many valuable discussions.

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Excited State Selectivity in the Thermolysis of a 3,4-Diaryl-3,4-dimethyl-1,2-dioxetane

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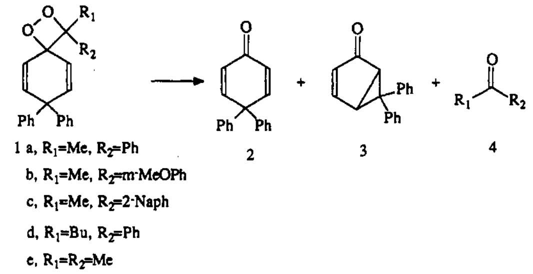
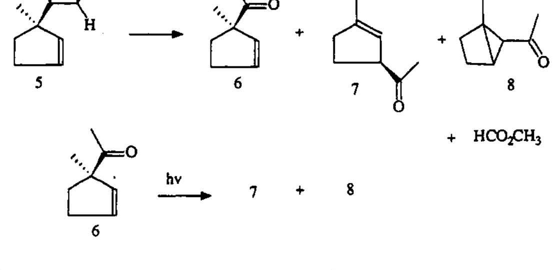
Total efficiencies for the production of triplet ketones from *cis-* and *trans*-3-(3,4-dimethylphenyl)-4-phenyl-1,2-dioxetane (11) are 14.1 ± 0.2% and 21.3 ± 0.5%, respectively. The specific efficiency for the production of triplet acetophenone from *trans*-11 was determined to be 19 ± 4% by trapping the triplet with 2-methyl-2-butene to give the oxetane. These results show that the production of triplets from the dioxetane is state selective, since the n,π* acetophenone triplet is higher in energy than the alternative π,π* triplet of 3,4-dimethylacetophenone. This state-selective production of triplet ketone is most reasonably dictated by orbital symmetry control in the thermolysis of the dioxetane. With this assumption, implications on the mechanism of dioxetane decomposition in terms of biradical intermediates or a concerted biradicaloid process are considered. Activation parameters for thermolysis of *cis-* and *trans*-11 are consistent with a biradical or biradicaloid mechanism. From these activation parameters and molecular mechanics calculations, it was concluded that the transition state was not quite half-way between the dioxetane reactant and a biradical intermediate, if the reaction proceeded through a biradical intermediate. In conjunction with earlier reported triplet efficiencies of 3,4-diaryl-3,4-dimethyl-1,2-dioxetanes and the efficiencies of *cis-* and *trans*-11, the participation of a triplet exciplex was suggested.

One of the unusual features of the thermolysis of 1,2-dioxetanes is their reported selective formation of n,π* triplet state carbonyl products, even though a π,π* state of lower energy may be available. Although there are numerous reports of the production of triplet products from dioxetanes, there are few documented examples where a higher energy n,π* state triplet is formed at the expense of a lower energy π,π* state. In the first reported example of this energy reversal, Zimmerman and coworkers[1] studied a series of dioxetanes of structures **1a–e**, where the efficiency of producing triplet **2** was monitored by the formation of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (**3**) (Scheme I). The triplet efficiencies for all these dioxetanes ranged from 11.5% to 17.1% (average 16.6 ± 3.2%). The constancy of the triplet efficiency is remarkable, since the lowest triplet energies of **4a,b,d,e** (74, 72, 74, and 82 kcal/mol, respectively)[1] are above the lowest triplet energy of **2** (68.5 kcal/mol, n,π*), while the lowest triplet energy of **4c** (59 kcal/mol, π,π*) is below that of **2**. On the basis of Boltzmann distribution of *lowest* triplet energies of the product ketones,[2] all of the triplet energy is expected to reside in 2-acetonaphthone (**4c**) and none in dienone **2**. In order to explain this observation, it was proposed that the triplet energy distribution was state selective, such that n,π* triplets were produced in preference to π,π* states. Neither the total efficiencies nor the specific triplet efficiencies of the companion ketones **4** were measured, so that it is not known if 2-acetonaphthone or the other ketones (**4**) are produced in an excited state to any extent.

