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Photochemical Migratory Aptitudes in the Di-π-methane Rearrangement of 5,5-Diaryl-Substituted 2,5-Dihydrofurans[1a]

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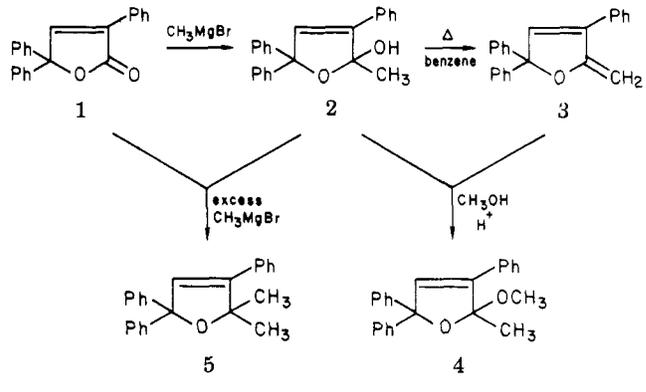
Irradiation of 3,3-dimethyl-4,5,5-triaryl-substituted 2,5-dihydrofurans in benzene results in a novel rearrangement to give 3-penten-1-one derivatives. Triplet sensitization leads to the formation of a 2-oxabicyclo[2.1.0]pentane intermediate which is extremely sensitive to heat and oxygen. Thermolysis of the labile 2-oxabicyclopentane results in central bond scission followed by a subsequent fragmentation to give 3-penten-1-one derivatives. The initially generated diradical intermediate can be readily trapped with oxygen to give a trioxabicyclo[2.2.1]heptane ring. The mechanism involved in these reactions consists of a di-π-methane rearrangement. Competitive migratory aptitude studies indicate that the phenyl group migrates in slight preference to *p*-anisyl, *p*-cyanophenyl, and *p*-tolyl. The products of migration are basically independent of the multiplicity of the excited state. The results obtained indicate that migratory aptitudes in the excited state can be controlled by the reluctance of phenyl groups to remain behind rather than from an inherent tendency of the substituted aryl group to migrate.

Migratory aptitudes of substituted aryl groups in reactive intermediates have been used to determine the transition state structure for the migration in both the ground state and excited state.[2-22] In the β-aryl rearrangement to a cationic terminus in saturated systems,[5-14] electron-rich aromatic rings show a superior migratory aptitude compared with electron-deficient groups. For example, the β-*p*-anisyl/β-phenyl migratory ratios are ca. 5–600 for solvolysis[5,6] and related reactions such as the Schmidt rearrangement.[7] The difference in migratory aptitude can be attributed to the larger charge stabilization by the *p*-methoxy group in the bridged ion.[10-14] Migratory

Scheme I



(1) (a) Photochemical Transformations of Small Ring Compounds. 109. For part 108, see: Padwa, A. *Acc. Chem. Res.* **1979**, *12*, 310. (b) Author to whom correspondence concerning this study should be addressed at the Department of Chemistry, Emory University, Atlanta, Georgia 30322.

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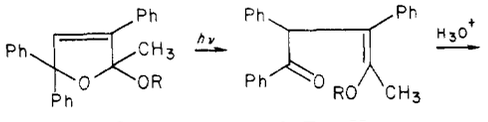
aptitudes of substituted aryl groups have also been used to probe the excited state electronic makeup and reactivity of α,β-unsaturated carbonyl compounds.[15,16] Zimmerman and co-workers found that phenyl groups having *p*-methoxy and *p*-cyano substituents migrated in preference to an unsubstituted phenyl group.[15] 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.[16]

During the course of our studies dealing with the photochemical rearrangement of 5,5-diaryl-2(5*H*)-furanones,[22] we uncovered a striking and rare crossover in the competitive migratory aptitude of aryl groups. The results obtained suggested that in certain cases excited state migratory aptitudes can be controlled by stabilization of the reactive intermediate by the nonmigrating aryl group. This is clearly different from the situation which usually prevails in the ground state.[2-14] Because of the intriguing nature of this effect, we decided to explore the photochemistry of some related systems in order to determine its generality. The systems selected for study consisted of a series of 5,5-diaryl-substituted 2,5-dihydrofurans. These compounds promised to provide additional information concerning photochemical migratory aptitudes. We report here the results of this study.

Results and Discussion

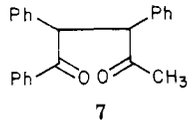
The 2,5-dihydrofurans of interest were synthesized as outlined below; details are given in the Experimental Section. Treatment of 2(5*H*)-furanone **1** with 1 equiv of methyl Grignard reagent afforded lactol **2** in 95% yield (Scheme I). Attempts to recrystallize **2** from benzene resulted in dehydration to give methylene dihydrofuran **3**. Heating a solution of **2** or **3** in methanol containing a trace of acid gave rise to methoxy dihydrofuran **4** in quantitative yield. The reaction of **1** or **2** with excess methyl Grignard reagent afforded the 2,2-dimethyl-substituted 2,5-dihydrofuran **5** in high yield.[23] A similar sequence of reactions was used to prepare a series of related 5,5-diaryl-substituted 2,5-dihydrofurans. This synthetic approach has proved both practical and general.

Irradiation of 2-hydroxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (**2**) in benzene under an argon atmosphere with Vycor-filtered light for 30 min gave 1,2,3-triphenyl-4-hydroxy-3-penten-1-one (**6**) in high yield. The structure of this material was unambiguously established by an acid-catalyzed tautomerization to the known 1,2,3-triphenyl-1,4-pentanedione (**7**) (3:2 mixture of diastereomers).[23] Enol **6** has a relatively long lifetime (ca. 4 h)



2, R = H
4, R = CH_3

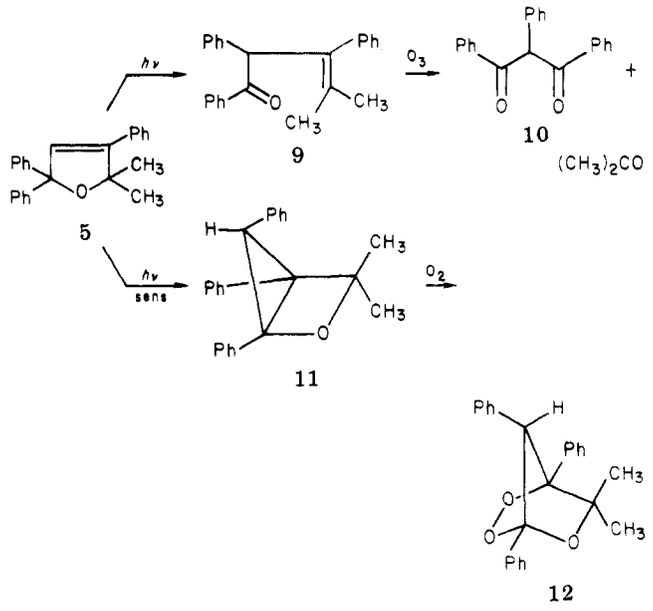
6, R = H
8, R = CH_3



7

which is probably the result of the absence of catalytic ionic contaminants in the benzene solution. When trace amounts of an acid or base were added to the solution, enol **6** spontaneously isomerized to the more stable keto tautomer. A similar irradiation of dihydrofuran **4** gave enol ether **8**, which could readily be converted to **7** on treatment with aqueous acid.

Scheme II



9 **10** **5** **11** **12**

Attention was next turned to the photochemical behavior of 2,2-dimethyl-3,5,5-triphenyl-2,5-dihydrofuran (**5**). Irradiation of a dilute solution of this compound in benzene gave 1,2,3-triphenyl-4-methyl-3-penten-1-one (**9**, 76%) as a crystalline solid, mp 115–116 °C (Scheme II). The structure of **7** was established on the basis of its spectral properties and was further confirmed by ozonization to acetone and 1,2,3-triphenyl-1,3-propanedione (**10**). Diketone **10** was verified by comparison with an authentic sample.[24]

In order to establish the nature of the reactive state involved in the photorearrangement, quenching and sensitization experiments were carried out. Identical 2,5-dihydrofuran solutions containing 1,3-cyclohexadiene or piperylene were irradiated. Neither the rate of dihydrofuran disappearance nor that of product formation was affected by the quenchers, each of which was present in concentrations known to diminish markedly the rates of established triplet processes.[25] To determine if a triplet excited state could give rise to the observed photoproduct, thioxanthone sensitization was employed under conditions where only the sensitizer absorbed light. In this run, concentrations were adjusted so that sensitizer singlets would decay to triplets before collision with the acceptor, but triplet energy transfer would be efficient. The results obtained clearly show that the photochemical rearrangement encountered on the direct irradiation of dihydrofuran **5** proceeds through the singlet manifold, since triplet sensitization of this compound resulted in the exclusive formation of 3,3-dimethyl-1,4,5-triphenyl-2-oxabicyclo[2.1.0]pentane (**11**) [NMR ($CDCl_3$, 100 MHz) δ 0.92 (s, 3 H), 1.40 (s, 3 H), 3.08 (s, 1 H), and 6.9–7.8 (m, 15 H)]. The stereochemical assignment of structure **11** is based on the chemical shift of the cyclopropyl hydrogen atom and the fact that the thermodynamically most stable

