHz) δ 3.71 (s, 3 H), 3.79 (s, 2 H), 6.82–8.01 (complex m, 15 H).

Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_4$: C, 76.65; H, 5.59. Found: C, 76.56; H, 5.60.

To a solution containing 1.0 g of 4-methoxybenzoin phenylacetate (**22**) in 25 mL of dry dimethyl sulfoxide was added 65 mg (1 equiv) of sodium hydride. The reaction mixture was stirred at room temperature for 2 h and then warmed to 60–70 °C for 10 min. The cooled reaction mixture was poured into cold water and extracted several times with ether. The ether layer was washed with a 2% hydrochloric acid solution and then repeatedly with water. Evaporation of the dried ethereal layer gave an oily residue which was recrystallized from absolute ethanol to give 622 mg (65%) of 3,4-diphenyl-5-(*p*-anisyl)-2(5H)-furanone (**20**): mp 112–113 °C; IR (KBr) 1755 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.64 (s, 3 H), 6.02 (s, 1 H), 6.62 (d, 1 H, $J = 8$ Hz), 6.8–7.4 (m, 12 H); m/e 342 (M^+), 241, 227, 196, 185, 170 (base), 157 and 156; UV (95% ethanol) 283 nm (ϵ 12 800).

Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3$: C, 80.68; H, 5.30. Found: C, 80.62; H, 5.30.

Irradiation of 3,5-Diphenyl-5-(*p*-anisyl)-2(5H)-furanone (18**) in Methanol.** A solution containing 100 mg of **18** in 475 mL of methanol was irradiated with a 450-W Hanovia lamp through a Corex filter sleeve for 1 h. Evaporation of the solvent under reduced pressure left a yellow oil which contained two components as shown by NMR spectroscopy: δ 6.5–7.4 (complex m), 5.12 (d, $J = 8$ Hz), 4.30 (d, $J = 8$ Hz), 3.70 (s, 3 H), 3.50 (s, 3 H), and 3.21 (s, 3 H). Treatment of the crude photolysate with 200 mg of stannous chloride in refluxing acetic acid (10 mL) for 24 h gave a mixture of 3,5-diphenyl-4-(*p*-anisyl)- (**19**) and 3,4-diphenyl-5-(*p*-anisyl)-2(5H)-furanone (**20**) (ratio 0.72). The two pure photoproducts could be obtained by extensive fractional crystallization from ether-hexane. The less soluble isomer was identified as 3,4-diphenyl-5-(*p*-anisyl)-5-methoxy- γ -lactone (**24**): mp 154–155 °C (58%); IR (KBr) 1770 cm^{-1} ; NMR (CDCl_3) δ 3.20 (s, 3 H), 3.69 (s, 3 H), 4.30 (d, 1 H, $J = 8.0$ Hz), 5.12 (d, 1 H, $J = 8.0$ Hz), 6.57–7.4 (m, 14 H); m/e 374, 343, 254, 180, 135, and 77.

The more soluble isomer was purified by chromatography on a thick layer plate followed by recrystallization from pentane to give 3,5-diphenyl-4-(*p*-anisyl)-5-methoxy- δ -lactone (**23**): mp 107–108 °C (42%); IR (KBr) 1770 cm^{-1} ; NMR (CDCl_3) δ 3.20 (s, 3 H), 3.51 (s, 3 H), 4.28 (d, 1 H, $J = 8.0$ Hz), 5.08 (d, 1 H, $J = 8.0$ Hz), 6.30 (d, 2 H, $J = 8.0$ Hz), 6.56 (d, 2 H, $J = 8.0$ Hz), 7.1–7.4 (m, 10 H); m/e 374, 343, 223, 208, 105, and 77.

The assignments of the two photoadducts were verified by treating each isomer separately with stannous chloride in refluxing acetic acid and isolating the corresponding 3,4,5-triaryl-substituted 2(5H)-furanone.

Synthesis of 3,5-Diphenyl-5-(*p*-cyanophenyl)-2(5H)-furanone (25**).** To a stirred solution of 2.3 g of 2-*p*-bromophenyl-2-phenylacetaldehyde⁶³ in 30 mL of chloroform was added a solution of 3.5 g of bromine in 5 mL of chloroform. After stirring for 1 h at room temperature the reaction mixture was quenched by the addition of 20 mL of a 5% aqueous sodium thiosulfate solution. The reaction mixture was washed with water and dried over sodium sulfate. Removal of the solvent left a yellow oil. A 1.5-g sample of this material was taken up in 25 mL of benzene and 1.40 g of potassium phenylacetate and 660 mg of 18-crown-6 were added to the solution. The mixture was heated at reflux for 24 h with an attached Dean-Stark tube. At the end of this time the solution was concentrated under reduced pressure and passed through a short silica gel column with benzene. Evaporation of the solvent and recrystallization from methanol gave 3,5-diphenyl-5-(*p*-bromophenyl)-2(5H)-furanone (62%): mp 134–135 °C; IR (KBr) 1760 cm^{-1} ; NMR (100 MHz, CDCl_3) δ 7.13–8.00 (m, 14 H), 8.03 (s, 1 H).