Scheme I



Scheme II



State selectivity was also called upon in the comparison of the thermolysis of dioxetane **5** to the photolysis of enone **6** (Scheme II).[3] The ratios of the 1,3-acyl shift product (**7**) to the oxadi-π-methane product (**8**) for direct photolysis of enone **6**, acetone triplet-sensitized photolysis of **6**, and the thermolysis of dioxetane **5** is 2.73, 0.031, and 0.70, respectively. The 1,3-acyl shift is then favored from the S_1 state of **6** as seen from the 2.73 ratio of **7**/**8** obtained

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[1] (a) Zimmerman, H. E.; Keck, G. E.; Pflederer, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 5574. (b) Zimmerman, H. E.; Keck, G. E. *J. Am. Chem. Soc.* **1975**, *97*, 3527.

[2] Richardson, W. H.; Lovett, M. B.; Price, M. E.; Anderegg, J. H. *J. Am. Chem. Soc.* **1979**, *101*, 4683.

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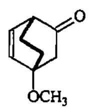
0022-3263/91/1956-6140$02.50/0

by direct photolysis. It is proposed that triplet acetone sensitization selectively populates the lower energy π,π^* state of 6 and that 8 arises from this T_1 triplet. To explain the greatly increased ratio of 7/8 in the thermolysis of the dioxetane, relative to triplet sensitized photolysis of 6, it is suggested that a higher energy T_2 n,π^* triplet of 6 is selectively generated from the dioxetane and that it leads to 7. Internal conversion of the T_2 to the T_1 state occurs so that some of 8 is produced as well.

In a similar study of the photolysis of enone 9 in comparison to the thermolysis of dioxetane 10, state selectivity in the production of n,π^* triplets from 10 was considered.[4] However, these authors point out that their results may be explained in terms of other than state selective production of n,π^* triplets from the dioxetane.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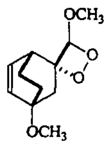
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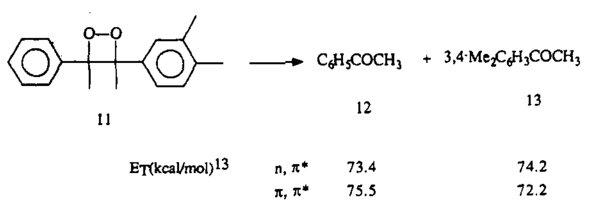
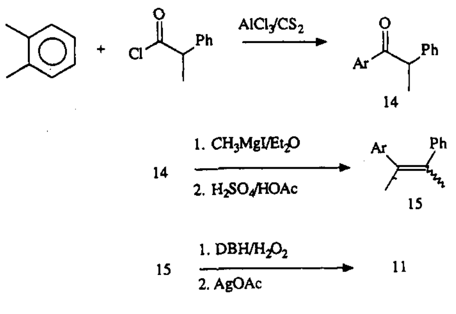
State-selective production of triplet carbonyl products is indeed remarkable, since a stepwise biradical decomposition path is usually proposed for the decomposition of dioxetanes.[5-10] Although n,π^* state formation was rationalized in terms of concerted biradicaloid dioxetane decomposition,[11] such a rationale would not seem applicable to stepwise process with long-lived 1,4-dioxybutane biradical intermediates. With an appreciable lifetime, the biradical would loose orbital symmetry memory and the rationale used to explain state selectivity in the context of a concerted thermolysis would not be applicable.

Considering the remarkable nature of n,π^* triplet state selectivity, it appeared worthwhile to pursue this phenomenon further with a 3,4-diaryl-3,4-dimethyl-1,2-dioxetane.[12] The particular peroxide that is selected for study in this series is 3-(3,4-dimethylphenyl)-4-phenyl-3,4-dimethyl-1,2-dioxetane (11), where the π,π^* state of 13 is the *lowest* energy triplet ketone product (Scheme III). However, the lowest energy n,π^* state is found in acetophenone (12). According to the n,π^* state-selectivity proposal, the favored first-born triplet will be the n,π^* triplet of 12. If energy distribution is not governed by state selectivity, then the lowest energy triplet (13 π,π^*) is expected to be favored.[2]

Scheme III



Scheme IV[a]



[a] Ar = 3,4-$(CH_3)_2C_6H_3$. DBH = 1,3-dibromo-5,5-dimethylhydantoin.