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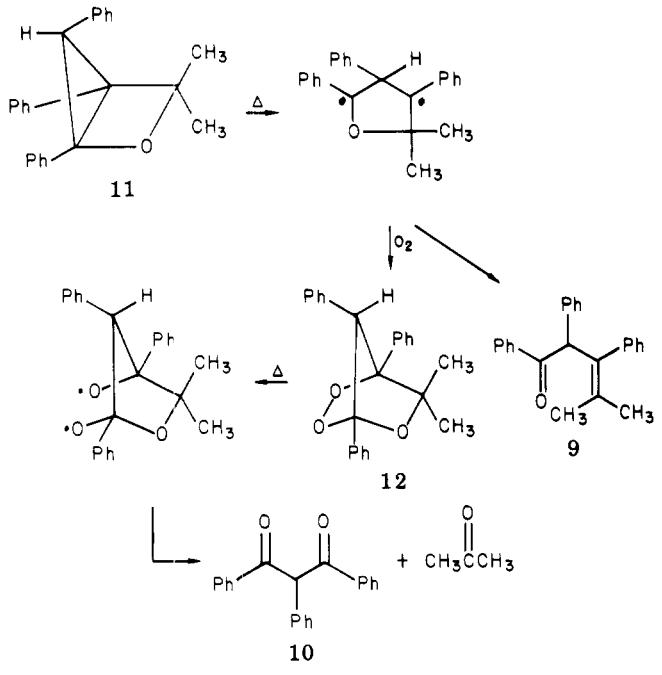
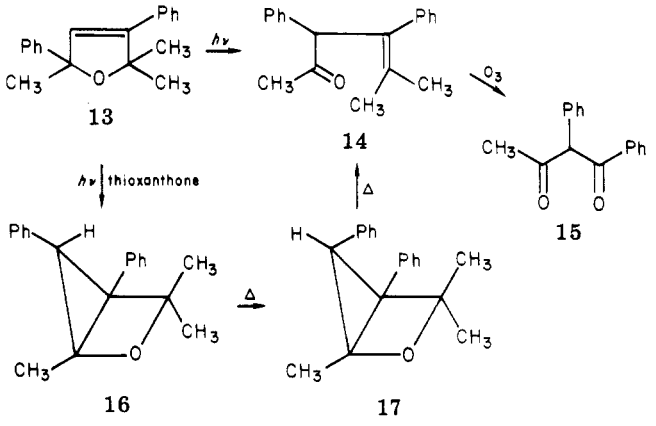
Scheme III



Scheme IV

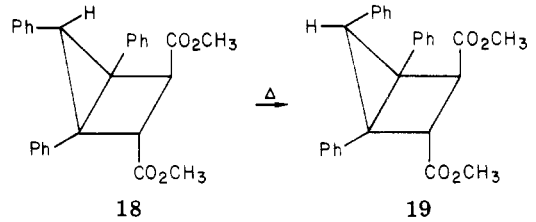


isomer has the 5-phenyl group located in the endo position (vide infra). This material was found to be quite sensitive to heat and oxygen. Heating a degassed sample of **11** at 50 °C for 15 min resulted in the quantitative formation of pentenone **9**. When **11** was exposed to oxygen at room temperature, it was rapidly converted to 1,4,7-triphenyl-2,5,6-trioxabicyclo[2.2.1]heptane (**12**) in 90% yield. The structure of this material was assigned on the basis of its spectroscopic and chemical properties [NMR ($CDCl_3$, 100 MHz) δ 1.10 (s, 3 H), 1.57 (s, 3 H), 4.34 (s, 1 H), 7.1–7.7 (m, 15 H); *m/e* 300 ($M^+ - (CH_3)_2CO$)]. Structure **12** was further supported by the finding that thermolysis at 120 °C resulted in the formation of acetone and propanedione **10** in high yield.

The formation of **9** and **12** from the thermolysis of **11** can be readily explained in terms of cleavage of the central σ bond to give a diradical intermediate which either undergoes fragmentation to **9** or is trapped by oxygen to give **12** (Scheme III). Related diradical intermediates have been implicated in the cis–trans isomerization of bicyclo[2.1.0]pentanes[26–32] and in the addition of olefins and acetylenes to the strained σ bond.[33–35] The radical stabilizing effect of the bridgehead phenyl groups present in **11** is undoubtedly responsible for the low activation energy for central bond scission. The conversion of cyclic peroxide **12** to propanedione **10** and acetone can be rationalized in terms of oxygen–oxygen bond cleavage to give a 1,5-diradical which subsequently undergoes fragmentation. A related set of reactions has been observed by Adam and co-workers in the thermolysis of cyclic peroxides such as 1,2-dioxolanes,[36] β- and γ-peroxy lactones,[37,38] and 1,2-dioxanes.[39] The thermal instability of **12**, especially when contrasted with the related 2,3-dioxabicyclo[2.2.1]heptane ring,[40,41] probably derives from the ease of acetone ejection and formation of the thermodynamically stable diketone system.

The photochemical behavior of the closely related 2,2,-5-trimethyl-3,5-diphenyl-2,5-dihydrofuran (**13**) was also studied in order to assess the generality of the rearrangement. Irradiation of **13** in benzene afforded β,γ-unsaturated ketone **14** in high yield (Scheme IV). The structure of **14** was supported by its spectral data and was confirmed by subsequent ozonization to acetone and the known diketone **15**.[42]

In contrast to the direct irradiation experiments, sensitization of **13** with thioxanthone gave rise to a single photoproduct whose structure was assigned as *exo*-1,3,3-trimethyl-4,5-diphenyl-2-oxabicyclo[2.1.0]pentane (**16**) on the basis of its spectral and chemical properties (see Experimental Section). At room temperature, compound **16** slowly isomerizes to give an isomeric oxabicyclopentane **17**. Arnold and Morchat observed a similar thermal isomerization with the bicyclo[2.1.0]pentane derived from the cycloaddition reaction of triphenylcyclopropene with dimethyl fumarate.[43] These workers found that the exo-substituted isomer **18** was readily isomerized to the thermodynamically more stable endo isomer **19** on heating.



Relief of steric interaction of the three phenyl groups present in **18** was suggested as the major reason for the greater thermodynamic stability of the endo isomer **19**. A similar relief of steric congestion would also account for the ready isomerization of **16** to **17**. The mechanism for isomerization of **16** to **17** most likely involves central bond cleavage followed by ring flipping and diradical reclosure.

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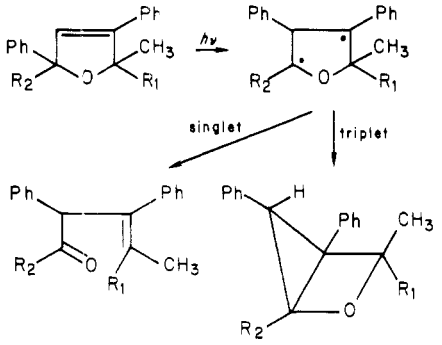
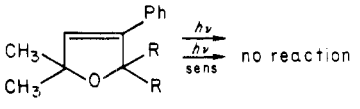
Scheme V



Heating a sample of 17 at 100 °C for 15 min resulted in the formation of ketone 14, thereby providing additional support for the structural assignments.

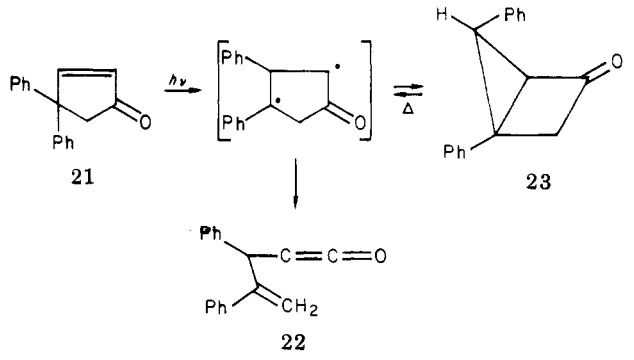
In order to determine whether the photorearrangement of a 2,5-dihydrofuran devoid of an aryl group in the 5-position would occur, we subjected dihydrofuran **20** to ultraviolet irradiation. We found that this system was perfectly stable to prolonged photolysis. This observation would tend to indicate that the rearrangement of the 5-aryl-substituted 2,5-dihydrofuran system proceeds via a di-π-methane mechanism.[44]



20a, R = CH_3
b, R = Ph

The mechanism involved in these reactions can be most readily accounted for by the pathway outlined in Scheme V. The nature of the photoproducts clearly points to a di-π-methane rearrangement as the primary photochemical step.[44] Fragmentation of the singlet 1,3-diradical yields the observed β,γ-unsaturated ketone directly. This transformation is analogous to the well-studied di-π-methane rearrangement of 4,4-diphenylcyclopentenones[45,46] and 2,-3,5,5-tetraphenyl-2,5-dihydrofuran.[47] Agosta[45] and Zimmerman[46] had previously reported that the photolysis of 4,4-diphenylcyclopentenone **21** proceeds via the triplet state to give the unsaturated ketene **22** (Scheme VI). When the irradiation was carried out at low temperatures, a reaction intermediate was observed and assigned the bicyclo[2.1.0]pentane (**23**) structure. The bicyclopentane was shown to proceed both photochemically and thermally to the ketene product observed at room temperature. There have also been a number of related reports dealing with the photochemistry of cyclopentenones where bicyclo[2.1.0]pentanones have been isolated as stable products.[48,49] These transformations provide good analogy for the mechanism suggested to occur in the 2,5-dihydrofuran system. The gross difference in the nature of the product obtained on direct irradiation and on triplet sensitization is attributable to the fact that fragmentation of the triplet diradical represents a higher energy pathway. The parallel spins in the triplet diradical delays ring fragmentation and the eventual spin inversion, which must precede reaction,

Scheme VI



21 **23**

22

is more likely to occur while the triplet diradical is in a conformation which is more favorable to ring closure than bond fragmentation. The mechanism outlined above also provides an explanation for the fact that phenyl but not methyl may undergo this rearrangement. Thus, no photoreaction occurs when 2,2,5,5-tetramethyl-3-phenyl-2,5-dihydrofuran (**20a**) is subjected to irradiation.

