Molecular Rearrangements of Excited States Generated by Intramolecular Dioxetane Scission. Photochemistry without Light. Mechanistic and Exploratory Organic Photochemistry[1,2]

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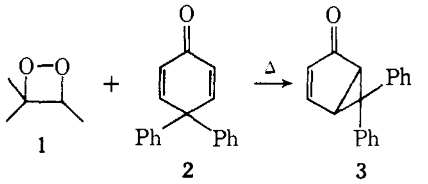
Abstract: A series of 1-methylene-4,4-diphenyl-2,5-cyclohexadienes was synthesized. Singlet oxygen reacted selectively with the exocyclic double bond affording a parallel series of dioxetanes. Thermolysis of the dioxetanes gave, in each case, 4,4-diphenyl-2,5-cyclohexadienone, 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, and the ketone derived from exocyclic double bond fission (i.e., acetone, acetophenone, *m*-methoxyacetophenone, valerophenone, 2-acetonaphthone). This provides a first example of dioxetane fission to afford a rearranging excited state. Since the efficiency of Type A rearrangement to give bicyclic ketone is known, efficiencies of excited state generation are available. Interestingly, these efficiencies proved to be 16.6 ± 3.2% and not dependent on the structure of the methyl ketone by-product. Thus, independent of the triplet energy of the methyl ketone, it is the diphenylcyclohexadienone which captures triplet excitation energy and rearranges. Surprisingly excitation remains in the 68.5 kcal/mol dienone chromophore rather than the 59 kcal/mol 2-acetonaphthone moiety. This is understood on the basis of the dioxetane decomposition leading only to n-π^* triplets and provides evidence for n-π^* excited triplet being the rearranging species in the Type A dienone process. Finally, no Type II rearrangement was encountered where excited valerophenone was potentially available, providing evidence against escape of the higher energy ketone triplets from the solvent cage.

Introduction

It was first reported 6 years ago by Kopecky[3] that thermolysis of dioxetanes affords excited carbonyl compounds. Since that time evidence has mounted that simple dioxetanes give rise to triplet excited states.[4] Kearns[5] and others[6] have provided theoretical reasoning, based on correlation diagrams and molecular orbital calculations, that the n-π^* triplet should be kinetically preferred.

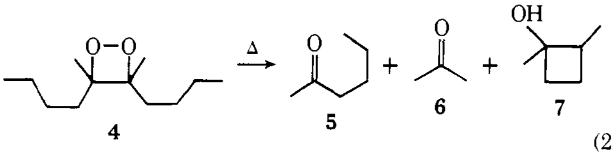
The idea of using a dioxetane as a source of acetone triplet sensitizer to effect a photochemical reaction was successfully demonstrated by White.[7] One example[7] was the bimolecular delivery of triplet excitation to effect the known[8] Type A rearrangement of 4,4-diphenyl-2,5-cyclohexadienone (**2**); note eq 1.

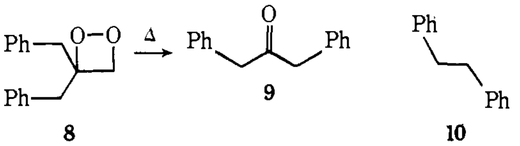


This example illustrates one type of "photochemistry without light".[9] Thus, the photochemistry here begins with the excited state itself.[7] This should not be confused with the original use[9] of the expression in which photochemical species (e.g., zwitterionic) were generated midway on a hypersurface leading from excited state reactant to ground state product. Thus there are two variations of photochemistry without light. The version starting with the initial excited state could aptly be designated "vertical" while that beginning further along the reaction coordinate could be designated "nonvertical".

Recently, examples of a very novel kind of vertical photochemistry without light were described by Foote[10] and by Richardson[11] in which the dioxetane moiety was incorporated in the reacting molecule and where any energy transfer must therefore be intramolecular; note eq 2 and 3.

The present study began with the idea of effecting an excited state unimolecular rearrangement by internal incorporation of a dioxetane moiety to give intramolecular electronic excitation.





For our study we selected dioxetanes of the general structure **11**, since thermal cleavage with attendant intramolecular electronic excitation promised to lead to the well-studied excited state of 4,4-diphenyl-2,5-cyclohexadienone (**2**).

Additionally, we were interested in the role played by the second ketonic fragment released in the reaction and in the triplet energy partition between this ketone and 4,4-diphenyl-2,5-cyclohexadienone (**2**). Thus, in the thermolysis of a dioxetane such as **11** there are two a priori modes of 2 + 2 cycloreversion as depicted in eq 4. One might anticipate that the mode of fission would depend on the relative energies of the two possible triplet excited states engendered and thus on the substituents R$_1$ and R$_2$ in this equation.

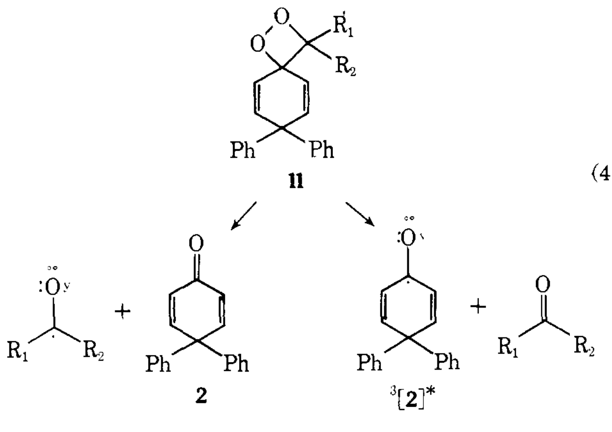
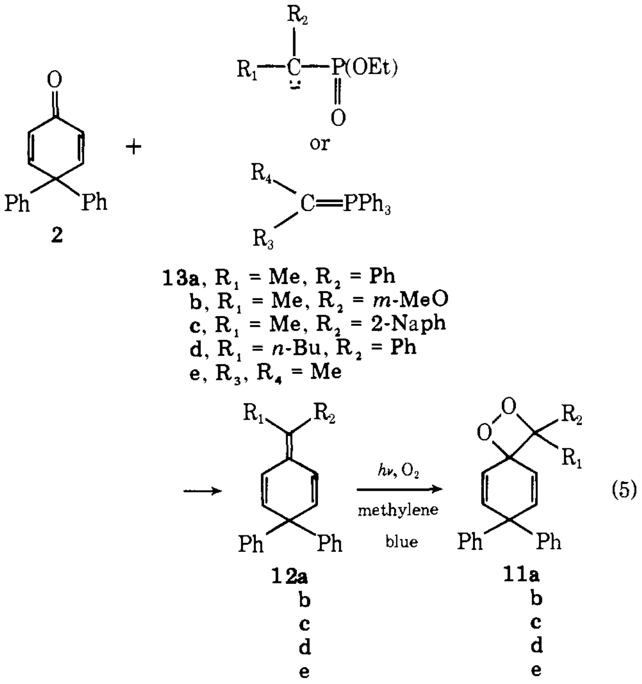


Table I

Inert triplet	Triplet energy	Bicyclic ketone yield, %	Dienone yield, %	Efficiency of dienone triplet generation, %
Acetone	82	11.5	88.5	13.4
Acetophenone	74	17.1	82.9	19.8
m-Methoxyacetophenone	72	14.0	86.0	16.3
2-Acetonaphthone	59	12.0	88.0	14.0
Valerophenone	74	15.0	85.0	17.4

Synthesis of Dioxetanes. Our synthesis utilized the reaction of 4,4-diphenyl-2,5-cyclohexadienone (**2**) with the corresponding Wittig[12] or Emmons-Wadsworth[13] reagents to afford the desired 1-methylene-4,4-diphenyl-2,5-cyclohexadiene derivative **12a–e** as shown in eq 5. Photooxidation with singlet oxygen generated at −78 °C in methanol-acetone led to regioselective attack on the exocyclic double bond to afford the desired dioxetanes **11a–e**. These were obtained free of byproducts by chromatogrphy at −20 °C. Dioxetanes **11a**, **11c**, and **11e** crystallized nicely and proved relatively stable in this form.