Table I. Specific Acetophenone Triplet Efficiency Produced from the Thermolysis of *trans*-11 with 1.89 M 2-Methyl-2-butene in *o*-Xylene at 60 °C

10^2[*trans*-11], M	$\alpha_T(C_6H_5COCH_3)$, %
1.20	17
1.72	14
1.86	23
2.20	21
	av 19 ± 4

Results

The synthesis of dioxetane 11 is outlined in Scheme IV, where the olefin is converted to the bromo hydroperoxide and this peroxide is used to prepare the dioxetane, according to the method of Kopecky.[14] Olefin 15 was obtained as a 2.2/1.0 mixture of the trans/cis isomers. Column chromatography could improve the trans/cis ratio to 20/1.0 and this mixture was used in the preparation of the dioxetane to give mainly *trans*-11. By low temperature chromatography of silica gel, the cis and trans isomers of 11 could be separated.

The total triplet efficiencies of cis and trans dioxetanes 11 were determined by induced chemiluminescence with 9,10-dibromoanthracene (DBA).[15] The total triplet efficiency of the cis isomer ($\alpha_T = 14.1 \pm 0.2\%$) was less than that of the trans isomer ($21.3 \pm 0.5\%$). The specific triplet efficiency of acetophenone was determined by trapping the triplet ketone with 2-methyl-2-butene in *o*-xylene solvent in a Paterno–Büchi-type reaction.[2] From eqs 1 and 2, the

$$\Phi_{App(Ox)} = [Ox]/[D] \quad (1)$$

$$\Phi_{App(Ox)} = \alpha_T(PhCOMe)\Phi_{Ox} \quad (2)$$

value of α_T(PhCOMe) was obtained for acetophenone, where $\Phi_{App(Ox)}$ is the apparent quantum yield for the for-

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Table II. Activation Parameters and Relative Rates for Dioxetane Thermolysis

dioxetane	E_a[a]	log A	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	k_{rel}(60°)
cis-11[c]	24.2 ± 0.2	11.79 ± 0.14	23.5 ± 0.2	−6.9 ± 0.5	1.11
trans-11[c]	26.0 ± 0.2	12.26 ± 0.14	25.2 ± 0.2	−4.8 ± 0.7	0.22
TMD[d-f]	27.8 ± 0.8	14.17	27.0 ± 0.6	3.2	1.00

[a] Kcal/mol. [b] eu. [c] *o*-Xylene solvent. [d] Toluene solent. [e] Tetramethyl-1,2-dioxetane. [f] Reference 18a.

mation of the oxetane derived from acetophenone, [Ox] is the concentration of oxetane produced as determined by GC, [D] is the initial concentration of dioxetane, and Φ_{Ox} is the quantum yield ((0.10)[16]) for the formation of the oxetane by photoexcitation. These results are presented in Table I, where the average value for the specific triplet efficiency of acetophenone is 19 ± 4%. By photoexcitation, it was shown that acetophenone yields the oxetane with 2-methyl-2-butene and irradiation, while 3,4-dimethylacetophenone gives no detectable oxetane.

Activation parameters for *cis*- and *trans*-11 are given in Table II along with relative rates at 60 °C. For comparison, tetramethyl-1,2-dioxetane (TMD) is included.

Discussion

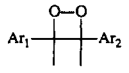
As seen from Scheme III, 3,4-dimethylacetophenone should be the major triplet product *if* the triplet energy is directed to the *lowest* energy triplet ketone product. A qualitative comparison of the specific triplet efficiency of acetophenone (α_T(PhCOMe) = 19 ± 4%)) with the total triplet efficiency (α_T = 21.3 ± 0.5%), produced from dioxetane *trans*-11, shows that the triplet excitation energy is *not* distributed preferentially according to the *lowest* triplet ketone product. A more quantitative picture of the expected distribution of triplet energy, based on the *lowest* energy triplet ketone products, may be calculated from a Boltzmann distribution (eq 3).[2] In this case, the E_T values represent the *lowest* triplet energies of acetophenone (12) and 3,4-dimethylacetophenone (13). At 60 °C, eq 3 predicts

$$RT \ln (\alpha_T(12)/\alpha_T(13) = E_T(13) - E_T(12) \qquad (3)$$

dicts that 99% of the triplet energy should reside in 3,4-dimethylacetophenone, which is clearly not what was observed experimentally. If n,π^* triplet ketones are produced exclusively, eq 3 predicts instead that 77% of the total triplet excitation energy should reside in acetophenone. With the observed total triplet efficiency of 21% from *trans*-11, this means that a specific acetophenone triplet efficiency of 16% is expected, which compares favorably to the observed value of 19 ± 4%. Whether or not this correction is applied, the data indicate that all of the triplets produced are those of acetophenone within experimental error.