Anal. Calcd for $\text{C}_{22}\text{H}_{15}\text{OBr}$: C, 67.53; H, 3.86; Br, 20.43. Found:

C, 67.52; H, 3.87; Br, 20.48.

A mixture containing 2.1 g of 3,5-diphenyl-5-(*p*-bromophenyl)-2(5H)-furanone and 600 mg of copper(I) cyanide in 10 mL of dimethylformamide was refluxed for 10 h under nitrogen. The reaction mixture was poured into 100 mL of a 10% sodium cyanide solution and shaken vigorously. The suspension was extracted thoroughly with benzene. The benzene layer was washed successively with 50 mL of a 10% sodium cyanide solution and water and then dried over sodium sulfate. The benzene was removed under reduced pressure leaving an orange oil which solidified on standing. Chromatography on silica gel using a 1:1 chloroform-hexane mixture as the eluent gave 1.5 g (84%) of 5-(4'-cyanophenyl)-3,5-diphenyl-2(5H)-furanone (**25**): mp 117–118 °C; IR (KBr) 1765 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 7.38–7.92 (complex m, 14 H), 8.01 (s, 1 H); UV (95% ethanol) 268 nm (ϵ 15 400); m/e 337 (M^+), 207, 186, 179, and 105.

Anal. Calcd for $\text{C}_{23}\text{H}_{15}\text{NO}_2$: C, 81.88; H, 4.48; N, 4.15. Found: C, 81.91; H, 4.52; N, 4.19.

Irradiation of 3,5-Diphenyl-5-(*p*-cyanophenyl)-2(5H)-furanone (25**) in Benzene.** A deaerated solution containing 100 mg of 3,5-diphenyl-5-(*p*-cyanophenyl)-2(5H)-furanone (**25**) in 450 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 1 h. Evaporation of the solvent under reduced pressure left a solid residue which contained two components. When the NMR spectra of independently synthesized samples of the two photoproducts were compared to an NMR spectrum of the crude photolysate (benzene solvent), a preferential *p*-cyanophenyl migration was observed (ratio found 3.5/1).

Independent Synthesis of 3,4-Diphenyl-5-(*p*-cyanophenyl)-2(5H)-furanone (27**).** A mixture of 12.5 g of 4-bromodeoxybenzoin⁶⁴ (mp 145–147 °C) and 5.40 g of copper(I) cyanide in 20 mL of dimethylformamide was refluxed under nitrogen for 10 h while being stirred. The hot reaction mixture was then poured into 50 mL of cold water. The tan precipitate was collected, washed thoroughly with water, and then shaken with a warm solution of ethylenediamine (30 mL) in water (70 mL). Benzene was added and the mixture was shaken thoroughly and the aqueous layer discarded. The benzene extracts were washed with a 10% aqueous sodium cyanide solution and water, and dried over sodium sulfate. After removal of the solvent, the residue was passed through a short column of silica gel to remove polar impurities and recrystallized from ethanol giving 8.55 g (86%) of 4-cyanodeoxybenzoin: mp 112–113 °C; IR (KBr) 2250 and 1695 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 4.41 (s, 2 H), 7.10–8.05 (complex m, 9 H); m/e 221 (M^+), 116, 105 (base), 89, and 77.

Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{NO}$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.39; H, 5.01; N, 6.28.

To a stirred solution containing 1.0 g of 4-cyanodeoxybenzoin in 50 mL of carbon disulfide was added a solution of 0.725 g of bromine in 5 mL of carbon disulfide. After stirring for 2 h the reaction mixture was quenched by the addition of 20 mL of a 1% aqueous sodium thiosulfate solution. The reaction mixture was washed with water and dried. Removal of the solvent gave 4-cyanodesyl bromide in quantitative yield: NMR (CDCl_3 , 100 MHz) δ 6.28 (s, 1 H), 7.09–7.80 (complex m, 9 H). The crude bromo ketone was taken up in 75 mL of acetonitrile and 1.0 g of potassium phenylacetate and 300 mg of 18-crown-6 were added to the solution. The mixture was heated at reflux for 1 h. The salt was removed by filtration and the benzene solution was washed through a short column of silica gel. Evaporation of the solvent under reduced pressure gave an oily residue which was recrystallized several times from ethanol to give 1.48 g (93%) of 4-cyanobenzoin phenylacetate: mp 96–97 °C; IR (KBr) 2200, 1750, and 1690 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.75 (s, 2 H), 6.81 (s, 1 H), 7.20–7.88 (complex m, 14 H).

Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{O}_3\text{N}$: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.72; H, 4.86; N, 3.93.

