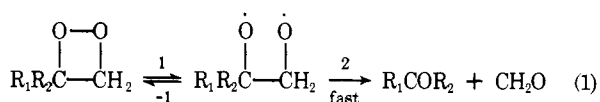# Kinetics of the Thermal Decomposition of 3,3-Diphenyl- and 3,3-Dibenzyl-1,2-dioxetane. A Consideration of Stepwise and Concerted Mechanisms

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Abstract: The preparation and kinetics for the thermal decomposition of 3,3-diphenyl-1,2-dioxetane (1c) and 3,3-dibenzyl-1,2-dioxetane (1d) in benzene and carbon tetrachloride are reported. Benzophenone was produced in approximately quantitative yield from 1c, while 1d gave dibenzyl ketone and bibenzyl in 88 and 2.2% yield, respectively. The decompositions of 1c and 1d were both first order. Experimental activation parameters for 1c and 1d in benzene solution were E_a = 22.7 ± 0.1 kcal/mol, log A = 12.36, ΔH^* = 22.0 ± 0.1 kcal/mol, ΔS^* = −4.1 ±0.3 eu and E_a = 24.3 ± 0.1 kcal/mol, log A = 12.83, ΔH^* = 23.6 ± 0.1 kcal/mol, and ΔS^* = −2.0 ± 0.5 eu, respectively. Calculated activation parameters for 1c and 1d, based on a two-step mechanism, were E_a = 22.6 kcal/mol, log A = 12.7, and ΔS^* = −2.5 eu and E_a = 24.6 kcal/mol, log A = 12.7, and ΔS^* = −2.5 eu, respectively. Agreement between the experimental and calculated activation parameters for 1c and 1d is consistent with a stepwise biradical decomposition mechanism for both peroxides. Further support for the biradical mechanism is given by comparison to kinetic data for other 1,2-dioxetanes. At present, all 1,2-dioxetanes for which kinetic data are available appear to be best accommodated by a stepwise rather than a concerted mechanism for their decomposition. An extended biradical decomposition mechanism for 1,2-dioxetanes is presented, where both singlet (S_R) and triplet (T_R) biradicals are included. By this means, triplet state carbonyl products can arise from T_R, while excited singlet state (S_1) and ground state (S_0) carbonyl products can be formed from S_R. A detailed kinetic analysis of this extended mechanism indicates that S_R and T_R can be viewed as true reaction intermediates. The extended biradical mechanism can then accommodate the available kinetic data as well as explain the electronic states of the carbonyl products. The biradical mechanism then avoids the problem of nonspin conservation, which is required for a concerted decomposition of a dioxetane. In addition, abnormally low entropies of activation are expected for the latter process. The observed activation entropies are not abnormally low and in fact they are in good agreement with the biradical mechanism. Although the extended biradical mechanism best accommodates all the features of dioxetane thermolysis, the simple two-step process can still be employed to predict activation parameters.

1,2-Dioxetanes are a unique class of compounds, since they produce excited state carbonyl molecules upon *thermal* decomposition.[1] An understanding of the mechanism of this reaction is of interest in order to appreciate this unusual conversion of a ground state reactant into an excited state product. Two general types of mechanisms can be considered: (1) a stepwise process with biradical intermediates[2] and (2) a concerted decomposition.[3] The stepwise mechanism in its most simple form (*cf.* eq 1) is amenable to thermochemical kinetic analysis employing procedures developed in the successful analysis of numerous cyclobutane decompositions and isomerizations.[4] The latter reactions are generally regarded to be stepwise processes involving 1,4-biradical intermediates. Thermochemical kinetic analysis of 1,2-dioxetanes provides estimated Arrhenius parameters which are in reasonably good agreement with observed values for the few dioxetanes for which kinetic data are available.[2a-c]

An important prediction of the stepwise mechanism is that dioxetane decomposition rates should be rather insensitive to substitution, since such substitution is one bond removed from the O–O bond broken in the rate determining step. Variations in rate, according to the stepwise mechanism (eq 1), are attributed solely to steric effects.[2c] By contrast, if the decomposition reactions are concerted, with some C–C as well as O–O bond rupture developing at the

transition state, substituent effects could be significant. For example, phenyl substitution should stabilize the developing carbonyl π-bond by resonance in the activated complex and hence lower the activation energy for decomposition. Thus, electronic as well as steric effects are expected with substituent changes if the concerted process is operative. The choice of a model concerted reaction involving a four-membered ring from which substituent effects can be evaluated is difficult. However, one of the best available model reactions may be the classic concerted electrocyclic decompositions of cyclobutenes. Here, replacement of methyl by phenyl substituents causes sizeable decreases in the observed activation energies and reaction rates (*cf.* Table I). In contrast, prior results with 1,2-dioxetanes have shown that replacement of one methyl by a phenyl group (1a to 1b), causes no significant change in either reaction rate or experimental activation energy within experimental error.[2b] This suggests that both 1a and 1b decompose by biradical processes.