In agreement with previous reports of the selective population of n,π^* triplets,[1,3,4] we find that *trans*-11 produces n,π^* triplets even though this triplet state of acetophenone is 2 kcal/mol higher in energy than the π,π^* state of 3,4-dimethylacetophenone.[13] It is most reasonable to expect that this preference for n,π^* states is dictated by orbital symmetry. Some time ago Turro and co-workers[11] rationalized n,π^* state formation of ketones from dioxetanes in terms of an orbital symmetry correlation diagram, based on a concerted biradicaloid decomposition of the dioxetane. With the data that are currently available, it appears that simply substituted dioxetanes undergo a stepwise biradical decomposition[5-10] or possibly a concerted biradicaloid reaction.[18] In fact, we have recently reported the trapping of a 1,4-dioxy biradical intermediate in thermolysis of 3,3-dimethyl-1,2-dioxetane.[19] Once the reaction has proceeded to a biradical intermediate with appreciable lifetime, preference for an antisymmetric state with respect to the original plane of the dioxetane ring is lost and the basis for correlation with the antisymmetric n,π^* state of the ketone product is lost as well. So how is the observed n,π^* state selectively rationalized? One possibility is that a concerted biradicaloid mechanism is operative with highly substituted as well as arylated dioxetanes. With this type of substitution, C–C bond breaking is expected to become more competitive with O–O bond rupture. It can also be noted that for the more highly methylated dioxetanes, trimethyl- and tetramethyl-1,2-dioxetanes, a biradical intermediate could not be detected under the same conditions under which this intermediate was trapped from 3,3-dimethyl-1,2-dioxetane.[19] It was estimated that the lifetime of a biradical intermediate from trimethyl- or tetramethyl-1,2-dioxetane could be no longer than 7 ps, which approaches the vibrational lifetime of the C–C bond in the proposed biradical (0.1 ps). With the lifetimes near the vibrational lifetime of the C–C bond, the biradical is no longer a true intermediate, but instead the reaction merges into a concerted biradicaloid process.

Earlier, we had studied a series of symmetrically substituted 3,4-diaryl-3,4-dimethyl-1,2-dioxetanes (16, $Ar_1 = Ar_2$) and proposed that the reaction proceeded in part through a triplet exciplex of the ketone products whereby energy wastage occurred.[12] As the triplet energy of the ketone products decreased, exciplex formation was facilitated and the triplet efficiency decreased. According to this proposal the triplet efficiency was dependent upon the companion ketone product and not just on the excited state energy of the ketone product. If on the other hand there was no exciplex formation, the companion ketone product should not affect the triplet efficiency and only the aryl substituents should affect α_T. In this case, an additivity of triplet efficiencies is expected such that a weighted sum of the triplet efficiencies of two symmetrically substituted dioxetanes could be used to predict the triplet efficiency of an unsymmetrically substituted dioxetane. For example, a Bolzmann distribution could be used to determine the weighting factor for distribution of triplet excitation between the two ketone products 12 and 13 from dioxetane 11. Since n,π^* state selectivity was observed for dioxetane 11, the Boltzmann equation (eq 3) is used with the n,π^* triplet energies of ketones 12 and 13. As stated above, this calculation predicts that the total triplet energy will be distributed into the ketone products as 77% triplet



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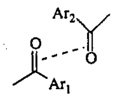
12 and 23% triplet **13**. Now with triplet efficiencies for the symmetrically substituted dioxetanes **16** ($Ar_1 = Ar_2 = C_6H_5$, cis = 44%, trans = 52%) and **16** ($Ar_1 = Ar_2 = 3,4\text{-}(CH_3)_2C_6H_3$, cis = 6%, trans(est) = 7%), eq 4 can be

$$\alpha_T(NX) = 0.77[\alpha_T(\mathbf{16}, Ar_1 = Ar_2 = Ph)] + 0.23[\alpha_T(\mathbf{16}, Ar_1 = Ar_2 = Me_2Ph] \quad (4)$$

used to calculate total triplet efficiencies in the *absence* of exciplex formation. For the cis isomers, $\alpha_T(NX)$ = 35% compared to the observed value of 14% for *cis*-**11**, and for the trans isomers $\alpha_T(NX)$ = 41% compared to the observed value of 21% for *trans*-**11**. The lack of agreement between the observed triplet efficiencies and those calculated on the basis of no exciplex formation points out the need to include this intermediate in order to adequately explain the triplet efficiencies.