13a, R_1 = Me, R_2 = Ph
b, R_1 = Me, R_2 = *m*-MeO
c, R_1 = Me, R_2 = 2-Naph
d, R_1 = *n*-Bu, R_2 = Ph
e, R_3, R_4 = Me

Results. Thermolysis of Dioxetanes. It was found that the dioxetanes decomposed smoothly in carbon tetrachloride at 77 °C. In each case the reaction proceeded cleanly to give three products: the ketone formed by scission of the exocyclic moiety (i.e., **14a–e** in Chart I), 4,4-diphenyl-2,5-cyclohexadienone (**2**), and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**3**). It was observed that clean and reproducible reaction required the use of base-washed glassware; ammonium hydroxide was used. Erratic results obtained otherwise may derive from traces of acid or heavy metals.

The products and yields are listed in Table I. Also given in Table I are the triplet excitation energies for the ketonic byproducts. Finally, Table I includes the efficiencies of generation of the triplet of 4,4-diphenyl-2,5-cyclohexadienone, a value which can be derived from the yield of bicyclic product **3** by multiplication by 1/0.86. Here 0.86 is the quantum yield[8b] of formation of bicyclic ketone from triplet of dienone **2**.

One concern was that the thermolysis might not be the simple unimolecular decomposition supposed and that chain, free-radical mechanisms might intervene. For this reason, the kinetics were investigated in one case, that of the phenylmethyl dioxetane **11a**. Unimolecular kinetics were observed, and a rate constant of 4.5×10^{-4} s^{-1} at 71.3 °C was obtained.

Control Experiments; Sensitization and Quenching. Results. Particular interest was focused on the naphthyl methyl dioxetane (**11c**) case in which it appeared that dienone triplet was formed in the same amount (note Table I) as in the cases where ketones with higher energy triplets than 4,4-diphenyl-2,5-cyclohexadienone were produced. It seemed important to ascertain whether free 2-acetonaphthone triplet (i.e., having escaped from the solvent cage) might actually be produced but then return energy to 4,4-diphenyl-2,5-cyclohexadienone.

Two control experiments were devised. One was designed to intercept any such free acetonaphthone triplets by addition of 0.1 M cyclohexadiene triplet quencher. The other was the inverse (i.e., sensitization) experiment, namely determination of the fate of 4,4-diphenyl-2,5-cyclohexadienone in presence of triplet 2-acetonaphthone generated artificially, again external to the solvent cage.

The results of quenching and sensitization are summarized in Table II. It is seen that cyclohexadiene quencher (E_T = 53 kcal/mol) did not inhibit formation of bicyclic ketone photoproduct **3** and thus had not intercepted 2-acetonaphthone triplets (E_T = 59 kcal/mol) capable of transferring energy back to dienone. This is despite the much lower (10^{-3}-fold) concentration of dienone **2** relative to cyclohexadiene.

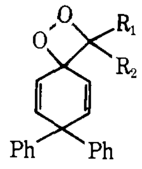
It is to be noted that the quenching experiments do not exclude the presence of 2-acetonaphthone triplets within the solvent cage which then return energy to the dienone. Such energy exchange would have to be without loss of the $n-\pi^*$ nature of the excitation, and a least complex interpretation does not invoke such exchange.

Turning to the sensitization experiment, we note that use of 335-nm light, selectively absorbed by 2-acetonaphthone by a factor of >99:1, led to a very low efficiency of bicyclic ketone formation. Knowing the quantum yield of formation of this product from triplet dienone as 0.86, we can calculate the efficiency of effective triplet energy transfer to be only 0.015.

Table II. Summary of Quenching and Sensitization Experiments

Experiment	Reactant	Additive	Yield (or quantum yield) of bicyclic ketone **3**
Sensitization	Dienone **2**	2-Acetonaphthone	Φ = 0.013
Sensitization	Dienone **2**	2-Acetonaphthone	Φ = 0.017
Sensitization	Dienone **2**	2-Acetonaphthone	Φ = 0.013
Quenching	Dioxetane **11c**	Cyclohexadiene, 0.10 M	12 ± 1%
Quenching	Dioxetane **11c**	Cyclohexadiene, 0.10 M	12 ± 1%
Quenching	Dioxetane **11c**	None	12 ± 1%
Quenching	Dioxetane **11c**	None	12 ± 1%

Chart I. Thermolysis of Dioxetanes **11a–e**



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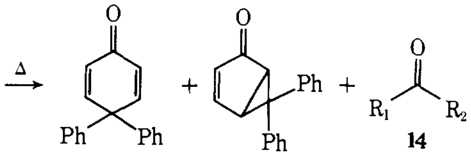
(a) R$_1$ = Me, R$_2$ = Ph
(b) R$_1$ = Me, R$_2$ = *m*-MeOPh
(c) R$_1$ = Me, R$_2$ = 2-Naph
(d) R$_1$ = Bu, R$_2$ = Ph
(e) R$_1$ = R$_2$ = Me



2 Yield, %	**3** Yield, %	**14** Triplet energy
82.9	17.1	74
86.0	14.0	72
88.0	12.0	59
85.0	15.0	74
88.5	11.5	82

Thus, 2-acetonaphthone triplets are quite ineffectual in effecting Type A rearrangement of 4,4-diphenyl-2,5-cyclohexadienone. These 2-acetonaphthone triplets are generated external to the solvent cage but should be able to penetrate the cage. That no appreciable reaction occurs indicates (*vide supra*) that caged acetonaphthone triplets are not involved.

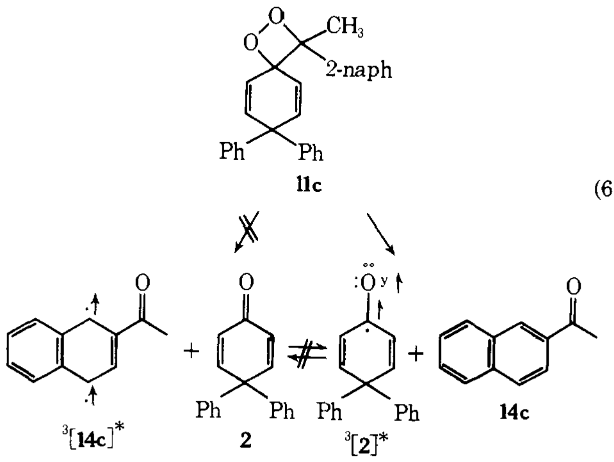
Interpretative Discussion of Results. The first striking result is the rearrangement itself (note Chart I). Thus, the formation of Type A dienone product (i.e., bicyclic ketone **3**) indicates that the original goal of intramolecular generation of dienone triplet was indeed successful.

The second remarkable observation is the constancy, within reasonable experimental error, of the efficiency of generation of the dienone triplet. Thus, Table I and Chart I show an average efficiency of 16.6 ± 3.2%. Comparison of the 68.5 kcal/mol triplet energy[8b] of 4,4-diphenyl-2,5-cyclohexadienone with the triplet energies of acetone (82 kcal/mol), acetophenone (74 kcal/mol), *m*-methoxyacetophenone (72 kcal/mol), and 2-acetonaphthone (59 kcal/mol) suggests that the partition of triplet excitation should be in favor of the dienone in the first three cases but in favor of 2-acetonaphthone in the last case. That the 2-acetonaphthone case does not have a very low or zero efficiency means that 2-acetonaphthone does not depart from the transition state for dioxetane fission with most of the triplet energy.

The question then is why the transition state is unaware of the availability of the low, 59 kcal/mol 2-acetonaphthone triplet. We should recognize, however, that the 59 kcal/mol triplet is of the π-π^* variety while the triplet of 4,4-diphenyl-2,5-cyclohexadienone is n-π^*.

This result brings to mind that it is the n-π^* triplet which is kinetically preferred (vide supra). Hence we can conclude that the failure of 2-acetonaphthone to pick up triplet excitation from the transition state derives from absence of a low-energy n-π^* state. It seems likely[14] that any n-π^* excited state available to 2-acetonaphthone is of much higher energy than the 68.5 kcal/mol n-π^* triplet of dienone **2**.