We have now pressed the substituent effect test further to determine whether or not evidence can be obtained for a concerted decomposition of a 1,2-dioxetane. To increase the possibility of a concerted reaction, the 1,2-dioxetane ring was substituted with two phenyl groups at the 3-position (1c). The structurally related cyclic peroxide, 3,3-dibenzyl-1,2-dioxetane (1d), is compared to 1c, where the phenyl groups are isolated by methylene groups from the peroxide ring in 1d. Previous results indicate that the latter peroxide should serve as a model for the biradical mechanism. An analysis is made of the existing kinetic data and observed electronic properties of the carbonyl products in terms of stepwise and concerted mechanisms.
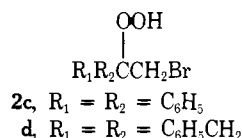

$$R_1R_2C\!\!-\!\!CH_2 \underset{-1}{\overset{1}{\rightleftharpoons}} R_1R_2\dot{C}\!\!-\!\!CH_2\dot{O} \xrightarrow[\text{fast}]{2} R_1COR_2 + CH_2O \quad (1)$$

1a, R_1 = R_2 = CH_3
  b, R_1 = CH_3; R_2 = C_6H_5
  c, R_1 = R_2 = C_6H_5
  d, R_1 = R_2 = $C_6H_5CH_2$

Results

Synthesis of 1,2-Dioxetanes. Both 1c and 1d were pre-

Table I. Substituent Effects in the Thermolysis of Cyclobutenes

Reactant	Product	E_a, kcal/mol	Log A	$10^3 k(60°)$,[a] sec⁻¹	Ref
(cyclobutene)	(diene)	37.4	14.10	3.69×10^{-8}	b
(cyclobutene)	(diene)	33.6	13.85	6.44×10^{-6}	b
Ph,Ph-cyclobutene	Ph,Ph-diene	25.0	12.74	0.219	c
Ph,Ph-cyclobutene	Ph,Ph-diene	21.0	10.78	1.01	c
Ph,Ph,Br-cyclobutene	Ph,Ph,Br-diene	25.1	13.6	1.36	b

[a] Calculated from the reported activation parameters. [b] G. R. Branton, H. M. Frey, and R. F. Skinner, *Trans. Faraday Soc.*, **62**, 1546 (1966). [c] H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Amer. Chem. Soc.*, **87**, 3019 (1965); G. A. Doorakian and H. H. Freedman, *ibid.*, **90**, 3583 (1968).

pared from the corresponding bromo hydroperoxides **2c** and **2d** with sodium methoxide in methanol at $-30°$, by a proce-

$$\begin{array}{c} \text{OOH} \\ | \\ R_1R_2CCH_2Br \end{array}$$

$$\textbf{2c, } R_1 = R_2 = C_6H_5$$
$$\textbf{d, } R_1 = R_2 = C_6H_5CH_2$$

dure similar to that described previously.[2b] Both cyclic peroxides could be purified by rapid low temperature chromatography on silica gel. Low temperature recrystallization could be used to further purify **1d**, to yield a light yellow crystalline solid, mp 60-61°. Crystallization of **1c** was not successful. Caution should be used with **1c** and **1d** when solvent is removed, since on occasion vigorous exothermic reactions occurred. Usually the peroxides were stored at about $-20°$ in benzene or carbon tetrachloride and peroxide concentrations were periodically checked by nmr with reference to methylene chloride as an internal standard.

Products. Product analyses from the thermal decomposition of **1c** and **1d** were obtained by glc, and the yield of dibenzyl ketone, produced from **1d** in carbon tetrachloride, was checked by nmr analysis. Previously the products from thermal decomposition of **1d** in benzene were reported.[1d] With 1.04×10^{-3} M **1d** in degassed benzene at 60°, the products and yields are dibenzyl ketone (88%) and bibenzyl (2.2%). The stoichiometry of the reaction dictates that formaldehyde should be formed along with dibenzyl ketone, but an analysis for formaldehyde was not made. Also carbon monoxide should be formed in a yield comparable to that of bibenzyl. Decomposition of **1c** (6.00×10^{-2} and 1.80×10^{-2} M) in carbon tetrachloride produces benzophenone in quantitative yield. In benzene solution, **1c** (9.80×10^{-4} M) gave benzophenone in 93% yield, which is probably within the experimental error of a quantitative yield as was observed in carbon tetrachloride.