We had previously noted a trend to higher triplet efficiencies for *trans*-**16** isomers compared to the cis isomers.[12] Now there is a clear difference between *trans*-**11** (21.3 ± 0.5%) and *cis*-**11** (14.1 ± 0.2%). A possible explanation for higher triplet efficiencies for the trans isomers in this series of dioxetanes may be found in the head-to-tail exciplex structures **17** and **18** that are derived from *cis*-**11** and *trans*-**11** dioxetanes, respectively. Gauche-type interactions between Ar_1 and Ar_2 would destabilize **18** relative to **17** or, in other words, exciplex formation is favored from the cis dioxetane relative to the trans dioxetane. Since triplet energy wastage occurs through the exciplex, lower efficiencies are expected from *cis*-dioxetanes, which is consistent with our observations.



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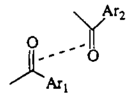

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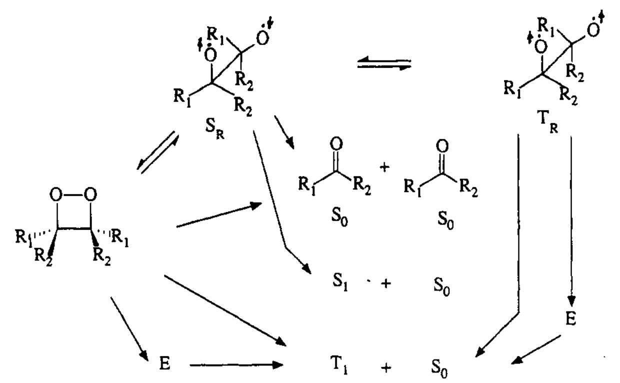
The relative rates for thermolysis of *cis*- and *trans*-**11** are consistent with a stepwise biradical mechanism, or possibly a concerted biradicaloid process where little or no C–C bond breaking of the dioxetane ring has occurred in the transition-state structure. The Arrhenius activation energy for *trans*-**11** is within the normal range for tetrasubstituted dioxetanes,[17] but the activation energy for *cis*-**11** appears low (cf. Table II). The apparent low activation energy is compensated by a low entropy of activation so that the relative rate is nearly the same as for tetramethyl-1,2-dioxetane so there is no reason to postulate a deviation from the biradical-type process. In order to see if the difference in activation energies between *trans*-**11** and *cis*-**11** (1.8 kcal/mol) was because of ground-state energy differences, an MM calculation with PCMODEL[20,21] was carried out on *trans*- and *cis*-**11** to obtain a difference in heat of formation of 3.9 kcal/mol (cis – trans). From the enthalpies of activation and this difference in heat of formation, the enthalpy difference between the transition-state structures of the two isomers is calculated to be 2.2 kcal/mol. Only 1.7 kcal/mol (= 3.9 – 2.2) or 44% of the enthalpy difference in the ground state is then relieved in going to the transition state. An MM calculation was also performed on the gauche dioxy biradicals that could result from *cis*- and *trans*-**11** to obtain a difference in heat of formation of 0.1 kcal/mol (cis – trans). This represents the difference in enthalpy of the transition-state structures, if the peroxide bond was completely broken at the transition state, and can be used as a model for either a stepwise biradical or concerted biradicaloid process. Since the energy of the biradical from either the cis or the trans dioxetane is essentially the same, the percent difference in ground-state energy that is released in going to the transition state for *cis*- and *trans*-**11** (44%) represents the percent of peroxide bond breaking at the transition state. That is, the transition state has proceeded along the reaction coordinate not to quite half-way from the dioxetane.