This means that not only the transition state for dioxetane fission but also the resulting ketone pair (i.e., cyclohexadienone plus 2-acetonaphthone) derived therefrom is unaware of the low-lying 2-acetonaphthone π-π^* excited state. We can conclude that any internal conversion as well as any energy repartition between ketonic moieties is slow compared with the very rapid rate of Type A triplet cyclohexadienone rearrangement.[15] The situation is summarized below:



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One further point deals with the use of the phenyl butyl dioxetane **11d**. Here no Type II products were discernable. This means that dioxetane fragmentation did not give free valerophenone triplets. Had such noncaged valerophenone triplets been generated, the known[16] rapid ($k_r = 1.4 \times 10^8$ s^{-1}) rate of Type II reaction is fast enough to compete successfully with energy transfer back to dienone at a diffusion-controlled rate ($k_{\text{pseudouni,diff}} = 10^5$ s^{-1} at the 0.0001 M dienone concentration present).

A final point is that the evidence demonstrates that it is the n-π^* 4,4-diphenylcyclohexadienone triplet which is kinetically formed and which rearranges prior to any equilibration with the π-π^* excited state. This resolves a long-standing question. Thus, many years ago[8,14] it was the n-π^* excited state which was postulated as the species accounting for the observed Type A rearrangement.

Experimental Section[17]

Diethyl 1-Phenylethylphosphonate. A mixture of 60.0 g (0.36 mol) of triethyl phosphite and 60.0 g (0.32 mol) of 1-phenylethyl bromide was heated to reflux and maintained at reflux for 1 h. Ethyl bromide which formed was allowed to distill out, and the temperature of the mixture rose to 180 °C. The mixture was maintained at 185 °C for 20 min, then cooled to room temperature. Styrene and triethyl phosphite were removed by short path distillation at 0.8 mm, and the material remaining in the pot, 57 g (74%), pure by NMR, was used without further purification. The product could be distilled, bp 185 °C at 0.8 mm, but considerable losses (ca. 50%) of material were sustained.

The spectral data were: ir 3.22, 3.25, 3.29, 3.33, 3.40, 3.42, 3.45, 6.24, 6.70, 6.90, 7.20, 7.31, 7.71, 8.03, 8.48, 8.61, 9.0–10.1, 10.1–11.0, 12.30, and 14.40 μ; NMR (CCl$_4$) τ 2.76 (s, 5 H, arom), 5.8–6.5 (complex m, 4 H, POCH_2CH$_3$), 6.98 (d of q partially obsured by POCH_2CH$_3$, 1 H, $J_{\text{PC-H}} = 22$ Hz, $J = 8$ Hz, methine), 8.50 (d of d, 3 H, $J_{\text{PC-CH}_3} = 19$ Hz, $J = 8$ Hz, -CH$_3$), 8.75 (t, 3 H, $J = 7$ Hz, CH_2CH$_3$).

Anal. Calcd for C$_{12}$H$_{19}$O$_3$P: *m/e* 242.1073. Found: *m/e* 242.1072.

Diethyl *m*-Methoxybenzylphosphonate. A mixture of 3.09 g (15.4 mmol) of *m*-methoxybenzyl bromide and 2.56 g (15.4 mmol) of triethyl phosphite was heated to 140 °C. Reflux was observed to commence at ca. 90 °C and ethyl bromide, bp 39 °C, was allowed to distill out. After 2 h at 140 °C, the mixture was heated at 180 °C for 10 min and then cooled to room temperature. Distillation afforded 3.58 g (90%) of the pure material, bp 121–124 °C at 0.05 mm.

The spectral data were: ir (CCl$_4$) 3.35, 3.38, 3.40, 3.41, 3.52, 3.54, 6.20 (sh), 6.24, 6.31, 6.70, 6.82, 6.88, 6.94, 6.97 (sh), 7.11, 7.18, 7.29, 7.69, 7.87, 7.98, 8.14, 8.40, 8.60, 8.68, 9.12, 9.50, 9.71, 10.38, 10.73, 10.94, 11.27, 11.61, 11.88, 12.33, 13.76, 14.45, and 16.13 μ; NMR (CCl$_4$) τ 2.86 (approx t, 3 H, $J = 8$ Hz, arom), 3.10–3.38 (m, 3 H, arom), 6.05 (d of q, partially obscured by s at 6.25, 4 H, $J_{\mathrm{POC-H}}$ = 8.5 Hz, J = 7 Hz, POCH_2CH$_3$), 6.25 (s, 3 H, OCH$_3$), 6.98 (d, 1 H, $J_{\mathrm{PC-H}}$ = 21.5 Hz, CH$_2$), 8.79 (t, 6 H, J = 7 Hz, -CH$_2$$CH_3$).

Anal. Calcd for $C_{12}H_{19}O_4P$: C, 55.79; H, 7.42. Found: C, 56.04; H, 7.55.

Diethyl β-Naphthylmethylphosphonate. A mixture of 4.42 g (20.0 mmol) of 2-bromomethylnaphthalene and 3.32 g (20.0 mmol) of triethyl phosphite was heated to 150 °C. Reflux was observed to commence at ca. 110 °C, and ethyl bromide was allowed to distill out. After 1 h at 150 °C, the reaction temperature was increased to 180 °C, maintained there for 15 min, and the mixture was then cooled to room temperature. Distillation afforded 4.47 g (80%) of the pure material, bp 148–153 °C at 0.05 mm.

The spectral data were: ir (CCl$_4$) 3.27, 3.31, 3.35, 3.39, 3.42, 3.49, 6.12, 6.24, 6.62, 6.76, 6.93, 7.10, 7.18, 7.29, 7.87, 7.97, 8.05, 8.18, 8.25, 8.59, 8.82, 8.88, 9.12, 9.45, 10.42, 11.09, 11.21, 11.67, 11.87, 12.31, and 15.58 μ; NMR (CCl$_4$) τ 2.16–2.40 (m, 4 H, arom), 2.56–2.78 (m, 3 H, arom), 6.10 (d of q, 4 H, $J_{\mathrm{POC-H}}$ = 8.5 Hz, J = 7 Hz, POCH_2CH$_3$), 6.85 (d, 2 H, $J_{\mathrm{PC-H}}$ = 22 Hz, CH$_2$), 8.92 (t, 6 H, J = 7 Hz, -CH$_2$$CH_3$).

Anal. Calcd for $C_{15}H_{19}O_3P$: C, 64.72; H, 6.89. Found: C, 64.50; H, 6.78.

Diethyl 1-Phenylpentylphosphonate. A stirred solution of 11.4 g (50 mmol) of diethyl benzylphosphonate in 100 ml of anhydrous tetrahydrofuran was cooled to −78 °C under nitrogen and 34.4 ml (50 mmol) of 1.45 M *n*-butyllithium in hexane was added over 20 min. The resulting solution was stirred at −78 °C for 30 min, and a solution of 10.2 g (55 mmol) of *n*-butyl iodide in 15 ml of anhydrous tetrahydrofuran was added dropwise. After addition was complete, the mixture was allowed to warm slowly to room temperature, stirred at room temperature for 2 h, then poured into ether, water washed, washed once with brine, dried, and concentrated in vacuo. Distillation yielded 8.69 g (61%) of the pure material, bp 122–125 °C at 0.05 mm.

The spectral data were: ir (NaCl) 3.23, 3.26, 3.29, 3.34 (sh), 3.36, 3.37, 3.38 (sh), 3.48, 6.23, 6.68, 6.80, 6,87, 7.18, 7.23 (sh), 7.30, 8.01, 8.45, 8.60, 9.09, 9.48, 9.71, 10.41, 11.78, 12.66, 13.25, 13.42, and 14.29 μ; NMR (CDCl$_3$) τ 2.65 (s, 5 H, arom), 5.8–6.4 (complex m, 4 H, POCH_2CH$_3$), 7.00 (d of d of d, 1 H, $J_{\mathrm{PC-H}}$ = 22 Hz, J = 10 Hz, J = 5 Hz, methine), 8.00 (br m, 2 H, diastereotopic CH$_2$), 8.30–9.16 (br m, 13 H, including sharp triplets for 3 H at 8.72, 8.90, and 9.16, -CH$_2$$CH_3$).

Anal. Calcd for $C_{15}H_{25}O_3P$: *m/e* 284.1535. Found: *m/e* 284.1541.