Kinetic Data. The primary method for following the disappearance of both **1c** and **1d** was by light emission produced from added 9,10-diphenylanthracene (DPA). First-order plots of the log of the intensity of light emission vs. time were typically linear through at least three half-lives.

This method was checked by following the disappearance of the peroxides, in the absence of DPA, both iodometrically and by nmr.

Kinetic data for thermal decomposition of **1c** are given in Table II. Rate coefficients for **1c** in carbon tetrachloride appear to be somewhat lower than in benzene as seen by the measurements at 76.30 and 76.65°, where the light emission technique was used for both runs. The concentration of **1c** was increased 60-fold in carbon tetrachloride solution and the rate was measured by nmr in the absence of DPA at 60.08°. The difference in rate between this measurement in carbon tetrachloride and the comparable run at 60.08° in benzene is similar to that observed at higher temperatures where initial concentrations are the same. This suggests that neither DPA nor changes in the initial concentration of **1c** affect the rate under these conditions and that the reaction is first order in **1c**. A further check on the validity of the emission data is seen by comparing the rate coefficients at 40°. Both the emission and iodometric (without DPA) measurements give the same values.

Table II. Rate Coefficients for the Thermal Decomposition of 3,3-Diphenyl-1,2-dioxetane (**1c**) in Benzene[a,b]

Temp, °C	$10^3 k$,[c] sec⁻¹	Temp, °C	$10^3 k$,[c] sec⁻¹
32.76	0.145 ± 0.001[d]	60.08	2.34 ± 0.04[f]
37.54	0.234 ± 0.001[d]	60.06	3.03 ± 0.01
40.01	0.320 ± 0.001	65.10	4.88 ± 0.01
40.01	0.322 ± 0.001	70.48	8.29 ± 0.08
40.01	0.327 ± 0.005[e]	70.99	9.34 ± 0.01
45.03	0.589 ± 0.001[d]	76.30	13.7 ± 0.03
49.31	0.973 ± 0.001	76.65	11.8 ± 0.04[g]
55.12	1.78 ± 0.01		

[a] $[\textbf{1c}]_0 = 1.0 \times 10^{-3}$ M. [b] Rates determined by following the decay of emission from DPA, with $[\text{DPA}] = 1.12 \times 10^{-5}$ M, unless noted otherwise. All measurements were made with aerated solutions. [c] Rate coefficients are reported with probable error within a given measurement and the values are determined by a least-squares computer program. [d] Benzene solvent treated with Na_2EDTA and Na_2SO_4. [e] Rate determined by iodometric titration without DPA. [f] Rate determined by nmr in carbon tetrachloride without DPA, $[\textbf{1c}]_0 = 60 \times 10^{-3}$ M. [g] Rate determined in carbon tetrachloride with 1.12×10^{-3} M DPA by emission.

Table III. Rate Coefficients for the Thermal Decomposition of 3,3-Dibenzyl-1,2-dioxetane (**1d**) in Benzene[a,b]

Temp, °C	$10^3k,^c$ sec^{-1}	Temp, °C	$10^3k,^c$ sec^{-1}
43.23	0.120 ± 0.001^d	60.66	0.830 ± 0.001^d
45.14	0.140 ± 0.001^d	65.23	1.28 ± 0.002^d
49.31	0.230 ± 0.001	70.01	2.11 ± 0.01^d
50.09	0.246 ± 0.001^e	70.41	2.11 ± 0.01
54.86	0.401 ± 0.001^d	75.59	3.84 ± 0.01^e
55.11	0.379 ± 0.004^f	77.30	4.60 ± 0.01^d
55.21	0.366 ± 0.006^g	77.72	4.83 ± 0.01^d
60.08	0.701 ± 0.019^h	77.80	5.17 ± 0.03

^{a} [**1d**]$_0$ = 1.0 × 10^{-2} M. ^{b} Rates determined by following the decay of emission from DPA, with [DPA] = 1.12 × 10^{-2} M, unless noted otherwise. All measurements were made with aerated solutions. ^{c} Rate coefficients are reported with probable error within a given measurement and the values are determined by a least-squares computer program. ^{d} Benzene solvent treated with Na$_2$EDTA and Na$_2$SO$_4$. ^{e} Rate determined by emission without DPA. ^{f} Rate determined by iodometric titration without DPA. ^{g} Rate determined by iodometric titration with DPA. ^{h} Rate determined by nmr in benzene without DPA.