In order to gain insight into the nature of the rearranging excited state, the photolysis of a series of 5,5-diaryl-substituted 2,5-dihydrofurans was investigated with the view that migratory aptitudes could be used as a probe for excited-state electronic makeup and reactivity. Irradiation of 2,5-dihydrofuran **24** gave two primary photoproducts, **25** and **26**, in a ratio of 1.2:1.0 (Scheme VII). The same two products were obtained on triplet sensitization of **24** followed by thermolysis of the transient oxabicyclo[2.1.0]-pentanes. Under these conditions the ratio of **25** to **26** was 1:1. The NMR, IR, and UV spectra suggested that the products were aryldiphenyl-substituted 4-methyl-3-penten-1-ones. The photoproducts were unequivocally identified by ozonization to propanediones **27** and **28** whose structures were established by comparison with authentic samples.

The preparation of the isomeric set of 1,3-diketones (i.e., **27** and **28**) turned out to be somewhat of a problem. Attempts to synthesize these 1,3-diketones by the 1:1 acylation of the alkali metal enolates with acyl halides was attended in practice by various problems: competing O-acylation, proton exchange between the enolate and product diketone, diacylation, and generally poor yields.[50,51] Some of these problems could be surmounted by strict control of the reaction conditions[52] or by the use of indirect methods, for example with regiospecifically generated enamines[53] rather than enolates. We eventually found that the C-acylation of silyl enol ethers was an effective method for the preparation of these compounds. The yields of the 1,3-diketones prepared by this method ranged from good to excellent and the di- and O-acylated side products were not formed.

Irradiation of 2,5-dihydrofurans **29** and **34** in benzene was found to proceed quite similarly to the case of **24**. Two rearranged unsaturated ketones were obtained whose structures were established by ozonization and comparison of the 1,3-diketones with independently synthesized samples. Rearrangement of 2,5-dihydrofuran **29** indicated that the phenyl group had migrated with slight preference over *p*-anisyl (ratio **30**/**31** = 3:2). The sensitized irradiation of

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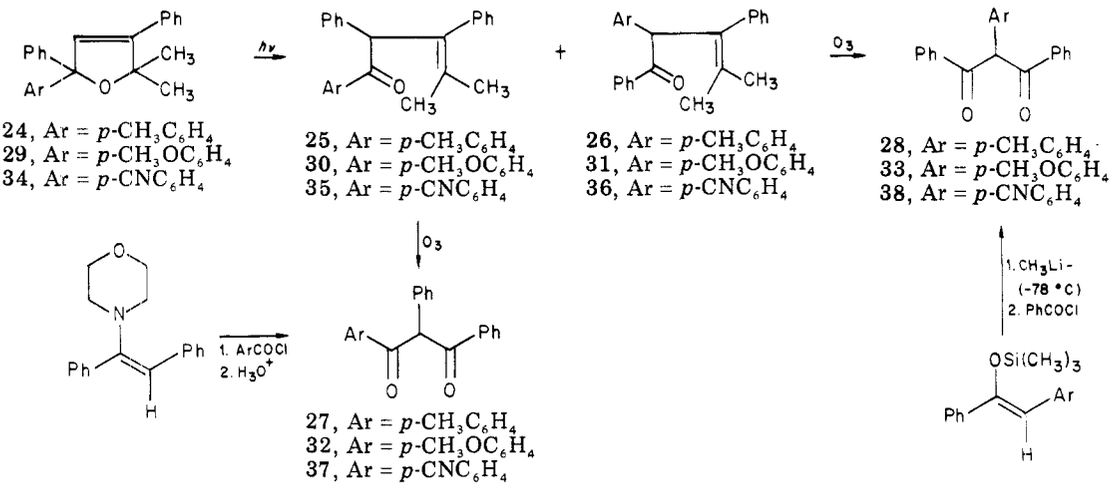
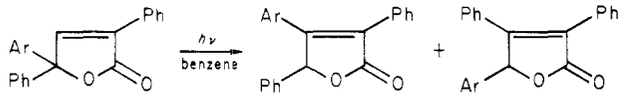
Scheme VII



29 followed by thermolysis of the crude reaction mixture also afforded the same two products (ratio **30**/**31** = 1.8:1). With the *p*-cyano-substituted dihydrofuran **34**, irradiation afforded ketones **37** and **38** (ratio **37**/**38** = 1.5:1). Under triplet-sensitized conditions, the phenyl group was also found to migrate with slight preference over *p*-cyanophenyl (ratio **37**/**38** = 1.4:1). These results clearly establish that the products of migration are basically independent of the multiplicity of the excited state.

The most striking feature of these rearrangements is that phenyl migrates in preference to the aryl group in both the direct and sensitized reactions.[54] The migratory aptitudes encountered here differ considerably with the results obtained in the 2(5*H*)-furanone system where the aryl group was found to migrate in preference to phenyl when the

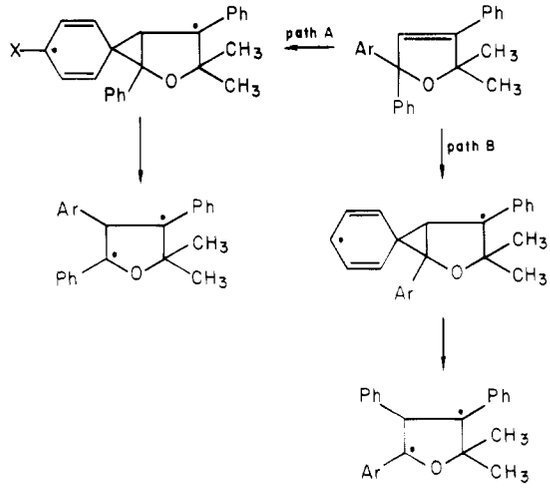


39 40 (major) 41 (minor)

irradiation was carried out in a nonpolar solvent.[22] Thus, we had previously observed that *p*-anisyl migrated in strong preference to phenyl (ratio *p*-An/Ph = 16:1) and that *p*-cyanophenyl also migrated in preference to phenyl (ratio *p*-CNPh/Ph = 3.5:1) when the irradiation of the 2(5*H*)-furanone (i.e., **39**) was carried out in benzene. Subsequent rate studies showed that *p*-An and *p*-CNPh were more reactive migrating groups than phenyl by factors of 7.2 and 5.0, respectively.[22] The results were rationalized by assuming that in a nonpolar solvent, the excited 2(5*H*)-furanone system possesses substantial odd electron character at the β-carbon atom of the unsaturated lactone. At the rate-controlling stage of the reaction, the free valence is more heavily localized at the para position of the migrating aryl group than in the nonmigrating aryl group. The results obtained with the 2(5*H*)-furanones parallel the migratory aptitudes generally observed in the ground state.[2-14] The nonmigrating group was found to have a very small effect on the rate of rearrangement, with an electron-donating group decreasing the rate and an electron-withdrawing group increasing the rate slightly.

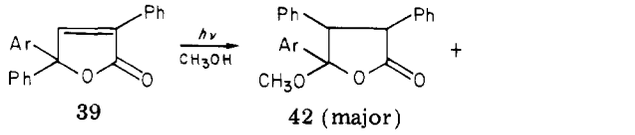
On the basis of the results encountered in the 2(5*H*)-furanone system, the migratory aptitudes observed on irradiation of the 5,5-diaryl-substituted 2,5-dihydrofurans are unexpected and striking. In the usual formulation of the di-π-methane reaction, where the free valence in the

Scheme VIII

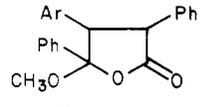


bridged species is represented as an odd-electron center, one would have anticipated a preference for path A rather than path B (Scheme VIII), since substituted aryl groups are known to stabilize odd electron centers in excited states better than phenyl. This is not the case and an alternate explanation must be sought.

At this point it should be noted that a substantial crossover in migratory aptitudes was found to occur in the 2(5*H*)-furanone system when the solvent was changed from benzene to methanol. A nonmigrating *p*-anisyl group



39 42 (major)



43 (minor)

significantly accelerated the rate of phenyl migration in methanol. Whereas the migration of *p*-anisyl in preference to phenyl in benzene was attributed to stabilization of the radical-like free valence by the migrating group, the slight preference for migration of phenyl over *p*-anisyl in methanol was explained in terms of stabilization of the electron deficiency which develops at C_5 by the nonmigrating *p*-anisyl group.[22] This observation suggests that, in certain cases, migratory aptitudes may be controlled by the reluctance of the phenyl group to "remain behind" rather than

(54) For a preliminary report of this work see Padwa, A.; Brookhart, T. *Tetrahedron Lett.* 1979, 1979.

from an inherent tendency of the substituted aryl group to migrate. The situation with the 5,5-diaryl-substituted 2,5-dihydrofurans seems to parallel the results obtained with the furanone system in methanol. Thus, migratory aptitudes in this system are seemingly determined at the stage of the mechanism where stabilization of the reactive center by the nonmigrating aryl group is the major factor responsible for the observed migrations.[55] This is clearly different from the situation which usually prevails in the ground state. Clearly, some caution needs to be exercised in correlating the nature of electronically excited states with migratory aptitudes of substituted aryl groups.