To a stirred solution containing 1.0 g of 4-cyanobenzoin phenylacetate in 15 mL of dry dimethyl sulfoxide was added 67 mg of sodium hydride. The reaction mixture was stirred at 70 °C for 2 h, cooled, poured into cold water, and extracted with ether. The ether layer was washed with a 2% hydrochloric acid solution and then repeatedly with water. Evaporation of the dried ethereal layer gave an oily residue which was recrystallized from ethanol to give 553 mg (58%) of 3,4-diphenyl-5-(*p*-cyanophenyl)-2(5H)-furanone (**27**): mp 117–118 °C; IR (KBr) 1745 and 2200 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 6.31 (s, 1 H), 7.02–7.69 (complex m, 14 H); UV (methanol) 276 nm (ϵ 12 400); m/e 337 (M^+), 207, 179 (base), 107, and 105.

Anal. Calcd for $\text{C}_{23}\text{H}_{15}\text{O}_2\text{N}$: C, 81.88; H, 4.48; N, 4.15. Found:

C, 81.93; H, 4.56; N, 4.21.

Independent Synthesis of 3,5-Diphenyl-4-(*p*-cyanophenyl)-2(5*H*)-furanone (26). A stirred suspension of magnesium turnings (1.20 g) and *p*-dibromobenzene (9.44 g) in 200 mL of anhydrous ether was refluxed under a nitrogen atmosphere for 24 h. To the cooled reaction mixture was added 4.80 g of phenylacetaldehyde in 50 mL of anhydrous ether. After refluxing for 5 h the reaction mixture was poured over dilute hydrochloric acid in ice and then stirred for 30 min. The mixture was extracted thoroughly with ether and the ether extracts were washed with water and then dried. Evaporation under reduced pressure left a colorless oil: IR (film) 3450 (broad) cm^{-1} ; NMR (CCl_4 , 100 MHz) δ 2.62 (m, 2 H), 3.02 (br s, 1 H), 4.42 (overlapping dd, 1 H, $J = 8.0$ Hz), 6.78–7.25 (complex m, 9 H). The oily residue (8.7 g) was dissolved in 200 mL of acetone and titrated with Jones reagent until an orange color persisted. A few drops of 2-propanol were added to destroy the Jones reagent. The mixture was filtered to remove the chromium salts followed by removal of the acetone under reduced pressure. The semisolid residue was dissolved in ether, washed with sodium bicarbonate solution and water, and then dried. Evaporation gave a white solid which was recrystallized from methanol to give 5.8 g (53%) of 4'-bromodeoxybenzoin:⁶⁵ mp 111–112 °C; IR (KBr) 1698 cm^{-1} ; NMR (CDCl_3) δ 4.18 (s, 2 H), 7.21 (br s, 5 H), 7.49–7.81 (dd, 4 H, $J = 8.0$ Hz).

A mixture of 4'-bromodeoxybenzoin (2.399 g) and copper(I) cyanide (785 mg) in 11 mL of 1-methyl-2-pyrrolidinone was refluxed under nitrogen for 5 h. The reaction mixture was cooled, poured into 150 mL of 10% potassium cyanide solution, and shaken thoroughly. The suspension was extracted with benzene and then filtered. The benzene extracts were washed with 10% potassium cyanide solution and water and then dried. Evaporation of the solvent under reduced pressure left a reddish-brown residue which was purified by chromatography on a silica gel column eluting with benzene. The yellow-white solid obtained was recrystallized several times from ethanol to give 1.44 g (75%) of 4'-cyanodeoxybenzoin: mp 108–109 °C; IR (KBr) 1698 and 2200 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 4.30 (s, 2 H), 7.31 (br s, 5 H), 7.71–8.19 (dd, 4 H, $J = 8.0$ Hz).

To a solution of 4'-cyanodeoxybenzoin (622 mg) in 50 mL of carbon disulfide containing several drops of 47% hydrobromic acid was added a solution of 450 mg of bromine in 5 mL of carbon disulfide. After stirring for 2 h at room temperature, the reaction mixture was quenched by the addition of 20 mL of a 1% aqueous sodium thiosulfate solution. The organic layer was then washed with water and dried. Removal of the solvent gave an almost quantitative yield of 4'-cyanodeoxybenzoin. The crude bromo ketone was taken up in 50 mL of acetonitrile and 489 mg of potassium phenylacetate and 44 mg of 18-crown-6 were added to the solution. The mixture was heated at reflux for 2 h. The solution was concentrated to 15 mL and then washed through a short column of silica gel. Evaporation of the solvent under reduced pressure gave an oily residue which was recrystallized from ethanol to give 250 mg (25%) of 4'-cyanobenzoin phenylacetate: mp 103–104 °C; IR (KBr) 2200, 1785, and 1695 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.79 (s, 2 H), 6.81 (s, 1 H), 7.32–7.45 (m, 10 H), 7.61 (d, 2 H, $J = 8.0$ Hz), 7.98 (d, 2 H, $J = 8.0$ Hz).

Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{NO}_3$: C, 77.73; H, 4.82; N, 3.94. Found: C, 77.61; H, 4.90; N, 3.88.