4,4-Diphenylcyclohexadienone. This material was prepared according to the procedure of Zimmerman et al.[18] from 4,4-diphenylcyclohexenone[19] by the sequence of enol acetate formation, bromination, and dehydrobromination in 51% overall yield, mp 124–125 °C (lit.[8] mp 124–125 °C).

1-(1′-Phenylethylidene)-4,4-diphenylcyclohexa-2,5-diene. A solution of 4.12 g (16.6 mmol) of diethyl 1-phenylethylphosphonate in 30 ml of anhydrous 1,2-dimethoxyethane was cooled to 0 °C with stirring under nitrogen and 10.0 ml (15.0 mmol) of 1.5 M *n*-butyllithium in hexane was added over 5 min. The resulting mixture was stirred at 0 °C for 5 min, a solution of 2.06 g (8.30 mmol) of 4,4-diphenylcyclohexadienone in 30 ml of anhydrous dimethoxyethane was added, and the mixture was heated to reflux. After refluxing for 16 h, the dark solution was cooled to room temperature, poured into water, ether extracted, water washed, washed once with brine, dried, concentrated in vacuo, and chromatographed on a 4 × 21 cm silica gel (MCB, Grade 62, 60–200 mesh) column slurry packed in hexane. Elution with 900 ml of 1% ether in hexane gave 1.80 g (63%) of the desired product as colorless oil, which was crystallized from methanol to afford 1.73 g (61%) of solid, mp 95–96.5 °C. Recrystallization from methanol gave needles, mp 96–97 °C.

The spectral data were: ir (CCl$_4$) 3.25, 3.27, 3.32, 3.43, 3.51, 6.25, 6.71, 6.91, 7.18, 7.26, 7.63, 8.15, 8.32, 8.45, 8.64, 9.12, 9.24, 9.53, 9.69, 9.79, 9.98, 10.24, 10.74, 11.05, 11.42, 11.76, 14.27, 14.84, and 15.06 μ; NMR (CCl$_4$) τ 2.86 (approx s, 15 H, arom), 3.32 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 3.70 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 3.90 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 4.18 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 7.84 (s, 3 H, -CH$_3$).

Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.43; H, 6.60.

1-(1′-*m*-Methoxyphenyl)ethylidene-4,4-diphenyl-2,5-cyclohexadiene. A solution of 2.72 g (10.5 mmol) of diethyl *m*-methoxybenzylphosphonate in 25 ml of anhydrous dimethoxyethane was cooled to 0 °C with stirring under nitrogen and 6.70 ml (10.5 mmol) of 1.5 M *n*-butyllithium in hexane was added slowly dropwise. The resulting mixture was stirred for 10 min at 0 °C, 1.43 g (10.5 mmol) of methyl iodide was added, and stirring was continued for 20 min at 0 °C. A second 6.70-ml portion of *n*-butyllithium was added, the resulting mixture stirred at 0 °C for 10 min, and then allowed to warm to room temperature. A solution of 1.24 g (5.00 mmol) of 4,4-diphenylcyclohexadienone in 20 ml of anhydrous dimethoxyethane was then added rapidly dropwise, and the mixture was heated at reflux for 11 h, cooled, poured into water, and ether extracted. The ether phases were water washed, dried, decolorized with Norite, concentrated in vacuo, and chromatographed on a 2 × 25 cm silica gel column slurry packed in hexane. Elution with 300 ml of 1% ether in hexane gave a colorless oil which crystallized from ether–pentane to afford 498 mg (27%) of the desired olefin as colorless prisms, mp 102–105 °C. Recrystallization from ether–pentane gave 473 mg (26%) with mp 107.5–108.5 °C.

The spectral data were: ir (CCl$_4$) 3.26, 3.27, 3.30, 3.34, 3.39, 3.41, 3.44, 3.53, 6.04, 6.27, 6.35, 6.73, 6.82, 6.91, 7.01, 7.27, 7.59, 7.78, 7.90, 8.10, 8.30, 8.49, 8.56, 8.64, 9.58, 9.65, 10.71, 11.04, 11.30, 11.68, 12.45, and 14.80 μ; NMR (CCl$_4$) τ 2.80 (approx s, 12 H, arom), 3.16–3.36 (m, 3 H, arom obscuring vinyl), 3.34 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 3.85 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 4.08 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 6.23 (s, 3 H, -OCH$_3$), 7.81 (s, 3 H, -CH$_3$).

Anal. Calcd for $C_{27}H_{24}O$: *m/e* 364.1826; C, 88.97; H, 6.64. Found: *m/e* 364.1827; C, 88.99; H, 6.74.

1-(1′-β-Naphthylethylidene)-4,4-diphenyl-2,5-cyclohexadiene. A solution of 1.67 g (6.00 mmol) of diethyl β-naphthylmethylphosphonate in 20 ml of anhydrous dimethoxyethane was cooled to 0 °C with stirring under nitrogen, and 4.00 ml (6.00 mmols) of 1.5 M *n*-butyllithium in hexane was added dropwise. The resulting mixture was stirred at 0 °C for 15 min, 0.916 g (6.75 mmol) of methyl iodide was added, and stirring was continued for 40 min at room temperature. The resulting mixture was recooled to 0 °C, a second 4.00-ml portion of *n*-butyllithium was added, and stirring was continued at 0 °C for 10 min. A solution of 0.992 g (3.00 mmol) of 4,4-diphenylcyclohexadienone in 10 ml of dimethoxyethane was added, cooling was removed, and the mixture was heated at reflux for 24 h, then stirred at room temperature for an additional 12 h. The solution was poured into water, ether extracted, dried, concentrated in vacuo, and passed through a 1.8 × 25 cm silica gel column, slurry packed in hexane, with 2% ether in hexane. The first 150 ml of eluent was concentrated in vacuo and chromatographed on a 1.8 × 25 cm silica gel column, slurry packed in hexane. Elution with 150 ml of 1% ether in hexane gave an oil which crystallized from methanol–ether to give 416 mg (34%) of colorless solid, mp 143–145 °C. Recrystallization from ether–hexane gave mp 146.5–148 °C.

The spectral data were: ir (CHCl$_3$) 3.27, 3.31, 3.33, 3.42, 3.49, 6.26, 6.72, 6.93, 7.40, 8.15, 8.32, 8.84, 9.56, 9.70, 10.46, 10.75, 11.09, 11.62, 12.17, 12.63, and 14.27 μ; NMR (CDCl$_3$) τ 2.1–2.35 (m, 3 H, arom), 2.45–2.90 (m, 14 H, including sharp singlet for 10 H at 2.78, arom), 3.18 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 3.59 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 3.80 (br d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 4.01 (br d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 7.84 (s, 3 H, CH$_3$).

Anal. Calcd for $C_{30}H_{24}$: *m/e* 384.1879; C, 93.71; H, 6.29. Found: *m/e* 384.1878; C, 93.67; H, 6.36.

1-(1′-Phenylpentylidene)-4,4-diphenyl-2,5-cyclohexadiene. A solution of 1.70 g (6.00 mmol) of diethyl 1-phenylpentylphosphonate in 20 ml of anhydrous dimethoxyethane was stirred at room temperature under nitrogen as 4.40 ml (6.00 mmol) of 1.45 M *n*-butyllithium in hexane was added slowly dropwise. After the addition was completed, the mixture was stirred at room temperature for 15 min, and a solution of 0.992 g (3.00 mmol) of 4,4-diphenylcyclohexadienone in 15 ml of dimethoxyethane was added. The mixture was then heated at reflux for 9 h, cooled, poured into water, and ether extracted. The ether phases were washed with brine, dried, concentrated in vacuo, and chromatographed on a 2 × 38 cm silica gel column, slurry packed in hexane. Elution with 200 ml of hexane gave 533 mg of a slightly yellow oil, which was decolorized by passage through a 1.2 × 20 cm column of silica gel with hexane, to yield 512 mg (33%) of the desired olefin as a viscous colorless oil.