Experimental Section[56]

Preparation of 2-Hydroxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (2). To a solution containing 4.0 g of 3,5,5-triphenyl-2(5*H*)-furanone[22] (**1**) in 250 mL of ether was added 1.5 equiv of methylmagnesium bromide. The solution was heated to reflux for 24 h, cooled, neutralized with an ammonium chloride solution, and extracted with ether. The organic layer was washed with a sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a white solid which was triturated with pentane and ether to give 4.0 g (95%) of 2-hydroxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (**2**): mp 125–126 °C; IR (KBr) 3400, 1500, and 1450 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.72 (s, 3 H), 2.78 (s, 1 H), 6.80 (s, 1 H), 7.2–7.9 (m, 15 H); *m/e* 310 (base, $M^+ - H_2O$), 233, 91, and 77. All attempts to obtain analytical data with this system were unsuccessful as a result of the lability of this compound. On recrystallization from benzene, **2** readily dehydrates to give 2-methylene-3,5,5-triphenyl-2,5-dihydrofuran (**3**) as a white solid: mp 112–113.5 °C; IR (KBr) 1650, 1600, 1500, and 1450 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 4.32 (d, 1 H, J = 2.0 Hz), 4.70 (d, 1 H, J = 2.0 Hz), 6.80 (s, 1 H), 7.3–7.6 (m, 15 H).

Irradiation of 2-Hydroxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (2). A solution containing 104 mg of dihydrofuran **2** in 450 mL of benzene under an argon atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Vycor filter sleeve for 30 min. Removal of the solvent under reduced pressure left a yellow oil which was identified as 1,2,3-triphenyl-4-hydroxy-3-penten-1-one (**6**): IR ($CHCl_3$) 3500, 1700, and 1600 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 2.3 (s, 3 H), 6.9 (s, 1 H), 7.0–7.6 (m, 15 H), 14.5 (s, 1 H). After chromatography on silica gel with a 75% pentane–ether mixture, a crystalline solid was isolated which consisted of a 3:2 mixture of the two diastereomers of 1,2,3-triphenyl-1,4-pentanedione (**7**). These diastereomers were separated by fractional crystallization from methanol. The less soluble isomer (major component) was recrystallized from methanol to give 51 mg (49%) of a white solid: mp 187–188 °C (lit.[23] 187–188 °C); IR (KBr) 1700 and 1600 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.93 (s, 3 H), 4.82 (s, 1 H, J = 11.0 Hz), 5.59 (d, 1 H, J = 11.0 Hz), 7.0–8.0 (m, 15 H). The more soluble isomer (minor component) was recrystallized from methanol to give 34 mg (33%) of a white solid: mp 154–155 °C (lit.[23] 155–156 °C); IR (KBr) 1700 and 1660 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 2.14 (s, 3 H), 4.57 (d, 1 H, J = 11.0 Hz), 5.19 (d, 1 H, J = 11.0 Hz), 7.1–8.1 (m, 15 H). The structure of the diastereomers was unambiguously established by comparison with authentic samples.[23]

Synthesis of 2-Methoxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (4). A solution containing 1.92 g of 2-hydroxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (**2**) in 10 mL of methanol was heated at reflux for 30 min and was then cooled. The white solid (1.8 g, 40%) which crystallized out of the reaction mixture was identified as 2-methoxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (**4**): mp 145–146 °C; IR (KBr) 1500 and 1450 cm^{-1}; UV (methanol) 252 nm (ϵ 21 300); NMR ($CDCl_3$, 100 MHz) δ 1.85 (s, 3 H), 2.94 (s, 3 H), 6.92 (s, 1 H), 7.2–7.7 (m, 15 H); *m/e* 310 (base, $M^+ - CH_3OH$), 233, 205, 105, 91, and 77.

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47. Found: C, 83.96; H, 6.51.

This compound could also be prepared in quantitative yield by refluxing a solution of 2-methylene-3,5,5-triphenyl-2,5-dihydrofuran (**3**) in methanol for 30 min.

Irradiation of 2-Methoxy-2-methyl-3,5,5-triphenyl-2,5-dihydrofuran (4). A solution containing 187 mg of dihydrofuran **4** in 450 mL of benzene under an argon atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Vycor filter sleeve for 1 h. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on silica gel with a 90% hexane–ethyl acetate mixture to give 51 mg (27%) of a 3:2 mixture of *cis*- and *trans*-1,2,3-triphenyl-4-methoxy-3-penten-1-one (**8**) as a light yellow oil: IR ($CHCl_3$) 1660 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.70 (s, 3 H), 1.88 (s, 3 H), 3.36 (s, 3 H), 3.38 (s, 3 H), 5.66 (s, 1 H), 5.70 (s, 1 H), 7.0–7.7 (m, 30 H); *m/e* 310 (base, $M^+ - CH_3OH$), 267, 205, 105, 91, and 77.

A solution containing 53 mg of the above pentenone **8** and 3 mL of a 10% hydrochloric acid solution in 20 mL of *p*-dioxane was stirred at 25 °C for 3 h. The solution was extracted with ether and the ether layer was washed with a sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind 25 mg (50%) of a yellow solid which was shown by NMR analysis to contain a 5:1 mixture of the two diastereomers of 1,2,3-triphenyl-1,4-pentanedione (**7**). The diastereomers were separated by fractional crystallization and were identical in every detail with authentic samples.[23]

Synthesis of 2,2-Dimethyl-3,5,5-triphenyl-2,5-dihydrofuran (5). To a solution containing 3.88 g of 3,5,5-triphenyl-2(5*H*)-furanone[22] (**1**) in 125 mL of ether was added 10 equiv of methylmagnesium bromide. The solution was heated at reflux for 20 h, cooled, neutralized with an ammonium chloride solution, and extracted with ether. The organic layer was washed with a sodium bicarbonate solution and was then dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow solid, which on recrystallization from benzene gave 3.0 g (70%) of 2-methyl-3,5,5-triphenyl-3-pentene-2,5-diol as a white solid: mp 166.0–166.5 °C; IR (KBr) 3500 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 1.4 (s, 6 H), 6.1 (s, 1 H), 7.1–7.7 (m, 15 H). The hydroxylic protons could not be detected in the NMR spectrum.

Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.59; H, 7.11.

A solution containing 202 mg of 2-methyl-3,5,5-triphenyl-3-pentane-2,5-diol and 2 mL of sulfuric acid in 100 mL of methanol was heated at reflux for 30 min. The solution was then cooled, diluted with 100 mL of water, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow solid which was recrystallized from methanol to give 153 mg (80%) of 2,2-dimethyl-3,5,5-triphenyl-2,5-dihydrofuran (**5**) as a white solid: mp 112.5–113 °C; IR (KBr) 1500 and 1450 cm^{-1}; UV (methanol) 253 nm (ϵ 18 500); NMR ($CDCl_3$, 100 MHz) δ 1.54 (s, 6 H), 6.44 (s, 1 H), 7.2–7.6 (m, 15 H); *m/e* 326 (M^+), 250, 222 (base), 105, 91, and 77.

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.47; H, 7.17.

Direct Irradiation of 2,2-Dimethyl-3,5,5-triphenyl-2,5-dihydrofuran (5). A solution containing 145 mg of dihydrofuran **5** in 450 mL of benzene under an argon atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Vycor filter sleeve for 25 min. Removal of the solvent under reduced pressure left behind a yellow oil. Chromatography of this material on silica gel with a 75% pentane–ether mixture afforded a yellow solid which on recrystallization from methanol gave 91 mg (76%) of 1,2,3-triphenyl-4-methyl-3-penten-1-one (**9**) as a white solid: mp 115–116 °C; IR (KBr) 1660 cm^{-1}; UV (methanol) 242 nm (ϵ 15 200); NMR ($CDCl_3$, 100 MHz) δ 1.54 (s, 3 H), 1.84 (s, 3 H), 5.88 (s, 1 H), 6.7–7.3 (m, 13 H), 7.7–7.8 (m, 2 H); *m/e* 326 (M^+), 324, 309, 221, 105 (base), 91, and 77.

(55) The migratory aptitudes encountered in this study can not be due to an equilibration of the bicyclic compounds with starting material since the products are not converted back to the reactants either photochemically or thermally.

(56) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Varian XL-100 and a Jeolco MH-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All preparative irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc.

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 87.98; H, 6.53.

The structure of the above photoproduct was further verified by an ozonative degradation experiment. Ozone was bubbled into a solution containing 48 mg of 1,2,3-triphenyl-4-methyl-3-penten-1-one (**9**) in 200 mL of methylene chloride which had been cooled to −78 °C for 15 min. The solution was flushed with nitrogen for 10 min and then 20 mL of dimethyl sulfide was added. The reaction mixture was stirred at 25 °C for 3 h. After the solvent was removed under reduced pressure, the oily residue was extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on silica gel using a 75% pentane–ether mixture as the eluent. Crystallization of the resulting solid with methanol gave 26 mg (59%) of 1,2,3-triphenyl-1,3-propanedione (**10**) as a white solid: mp 147–148 °C (lit.[24] 149 °C); IR (KBr) 1680 and 1650 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 6.50 (s, 1 H), 7.2–7.4 (m, 13 H), 7.8–7.9 (m, 2 H). The structure of this compound was further verified by comparison with an independently synthesized sample.