Scheme V



Conclusions

Selective production of n,π* triplet-state acetophenone was observed in the thermolysis of dioxetane *trans*-**11**, even though a lower energy π,π* triplet state of 3,4-dimethylacetophenone was available. This orbital symmetry dictated process could result from extremely short-lived biradicals or from a concerted biradicaloid decomposition of the dioxetane. In comparison to the triplet efficiencies of other 3,4-diaryl-3,4-dimethyl-1,2-dioxetanes, the triplet efficiencies of *cis*- and *trans*-**11** supported participation of a triplet exciplex in thermolysis of these dioxetanes. Activation parameters for the decomposition of *cis*- and *trans*-**11** were consistent with a biradical or biradicaloid process. On the basis of a stepwise biradical process, MM calculations combined with activation energies for thermolysis of *cis*- and *trans*-**11** suggested that the transition state is located somewhat less than half-way between the dioxetane reactant and the biradical intermediate. The present status of the dioxetane thermolysis mechanism is outlined in Scheme V, where there may be a spectrum of biradical-stepwise to concerted reaction, which depends on dioxetane substitution. In this scheme, the triplet carbonyl product is formed from two competing paths, one of which involves a triplet exciplex (E).[12]

Experimental Section[22]

1-(3,4-Dimethylphenyl)-2-phenyl-1-propanone (14). A procedure similar to those reported for other Friedel–Crafts acylation reactions[23,24] was used. A solution of 2.86 g (17.0 mmol) of 2-phenylpropanoyl chloride[23] and 2.15 mL (17.8 mmol) of *o*-xylene (MCB, bp 143.3–144.5 °C) in 7 mL of carbon disulfide (Baker, bp 46.3 °C) was added to a mixture of 2.31 g (17.3 mmol)

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[20] PCMODEL, Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076. PCMODEL is a modified version of C. Still's (Columbia University) MODEL program (VAX version 1.1) modified by Kosta Steliou (University of Montreal) and adapted to the IBM-PC by Mark Midland (University of California, Riverside) and worked on further by K. E. Gilbert and J. J. Gajewski (Indiana University).

[21] Richardson, W. H. *J. Org. Chem.* **1989**, *54*, 4677.

[22] *Caution*! Hydroperoxides and dioxetanes are potentially explosive compounds. Temperatures of kinetic measurements and melting points are corrected, but boiling points are uncorrected. NMR, IR, and MS were measured with a Varian EM-390 or a Magnachem A-200 (200 MHz), a Perkin-Elmer 337 or 1750FT, and a Hitachi RMU-6E or Finnegan 3000 spectrometer, respectively. The NMR data are reported on the δ scale, the IR are reported in cm^{-1}, and the MS are obtained at 70 eV unless stated otherwise and are reported as *m/e*.

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of aluminum chloride in 7 mL of carbon disulfide and the reaction mixture was allowed to stand for 14 h at room temperature. The reaction mixture was then poured onto a mixture of 15 g of ice and 3 mL of concd hydrochloric acid. After extraction with ether, washing with brine, drying the ether phase over magnesium sulfate, and evaporation of the ether, 4.01 g (99% yield) of a liquid (bp 160 °C/1 mm) was obtained. Recrystallization from 10% methylene chloride/hexane gave a solid: mp 50.0–50.5 °C; NMR (CCl_4) 1.42 (d, J = 7.2 Hz, 3 H), 2.19 (s, 6 H), 4.42 (q, J = 7.2 Hz, 1 H), 6.1–7.1 (m, 5 H), 7.3–7.6 (m, 3 H); IR (CCl_4) 3100, 3075, 3060, 3020, 2970, 2925, 2865, 1680, 1605, 1495; MS 238 (M^+, 3.97), 133 ($(CH_3)_2C_6H_3CO^+$, 100), 105 ($C_7H_6CH_3$, 100). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.78; H, 7.53.