The spectral data were: ir (CHCl$_3$) 3.27, 3.33, 3.36, 3.41, 3.45 (sh), 3.46, 3.47, 6.25, 6.33, 6.71, 6.80, 6.85, 6.92, 7.25, 7.69, 8.46, 9.01, 9.30, 9.70, 10.00, 10.20, 10.75, 11.05, 11.63, 11.90, 12.50, and 14.25 μ; NMR (CCl_4) τ 2.83 (approx s, 15 H, arom), 3.29 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 3.82 (AB q collapsed to approx t, 2 H, J_{AB} = 10 Hz, J = 2 Hz, vinyl), 4.20 (d of d, 1 H, J = 10 Hz, J = 2 Hz, vinyl), 7.47 (distorted t, 2 H, J = 7 Hz, allylic), 8.60–8.85 (m, 4 H, -$CH_2CH_2CH_3$), 9.14 (m, 3 H, CH_3).

Anal. Calcd for $C_{29}H_{28}$: C, 92.50; H, 7.50. Found: C, 92.60; H, 7.54.

1-Isopropylidene-4,4-diphenyl-2,5-cyclohexadiene. To a stirred suspension of 4.30 g (10.0 mmol) of isopropyl triphenylphosphonium iodide[12] in 30 ml of anhydrous tetrahydrofuran was added 7.00 ml (10.0 mmol) of 1.45 M *n*-butyllithium in hexane dropwise at room temperature under nitrogen. After stirring at room temperature for 30 min, a solution of 2.40 g (10.0 mmol) of 4,4-diphenylcyclohexadienone in 25 ml of tetrahydrofuran was added over 20 min. After stirring the dark orange-red suspension for 2 h at room temperature, the mixture was poured into hexane, filtered, washed with saturated aqueous ammonium chloride, dried, and concentrated in vacuo to afford a light yellow oil, which crystallized on standing. Recrystallization from ethanol yielded 2.60 g (95%) of the olefin, mp 89–91 °C.

The spectral data were: ir (CCl_4) 3.27, 3.28, 3.31, 3.38, 3.41, 3.50, 6.29, 6.75, 6.94, 7.27, 9.31, 10.75, 11.05, and 14.67 μ; NMR (CCl_4) τ 2.84–3.00 (m, 10 H, arom), 3.46 (d, 2 H, J = 10 Hz, vinyl), 4.10 (d, 2 H, J = 10 Hz, vinyl), 8.12 (s, 6 H, -CH_3).

Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.63; H, 7.29.

Photooxidation of 1-(1′-Phenylethylidene)-4,4-diphenyl-2,5-cyclohexadiene. A solution of 140 mg (0.407 mmol) of 1-(1-phenylethylidene)-4,4-diphenyl-2,5-cylohexadiene and 30 mg of methylene blue in 130 ml of 1:1 methanol–acetone was photooxidized at −70 °C, using a low-temperature immersion well apparatus and a 450-W Hanovia lamp. A continuous stream of dry oxygen was passed through the solution, and a combination of Pyrex glass and aqueous basic potassium chromate filters (ca. 0.1 M) were used to exclude light of wavelengths shorter than 470 nm. The basic apparatus used has been previously described by Zimmerman and Iwamura.[20]

The progress of the photooxidation was monitored by TLC, using 20% ether in hexane as eluent with development of the plates at −12 °C. The starting material was smoothly consumed over the course of 3–4 h with production of only one product. After complete consumption of starting material, there was no evidence for the presence of 4,4-diphenylcyclohexadienone in the cold mixture. The observed R_f's were: starting olefin, 0.62; dioxetane product, 0.46; dienone 0.23. The spots were observed by fluorescence quenching of short wave uv indicator. The reaction mixture was transferred to a 500-ml round-bottom flask maintained at −70 °C, and the photolysis well was rinsed out with chilled ether. This solution was maintained at −70 °C and diluted with 225 ml of brine (precooled to ca. −12 °C); chilled ether (precooled to −70 °C) was then added until the flask was nearly full. The flask was stoppered, removed from the cooling bath, and shaken vigorously until the ice which had formed had broken up enough to allow pouring. The mixture was then poured into a separatory funnel (precooled to −28 °C), and the layers were separated and maintained in −70 °C baths. The aqueous phase was extracted twice more with ether to give a total volume of 300–400 ml of ether phase. The combined ether phases were then washed twice quickly with ice water, dried over potassium carbonate at −28 °C, and concentrated in vacuo at −10 °C. The residue was dissolved in methylene chloride at −20 °C and applied to a 40-g 20 × 20 cm silica gel thick plate (GF-254) which had been precooled to −20 °C, then eluted (still at −20 °C) with 20% ether in pentane. The fastest moving uv active band was removed, ether extracted at −20 °C, filtered, and concentrated in vacuo at −10 °C. The residue was crystallized evaporatively by dissolution in excess ether–pentane at 0 to −10 °C, followed by evaporation of solvent under a stream of nitrogen at −10 °C. The solid so obtained was then recrystallized from ether–pentane between 0 and −70 °C to give 119 mg (80%) of 3-methyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene as colorless solid, mp 88–92 °C dec, pure by NMR and cold TLC analysis.

The spectral data were: NMR (CCl_4) τ 2.6–3.0 (m, 15 H, arom), 3.41 (AB q with additional fine coupling, 2 H, J = 10 Hz and ca. 2 Hz, vinyl), 3.99 (AB q with additional fine coupling, 2 H, J = 9.5 and ca. 2 Hz, vinyl), 8.14 (s, 3 H, CH_3).

Photooxidation of 1-(1′-*m*-Methoxyphenylethylidene)-4,4-diphenyl-2,5-cyclohexadiene. A solution of 150 mg of 1-(1′-*m*-methoxyphenylethylidene)-4,4-diphenyl-2,5-cyclohexadiene and 23 mg of methylene blue in 130 ml of 1:1 methanol–acetone was photooxidized at −70 °C (external dry ice–ethanol cooling) using a 450-W medium pressure Hanovia lamp. A combination of Pyrex glass filters and circulated basic aqueous potassium chromate (ca. 0.1 M) was used to exclude uv light and provided a ca. 470-nm cutoff. Dry oxygen was passed through the solution continually. The progress of the photooxidation was conveniently monitored by TLC analysis with development of the plates at −28 °C. This procedure revealed the smooth consumption of starting material with the formation of a sole product. The product spot disappeared on warming the aliquot and was replaced by new spots for *m*-methoxyacetophenone and 4,4-diphenylcyclohexadienone. The observed R_f's (20% ether in hexane) were: starting material, 0.75; dioxetane product, 0.53; 4,4-diphenylcyclohexadienone, 0.23; and *m*-methoxyacetophenone, 0.33. After 3.5 h, consumption of starting material was complete, the reaction mixture was transferred to a 500-ml round-bottom flask maintained at −70 °C, and the photolysis well was rinsed out with chilled ether. This solution was maintained at −70 °C while 225 ml of aqueous sodium chloride was cooled to −12 °C and a 1-l. separatory funnel cooled to −28 °C. The mixture was then diluted with the cold sodium chloride solution, and prechilled (−70 °C) ether was then added until the flask was nearly full. The flask was then stoppered, removed from the cooling bath, and shaken vigorously until the ice which had formed had broken up enough to allow pouring. The resulting thick mixture was then transferred to the chilled separatory funnel and the phases were separated. The ether and aqueous phases were maintained in −70 °C baths. Ether extraction was repeated three times to give a total volume of 300–400 ml of ether phase. Periodic checks of the temperature in the separatory funnel during this process revealed that the temperature of the mixture never rose above −20 °C during these operations. The ether phases were then washed twice *quickly* with ice water, dried over potassium carbonate, and concentrated in vacuo at −10 °C. The residue was dissolved in a minimal amount of methylene chloride and applied (at −20 °C) to a precooled 20 × 20 cm thick plate of silica gel (GF-254), then eluted (−20 °C) with 20% ether in pentane. The fastest moving uv active band was removed, ether extracted (still at −20 °C), filtered, and finally concentrated in vacuo at −10 °C to give 140 mg (86%) of 3-methyl-3-*m*-methoxyphenyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene, as an oil which refused to crystallize, pure by NMR and TLC analysis.

The spectral data were: NMR (CCl_4) τ 2.65–3.05 (m, 12 H, arom), 3.2–3.6 (m, AB q at 3.42 obscured by arom, 4 H, J_{AB} = 10 Hz, vinyl and arom), 3.98 (AB q with additional ca. 3 Hz splitting, 2 H, J_{AB} = 10 Hz, vinyl), 6.33 (s, 3 H, OCH_3), 8.23 (s, 3 H, CH_3).