A mixture containing 32.4 mg of oil-free sodium hydride and 461 mg of 4'-cyanobenzoin phenylacetate in 25 mL of anhydrous dimethyl sulfoxide was stirred at 70 °C for 3 h. After cooling, the mixture was poured into 100 mL of a 2% hydrochloric acid solution and extracted with ether. The ethereal layer was washed with a 10% sodium bicarbonate solution, then water, and dried over anhydrous magnesium sulfate. Removal of the solvent left a yellow oil which crystallized upon addition of methanol to give the β,γ -unsaturated lactone: NMR (CDCl_3 , 100 MHz) δ 7.0–7.7 (m, 14 H) and 4.85 (s, 1 H). Further recrystallization of this material from methanol caused double bond isomerization to afford 365 mg (83%) of 3,5-diphenyl-4-(*p*-cyanophenyl)-2(5*H*)-furanone (26): mp 178–179 °C; IR (KBr) 1750 and 2200 cm^{-1} ; UV (methanol) 276 nm (ϵ 10 300); NMR (CDCl_3 , 100 MHz) δ 6.21 (s, 1 H) and 7.02–7.60 (m, 1 H); m/e 337 (M^+), 205, 186, and 105 (base).

Anal. Calcd for $\text{C}_{23}\text{H}_{15}\text{NO}_2$: C, 81.88; H, 4.48; N, 4.15. Found: C, 81.71; H, 4.43; N, 4.14.

Irradiation of 3,5-Diphenyl-5-(*p*-cyanophenyl)-2(5*H*)-furanone (25) in Methanol. A deaerated solution of 5-(4'-cyanophenyl)-3,5-diphenyl-2(5*H*)-furanone (25, 100 mg) in 475 mL of methanol was irradiated with a 450-W Hanovia mercury arc lamp equipped with a

Corex filter for 1 h. Evaporation of the solvent under reduced pressure gave an oil which crystallized on standing: IR (CHCl_3) 2250, 1775 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.10 (s, OCH_3), 4.40 (dd, $J = 8.0$ Hz), 5.18 (dd, $J = 8.0$ Hz), 6.62–7.61 (complex m). Treatment of the crude photolysate with 200 mg of stannous chloride in refluxing acetic acid (10 mL) for 24 h gave a mixture of 4-(4'-cyanophenyl)-3,5-diphenyl- (26) and 5-(4'-cyanophenyl)-3,4-diphenyl-2(5*H*)-furanone (27) (4.5/1). When the NMR spectrum of independently synthesized samples was compared to the crude spectrum, a preferential *p*-cyanophenyl migration was observed (4.5/1). The material balance for the above reactions was >90%.

Synthesis of 3,5-Diphenyl-5-(*m*-anisyl)-2(5*H*)-furanone (30). This lactone was prepared by the standard procedure previously outlined in 85% yield: mp 121–122 °C; IR (KBr) 1730 cm^{-1} ; NMR (CDCl_3 , 100 MHz) δ 3.7 (s, 3 H), 6.7–7.95 (m, 14 H), 8.0 (s, 1 H); UV (methanol) 267 nm (ϵ 13 900); m/e 342 (M^+), 237, 209 (base), 207, 179, and 105.

Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3$: C, 80.68; H, 5.30. Found: C, 80.55; H, 5.25.

Irradiation of 3,5-Diphenyl-5-(*m*-anisyl)-2(5*H*)-furanone (30) in Benzene. A deaerated solution containing 188 mg of furanone 30 in 450 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 1 h. Removal of the solvent under reduced pressure left an oil which contained two components as judged from its NMR spectrum. Integration of the signals indicated a 1.5/1 ratio of 3,5-diphenyl-4-(*m*-anisyl)-2(5*H*)-furanone (32) to 3,4-diphenyl-5-(*m*-anisyl)-2(5*H*)-furanone (33). The structures of the photoproducts were unambiguously established by comparison with independently synthesized samples.

Independent Synthesis of 3,5-Diphenyl-4-(*m*-anisyl)-2(5*H*)-furanone (32). A sample of 3'-methoxydeoxybenzoin⁶⁶ was converted to 3'-methoxybenzoin phenylacetate, mp 87–88 °C, in 90% yield using *N*-bromosuccinimide as the brominating agent. This material was converted to furanone 32 by the standard procedure. The desired furanone 32 showed the following spectral properties: mp 100–101 °C; IR (KBr) 1740 cm^{-1} ; UV (methanol) 284 nm (ϵ 18 200); NMR (CDCl_3 , 100 MHz) δ 3.38 (s, 3 H), 6.20 (s, 1 H), 6.5–7.6 (m, 14 H); m/e 342 (M^+), 281, 185, and 144 (base).

Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3$: C, 80.68; H, 5.30. Found: C, 80.34; H, 5.54.