Table IV. Experimental Activation Parameters for the Thermal Decomposition of 3,3-Diphenyl-1,2-dioxetane (**1c**) and 3,3-Dibenzyl-1,2-dioxetane (**1d**) in Benzene[a]

Dioxetane	E_n^b	Log A	$\Delta H^{*\,b}$	$\Delta S^{*\,c}$
1c	22.7 ± 0.1	12.36	22.0 ± 0.1	-4.1 ± 0.3
1d	24.3 ± 0.1	12.83	23.6 ± 0.1	-2.0 ± 0.5

^{a} Data with least-squares fit and probable error. ^{b} In kcal/mol. ^{c} In eu.

Kinetic data for the thermal decomposition of **1d** in benzene are shown in Table III. Increasing the initial concentration of **1d** by 30-fold and measuring the rate by nmr (60°) produces a rate coefficient which is about 7% lower than predicted by the activation parameters obtained from emission data. Considering the change in kinetic method and the large change in initial concentration, this variation in rate is insignificant. Furthermore, induced decomposition[5] usually causes an increase in rate, but not a decrease, with an increase in initial concentration. The data then indicate that **1d** undergoes first-order decomposition as was suggested for **1c**. The iodometric rate coefficients are somewhat lower than the emission values. This small difference is most likely due to an inaccuracy in the infinity titers of the iodometric method. Iodometric measurements with and without DPA show no change in rate, which confirms that DPA is not responsible for this small difference between kinetic methods. Light emission was observed from **1d** in the absence of DPA. Rate coefficients obtained without DPA at 50.09 and 75.59° are in excellent agreement with those values with DPA, which again shows that DPA does not affect the rate under these conditions.

Activation parameters for **1c** and **1d**, based on emission data in benzene, are given in Table IV. Calculated and experimental activation parameters for thermal decomposition of 1,2-dioxetanes **1a–d**, based on the two-step mechanism (eq 1) are given in Table V. Thermochemical values used in the calculations are given in Table VI. The activation energy and entropy of activation are calculated from eq 2 and 3. There is a small difference in some of the thermochemical values from our previous calculations,[2a-c] which results in part from a recent revision of oxygen-containing

$$E_a = \Delta H_{1,-1}^\circ + E_{-1} \quad (2)$$

$$\Delta S^* = \Delta S_{1,-1}^\circ + \Delta S_{-1}^* + R \ln\left(\frac{\sigma n^*}{\sigma^* n}\right)^6 \quad (3)$$

Table V. Calculated and Experimental Activation Parameters for the Thermal Decomposition of 1,2-Dioxetanes **1a–d**

Dioxetane	E_a^a Obsd	Calcd	$-$Log A^b Obsd	Calcd	$-\Delta S^{*\,c}$ Obsd	Calcd
1a^d	23.0	(23.0)	12.2	12.9	-5.0	-2.3
1b^d	22.9	23.0	12.1	12.6$_5$	-5.3	-2.8
1c^e	22.7	22.6	12.36	12.7$_1$	-4.1	-2.5
1d^e	24.3	24.6	12.83	12.7$_1$	-2.0	-2.5

^{a} In kcal/mol. ^{b} In sec^{-1}, calculated at 60° ^{c} In eu. ^{d} Carbon tetrachloride solvent. ^{e} Benzene solvent.

Table VI. Thermochemical Parameters for 1,2-Dioxetanes **1a–d** and the Corresponding Biradicals **1ar–dr**

Species	S° (intrinsic)^a	$\Delta S_{1,-1}^{\circ\,a}$	$\Delta S^*_{-1}{}^a$	$\Delta H_f^{\circ\,b}$	$\Delta H_{1,-1}^{\circ\,b}$	E (strain)^b
1a	83.8	3.1	-5.4	-18.9	14.5	25
1ar	86.9			-4.4		0
1b	103.4	3.1	-5.9	14.5	14.2	25
1br	106.5			28.7		0
1c	121.7	3.1	-5.6	48.7	14.1	25
1cr	124.8			62.8		0
1d	141.6	3.1	-5.6	37.9	16.1	25
1dr	144.7			54.0		0

^{a} In eu. ^{b} In kcal/mol.

additivity values.[7] A gauche-oxy radical–methyl interaction is taken as one-half of the preferred hydroxyl cyclohexane A value (0.7 kcal/mol).[8] The same value is assumed for a gauche-oxy-oxy radical interaction. A more recent estimate of the strain energy (25 kcal/mol) for the dioxetanes is used, which is based on oxetane (25.2 kcal/mol).[7] In addition, from this revised value of $\Delta H_{1,-1}^\circ$ for **1a** and the previously reported E_a-value of 23.0 kcal/mol,[2b] E_{-1} is calculated to 8.5 kcal/mol from eq 2.