Photooxidation of 1-(1′-β-Naphthylethylidene)-4,4-diphenyl-2,5-cyclohexadiene. A solution of 100 mg of 1-(1′-β-naphthylethylidene)-4,4-diphenyl-2,5-cyclohexadiene and 20 mg of methylene blue in 130 ml of 1:1 methanol–acetone was photooxidized at −70 °C, using a 450-W medium pressure Hanovia lamp. A combination of Pyrex glass filters and circulated basic aqueous potassium chromate served to exclude uv light and provided a ca. 470-nm cutoff. Dry oxygen was passed through the solution continually. The progress of the photooxidation was conveniently followed by TLC with development of the plates at −28 °C. This revealed the smooth consumption of starting material with production of a sole product. The product was shown to be thermally labile, since warming of the aliquots resulted in disappearance of the product spot and the observation of spots for 2-acetonaphthone and 4,4-diphenylcyclohexadienone. The observed R_f's were: starting olefin, 0.59; dioxetane product, 0.49; 4,4-diphenylcyclohexadienone, 0.23; and 2-acetonaphthone, 0.31. After starting material had been completely consumed (3.7 h), the mixture was transferred to a 500-ml round-bottom flask and maintained at −70 °C while an aqueous sodium chloride solution was cooled to −12 °C and a 1-l. separatory funnel was cooled to −28 °C. The reaction mixture was diluted with the cold sodium chloride solution, then with ether which had been precooled to −70 °C. The mixture was shaken vigorously until pouring was possible, then transferred to the separatory funnel, and the layers were separated. The aqueous and ether phases were maintained in −70 °C baths. The aqueous phase was extracted with ether until a total volume of ca. 350 ml of ether phase was obtained. The ether phases were then washed twice quickly with ice water, dried over potassium carbonate at −28 °C, and concentrated in vacuo at −10 °C. The residue was dissolved in a minimal amount of methylene chloride, applied at −20 °C to a 20 × 20 cm thick plate of silica gel (GF-254), and eluted with 20% ether in pentane at −20 °C. The fastest moving uv active band was removed, ether extracted at −20 °C, filtered, and concentrated in vacuo at −10 °C. The material so obtained was crystallized twice from ether–pentane between 0 and −70 °C to give 61 mg (54%) of 3-methyl-3-(2′-naphthyl)-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene as colorless crystalline solid, mp 89–94 °C dec, pure by NMR and TLC analysis.

The spectral data were: NMR (CCl$_4$) τ 2.12–2.36 (m, 4 H, arom), 2.48–3.04 (m, 13 H, arom), 3.35 (AB q with additional 2 Hz coupling, 2 H, J_{AB} = 10 Hz, vinyl), 8.27 (s, 3 H, CH$_3$).

Photooxidation of 1-(1′-Phenylpentylidene)-4,4-diphenylcyclohexa-2,5-diene. A solution of 130 mg of 1-(1′-phenylpentylidene)-4,4-diphenylcyclohexa-2,5-diene and 31 mg of methylene blue in 130 ml of 1:1 methanol–acetone was photooxidized at −70 °C (external dry ice–ethanol cooling) using a 450-W medium pressure Hanovia lamp. A combination of Pyrex glass filters and circulated basic aqueous potassium chromate (ca. 0.1 M) was used to exclude light of wavelength shorter than 470 nm. Dry oxygen was passed through the solution continually. Consumption of starting material and production of the dioxetane product were monitored by TLC analysis at −28 °C using 20% ether in hexane as eluent. A total of 8.5 h of irradiation was required to consume the starting material completely. TLC analysis at the end of that time showed only one product which had R_f 0.6 in 20% ether–hexane. The reaction mixture was transferred to a 500-ml round-bottom flask and maintained at −70 °C as the photolysis well was rinsed out with chilled ether. This solution was then maintained at −70 °C while 225 ml of saturated aqueous sodium chloride was cooled to −12 °C and a 1-l. separatory funnel was cooled to −28 °C. The photooxidation mixture was then diluted with the cold sodium chloride solution, and precooled (−70 °C) ether was added until the flask was nearly full. The flask was then stoppered, removed from the cooling bath, shaken vigorously until the ice which had formed was broken up sufficiently to allow pouring, then transferred to the chilled separatory funnel, and the phases were separated. The ether and aqueous phases were maintained in −70 °C baths. Ether extraction was repeated three times to give a total volume of 300–400 ml of extract. Periodic checks of the temperature in the separatory funnel during this process revealed that the temperature of the mixture never rose above −20 °C during these operations. The ether layers were then washed twice *quickly* with ice water, dried over potassium carbonate, and concentrated in vacuo at −10 °C. The residue was dissolved in a minimal amount of methylene chloride and applied (at −20 °C) to a 20 × 20 cm silica gel thick plate which had been precooled at −20 °C. The plate was then eluted with 10% ether in pentane at −20 °C. An intense band with R_f 0.4 was removed and ether extracted at −20 °C, filtered, and concentrated in vacuo below 0 °C to yield 96 mg (68%) of pure 3-butyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene as a clear, slightly yellow oil.

The spectral data were: NMR (CCl$_4$) τ 2.7–3.3 (m, 15 H, arom), 3.53 (AB q with additional 2 Hz splitting, 2 H, J_{AB} = 10 Hz, vinyl), 7.29 (m, 2 H, diastereotopic CH$_2$), 8.0–9.0 (br m, 4 H, CH_2CH_2CH$_3$), 9.19 (distorted t, J = 7 Hz, 3 H, CH$_2$$CH_3$).

Photooxidation of 1-Isopropylidene-4,4-diphenylcyclohexa-2,5-diene. A solution of 220 mg of 1-isopropylidene-4,4-diphenylcyclohexa-2,5-diene and 25 mg of methylene blue in 130 ml of methanol was photooxidized at −70 °C using a 450-W Hanovia lamp. A combination of Pyrex glass and circulated basic aqueous potassium chromate (ca. 0.1 M) was used to exclude light of wavelengths shorter than 470 nm. Dry oxygen was passed through the solution continually. After 30 min of irradiation, TLC analysis (−12 °C) showed complete consumption of starting material with formation of a product which had R_f 0.62 in 20% ether–hexane. The reaction mixture was transferred to a 500-ml round-bottom flask and maintained at −70 °C as the photolysis well was rinsed out with chilled ether, an aqueous sodium chloride solution was cooled to −12 °C, and a 1-l. separatory funnel was cooled to −28 °C. The reaction mixture was then diluted with the cold sodium chloride solution, and precooled (−70 °C) ether was added until the flask was nearly full. The flask was then stoppered, removed from the cooling bath, shaken vigorously until the mixture was broken up enough to allow pouring; the resulting thick mixture was then transferred to the separatory funnel, and the layers were separated. The ether and aqueous phases were maintained in −70 °C baths after separation. Ether extraction was repeated three times, until a total volume of 350 ml of ether phase was obtained. The ether phases were then washed twice quickly with ice water, dried over potassium carbonate at −28 °C, and concentrated in vacuo at −5 °C to give a yellow oil, which was chromatographed on a 40-g 20 × 20 cm silica gel thick plate at −20 °C, using 20% of ether in hexane as eluent. Removal of the fastest moving uv active band, followed by ether extraction, filtration (both at −20 °C), and concentration in vacuo at −10 °C gave a colorless crystalline product, which was recrystallized from ether–pentane between −20 and −70 °C to give 201 mg (82%) of pure 3,3-dimethyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene as a colorless crystalline solid, mp 72–74 °C.

The spectral data were: NMR (CCl$_4$) τ 2.83–3.05 (m, 10 H, arom), 3.55 (AB q, 4 H, J = 10 Hz, vinyl), 8.56 (s, 6 H, CH$_3$).