Independent Synthesis of 3,4-Diphenyl-5-(*m*-anisyl)-2(5*H*)-furanone (33). A mixture containing 8.3 g of 3-methoxyphenylacetic acid and 5 mL of thionyl chloride was heated on a steam bath for 45 min. The excess thionyl chloride was removed under reduced pressure and the residue was distilled at 77 °C (0.2 mm). The resulting acid chloride in 100 mL of benzene was added dropwise to a slurry containing 7 g of aluminum chloride in 100 mL of benzene. The reaction mixture was heated at reflux for 2 h, poured onto 400 g of crushed ice and 40 mL of concentrated hydrochloric acid, and extracted with ether. The ether extracts were washed with a 10% sodium bicarbonate solution followed by water. After drying over magnesium sulfate the solvent was removed under reduced pressure and the residue was chromatographed on silica gel with a 5% acetone-hexane mixture to give a pure sample (70%) of 3-methoxydeoxybenzoin: NMR (CDCl_3 , 100 MHz) δ 3.88 (s, 3 H), 4.2 (s, 2 H), 6.6–8.2 (m, 9 H). This material was converted to 3-methoxybenzoin phenylacetate using pyrrolidone hydrotribromide as the brominating agent: NMR (CDCl_3 , 100 MHz) δ 3.54 (s, 3 H), 3.74 (s, 2 H), 6.7–8.1 (m, 14 H); IR (neat) 1680 and 1730 cm^{-1} . Subjection of this compound to the standard sodium hydride-dimethyl sulfoxide cyclization procedure gave 3,4-diphenyl-5-(*m*-anisyl)-2(5*H*)-furanone (33) in 83% yield: IR (CHCl_3) 1770 cm^{-1} ; UV (methanol) 280 nm (ϵ 12 500); NMR (CDCl_3 , 100 MHz) δ 3.6 (s, 3 H), 6.1 (s, 1 H), 6.5–7.4 (m, 14 H); m/e 336 (M^+), 324, 296, 281, 246, 205, 185, 144 (base), 91, and 77.

Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{O}_3$: C, 80.67; H, 5.30. Found: C, 80.77; H, 5.35.

Irradiation of 3,5-Diphenyl-5-(*m*-anisyl)-2(5*H*)-furanone (30) in Methanol. A deaerated solution of furanone 30 (153 mg) in 450 mL of methanol was irradiated with a 450-W Hanovia lamp through a Corex filter sleeve for 60 min. Removal of the solvent under reduced pressure left an oil which exhibited the following signals in the NMR (CDCl_3 , 100 MHz): δ 3.14 (s), 3.17 (s), 3.38 (s), 3.54 (s), 4.25 (dd, $J = 8.0$ Hz), 5.04 (dd, $J = 8.0$ Hz), 6.2–7.5 (m). Treatment of the crude photolysate with 250 mg of stannous chloride in the normal fashion afforded a 1.05/1 ratio of 3,4-diphenyl-5-(*m*-anisyl)- (33) and 3,5-diphenyl-4-(*m*-anisyl)-2(5*H*)-furanone (32).

Synthesis of 3,5-Diphenyl-5-(*p*-toluyl)-2(5H)-furanone (31). The above lactone was prepared by an identical procedure with that previously outlined for the synthesis of the other 3,5,5-triaryl-2(5H)-furanones. The desired lactone (31) was a crystalline solid; mp 133–134 °C; 88% overall yield; IR (KBr) 1740 cm⁻¹; UV (methanol) 266 nm (ϵ 14 600); NMR (CDCl₃, 100 MHz) δ 2.34 (s, 1 H), 7.13–8.00 (m, 14 H), and 8.02 (s, 1 H); *m/e* 326 (M⁺), 221, 193 (base), 186, and 179.

Anal. Calcd for C₂₃H₁₈O₂: C, 84.64; H, 5.56. Found: C, 84.43; H, 5.57.

Irradiation of 3,5-Diphenyl-5-(*p*-toluyl)-2(5H)-furanone (31) in Benzene. A deaerated solution containing 98.5 mg of furanone 31 in 450 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 1 h. Removal of the solvent under reduced pressure left an oil which contained two components as judged from the NMR spectrum of the crude photolysate. Integration of the signals indicated a 3.5/1 ratio of 3,5-diphenyl-4-(*p*-toluyl)- (36) to 3,4-diphenyl-5-(*p*-toluyl)-2(5H)-furanone (37). The structures of the photoproducts were unambiguously established by comparison with independently synthesized samples.

Independent Synthesis of 3,4-Diphenyl-5-(*p*-toluyl)-2(5H)-furanone (37). To a stirred solution containing 2.0 g of 4-methyldeoxybenzoin⁶⁷ in 400 mL of distilled tetrahydrofuran was added 5.20 g of pyrrolidone hydrotribromide in 250 mL of tetrahydrofuran over a 45-min interval. After stirring for 9 h, the mixture was washed with 1 sodium thiosulfate and water and dried over magnesium sulfate. Removal of the solvent left the monobrominated ketone as a yellow oil which was used without further purification. A 2.4-g sample of the α -bromo ketone and 1.74 g of potassium phenylacetate in 100 mL of acetonitrile which contained 500 mg of 18-crown-6 was stirred at 25 °C for 8 h. The 18-crown-6 was removed by filtration through a silica gel column to give 2.4 g (84%) of 4-methylbenzoin phenylacetate: mp 98–99 °C; IR (KBr) 1680 and 1750 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 2.66 (s, 3 H), 4.13 (s, 2 H), 7.25 (s, 1 H), 7.5–8.25 (m, 14 H); *m/e* 344 (M⁺), 239, 199, 119 (base), and 105.