Steric effects involving bulky geminal phenyl and benzyl groups as found in **1c** and **1d**, and the corresponding biradicals **1cr** and **1dr**, require special consideration. Steric interactions between phenyl and CH$_2$O· in biradicals **1br** and **1cr** amount to 0.5 kcal/mol (an alkene gauche-interaction).[9] The phenyl-oxy radical interaction in **1br** and **1cr** is interpolated from the gauche-methyl (0.8 kcal/mol)[9] and the alkene gauche (0.5 kcal/mol) interaction. Thus, with a gauche-methyl–oxy radical value of 0.35 kcal/mol (vide supra), the alkene (or phenyl)–oxy radical gauche interaction is 0.2 kcal/mol (= (0.5/0.8) × 0.35). In **1dr**, the gauche-phenyl–CH$_2$O interaction is estimated to be 1.55

1br, R = CH$_3$
1cr, R = C$_6$H$_5$

1dr
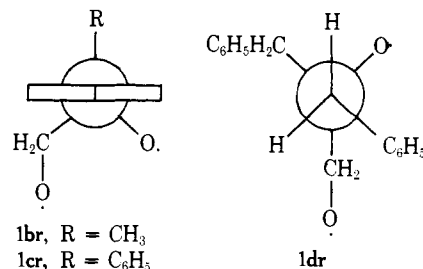
kcal/mol. There will be a total of two such interactions in **1dr**, one for each phenyl group, or 3.1 kcal/mol. The gauche-phenyl interaction is obtained by using one-half of the preferred phenyl cyclohexane A value (3.1 kcal/mol).[8] Similarly, there will be two phenyl–oxy radical gauche interactions, where each interaction is estimated to be 0.7 kcal/mol by interpolation in the carbon series (i.e., 0.35 × (1.55/0.8) = 0.7 kcal/mol). Less pronounced repulsions should occur in the 1,2-dioxetanes, since the bond angle between geminal groups is larger and the C–C–O ring angle is smaller. The interactions in the 1,2-dioxetanes can range

between zero and the values obtained in the corresponding biradicals. We have taken an average of these two extremes and set the geminal repulsions in the 1,2-dioxetanes to be one-half of that calculated for the parent biradicals (*i.e.*, 0.35 kcal/mol in **1b**, 0.7 kcal/mol in **1c**, and 2.25 kcal/mol in **1d**). These steric effects in the dioxetanes and biradicals are embodied in $\Delta H_{1,-1}^{\circ}$ and thus in the calculated E_a values.

All of the group contributions to ΔH_f° and S° (intrinsic) are reported, with the exception of [C-(O)(C$_B$)(C)$_2$], [C-(O)(C$_B$)$_2$(C)], [C-(Ȯ)(C$_B$)(C)$_2$], and [C-(Ȯ)(C$_B$)$_2$(C)], which are required for **1b**, **1c**, **1br**, and **1cr**, respectively. The ΔH_f° group values were estimated by calculating the change in ΔH_f° for the replacement of C with C$_B$ (+0.9 kcal) from reported values of [C-(O)(C$_B$)(H)$_2$][7] and [C-(O)(C)(H)$_2$].[7] The desired groups can then be calculated from reported groups with this correction. For example, [C-(O)(C$_B$)(C)$_2$] = [C-(O)(C)$_3$] + 0.9. A similar method was used to calculate the change in S° (intrinsic) (−0.6 eu) for the replacement of C with C$_B$ via [C-(O)(C$_B$)(H)$_2$][7] and [C-(O)(C)(H)$_2$].[7] Although these estimates may produce an error in the absolute entropies and heats of formations of the dioxetanes and their respective biradicals, the group values cancel in the calculations of $\Delta H_{1,-1}^{\circ}$ and $\Delta S_{1,-1}^{\circ}$, and therefore produce no error in these kinetically more important values.