Independent Synthesis of 1,2,3-Triphenyl-1,3-propanedione (10). A mixture of 500 mg of 4-(1,2-diphenylethenyl)morpholine (prepared by the method of Munk and Kim[57]), 290 mg of benzoyl chloride, and 228 mg of triethylamine was heated neat at 120 °C for 75 min. The reaction mixture was cooled, dissolved in *p*-dioxane, and added to 60 mL of a 10% hydrochloric acid solution with enough *p*-dioxane to give a clear solution. This mixture was refluxed for 3 h, cooled, diluted with 100 mL of water, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give a yellow oil. Chromatography of this material on silica gel with a 75% pentane–ether mixture afforded 1,2,3-triphenyl-1,3-propanedione (**10**) as a white solid which was recrystallized from methanol to afford material which was identical in every way with the material derived from the ozonolysis of 1,2,3-triphenyl-4-methyl-3-penten-1-one (**9**).

Sensitized Irradiation of 2,2-Dimethyl-3,5,5-triphenyl-2,5-dihydrofuran (5). A solution containing 15.6 mg of dihydrofuran **5** and 1.4 mg of thioxanthone in 0.5 mL of deuteriobenzene was degassed to 5×10^{-3} mm in three freeze–thaw cycles, and was then sealed and irradiated with a series of 3500-Å lamps in a Rayonet photochemical reactor for 3 h. The photoproduct, which was obtained in quantitative yield, was assigned the structure of 3,3-dimethyl-1,4,4-triphenyl-2-oxabicyclo[2.1.0]pentane (**11**) on the basis of its characteristic NMR spectrum: NMR (C_6D_6, 100 MHz) δ 0.92 (s, 3 H), 1.40 (s, 3 H), 3.08 (s, 1 H), 6.9–7.4 (m, 13 H), 7.5–7.8 (m, 2 H). This material was found to be quite sensitive to heat and oxygen. A sealed sample of 3,3-dimethyl-1,4,5-triphenyl-2-oxabicyclo[2.1.0]pentane (**11**), which had been prepared from the sensitized irradiation of dihydrofuran **5**, was heated at 100 °C for 75 min. At the end of this time the solvent was removed under reduced pressure to afford a quantitative yield of 1,2,3-triphenyl-4-methyl-3-penten-1-one (**9**). Another sample of 3,3-dimethyl-1,4,5-triphenyl-2-oxabicyclo[2.1.0]pentane (**11**), prepared in the same fashion as above, was opened to the atmosphere immediately following irradiation. The solvent was removed under reduced pressure leaving a yellow solid. This solid was recrystallized from methanol to give a 90% yield of 3,3-dimethyl-1,4,7-triphenyl-2,5,6-trioxabicyclo[2.2.1]heptane (**12**) as a white solid: mp 122–123 °C; IR (KBr) 1480, 1440, and 1325 cm^{-1}; UV (methanol) 250 nm (ε 2000); NMR ($CDCl_3$, 100 MHz) δ 1.1 (s, 3 H), 1.57 (s, 3 H), 4.34 (s, 1 H), 7.1–7.7 (m, 15 H); *m/e* 300, 252, 167, 128, 105 (base), 91, and 77.

Anal. Calcd for $C_{24}H_{22}O_3$: C, 80.42; H, 6.19. Found: C, 80.21; H, 6.23.

Synthesis of 2,2,5,5-Tetramethyl-3-phenyl-2,5-dihydrofuran (20a). To a solution containing 2.3 g of 5,5-dimethyl-3-phenyl-2(5*H*)-furanone[22] in 500 mL of ether was added 10 equiv of methylmagnesium bromide. The reaction mixture was heated at reflux for 24 h, cooled, neutralized with an ammonium chloride solution, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil, which was used without further purification for the next reaction step. A solution containing the above oil and 1 mL of sulfuric acid in 100 mL of methanol was heated at reflux for 30 min, cooled, diluted with 200 mL of water, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow liquid which was distilled to give 1.54 g (63%) of 2,2,5,5-tetramethyl-3-phenyl-2,5-dihydrofuran (**20a**) as a clear liquid: bp 48–54 °C (0.1 mm); IR (neat) 3000, 1600, and 1450 cm^{-1}; UV (methanol) 250 nm (ε 8270); NMR ($CDCl_3$, 100 MHz) δ 1.36 (s, 6 H), 1.46 (s, 6 H), 5.75 (s, 1 H), 7.1–7.4 (m, 5 H); *m/e* 202 (M^+), 187 (base), 159, 145, 128, 105, 91, and 77.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.22; H, 9.35.

Synthesis of 2,2,3-Triphenyl-5,5-dimethyl-2,5-dihydrofuran (20b). 4,5,5-Triphenyl-2(5*H*)-furanone was prepared by the method of Lehman[58] from 2-acetoxy-2,2-diphenylacetophenone.[59] This material, in turn, was prepared by the method of Stevens and DeYoung[59] from 2-hydroxy-2,2-diphenylacetophenone which was, in turn, prepared by the method of Ioffe.[60] To a solution containing 1.0 g of this 2(5*H*)-furanone in 500 mL of ether was added 10 equiv of methyllithium–lithium bromide complex. After the reaction had been stirred at 25 °C for 20 h, it was neutralized with an ammonium chloride solution, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left behind a yellow oil which was used without further purification in the next reaction step. The above yellow oil was heated at reflux in 150 mL of acetic anhydride for 2 h, cooled, poured into ice–water, stirred for 1 h, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure and chromatography of the oily residue on silica gel with a 75% pentane–ether mixture as the eluent afforded 205 mg (20%) of 2,2,3-triphenyl-5,5-dimethyl-2,5-dihydrofuran (**20b**) as a white solid: mp 135–136 °C; IR (KBr) 3000, 1600, 1500, and 1440 cm^{-1}; UV (methanol) 250 nm (ε 9860); NMR ($CDCl_3$, 100 MHz) δ 1.44 (s, 6 H), 6.24 (s, 1 H), 7.1–7.5 (m, 15 H); *m/e* 326 (M^+), 311 (base), 283, 249, 105, 91, and 77.

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 87.95; H, 6.71.

Synthesis of 2,2,5-Trimethyl-3,5-diphenyl-2,5-dihydrofuran (13). To a solution containing 3.2 g of 5-methyl-3,5-diphenyl-2(5*H*)-furanone[22] in 500 mL of ether was added 10 equiv of methylmagnesium bromide. The solution was heated at reflux for 18 h, cooled, neutralized with an ammonium chloride solution, and extracted with ether. The organic layer was washed with a sodium bicarbonate solution and was then dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was used in the next reaction step without further purification.

A solution containing the above yellow oil and 1 mL of sulfuric acid in 150 mL of methanol was heated at reflux for 30 min. The reaction mixture was cooled, diluted with 100 mL of water, and extracted with ether. The organic layer was washed with a sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which was distilled to give 2.36 g (70%) of 2,2,5-trimethyl-3,5-diphenyl-2,5-dihydrofuran (**13**) as a clear liquid: bp 68–70 °C (0.04 mm); IR (neat) 3000, 1600, 1480, and 1430 cm^{-1}; UV (methanol) 252 nm (ε 9850); NMR ($CDCl_3$, 100 MHz) δ 1.5 (s, 3 H), 1.6 (s, 3 H), 1.7 (s, 3 H), 6.06 (s, 1 H), 7.1–7.6 (m, 10 H); *m/e* 264 (M^+), 249 (base), 221, 105, 91, and 77.

Anal. Calcd for $C_{10}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.12; H, 7.74.

Photolysis of 2,2,5-Trimethyl-3,5-diphenyl-2,5-dihydrofuran (13). A solution containing 230 mg of dihydrofuran **13** in 450 mL of benzene under an argon atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Vycor filter sleeve for 20 min. Removal of the solvent under reduced pressure left

(57) Munk, M. E.; Kim, Y. K. *J. Org. Chem.* **1965**, *30*, 3705.

(58) Lehman, H. G. *Chem. Abstr.* **1965**, *63*, 16429.
(59) Stevens, C. L.; DeYoung, J. J. *J. Am. Chem. Soc.* **1954**, *76*, 718.
(60) Ioffe, D. V. *Zh. Obshch. Khim.* **1965**, *35*, 1851.

a yellow oil which was shown by thin-layer chromatography to consist of one major product. Purification of this material by thick-layer chromatography using a 3% acetone–hexane mixture as the eluent gave 3,4-diphenyl-5-methyl-4-hexen-2-one (**14**): IR (neat) 3500, 3000, 1720, and 1600 cm^{-1}; UV (methanol) 294 nm (ϵ 20 200); NMR ($CDCl_3$, 100 MHz) δ 1.56 (s, 3 H), 1.78 (s, 3 H), 2.07 (s, 3 H), 4.90 (s, 1 H), 6.8–7.4 (m, 10 H); *m/e* 264 (M^+), 262, 247 (base), 221, 143, 105, 91, and 77.

Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.14; H, 7.68.