A mixture containing 450 mg of the above compound and 34.6 mg of sodium hydride in 25 mL of dimethyl sulfoxide was stirred at 70 °C for 3 h. The normal workup procedure afforded 328 mg (77%) of 3,4-diphenyl-5-(*p*-toluyl)-2(5H)-furanone (37); mp 119–120 °C; IR (KBr) 1755 cm⁻¹; UV (methanol) 284 nm (ϵ 12 200); NMR (CDCl₃, 100 MHz) δ 2.17 (s, 3 H), 6.23 (s, 1 H), 6.9–7.6 (m, 14 H); *m/e* 326 (M⁺), 207, 179, and 119.

Anal. Calcd for C₂₃H₁₈O₂: C, 84.64; H, 5.56. Found: C, 84.59; H, 5.55.

Independent Synthesis of 3,5-Diphenyl-4-(*p*-toluyl)-2(5H)-furanone (36). A sample of 4'-methylbenzoin phenylacetate, prepared in an identical fashion with that described above, showed the following spectral properties: mp 96–97 °C; NMR (CDCl₃, 100 MHz) δ 3.46 (s, 2 H), 3.64 (s, 3 H), 6.72 (s, 1 H), 6.8–7.75 (m, 14 H). This material was converted to furanone 36 by treatment with potassium phenylacetate in acetonitrile with 18-crown-6 in quantitative yield. The desired furanone 36 showed the following spectral properties: mp 122–123 °C; IR (KBr) 1750 cm⁻¹; UV (methanol) 295 nm (ϵ 13 400); NMR (CDCl₃, 100 MHz) δ 2.04 (s, 3 H), 6.12 (s, 1 H), 6.5–7.6 (m, 14 H); *m/e* 326 (M⁺), 205, 180 (base), and 165.

Anal. Calcd for C₂₃H₁₈O₂: C, 84.64; H, 5.56. Found: C, 84.54; H, 5.64.

Irradiation of 3,5-Diphenyl-5-(*p*-toluyl)-2(5H)-furanone (31) in Methanol. A deaerated solution of furanone 31 (182 mg) in 450 mL of methanol was irradiated with a 450-W Hanovia lamp through a Corex filter sleeve for 75 min. Removal of the solvent under reduced pressure left an oil which exhibited the following signals in the NMR (CDCl₃, 100 MHz): δ 1.90 (s), 2.10 (s), 3.10 (s), 4.20 (dd, *J* = 8.0 Hz), 4.95 (dd, *J* = 8.0 Hz), 6.4–7.3 (m). Treatment of the crude photolysate with 250 mg of stannous chloride in refluxing acetic acid for 24 h afforded a 0.81 ratio of 3,5-diphenyl-4-(*p*-toluyl)- (36) and 3,4-diphenyl-5-(*p*-toluyl)-2(5H)-furanone (37).

Synthesis of 5-Methyl-3,5-diphenyl-2(5H)-furanone (40). To a solution containing 2.06 g of 2-bromo-2-phenylpropionaldehyde⁶⁸ in 125 mL of dry benzene were added 2.0 g of potassium phenylacetate and 800 mg of 18-crown-6. The mixture was heated at reflux for 24 h with an attached Dean-Stark tube to remove the water. The reaction mixture was then filtered and chromatographed through a short silica gel column to remove the crown ether. Removal of the solvent under reduced pressure left 2.7 g (73%) of 5-methyl-3,5-diphenyl-2(5H)-furanone (40) as a white, crystalline solid; mp 71–72 °C; IR (KBr)

1740 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 1.84 (s, 3 H), 7.81 (s, 1 H), 7.38–7.60 and 7.95–8.02 (m, 10 H); *m/e* 250 (M⁺), 207, 179 (base), and 144; UV (methanol) 260 nm (ϵ 19 900).

Anal. Calcd for C₁₇H₁₄O₂: C, 81.58; H, 5.64. Found: C, 81.47; H, 5.68.

Irradiation of 5-Methyl-3,5-diphenyl-2(5H)-furanone (40) in Benzene. A deaerated solution containing 100 mg of 5-methyl-3,5-diphenyl-2(5H)-furanone (40) in 475 mL of dry benzene was irradiated with a 450-W Hanovia mercury arc lamp equipped with a Corex filter for 35 min. Removal of the solvent under reduced pressure left a white solid which was crystallized from methanol to give 85 mg (85%) of 5-methyl-3,4-diphenyl-2(5H)-furanone (41); mp 139–140 °C; IR (KBr) 1760 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 1.43 (d, 1 H, *J* = 8.0 Hz), 5.63 (q, 1 H, *J* = 8.0 Hz), 7.40–7.80 (m, 10 H); *m/e* 250 (M⁺), 207, 179 (base), and 144; UV (methanol) 282 nm (ϵ 11 900).

Anal. Calcd for C₁₇H₁₄O₂: C, 81.58; H, 5.64. Found: C, 81.45; H, 5.66.