Discussion

Comparison of Experimental and Calculated Activation Parameters. As seen from Table V, the experimental activation energies for dioxetanes **1a–d** are in good agreement with calculated values based on the simple stepwise mechanism (eq. 1). The experimental E_a values for **1c** and **1d** are 0.1 kcal/mol greater and 0.3 kcal/mol less, respectively, than calculated values, but this is well within experimental error and the expected error (±1 kcal/mol) of the calculations. Dioxetane **1d** was originally chosen as the model compound (for stepwise decomposition) to be compared to **1c**. As seen from Table V, the experimental activation energy for **1d** is 1.6 kcal/mol greater than that observed for **1c**. Although this might be interpreted as a trend toward concerted decomposition for **1c**, this seems unlikely. First, the calculated E_a value for **1d**, based on the stepwise mechanism, is in excellent agreement with the experimental value. Second, the calculated E_a value for **1d** is 2.0 kcal/mol greater than that calculated for **1c**. This is approximately the difference between experimental E_a values (1.6 kcal/mol) for these dioxetanes and suggests that the difference is due to a change in steric effects. Third, with increasing replacement of methyl for phenyl groups, in proceeding from **1a** to **1c**, there is little change in experimental activation energies. Over this same series of dioxetanes, there is little change in calculated E_a values as well, based on the stepwise mechanism. Furthermore, the small changes in experimental and calculated E_a values with **1a–c** are coincident. In summary, the activation energies for **1a–d** suggest that all of these cyclic peroxides decompose in a stepwise manner. Our desire to force a concerted decomposition of a 1,2-dioxetane by appropriate substitution then does not appear to be realized as yet.

The experimental entropies of activation for dioxetanes **1a–d** deviate somewhat from calculated values as seen from Table V. However, the agreement is acceptable, considering experimental error and an error of at least ±2 eu in the calculated values.

Preliminary kinetic data for *cis*-3,4-diethoxy-1,2-dioxetane[1i] and tetramethoxy-1,2-dioxetane[1h] appear to be well approximated by calculated activation parameters based on

a stepwise decomposition.[2b] Agreement between experimental[10] and calculated activation parameters for trimethyl-1,2-dioxetane is also good.[2c] Recently the enthalpy of activation for tetramethyl-1,2-dioxetane (TMD) was reported to be 25 kcal/mol with an entropy of activation of −1 eu.[11,12] At 60° these values correspond to E_a = 25.7 kcal/mol and log A = 13.04. The calculated activation parameters for TMD, based on eq 1 are E_a = 23.9 kcal/mol and log A = 12.3 (with E_{-1} = 8.5 kcal/mol and a strain energy of 25 kcal/mol for TMD). At first sight, the agreement between experimental and calculated activation parameters does not appear to be as good as found with other dioxetanes. However, the experimental and calculated free energies of activation are in good agreement ($\Delta G^{*}(60°)$ = 25.3 and 24.7 kcal/mol, respectively). Thus, as is so often the case in kinetics, E_a and log A values are compensating, and probably reflect differences in the experimental and calculation errors rather than any real kinetic or mechanistic change.

Since it has been suggested that TMD undergoes a concerted decomposition,[11a] several other observations relevant to TMD are of interest. A comparison of experimental activation energies for 3,3-dimethyl-1,2-dioxetane (**1a**, 23.0 kcal/mol) and tetramethyl-1,2-dioxetane (TMD, 25.7 kcal/mol) indicates that a concerted decomposition is unlikely here. According to the stepwise mechanism, increased steric effects by substituents have a net effect of increasing the tendency of a biradical to revert to the dioxetane and thus to raise the activation energy.[2c] In contrast, a concerted decomposition should be accelerated by increased steric repulsions between substituents on the dioxetane ring. The increased activation energy for TMD relative to **1a** is then in agreement with a stepwise process but inconsistent with a concerted decomposition. In addition, increased alkyl substitution of 1,2-dioxetanes should result in the stabilization of the developing π-carbonyl bond in the activated complex. This, too, is in contradiction with the larger activation energy for TMD compared to the 3,3-dimethyl derivative (**1a**).

An Extended Biradical Mechanism. The simple two-step mechanism (eq 1) then adequately accounts for the existing *kinetic* data for 1,2-dioxetanes. However, in view of the important observation of Turro and Lechtken[11] that TMD directly produces mainly triplet acetone, this simple mechanism requires modification. A general biradical mechanism[1d] as shown in Scheme I can accommodate the kinetic

Scheme I
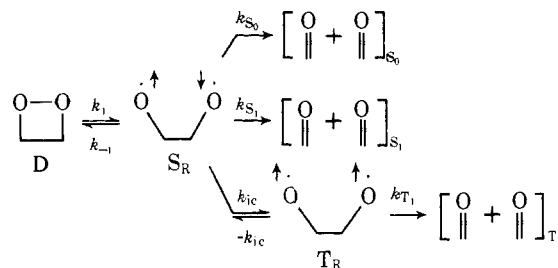
data and explain the electronic states of the carbonyl products. This extended mechanism does not require any revision in our prior estimates of activation parameters, based on the simple two-step process (eq 1), since the rate determining step is still ring opening ($k_{\text{exptl}} = k_1$). Thus, if decomposition of either the singlet or triplet biradicals (S$_R$ or T$_R$) were rate determining, reaction activation entropies would be large and positive[13] (rather than negative as observed), and if internal conversion from S$_R$ to T$_R$ were rate determining, the expected activation energy would be much lower than observed.[14] Scheme I accounts for both S$_1$ and