Preparative Decomposition of 3-Methyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. A solution of 366 mg (1.00 mmol) of 3-methyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene in 1500 ml of carbon tetrachloride was heated at reflux for 12 h, then concentrated in vacuo. VPC analysis showed only a ca. 8% yield of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in this large scale run. After removal of acetophenone under high vacuum, the residue was fractionally crystallized successively from methanol and ether–pentane to afford 194.6 mg (79.1%) of 4,4-diphenylcyclohexadienone, mp 123–125 °C, identical in all respects with authentic material. The mother liquors from the crystallization (53 mg) consisted (NMR analysis) of a 2:1 mixture of 4,4-diphenylcyclohexadienone and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. This material was chromatographed on a 1.0 × 50 cm silica gel column, slurry packed in hexane. Elution was with 80 ml of hexane, 20 ml of 2% ether in hexane, and 280 ml of 4% ether in hexane, and 5-ml fractions were collected. The results were: fractions 1–44, nil; fractions 45–55, 20.0 mg of 4,4-diphenylcyclohexadienone; 56–65. 26.3 mg of a mixture of 4,4-diphenylcyclohexadienone and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one; 66–76, essentially pure 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. Recrystallization of the contents of fractions 66–76 from ether–pentane afforded 3.5 mg (1.4%) of the bicyclic ketone, mp 137.5–138.5 °C, mixture melting point undepressed, identical by NMR and VPC (5% QF-1, 3% Carbowax, and 2% SE-54 columns) with authentic material.

Preparative Decomposition of 3-Methyl-3-*m*-methoxyphenyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. A solution of 110 mg of 3-methyl-3-*m*-methoxyphenyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene in 400 ml of CCl$_4$ was decomposed at reflux for 12 h. Removal of *m*-methoxyacetophenone under high vacuum gave 68 mg (100.6%) of a mixture of 4,4-diphenylcyclohexadienone and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one in a ratio of 89:11 by NMR analysis.

Preparative Decomposition of 3-Methyl-3-(2′-naphthyl)-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. A solution of 34 mg of 3-methyl-3-(2′-naphthyl)-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene in 300 ml of carbon tetrachloride was decomposed at reflux for 12 h, concentrated in vacuo, and chromatographed on a 1.0 × 34 cm silica gel column, slurry packed in hexane. Elution with 180 ml of 2.5% ether in hexane gave 14.1 mg (101.5%) of β-acetonaphthone, mp 52–53 °C, identical by NMR and VPC analysis with an authentic sample. Elution with 130 ml of 10% ether in hexane gave 19.7 mg (98%) of a mixture of 4,4-diphenylcyclohexadienone and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, in a ratio of ca. 85:15 by NMR analysis.

Preparative Decomposition of 3-Butyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. A solution of 88 mg of 3-butyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene in 400 ml of CCl$_4$ was decomposed at reflux for 12 h, concentrated in vacuo, and chromatographed on a 1.0 × 35 cm silica gel column, slurry packed in hexane. Elution with 150 ml of 3% ether in hexane gave 34.6 mg (99%) of valerophenone, identical by NMR, TLC, and VPC analysis with an authentic sample. Elution with 150 ml of 10% ether in hexane gave 53 mg (100%) of a mixture of 4,4-diphenylcyclohexadienone and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, in a ratio of 91:9 by NMR analysis.

Preparative Decomposition of 3,3-Dimethyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. A solution of 97 mg of 3,3-dimethyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene in 400 ml of carbon tetrachloride was decomposed at reflux for 12 h, then concentrated in vacuo to give 87 mg (99.2%) of a mixture of 4,4-diphenylcyclohexadienone and 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, in a ratio of 91:9 by NMR analysis.

Rate of Thermal Decomposition of 3-Methyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. Rate measurements were performed using a Jeolco MH-100 NMR spectrometer with variable temperature accessories. Temperature measurements employed a digital readout thermocouple. The methyl resonances of dioxetane starting material and acetophenone product were periodically recorded as was internal Me$_4$Si; the decrease in dioxetane peak height was taken as disappearance of dioxetane. This decrease was observed to be first order and was balanced by a first-order increase in acetophenone. Plots of the log of the dioxetane methyl peak height vs. time were used to determine the rate constant graphically. Three runs were made at 71.3 ± 0.3 °C using base-washed NMR tubes, which were sealed prior to the rate measurements. The derived rate constants were: **Run 1**, 4.6 $\times 10^{-4}$ s^{-1}; **Run 2**, 4.2 $\times 10^{-4}$ s^{-1}; **Run 3**, 4.6 $\times 10^{-4}$ s^{-1}; for an average rate of 4.5 $\times 10^{-4}$ s^{-1} with estimated error of ca. ±10%.

Decompositions of 3-Methyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]-nona-5,8-diene. Excited State Yields. Decompositions were carried out using base-washed glassware with carbon tetrachloride as solvent. All decompositions were accomplished by refluxing dilute solutions (open to the air) of the dioxetane in foil wrapped flasks with minimal room lighting for periods of 5–12 h. TLC monitoring prior to analysis insured that no dioxetane remained. After concentration in vacuo, a weighed amount of triphenylene internal standard was added, and the mixture was analyzed by VPC, using a 6 ft × ⅛ in. column of 5% QF-1 operated at either 180 or 190 °C with 24 ml/min flow rate of nitrogen carrier gas. Retention times at 190 °C were: 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, 8.0 min; 4,4-diphenylcyclohexadienone, 14.0 min; and triphenylene internal standard, 24.5 min. Peak areas were measured by planimetry. The flame ionization detector of the VPC was calibrated for the relative responses of the components using a standard mixture.

Data follow for run number, starting concentration of dioxetane, percentage of lumiketone product, percentage of dienone product, and finally, the efficiency of generation of triplet 4,4-diphenylcyclohexadienone derived from the data: **Run 1.** 3.0 $\times 10^{-4}$ M in dioxetane, 17.3% lumiketone, 82.7% dienone. **Run 2.** 5.9 $\times 10^{-5}$ M in dioxetane, 17.0% lumiketone, 83.0% dienone. **Run 3.** 1.0 $\times 10^{-4}$ M in dioxetane, 17.1% lumiketone, 82.9% dienone.

These data yield an average of 17.1 ± 0.2% of lumiketone, leading to an average of 19.8% efficiency for generation of triplet 4,4-diphenylcyclohexadienone.

Decompositions of 3-Methyl-3-*m*-methoxyphenyl-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. Excited State Yields. Decompositions were performed and analyzed as described above. Data follow for run number, starting concentration of dioxetane, percentage of lumiketone product, percentage of dienone product, and finally, the efficiency of generation of triplet 4,4-diphenylcyclohexadienone derived from the data: **Run 1.** 3.4 $\times 10^{-4}$ M in dioxetane, 13.9% lumiketone, 86.1% dienone. **Run 2.** 5.9 $\times 10^{-5}$ M in dioxetane, 14.1% lumiketone, 85.9% dienone. **Run 3.** 2.4 $\times 10^{-5}$ M in dioxetane, 14.1% lumiketone, 85.9% dienone.

These data yield an average of 14.0 ± 0.3% of lumiketone, leading to an average of 16.3% efficiency for generation of triplet 4,4-diphenylcyclohexadienone.

Decompositions of 3-Methyl-3-(2′-naphthyl)-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. Excited State Yields. Decompositions were performed and analyzed as described above. Data follow for run number, starting concentration of dioxetane, percentage of lumiketone product, percentage of dienone product, and finally, the efficiency of generation of triplet 4,4-diphenylcyclohexadienone derived from the data: **Run 1.** 5.4 $\times 10^{-4}$ M in dioxetane, 11.7% lumiketone, 87.6% dienone. **Run 2.** 3.1 $\times 10^{-4}$ M in dioxetane, 11.8% lumiketone, 88.2% dienone. **Run 3.** 7.3 $\times 10^{-4}$ M in dioxetane, 12.4% lumiketone, 87.6% dienone.

These data yield an average of 12.0 ± 0.3% of lumiketone, leading to an average of 14.0% efficiency for generation of triplet 4,4-diphenylcyclohexadienone.