The structure of the above photoproduct was further verified by ozonization to 3,4-diphenyl-2,4-butanedione (**15**): IR (neat) 1700 and 1650 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 2.15 (s, 3 H), 5.62 (s, 1 H), 7.0–7.4 (m, 8 H), 7.75–7.90 (m, 2 H). The structure of this diketone was established by comparison with an independently synthesized sample prepared by the method of Young and co-workers.[42]

The sensitized irradiation of **16** in benzene with thioxanthone as the sensitizer afforded *exo*-1,3,3-trimethyl-4,5-diphenyl-2-oxabicyclo[2.1.0]pentane (**16**) as the exclusive photoproduct: IR ($CHCl_3$) 3000, 1600, 1500, 1450, and 1380 cm^{-1}; UV (methanol) 218 nm (ϵ 11 600); NMR ($CDCl_3$, 100 MHz) δ 0.80 (s, 3 H), 1.36 (s, 3 H), 1.95 (s, 3 H), 2.18 (s, 1 H), 7.0–7.6 (m, 10 H); *m/e* 264 (M^+), 262, 247, 221 (base), 143, 128, 105, 91, and 77. Support for oxabicyclopentane **16** was obtained by its quantitative conversion to 3,4-diphenyl-5-methyl-4-hexen-2-one (**14**) on treatment with *p*-toluenesulfonic acid, by heating or by direct irradiation. When a solution of **16** in benzene was stirred at 25 °C in the dark it afforded *endo*-1,3,3-trimethyl-4,5-diphenyl-2-oxabicyclo[2.1.0]pentane (**17**): NMR ($CDCl_3$, 100 MHz) δ 1.34 (s, 6 H), 1.68 (s, 3 H), 3.04 (s, 1 H), 6.6–7.4 (m, 10 H). This material was rapidly converted to **14** on treatment with acid or on heating at 100 °C for 15 min.

Synthesis of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-tolyl)-2,5-dihydrofuran (24). To a solution containing 1.0 g of 3,5-diphenyl-5-(*p*-tolyl)-2(5*H*)-furanone[22] in 125 mL of ether was added 10 equiv of methylmagnesium bromide. The solution was heated at reflux for 20 h, cooled, neutralized with an ammonium chloride solution, and extracted with ether. The organic layer was washed with a sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil. A solution containing 1.31 g of the above oil and 2 mL of sulfuric acid in 200 mL of methanol was heated at reflux for 30 min. The solution was then cooled, diluted with 200 mL of water, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow solid which was recrystallized from methanol to give 740 mg (71%) of 2,2-dimethyl-3,5-diphenyl-5-(*p*-tolyl)-2,5-dihydrofuran (**24**) as a white solid: mp 109–110 °C; IR (KBr) 1500 and 1450 cm^{-1}; UV (methanol) 253 nm (ϵ 14 400); NMR ($CDCl_3$, 100 MHz) δ 1.5 (s, 6 H), 2.28 (s, 3 H), 6.33 (s, 1 H), 7.0–7.4 (m, 14 H); *m/e* 340 (M^+), 325, 263, 240, 235 (base), 119, 105, 91, and 77.

Anal. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.11. Found: C, 87.92; H, 7.05.

Direct Irradiation of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-tolyl)-2,5-dihydrofuran (24). A solution containing 81 mg of dihydrofuran **24** in 450 mL of benzene under an argon atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Vycor filter sleeve for 25 min. Removal of the solvent under reduced pressure left behind an oil which was shown to contain two photoproducts as judged from the NMR spectrum of the crude photolysate. Integration of the signals indicated a 1.2:1.0 ratio of 1-(*p*-tolyl)-2,3-diphenyl-3-penten-1-one (**25**) [NMR ($CDCl_3$, 100 MHz) δ 1.58 (s, 3 H), 1.87 (s, 3 H), 2.27 (s, 3 H), 5.87 (s, 1 H), 6.8–8.0 (m, 14 H)] and 2-(*p*-tolyl)-1,3-diphenyl-3-penten-1-one (**26**) [NMR ($CDCl_3$, 100 MHz) δ 1.58 (s, 3 H), 1.87 (s, 3 H), 2.35 (s, 3 H), 5.90 (s, 1 H), 6.8–8.0 (m, 14 H)]. The two photoproducts could be separated from unreacted starting material by chromatography on a silica gel column using a 75% pentane–ether mixture as the eluent. The identity of these compounds was determined by an ozonative degradation experiment. Ozone was bubbled into a solution containing 29 mg of the mixture of photoproducts in 200 mL of methylene chloride which had been cooled to −78 °C for 15 min. The solution was flushed with nitrogen for 10 min and then 20 mL of dimethyl sulfide was added. The reaction mixture was stirred at 25 °C for 3 h. After the solvent was removed under reduced pressure, the oily residue was extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which contained two compounds as judged from the NMR spectrum of the crude reaction mixture. Integration of the signals indicated a 1.2:1 ratio of 1-(*p*-tolyl)-2,3-diphenyl-1,3-propanedione (**27**) [NMR ($CDCl_3$, 100 MHz) δ 2.33 (s, 3 H), 6.55 (s, 1 H), 7.2–8.1 (m, 14 H)] and 2-(*p*-tolyl)-1,3-diphenyl-1,3-propanedione (**28**) [NMR ($CDCl_3$, 100 MHz) δ 2.38 (s, 3 H), 6.57 (s, 1 H), 7.2–8.1 (m, 14 H)]. The identity of the two products was further established by comparison with independently synthesized samples.

Independent Synthesis of 1-(*p*-Tolyl)-2,3-diphenyl-1,3-propanedione (27). A mixture containing 515 mg of 4-(1,2-diphenylethenyl)morpholine,[57] 330 mg of *p*-toluoyl chloride, and 246 mg of triethylamine was heated neat at 120 °C for 75 min. The reaction mixture was cooled and dissolved in *p*-dioxane, and 60 mL of a 10% hydrochloric acid solution was added with enough *p*-dioxane to afford a clear solution. This mixture was refluxed for 3 h, cooled, diluted with 100 mL of water, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure leaving behind a yellow oil. Chromatography of this material on a silica gel column using a 75% pentane–ether mixture as the eluent afforded a yellow solid. Recrystallization of this material from methanol gave 150 mg (25%) of 1-(*p*-tolyl)-2,3-diphenyl-1,3-propanedione (**27**) as a white solid: mp 133–134 °C; IR (KBr) 1680, 1660 and 1600 cm^{-1}; UV (methanol) 252 nm (ϵ 26 700); NMR ($CDCl_3$, 100 MHz) δ 2.3 (s, 3 H), 6.67 (s, 1 H), 7.0–7.5 (m, 10 H), 3.8–8.0 (m, 4 H); *m/e* 119 (base), 105, 91, and 77.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.00; H, 5.81.

Independent Synthesis of 2-(*p*-Tolyl)-1,3-diphenyl-1,3-propanedione (28). A mixture containing 2.1 g of 4-methyldeoxybenzoin,[61] 4.32 g of trimethylsilyl chloride, and 4.4 g of triethylamine in 40 mL of dimethylformamide was heated at reflux for 12 h. The reaction mixture was cooled, dissolved in hexane, and washed with a saturated sodium bicarbonate solution, followed by a 10% hydrochloric acid solution, and washed again with water. The solvent was removed under reduced pressure and the residue was distilled at 115 °C (0.5 mm) to give 3.0 g of the corresponding silyl enol ether of 4-methyldeoxybenzoin: NMR ($CDCl_3$, 100 MHz) δ 0.04 (s, 9 H), 2.28 (s, 3 H), 6.05 (s, 1 H), 7.0–7.6 (m, 9 H). To a solution containing 1.4 g of the above silyl enol ether in 20 mL of tetrahydrofuran at −60 °C was added 0.1 g of methyllithium in 8 mL of tetrahydrofuran. After stirring for 30 min at −60 °C, the mixture was warmed to −10 °C and held at this temperature for 45 min. A 0.7-g sample of benzoyl chloride in 10 mL of tetrahydrofuran was added to the above solution at −10 °C. After stirring for 45 min at −10 °C, the mixture was allowed to warm to room temperature. The solution was washed with a saturated ammonium chloride solution and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left 20 mg of 2-(*p*-tolyl)-1,3-diphenyl-1,3-propanedione (**28**) as a crystalline solid: mp 150–151 °C; NMR ($CDCl_3$, 100 MHz) δ 2.28 (s, 3 H), 6.56 (s, 1 H), 7.1–8.0 (m, 14 H); IR (KBr) 1670 cm^{-1}; *m/e* 314 (M^+).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.09; H, 5.80.

Sensitized Irradiation of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-tolyl)-2,5-dihydrofuran (24). A solution containing 27.5 mg of dihydrofuran **24** and 3.1 mg of thioxanthone in 8 mL of benzene was degassed to 5×10^{-3} mm in three freeze–thaw cycles and was then sealed and irradiated with a series of 3500-Å lamps in a Rayonet photochemical reactor for 3 h. At the end of this time the photolysate was heated at 100 °C for 75 min. The solvent was removed under reduced pressure to afford a quantitative yield of a 1:1 mixture of 1-(*p*-tolyl)-2,3-diphenyl-4-methyl-3-penten-1-one (**25**) (50%) and 2-(*p*-tolyl)-1,3-diphenyl-4-methyl-3-penten-1-one (**26**) (50%). The identity of the photoproducts was confirmed by ozonization to a 1:1 mixture of **27** and **28** whose structures were verified by comparison with authentic samples.