This material was further verified by comparison with an authentic sample. A sample of 1-benzoyl ethyl phenylacetate was prepared by treating α -bromopropiophenone with potassium phenylacetate in acetonitrile with 18-crown-6: NMR (CDCl₃, 100 MHz) δ 1.41 (d, 3 H, *J* = 7.0 Hz), 3.6 (s, 2 H), 5.82 (q, 1 H, *J* = 7.0 Hz), 7.05–7.80 (m, 10 H); IR (neat) 1690 and 1740 cm⁻¹. This compound was converted to furanone 41 in 90% yield by the standard sodium hydride cyclization procedure. The furanone (41) obtained from this synthesis was identical in every detail with that obtained from the photolysis of furanone 40.

Irradiation of 5-Methyl-3,5-diphenyl-2(5H)-furanone (40) in Methanol. A deaerated solution of 3,5-diphenyl-5-methyl-2(5H)-furanone (140 mg, 40) in 450 mL of methanol was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 1 h. Removal of the solvent left a crude oil whose NMR spectrum (CDCl₃, 100 MHz) showed peaks at δ 1.18 (s), 1.28 (s), 3.64 (s), 3.68 (s), 3.86 (d, *J* = 8.0 Hz), 4.02 (d, *J* = 12.0 Hz), 4.35 (d, *J* = 12.0 Hz), 4.90 (d, *J* = 8.0 Hz), 6.9–7.6 (m). Treatment of the crude photolysate with stannous chloride in the normal fashion afforded 3,4-diphenyl-5-methyl-2(5H)-furanone (41) as the only detectable product in 95% yield.

Synthesis of 5-Methyl-5-(*p*-anisyl)-3-phenyl-2(5H)-furanone (43). The preparation of furanone 43 was carried out by the standard method previously described and 43 was obtained in 89% yield; mp 83–84 °C; IR (KBr) 1770 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 1.87 (s, 3 H), 3.78 (s, 3 H), 6.8–7.95 (m, 9 H), and 7.70 (s, 1 H); UV (methanol) 263 nm (ϵ 12 800); *m/e* 280 (M⁺), 237 (base), 209, and 135.

Anal. Calcd for C₁₈H₁₆O₃: C, 77.12; H, 5.75. Found: C, 77.17; H, 6.11.

Irradiation of 5-Methyl-5-(*p*-anisyl)-3-phenyl-2(5H)-furanone (43) in Benzene. A deaerated solution containing 95 mg of furanone 43 in 450 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 1 h. Removal of the solvent under reduced pressure left a pale oil which was recrystallized from methanol to give 5-methyl-4-(*p*-anisyl)-3-phenyl-2(5H)-furanone (44) in 90% yield; mp 130–131 °C; IR (KBr) 1745 cm⁻¹; UV (methanol) 307 nm (ϵ 19 000); NMR (CDCl₃, 100 MHz) δ 1.40 (d, 3 H, *J* = 6.0 Hz), 3.72 (s, 3 H), 5.47 (q, 1 H, *J* = 6.0 Hz), 6.7–7.5 (m, 9 H); *m/e* 280, 278, 237, 209 (base), and 165.

Anal. Calcd for C₁₈H₁₆O₃: C, 77.12; H, 5.75. Found: C, 77.03; H, 6.01.

The structure of this material was further verified by comparison with an independently synthesized sample. A 3.3-g sample of *p*-methoxypropiophenone was brominated in the usual fashion and was then heated with a sample of potassium phenylacetate and 500 mg of 18-crown-6 in refluxing benzene for 24 h. Standard workup of the reaction mixture afforded a 94% yield of furanone 44 which was identical in every detail with a sample prepared from the irradiation of 43.

Irradiation of 5-Methyl-5-(*p*-anisyl)-3-phenyl-2(5H)-furanone (43) in Methanol. A deaerated solution of furanone 43 (71 mg) in 450 mL of methanol was irradiated with a 450-W Hanovia lamp equipped with a Corex filter sleeve for 1 h. Removal of the solvent followed by reaction of the residue with stannous chloride in the usual manner afforded 5-methyl-4-(*p*-anisyl)-3-phenyl-2(5H)-furanone (44) which was identical with the independently synthesized sample.

Synthesis and Attempted Photolysis of 5,5-Dimethyl-3-phenyl-2(5H)-furanone (46). In a 250-mL round-bottom flask equipped with

a Dean-Stark trap and a condenser were placed 4.02 g of 2-bromo-2-methylpropanol,⁶⁹ 5.1 g of potassium phenylacetate, 1.76 g of 18-crown-6, and 125 mL of benzene. The mixture was heated at reflux for 10 h. At the end of this time the mixture was filtered through 40 g of silica gel to remove the crown ether. The major component contained 4.46 g (93%) of 5,5-dimethyl-3-phenyl-2(5*H*)-furanone (**46**) as a white, crystalline solid: mp 67–68 °C; IR (KBr) 1750 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 1.52 (s, 6 H), 7.47 (s, 1 H), 7.37–7.82 (m, 5 H); UV (cyclohexane) 295, 257, and 224 nm (ε 1100, 11 000, and 10 000); *m/e* 188 (M⁺), 145, 117 (base).