2-(3,4-Dimethylphenyl)-3-phenyl-2-butanol. A solution of 18.2 g (76.5 mmol) of 14 in 50 mL of ether was added to methylmagnesium iodide (prepared from 8.2 mL (132 mmol) of methyl iodide and 2.07 g (85.2 mg-atom of magnesium) in 75 mL of ether) over a 15-min period. The solution was allowed to stir for 30 min at room temperature and then the mixture was allowed to reflux for 1 h. Stirring was continued for 20 h at room temperature and then the reaction mixture was poured onto 30 g of ammonium chloride, 120 mL of water, and 200 g of ice. The aqueous phase was extracted with ether and the combined organic extracts were washed with 0.1 N sodium hydroxide solution, brine, and water. After drying over sodium sulfate, the solvent was evaporated to give 16.8 g of semisolid (87% yield): NMR (CCl_4) 1.1 (d, J = 6.3 Hz, 2.5 H, erythro), 1.2 (d, J = 6.3 Hz, 0.5 H, threo), 1.3 (s, 2.5 H, erythro), 1.4 (s, 0.3 H, threo), 2.2 (s, 6 H), 3.0 (q, J = 6.3 Hz, 1 H), 6.7–7.1 (m, 8 H); IR (CCl_4) 3600, 3570, 3450 (br), 3080, 3060, 3025, 2970, 2930, 2870, 1600, 1500, 1128, 1078, 1052, 1028; MS (25 eV) 254 (M^+, 0.75), 239 ($M^+ - CH_3$, 1.00), 237 ($M^+ - OH$, 17.3), 149 ($(CH_3)_2C_6H_3C(OH)CH_3{}^+$, 19.4), 148 ($(CH_3)_2C_6H_3COCH_3{}^+$, 86.7), 105 ($C_7H_6CH_3{}^+$, 98.8); high resolution MS (9.3 eV) calcd for $C_{18}H_{22}O$ 254.1671, found 254.1695.

2-(3,4-Dimethylphenyl)-3-phenyl-2-butene (15). To a rapidly stirred mixture of 150 mL of acetic acid and 3.42 mL of concd sulfuric acid was added 16.0 g (63.0 mmol) of 2-(3,4-dimethylphenyl)-3-phenyl-2-butanol, and the solution was allowed to reflux for 25 min. The reaction mixture was allowed to cool to room temperature (total reaction period 75 min) and then it was poured onto 100 mL of water. The aqueous phase was extracted with methylene chloride and the combined extracts were washed with 0.1 N sodium hydroxide solution, brine, and water. The extract was dried over sodium sulfate, the solvent was evaporated, and the residue (trans/cis = 2.2/1.0 by NMR) was chromatographed on 150 g of neutral alumina (Woelm), which was activated at 300 °C/2 mm for 2 h. The olefin was eluted from the column with hexane to give a total of 11.3 g (76% yield) of **15** (trans/cis = 20/1): NMR (CCl_4), cis 2.03 (s, 3 H), 2.07 (s, 3 H), 2.13 (s, 6 H), 6.3–6.7 (m, 3 H), 6.85 (s, 5 H); trans 1.86 (s, 6 H), 2.21 (s, 6 H), 6.86 (s, 3 H), 7.06 (s, 5 H); MS 236 (M^+, 81.4), 221 ($M - CH_3$, 46.2), 206 ($M - 30$, 68.8). A sample of the product, before chromatography, was distilled for analysis (bp 140–143 °C/0.8 mm, trans/cis = 1.9/1.0). Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.07; H, 8.53.

2-Bromo-2-(3,4-dimethylphenyl)-3-phenyl-3-hydroperoxybutane. The general procedure of Kopecky[14] was used to prepare this compound. A solution of 430 mg (1.82 mmol) of olefin **15** (trans/cis = 20/1) in 5 mL of anhydrous THF under nitrogen was maintained at −25 ± 5 °C with an isopropyl alcohol–dry ice bath. Then, 3.5 mL of 6.13 M hydrogen peroxide in THF, prepared from 3.00 mL of 90% hydrogen peroxide (DuPont) and 15.0 mL of THF and dried over sodium sulfate with disodium EDTA, was added with stirring. Small portions of 261 mg (0.913 mmol) of 1,3-dibromo-5,5-dimethylhydantoin (Aldrich) were added over 3.5 h and the solution was stirred for an additional 1 h and then placed in the freezer at −20 °C for 20 h. The reaction mixture was then poured onto cold water containing disodium EDTA and extracted with ether. The organic extract was washed with 10% sodium bicarbonate solution and water and dried over sodium sulfate. The solvent was removed by rotary evaporation under reduced pressure and the residual oil was crystallized from hexane (9 mL hexane/g of crude bromo hydroperoxide) at −78 °C in an isopropyl alcohol–dry ice bath. Repeated recrystallization gave the product in 32% yield with only small impurity peaks in the NMR (CCl_4): 1.90, 1.95 (s, 3 H, erythro and threo $BrCCH_3$), 2.20–2.30 (unresolved singlets, 9 H, Ar-CH_3 and $HOOC\underline{CH_3}$), 6.45–7.2 (m, 9 H, ArH and OOH).