(61) McKenzie, A.; Mills, A. K.; Miles, J. R. *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 904.

Synthesis of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-anisyl)-2,5-dihydrofuran (29). To a solution containing 1.0 g of 3,5-diphenyl-5-(*p*-anisyl)-2(5*H*)-furanone[22] in 125 mL of ether was added 10 equiv of methylmagnesium bromide. The solution was heated at reflux for 20 h, cooled, neutralized with an ammonium chloride solution, and extracted with ether. The organic layer was washed with a sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil. A solution containing 1.08 g of the above oil and 2 mL of sulfuric acid in 200 mL of methanol was heated at reflux for 30 min. The solution was cooled, diluted with 200 mL of water, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow solid which was recrystallized from methanol to give 770 mg (74%) of 2,2-dimethyl-3,5-diphenyl-5-diphenyl-5-(*p*-anisyl)-2,5-dihydrofuran (**29**) as a white solid: mp 90–91 °C; IR 1600, 1500, and 1450 cm^{-1}; UV (methanol) 253 nm (ϵ 12 900); NMR ($CDCl_3$, 100 MHz) δ 1.52 (s, 6 H), 3.74 (s, 3 H), 6.36 (s, 1 H), 6.7–7.4 (m, 14 H); *m/e* 356 (M^+), 341, 279, 251 (base), 249, 135, 115, 105, 91, and 77.

Anal. Calcd for $C_{25}H_{24}O_2$: C, 84.24; H, 6.79. Found: C, 84.25; H, 7.06.

Sensitized Irradiation of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-anisyl)-2,5-dihydrofuran (29). A solution containing 50.6 mg of dihydrofuran **29** and 3.4 mg of thioxanthone in 8 mL of benzene was degassed to 5×10^{-3} mm in three freeze–thaw cycles and was then sealed and irradiated with a series of 3500-Å lamps in a Rayonet photochemical reactor for 3 h. At the end of this time the photolysate was heated at 100 °C for 75 min. The solvent was removed under reduced pressure to afford a quantitative yield of a 1.8:1.0 mixture of 1-(*p*-anisyl)-2,3-diphenyl-4-methyl-3-penten-1-one (**30**) [NMR ($CDCl_3$, 100 MHz) δ 1.56 (s, 3 H), 1.87 (s, 3 H), 3.76 (s, 3 H), 5.88 (s, 1 H), 6.7–8.0 (m, 14 H)] and 2-(*p*-anisyl)-1,3-diphenyl-4-methyl-3-penten-1-one (**31**) [NMR ($CDCl_3$, 100 MHz) δ 1.56 (s, 3 H), 1.87 (s, 3 H), 3.68 (s, 3 H), 5.87 (s, 1 H), 6.7–8.0 (m, 14 H)]. The identity of the two photoproducts was established by ozonization to a 1.8:1 mixture of 1-(*p*-anisyl)-2,3-diphenyl-1,3-propanedione (**32**) [NMR ($CDCl_3$, 100 MHz) δ 3.8 (s, 3 H), 6.55 (s, 1 H), 6.8–8.0 (m, 14 H] and 2-(*p*-anisyl)-1,3-diphenyl-1,3-propanedione (**33**) [NMR ($CDCl_3$, 100 MHz) δ 3.76 (s, 3 H), 6.55 (s, 1 H), 6.8–8.0 (m, 14 H)]. The identity of the two products was determined by comparison with independently synthesized samples.

Independent Synthesis of 1-(*p*-Anisyl)-2,3-diphenyl-1,3-propanedione (32). A mixture containing 2.0 g of 4-(1,2-diphenylethenyl)morpholine,[57] 1.42 g of *p*-anisoyl chloride, and 1.53 g of triethylamine was heated neat at 120 °C for 75 min. The reaction mixture was cooled and dissolved in *p*-dioxane and 60 mL of a 10% hydrochloric acid solution was added with enough *p*-dioxane to afford a clear solution. This mixture was refluxed for 3 h, cooled, diluted with 100 mL of water, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure, leaving behind a yellow oil. Chromatography of this material on a silica gel column using a 75% pentane–ether mixture as the eluent was followed by bulb-to-bulb distillation at 0.5 mm to give 1-(*p*-anisyl)-2,3-diphenyl-1,3-propanedione (**32**) as a pale yellow oil: bp 150 °C (0.05 mm); IR ($CHCl_3$) 1700, 1680, 1600, and 1560 cm^{-1}; UV (methanol) 283 nm (ϵ 18 600); NMR ($CDCl_3$, 100 MHz) δ 3.76 (s, 3 H), 6.5 (s, 1 H), 6.8–8.0 (m, 14 H); *m/e* 204 (base), 135, 105, 91, and 77.

Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.43; H, 5.68.

Independent Synthesis of 2-(*p*-Anisyl)-1,3-diphenyl-1,3-propanedione (33). A mixture containing 1.13 g of 4-methoxydeoxybenzoin,[62] 1.5 g of trimethylsilyl chloride, and 1.5 g of triethylamine in 50 mL of dimethylformamide was heated at reflux for 36 h. The reaction mixture was cooled, dissolved in hexane, and washed with a saturated sodium bicarbonate solution, followed by a 10% hydrochloric acid solution, and then with water. The solvent was removed under reduced pressure to give the corresponding trimethylsilyl enol ether of 4-methoxydeoxybenzoin: NMR ($CDCl_3$, 100 MHz) δ 0.04 (s, 9 H), 3.66 (s, 3 H), 6.02 (s, 1 H), 6.7–7.8 (m, 9 H). To a solution containing 400 mg of the crude enol ether in 10 mL of tetrahydrofuran at −60 °C was added 30 mg of methyllithium in 5 mL of tetrahydrofuran. After stirring for 30 min at −60 °C, the solution was warmed to −20 °C and stirred at this temperature for 45 min. A 200-mg sample of benzoyl chloride in 5 mL of tetrahydrofuran was added at −20 °C. The mixture was then allowed to warm to room temperature. The solution was washed with a saturated ammonium chloride solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 250 mg of a crystalline solid: mp 151–152 °C; IR (KBr) 1675 and 1600 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 3.76 (s, 3 H), 6.55 (s, 1 H), 6.8–8.0 (m, 14 H); *m/e* 330 (M^+).

Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.88; H, 5.49. Found: C, 79.77; H, 5.73.

Direct Irradiation of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-anisyl)-2,5-dihydrofuran (29). A solution containing 40.8 mg of dihydrofuran **29** in 8 mL of benzene was degassed to 5×10^{-3} mm in three freeze–thaw cycles and sealed and irradiated with a series of 3000-Å lamps in a Rayonet photochemical reactor for 4 h. Removal of the solvent under reduced pressure left behind an oil which was shown to contain a 1.5:1 mixture of 1-(*p*-anisyl)-2,3-diphenyl-3-penten-1-one (**30**) and 2-(*p*-anisyl)-1,3-diphenyl-3-penten-1-one (**31**). The structure of these compounds was further verified by ozonization to a mixture of diketones **32** and **33**.

Synthesis of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-cyanophenyl)-2,5-dihydrofuran (34). To a solution containing 1.0 g of 3,5-diphenyl-5-(*p*-bromophenyl)-2(5*H*)-furanone[22] in 125 mL of ether was added 10 equiv of methylmagnesium bromide. The solution was heated at reflux for 20 h, cooled, neutralized with an ammonium chloride solution, and extracted with ether. The organic layer was washed with a sodium bicarbonate solution and then dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil. A solution containing 909 mg of the above oil and 2 mL of sulfuric acid in 200 mL of methanol was heated at reflux for 30 min. The solution was then cooled, diluted with 200 mL of water, extracted with ether, washed with a sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow solid which was recrystallized from methanol to give 720 mg (82%) of 2,2-dimethyl-3,5-diphenyl-5-(*p*-bromophenyl)-2,5-dihydrofuran as a white solid: mp 98–99 °C; NMR ($CDCl_3$, 100 MHz) δ 2.48 (s, 6 H), 6.2 (s, 1 H), 7.1–7.5 (m, 14 H). A solution containing 4.1 g of the above dihydrofuran and 1.89 g of cuprous cyanide in 50 mL of dimethylformamide was heated at reflux for 67 h. The reaction mixture was cooled, diluted with 150 mL of a 100% sodium cyanide solution, extracted with a 10% sodium cyanide solution and water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a brown oil which was chromatographed on a silica gel column using an 88% hexane–ether mixture as the eluent. The yellow solid obtained was recrystallized from methanol to give 2.87 g (81%) of 2,2-dimethyl-3,5-diphenyl-5-(*p*-cyanophenyl)-2,5-dihydrofuran (**34**) as a white solid: mp 121–121.5 °C; IR (KBr) 3000, 2220, 1610, 1500, and 1450 cm^{-1}; UV (methanol) 238 nm (ϵ 24 400); NMR ($CDCl_3$, 100 MHz) δ 1.52 (s, 6 H), 6.33 (s, 1 H), 7.2–7.6 (m, 14 H); *m/e* 351 (M^+), 336, 274, 249, 222 (base), 105, 103, 91, and 77.

Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.42; H, 6.05; N, 3.98.