Anal. Calcd for C₁₂H₁₂O₂: C, 76.57; H, 6.43. Found: C, 76.57; H, 6.42.

Extended irradiation of this material in benzene or methanol gave only recovered starting material with no indication of any other photoproduct.

Synthesis of 3,5,5-Triphenyl-4-methyl-2(5*H*)-furanone (48). To a stirred solution containing 1.56 g of 3,5,5-triphenyl-2(5*H*)-furanone (**12**) in 50 mL of ether was added a solution containing 1.0 g of diazomethane in 100 mL of ether. The solution was allowed to stir at 25 °C for 3 days. At the end of this time the precipitate which had formed was collected by filtration. This material contained 867 mg (49%) of 3,7,7-triphenyl-1-oxa-4,5-diazabicyclo[3.3.0^{3,7}]oct-4-en-2-one (**47**): mp 128–129 °C; NMR (CDCl₃, 100 MHz) δ 3.92 (dd, 1 H, *J* = 9.0 and 5.0 Hz), 4.42 (dd, 1 H, *J* = 19.0 and 5.0 Hz), 5.05 (dd, 1 H, *J* = 19.0 and 9.0 Hz), 7.0–7.5 (m, 15 H); IR (KBr) 1770 cm⁻¹. A 130-mg sample of this solid was heated under a nitrogen atmosphere for 30 min to give a 1:1 mixture of 3,5,5-triphenyl-4-methyl-2(5*H*)-furanone (**48**) and 3,6,6-triphenyl-1-oxabicyclo[3.1.0^{3,5}]hexan-2-one (**49**). These two compounds were separated by fractional crystallization from acetone-hexane. The bicyclohexan-2-one **49** was a crystalline solid: mp 155–156 °C; IR (KBr) 1770 cm⁻¹; NMR (CDCl₃, 100 MHz) δ 1.36 (t, 1 H, *J* = 5.0 Hz), 1.70 (dd, 1 H, *J* = 7.0 and 5.0 Hz), 3.07 (dd, 1 H, *J* = 7.0 and 5.0 Hz), 7.2–8.0 (m, 15 H); UV (methanol) 260 nm (ε 980); *m/e* 326 (M⁺), 298, 282, 280, 131, and 104 (base).

Anal. Calcd for C₂₃H₁₈O₂: C, 84.64; H, 5.56. Found: C, 84.62; H, 5.55.

A pure sample of 3,5,5-triphenyl-4-methyl-2(5*H*)-furanone (**48**) exhibited the following spectral properties: mp 103–104 °C; IR (KBr) 1745 cm⁻¹; UV (methanol) 256 nm (ε 48 000); NMR (CDCl₃, 100 MHz) δ 2.11 (s, 3 H) and 7.1–7.55 (m, 15 H); *m/e* 326 (M⁺), 280, 237, 209 (base), and 193.

Anal. Calcd for C₂₃H₁₈O₂: C, 84.64; H, 5.56. Found: C, 84.62; H, 5.47.

Irradiation of 3,5,5-Triphenyl-4-methyl-2(5*H*)-furanone (48). A deaerated solution containing 144 mg of furanone **48** in 250 mL of methanol was irradiated with a 450-W Hanovia lamp equipped with a Correx filter sleeve for 1 h. Removal of the solvent left a pale oil which was chromatographed on a thick layer plate using hexane-benzene as the eluent. The major band contained an inseparable mixture of the *cis* and *trans* isomers of 4-methoxy-4-methyl-3,5,5-triphenyl-γ-lactone (**50**) as evidenced by NMR analysis: NMR (CDCl₃, 100 MHz) minor isomer δ 0.85 (s, 3 H), 3.11 (s, 3 H), 5.20 (s, 1 H), and 6.8–7.4 (m, 15 H); major isomer δ 1.43 (s, 3 H), 3.20 (s, 3 H), 4.58 (s, 1 H), and 6.8–7.4 (m, 15 H). When the irradiation of **48** was carried out in benzene for 20 h the only material present was unreacted starting material.

Quantum Yield Determinations. Quantum yields were determined using a "merry-go-round" apparatus⁷⁰ equipped with a 450-W Hanovia lamp housed in a quartz well at the center of the carriage. Samples in 13-mm Pyrex test tubes were degassed to 5 × 10⁻³ mm in three freeze-thaw cycles and then sealed. Benzophenone-benzhydrol actinometry was used for quantum yield determinations. An actinometer yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 M.³⁰ For the sensitized runs a filter solution of potassium dichromate in aqueous potassium carbonate was circulated through the well and the entire unit allowed to run for 1 h prior to use.⁷¹ The concentrations were adjusted so that the sensitizer absorbed more than 98% of the light. Analyses were performed on a Waters liquid partition chromatography (M-6000) equipped with a 2537-Å source using a 0.125 in. × 4 ft Corasil II column. The conversions were run to 15% of less. The mass balance in these runs was generally better than 95%. *cis*-Piperylene was used as the triplet quencher in the Stern-Volmer plots.

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