3-(3,4-Dimethylphenyl)-4-phenyl-1,2-dioxetane (11). All solvents, solutions, and glassware were treated with disodium EDTA and the reaction flask was protected from light by wrapping it with aluminum foil. To a solution of 403 mg (1.15 mmol) of the bromo hydroperoxide in 7 mL of carbon tetrachloride, cooled in an ice bath, was added 768 mg (4.60 mmol) of silver acetate in a stream of nitrogen. The mixture was magnetically stirred under nitrogen for 1 h at 0 °C and then vacuum filtered through a scintered glass funnel. The solid was washed with carbon tetrachloride and the combined organic solution was washed with 10% sodium bicarbonate and then with water. The solution was dried over soduim sulfate and concentrated to about 0.5 mL on a rotary evaporator under reduced pressure. The major compound in the crude product was 3-(3,4-dimethylphenyl)-3-phenyl-2-butanone:[12] NMR (CCl_4) 1.64 (s, 3 H), 1.90 (s, 3 H), 2.16 (s, 6 H), 6.7–7.1 (m, 8 H); MS 252 (M^+), 209 ($M^+ - COCH_3$). The crude mixture was flash-chromatographed on silica gel (Baker's 40-μm flash chromatography silica gel) at approximately −30 °C with a methylene chloride (5–30%)–pentane gradient elution. The first fractions contained *cis*-**11** (NMR (CCl_4) 1.91, 1.92 (s, 6 H), 2.06 (s, 6 H), 6.58–6.90 (m, 8 H)) then *trans*-**11** was eluted (NMR (CCl_4) 1.39 (s, 3 H), 1.42 (s, 3 H), 2.27 (s, 3 H), 2.32 (s, 3 H), 6.90–7.15 (m, 3 H), 7.20–7.40 (m, 5 H)). The concentrations of dioxetane solutions were determined by one of three different methods: iodometric titration,[25] NMR (aryl methyl protons relative a known amount of methylene chloride), or the acetophenone product, which is produced in quantitative yield (GC analysis on a 0.25-mm, 25-m OV-17 column temperature programmed from 60 to 210 °C at 4°/min, where the retention times of acetophenone and the 1-chloronapthalene are 17 and 28.5 min, respectively).

Specific Triplet Efficiency of Acetophenone Generated from *trans*-11. An aliquot of a solution of *trans*-**11** and 1-chloronaphthalene internal standard in *o*-xylene was mixed with 2-methyl-2-butene and heated for 73 h (ca. 12 half-lives) at 60 °C. The concentrations of acetophenone, 4-phenyl-2,3,3,4-tetramethyloxetane,[2] and 1-chloronaphthalene were determined by GC analysis on an OV-17 capillary column as indicated above (t_R(oxetane) = 24.5 min) by comparison to authentic compounds.

Total Triplet Efficiencies and Kinetic Studies. Methods for determining triplet efficiencies by light emission in the presence of DBA[15] were previously described.[12,26] Rate constants were measured by the decay of ligth emission in the presence of DBA as was previously described.[12,26]

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Registry No. *cis*-**11**, 135584-35-9; *trans*-**11**, 135584-36-0; **12**, 98-86-2; **14**, 135584-30-4; (*E*)-**15**, 135584-32-6; (*Z*)-**15**, 135584-33-7; 2-phenylpropanoyl chloride, 22414-26-2; *o*-xylene, 95-47-6; 2-(3,4-dimethylphenyl)-3-phenyl-2-butanol, 135584-31-5; 2-bromo-2-(3,4-dimethylphenyl)-3-phenyl-3-hydroperoxybutane, 135584-34-8.

Supplementary Material Available: The preparation of 2-phenylpropanoyl chloride and the proton NMR of 2-(3,4-dimethylphenyl)-3-phenyl-2-butanol (2 pages). Ordering information is given on any current masthead page.

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