T_1 excited state acetone production from TMD.[11] Where efficiencies of excited state carbonyl (S_1 and T_1) production are less than one per dioxetane decomposed,[1e-g,p,r,s,u] ground state carbonyl (S_0) products can arise from S_R. Only one of the two carbonyl molecules shown in brackets (S_1 and T_1) can be in an excited state as shown by thermochemical calculations.[2a-c] The most appealing feature of Scheme I as a mechanistic interpretation of dioxetane reactions, as opposed to a concerted process,[11a] is that it strictly adheres to spin conservation rules.

The simple biradical mechanism (eq 1) has been criticized by Turro and Lechtken[11a] and these comments apply to the general biradical mechanism (Scheme I) as well. They propose that the biradical mechanism might be expected: (a) "to proceed in nonpolar solvents with the occurrence of a substantially positive value of ΔS^*, based on analogy to the decomposition of di-*tert*-butyl peroxide ($\Delta S^* \sim +10$ eu)[15] and the biradical-like fragmentation of cyclobutanes ($\Delta S^* \sim +10$ eu);[16] (b) to show little variation in rate with structural substitution since the O–O bond breaking is dominant in achieving the transition state; (c) to exhibit a substantial rate increase in polar solvents such as acetonitrile and methanol, in analogy to the work of Walling and Wagner[17] on solvent effects on alkoxy radical decompositions; (d) to show a statistical production of three triplets per (excited) singlet." It was concluded[11a] that only criterion b is actually observed.

This criticism of the biradical mechanism appears unwarranted. With regard to criterion a, neither the decomposition of di-*tert*-butyl peroxide nor the fragmentation of cyclobutanes are good analogies to the stepwise decomposition of dioxetanes. The cyclobutane activation entropies are large and positive, because in opening to the tetramethylene 1,4-biradical *three* internal rotations are produced (the dioxy 1,4-biradical produced from dioxetanes has only one internal rotation). Also, the reaction path degeneracy of cyclobutane is four (*i.e.*, any one of four bonds may be ruptured), while that of the dioxetane is one (*i.e.*, only the O–O bond is ruptured). Reducing the entropy of activation of cyclobutane by the entropy associated with the above differences gives $\Delta S^* = -2.5$ eu, which is in perfect agreement with our estimates for dioxetanes. The entropy of activation for di-*tert*-butyl peroxide is large and positive, because two fragments are forming at the transition state. The large activation entropies of such simple single bond fission reactions can be attributed primarily to a considerable reduction in the frequencies of the four rocking motions of the separating fragments.[18] No such separation occurs in the dioxetane ring opening process, and therefore the two reactions are not at all analogous.

Alternatively, it was suggested that the observed activation entropies for dioxetane decompositions were more consistent with a concerted mechanism, where triplet acetone is produced directly by a nonspin conservation process.[11a] A low entropy of activation is expected for such a process, due to a low probability of crossing from a singlet to a triplet state along the reaction coordinate. Unfortunately, most reactions initially reported to be nonadiabatic have on further study been found to be homogeneous processes complicated by either catalytic or heterogeneous effects. Hence, a number of model reactions are not available to estimate the expected decrease in ΔS^* for such a reaction. To our knowledge, the single reaction whose nonspin conservation behavior remains unquestioned is the thermolysis of nitrous oxide.[19] Here, log A is lower by 4.0 units (*i.e.*, $\Delta S^* = -18.4$ eu) compared to that expected for a singlet unimolecular reaction. This result suggests that nonadiabatic behavior results in a sizeable decrease in log A; whereas dioxetane A factors do not appear to be unusually low (*i.e.*,

lower than normal by less than 1.0 log A unit). They are, in fact, in good agreement with those calculated from transition state theory and a stepwise mechanism.

We defer discussion on the expected solvent effects (criterion c) to a future publication, except to note that the activation energy for TMD in methanol is similar to that in benzene.[12a] The initially reported low activation parameters[11a] cannot be used then as an argument against the biradical mechanism.