Direct Irradiation of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-cyanophenyl)-2,5-dihydrofuran (34). A solution containing 73 mg of dihydrofuran **34** in 450 mL of benzene under an argon atmosphere was irradiated with a 450-W Hanovia lamp equipped with a Vycor filter sleeve for 1 h. Removal of the solvent under reduced pressure left behind an oil which was later shown to contain two photoproducts. As a result of the similarity of the NMR spectra, the ratio of the two photoproducts could not be determined at this stage [NMR ($CDCl_3$, 100 MHz) δ 1.56 (s, 3 H), 1.83 (s, 3 H), 5.88 (s, 1 H), 6.7–7.9 (m, 14 H)]. The two photoproducts could be separated from unreacted starting material by chromatography on a silica gel column using a 75% pentane–ether mixture as the eluent. The ratio of the two photoproducts was then determined by an ozonative degradation experiment. Ozone was bubbled into a solution containing 25 mg of the mixture of photoproducts in 200 mL of methylene chloride which had been cooled to −78 °C for 15 min. The solution was flushed with

(62) Jenkins, S. S. *J. Am. Chem. Soc.* **1934**, *56*, 682.

nitrogen for 10 min and then 20 mL of dimethyl sulfide was added. The reaction mixture was stirred at 25 °C for 3 h. After the solvent was removed under reduced pressure, the oily residue was extracted with ether, washed with water, and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow oil which contained a 1.5:1.0 mixture of 1-(*p*-cyano)-2,3-diphenyl-1,3-propanedione (**37**) [NMR (benzene-d_6, 100 MHz) δ 6.01 (s, 1 H), 6.6–7.7 (m, 14 H)] and 2-(*p*-cyano)-1,3-diphenyl-1,3-propanedione (**38**) [NMR (benzene-d_6, 100 MHz) δ 6.05 (s, 1 H), 6.6–7.7 (m, 14 H)]. The identity of the two products was determined by comparison with independently synthesized samples.

Independent Synthesis of 1-(*p*-Cyano)-2,3-diphenyl-1,3-propanedione (37). A mixture containing 5.98 of deoxybenzoin, 5.4 g of trimethylsilyl chloride, and 7.07 g of triethylamine in 30 mL of dimethylformamide was heated at reflux for 12 h. The usual workup followed by distillation at 115 °C (0.05 mm) gave 5.0 g of the silyl enol ether of deoxybenzoin: NMR ($CDCl_3$, 60 MHz) δ 0.04 (s, 9H), 6.08 (s, 1 H), 7.2–7.8 (m, 10 H). To a solution containing 540 mg of the silyl enol ether in 10 mL of tetrahydrofuran at −60 °C was added 45 mg of methyllithium in 8 mL of tetrahydrofuran at −60 °C. After stirring for 30 min at −60 °C, the solution was warmed to −20 °C and stirred at this temperature for an additional 45 min. A 330-mg sample of *p*-cyanobenzoyl chloride in 10 mL of tetrahydrofuran was added and the mixture was warmed to 25 °C, washed with a saturated ammonium chloride solution, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting solid was recrystallized from methanol to give 380 mg of 1-(*p*-cyano)-2,3-diphenyl-1,3-propanedione (**37**): mp 141–142 °C; IR (KBr) 2230, 1700, and 1670 cm^{-1}; NMR ($CDCl_3$, 100 MHz) δ 6.51 (s, 1 H), 7.1–8.0 (m, 14 H); *m/e* 325 (M^+).

Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31. Found: C, 81.09; H, 4.73; N, 4.26.

Independent Synthesis of 2-(*p*-Cyano)-1,3-diphenyl-1,3-propanedione (38). A mixture containing 2.2 g of 4-cyanodeoxybenzoin,[22] 4.4 g of trimethylsilyl chloride, and 4.4 g of triethylamine in 30 mL of dimethylformamide was heated at reflux for 12 h. The usual workup followed by bulb-to-bulb distillation at 120 °C (0.5 mm) gave 1.5 g of the trimethylsilyl enol ether of 4-cyanodeoxybenzoin as a colorless oil: NMR ($CDCl_3$, 100 MHz) δ 0.04 (s, 9 H), 6.0 (s, 1 H), 7.1–7.7 (m, 9 H). To a solution containing 1.45 g of the silyl enol ether in 20 mL of tetrahydrofuran at −60 °C was added 0.1 g of methyllithium in 10 mL of tetrahydrofuran. After stirring for 30 min at −60 °C, the solution was warmed to −20 °C and stirred at this temperature for 45 min. A 700-mg sample of benzoyl chloride in 10 mL of tetrahydrofuran was then added and the mixture was stirred for 45 min at −15 °C. After warming to room temperature, the mixture was washed with a saturated ammonium chloride solution followed by drying over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left an oily residue which was chromatographed on a silica gel column using a 10% ether–hexane mixture. The crystalline solid obtained was identified as 2-(*p*-cyano)-1,3-diphenyl-1,3-propanedione (**38**) on the basis of its spectral properties: mp 139–140 °C; NMR ($CDCl_3$, 100 MHz) δ 6.51 (s, 1 H), 7.1–8.0 (m, 14 H); IR (KBr) 2230 and 1680 cm^{-1}; *m/e* 325 (M^+).

Anal. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31. Found: C, 81.08; H, 4.57; N, 4.28.

Sensitized Irradiation of 2,2-Dimethyl-3,5-diphenyl-5-(*p*-cyanophenyl)-2,5-dihydrofuran (34). A solution containing 32.1 mg of dihydrofuran **34** and 3.3 mg of thioxanthone in 8 mL of benzene was degassed to 5×10^{-3} mm in three freeze–thaw cycles and was then sealed and irradiated with a series of 3500-Å lamps in a Rayonet photochemical reactor for 3 h. At the end of this time the photolysate was heated at 100 °C for 75 min. The solvent was removed under reduced pressure to afford a quantitative yield of an oil which was shown to contain a 1.4:1 mixture of enones **35** and **36**. The structures of these compounds were further verified by ozonization to a mixture of diketones **37** and **38**.

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Registry No. 1, 36859-02-6; **2**, 71597-51-8; **3**, 71597-52-9; **4**, 71597-53-0; **5**, 71597-54-1; **6**, 71597-55-2; **7** isomer 1, 31502-11-1; **7** isomer 2, 31615-95-9; *cis*-**8**, 71597-56-3; *trans*-**8**, 71597-57-4; **9**, 71597-58-5; **10**, 4888-39-5; **11**, 71597-59-6; **12**, 71597-60-9; **13**, 71597-61-0; **14**, 71597-62-1; **15**, 13148-19-1; **16**, 71597-63-2; **17**, 71629-34-0; **20a**, 71597-64-3; **20b**, 71597-65-4; **24**, 71597-66-5; **25**, 71597-67-6; **26**, 71597-68-7; **27**, 71597-69-8; **28**, 71597-70-1; **29**, 71597-71-2; **30**, 71597-72-3; **31**, 71597-73-4; **32**, 71597-74-5; **33**, 71597-75-6; **34**, 71597-76-7; **37**, 71597-77-8; **38**, 71597-78-9; **39** (Ar = *p*-$CH_3C_6H_4$), 68727-78-6; **39** (Ar = *p*-anisyl), 56258-94-7; **39** (Ar = *p*-BrC_6H_4), 56258-97-0; 2-methyl-3,5,5-triphenyl-3-pentene-2,5-diol, 71597-79-0; 4-(1,2-diphenylethenyl)morpholine, 18239-50-4; benzoyl chloride, 98-88-4; 5,5-dimethyl-3-phenyl-2(5*H*)-furanone, 68727-84-4; 4,5,5-triphenyl-2(5*H*)-furanone, 4080-72-2; 2-acetoxy-2,2-diphenylacetophenone, 4917-96-8; 2-hydroxy-2,2-diphenylacetophenone, 4237-46-1; 5-methyl-3,5-diphenyl-2(5*H*)-furanone, 68727-81-1; *p*-toluoyl chloride, 874-60-2; 4-methyldeoxybenzoin, 2001-28-7; trimethylsilyl chloride, 75-77-4; 4-methyldeoxybenzoin trimethylsilyl enol ether, 71597-80-3; *p*-anisoyl chloride, 100-07-2; 4-methoxydeoxybenzoin, 1023-17-2; 4-methoxydeoxybenzoin trimethylsilyl enol ether, 71597-81-4; 2,2-dimethyl-3,5-diphenyl-5-(*p*-bromophenyl)-2,5-dihydrofuran, 71597-82-5; deoxybenzoin, 451-40-1; deoxybenzoin silyl enol ether, 71597-83-6; tetrahydrofuran, 109-99-9; *p*-cyanobenzoyl chloride, 6068-72-0; 4-cyanodeoxybenzoin, 60694-99-7; 4-cyanodeoxybenzoin trimethylsilyl enol ether, 71597-84-7.

Nogalamycin. Stereochemistry and Chemical Modification

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The conversion of nogalamycin (**1a**) to a number of analogues in which the nogalose moiety is replaced by alkoxy groups and hydrogen is described. In one series of analogues the carbomethoxy group at C-10 of **1a** is removed, but in the other series this group has been retained. Preparation of these compounds by acidic alcoholysis results in formation of pairs of isomers differing only in configuration at C-7. The absolute configuration of the chiral centers at C-7, C-9, and C-10 of **1a** are assigned on the basis of CD studies.

Nogalamycin[1-3] (**1a**) is an anthracycline antibiotic which has activity against gram-positive microorganisms and is an antitumor agent.[4] As a result of previous studies[4] of compounds prepared by chemical modification of **1a**, it

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