Decompositions of 3-Butyl-3,7,7-triphenyl-1,2-dioxaspiro[3.5]-nona-5,8-diene. Excited State Yields. Decompositions were performed and analyzed as described above, except that in this case all decompositions were carried out under nitrogen in thoroughly degassed solvents. Data follow for run number, starting concentration of dioxetane, percentage of lumiketone product, percentage of dienone product, and, finally, the efficiency of generation of triplet 4,4-diphenylcyclohexadienone derived from the data: **Run 1.** 3.2 $\times 10^{-4}$ M in dioxetane, 15.0% lumiketone, 85.0% dienone. **Run 2.** 4.3 $\times 10^{-4}$ M in dioxetane, 15.3% lumiketone, 84.7% dienone. **Run 3.** 2.7 $\times 10^{-4}$ M in dioxetane, 14.7% lumiketone, 85.3% dienone.

These data thus yield an average of 15.0% of lumiketone, corresponding to 17.4% efficiency of generation of triplet dienone.

Analysis for acetophenone was performed on 5% QF-1 at 120 °C, using dioxetane decompositions which were concentrated in vacuo below room temperature prior to analysis. No acetophenone was detected, although as little as 0.5% should have been readily detectable.

Decompositions of 3,3-Dimethyl-7,7-diphenyl-1,2-dioxaspiro-[3.5]nona-5,8-diene. Excited State Yields. Decompositions were performed and analyzed as described above. Data follow for run number, starting concentration of dioxetane, percentage of lumiketone produced, percentage of dienone produced, and, finally, the efficiency of generation of triplet 4,4-diphenylcyclohexadienone derived from the data: **Run 1.** 1.2 $\times 10^{-4}$ M in dioxetane, 11.8% lumiketone, 88.2% dienone. **Run 2.** 2.3 $\times 10^{-4}$ M in dioxetane, 11.2% of lumiketone, 88.8% dienone. **Run 3.** 9 $\times 10^{-5}$ M in dioxetane, 11.6% of lumiketone, 88.4% dienone.

These data thus yield an average of 15.0% of lumiketone, corresponding to 17.4% efficiency of generation of triplet dienone.

β-Acetonaphthone Sensitized Irradiations of 4,4-Diphenylcyclohexadienone. Quantum yields for this sensitized irradiation were measured using our micro optical bench apparatus[21] with a wavelength of 335 nm and a 22-nm bandpass at half-height. Carbon tetrachloride was used as the solvent for all irradiations. Ferrioxalate actinometry was employed. Analysis of the photolysates was via VPC using a 5% QF-1 column operated at 180 °C, using triphenylene internal standard as described for the dioxetane thermolyses. Peak areas were measured by planimetry. The concentration of sensitizer and substrate was adjusted to allow for >99% light capture by the sensitizer, and the quantum yields are corrected for small amounts of direct absorption by 4,4-diphenylcyclohexadienone at 335 nm. Data follow for run number, concentration of dienone, concentration of β-acetonaphthone, quantum yield for appearance of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, percentage conversion, and, finally, the average quantum yields of reaction and energy transfer derived from the data: **Run 1.** 1.0 $\times 10^{-3}$ M in dienone, 1.5 $\times 10^{-2}$ M in β-acetonaphthone, $\Phi_r = 0.013$, 2.4% conversion. **Run 2.** 2.0 $\times 10^{-3}$ M in dienone, 1.5 $\times 10^{-3}$ M in β-acetonaphthone, $\Phi_r = 0.017$, 3.0% conversion. **Run 3.** 2.0 $\times 10^{-3}$ M in dienone, 1.5 $\times 10^{-2}$ M in β-acetonaphthone, $\Phi_r = 0.013$, 3.6% conversion.

The data from runs 1–3 yield an average quantum yield for reaction of 0.014, which corresponds to an average quantum yield of energy transfer of 0.015.

Attempted Quenching of Production of 6,6-Diphenylbicyclo[3.1.0]-hex-3-en-2-one from 3-Methyl-3-(2′-naphthyl)-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene. A stock solution of 3-methyl-3-(2′-naphthyl)-7,7-diphenyl-1,2-dioxaspiro[3.5]nona-5,8-diene in carbon tetrachloride was prepared. Aliquots of this solution were then withdrawn to provide ca. 10^{-4} M dioxetane on dilution to 50 ml and decomposed in refluxing carbon tetrachloride as previously described. In this case, however, two samples were decomposed normally to serve as blanks, while the other two samples were decomposed in the presence of 10^{-1} M cyclohexadiene. This procedure insured that the only difference between the two sets of decompositions was the presence of cyclohexadiene in the quencher containing samples. After complete decomposition of the dioxetane, the samples were analyzed by VPC. No effect of 10^{-1} M cyclohexadiene was observed on the efficiency of production of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one; identical efficiency was obtained between the blank and quencher containing decompositions: **Run 1.** No additive, 12 ± 1% bicyclic ketone. **Run 2.** No additive, 12 ± 1% bicyclic ketone. **Run 3:** 10^{-1} M in cyclohexadiene, 12 ± 1% bicyclic ketone. **Run 4.** 10^{-1} M in cyclohexadiene, 12 ± 1% bicyclic ketone.

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References and Notes

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Involvement of Enol Tautomers in the Photoisomerization of 3-Substituted Isochromanones[1]

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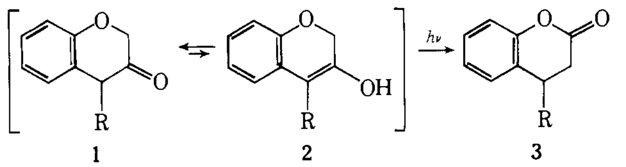
Abstract: Irradiation of 3-carbomethoxyisochromanone (**4**) in methanol under an argon atmosphere produced a mixture of 1-hydroxy-3-carbomethoxyisochromene (**7**) and 2-hydroxy-2-carbomethoxyindanone (**6**) in high yield. A study of the product distribution as a function of time showed that indanone **6** was produced initially. On further irradiation **6** was quantitatively transformed into **7**. When the irradiation of **4** was carried out in the presence of oxygen, 3-hydroxy-3-carbomethoxyisochromanone was the major product formed. The photochemical rearrangement of **4** → **6** has been rationalized by a ring opening reaction of the excited enol tautomer followed by an internal aldol cyclization. The conversion of **6** → **7** involves a Norrish type I reaction followed by a 1,4-hydrogen transfer and subsequent cyclization. The excited-state behavior of the 3-phenylisochromanone system was also examined. In this case, the major photochemical path resulted in photoreduction and occurred from the n-π^* triplet state of the keto tautomer. In the presence of a triplet quencher, the photoreduction route was suppressed and the system reacted from the singlet state of the enol tautomer.

Introduction

Photoenolization of carbonyl compounds is a reaction of considerable importance and current interest.[2-19] The concept of internal photoactivated hydrogen transfer (photoenolization) was originally postulated to explain the apparent lack of bimolecular photoreduction of 2-alkyl-, 2-amino-, and 2-hydroxybenzophenones.[2-5] Yang[2-4] and other workers[5-8] have provided chemical and physical evidence which demonstrate that the photoenolization process is an intramolecular photochemical reaction analogous to the Norrish type II process.[20] Enols generated in this fashion have relatively long lifetimes[4,8] and can be trapped with dienophiles.[2,15] The remarkable stability of these enols is probably due principally to the absence of catalytic ionic contaminants which are generally present in nonphotochemical reactions. Recently, a number of widely scattered and isolated reports have appeared which indicate that 1,3-tautomerization of certain ketones can also occur upon electronic excitation.[21-26] In earlier reports from this laboratory,[27] evidence was presented which demonstrated that the enol content can be an overriding factor in determining the excited-state behavior of a carbonyl group. Particular attention was focused on relativly acidic ketones[28-32] and esters[27] and the question as to whether it is possible to observe photochemistry from an excited enol (or enolate) when the carbonyl tautomer is the absorbing species. As part of a program directed toward determining the scope and limitations of enol photochemistry, we studied the photorearrangement of 4-substituted-3-chromanones (**1**) to 4-substituted dihydrocoumarins (**3**) and found that the reaction involves the prior conversion of **1** into its enol tautomer **2**, which is subsequently converted to **3** on exposure to uv light.[27,33,34] In view of the fascinating rearrangement uncovered with this system, we thought it of considerable interest to determine if comparable photochemistry might occur with the closely related 3-substituted isochromanone system. In order to probe this possibility, the excited-state behavior of 3-carbomethoxyisochromanone (**4**) was examined.[32]



1 **2** **3**