We move on to consider criterion d, *i.e.*, how Scheme I can explain the high efficiency of triplet carbonyl production from dioxetanes. This requires a detailed kinetic analysis of Scheme I, complete with estimates for the various rate coefficients. This analysis is presented in the next section. The resulting rate coefficient estimates indicate that the biradical mechanism can, in fact, accommodate the observed efficiencies of excited state carbonyl production and that biradicals S_R and T_R can be viewed as true reaction intermediates. This latter result is critical, since if S_R and T_R were not true intermediates, the biradical process (Scheme I) would reduce to a concerted mechanism.

Kinetic Analysis of Scheme I. A steady state treatment of Scheme I yields the relationships below, where $\tau_{T_R} = [k_{T_1} + k_{ic}]^{-1}$, $\tau_{S_R} = [k_{-1} + k_{S_1} + k_{ic}]$, and v represents velocities.

$$v_{S_0} = \frac{k_{S_0} \tau_{S_R} k_1 [D]}{[1 - k_{-ic} \tau_{T_R} k_{ic} \tau_{S_R}]} \quad (4)$$

$$v_{S_1} = \frac{k_{S_1} \tau_{S_R} k_1 [D]}{[1 - k_{-ic} \tau_{T_R} k_{ic} \tau_{S_R}]} \quad (5)$$

$$v_{T_1} = \frac{k_{T_1} k_{ic} \tau_{T_R} \tau_{S_R} k_1 [D]}{[1 - k_{-ic} \tau_{T_R} k_{ic} \tau_{S_R}]} \quad (6)$$

$$\frac{v_{T_1}}{v_{S_0}} = \frac{k_{T_1} k_{ic}}{k_{S_0} (k_{T_1} + k_{-1c})} \quad (7)$$

$$\frac{v_{T_1}}{v_{S_1}} = \frac{k_{T_1} k_{1c}}{k_{S_1} (k_{T_1} + k_{-ic})} \quad (8)$$

High triplet efficiencies ($\alpha_{T_1} \rightarrow 1$, where $\alpha_{T_1} =$ no. of T_1 product molecules/no. dioxetane molecules decomposed) can occur only when the equilibrium constant between S_R and T_R strongly favors T_R. If the equilibrium constant K_{ic} ($= k_{ic}/k_{-ic}$) reflected only spin multiplicity differences (*i.e.*, $K_{ic} = R \ln 3 = 2.2$), then Turro and Lechtken's argument[11a] against the biradical mechanism would be valid. However, K_{ic} could be significantly larger. Thus, while the entropy charge for the $S_R \rightleftharpoons T_R$ equilibrium may be given by the spin multiplicity charge of $\Delta S_{ic}^\circ = 2.2$ eu, the enthalpy charge could well be nonzero. An estimate of this enthalpy charge (ΔH_{ic}°) is not easily made. Alkanone triplet (T_1) and excited singlet (S_1) states are separated by about 8 kcal/mol,[20] but the interacting electrons of such species are physically close. Stephenson, Gibson, and Brauman, using INDO calculations, have concluded that there may be significant energy differences (6–10 kcal/mol) between the triplet and singlet states[21] of trimethylene and tetramethylene. However, they suggested that all quantum mechanical calculations of biradical energies (including their own) are suspect because of the many necessary but perhaps questionable assumptions employed in the calculation methods. An enthalpy difference smaller than 6–10 kcal/mol between T_R and S_R is intuitively appealing, and a recent measurement of about 2.5 kcal/mol for the enthalpy difference between triplet and singlet states of the 2-pentanol-2,5-bira-

dical,[22] is consistent with this expectation. Therefore we estimate $\Delta H^\circ_{S_R \to T_R} \simeq -2.5$ kcal/mol and obtain $\Delta G^\circ(60^\circ) = -3.2$ kcal/mol or $K_{ic} \simeq 10^{2.2}$ (60°).

It now remains to be shown that this value for K_{ic} is sufficiently large to accommodate the experimental data. A considerable variation in the efficiency (α) of excited state carbonyl production from dioxetanes is reported. Values of α range from a high of about $1.0^{11,1k}$ to lower values in the region 0.14 to 0.035.[1f,g,r,s,u] For convenience, we will consider α values approaching 1.0 to 0.09. Based on the results with TMD,[11] the excited state carbonyl species are mainly in the T_1 state. Assuming that at least 1% of the S_R biradicals give S_0 products when α_{T_1} approaches 1.0, the range of α-values gives $v_{T_1}/v_{S_0} \simeq 10^2$ ($\alpha_{T_1} \to 1.0$) and $v_{T_1}/v_{S_0} \simeq 10^{-1}$ ($\alpha_{T_1} = 0.09$). Thus, eq 7 can be equated to this range of relative velocities. This relationship does not immediately allow us to decide whether or not the estimated K_{ic} value is sufficiently large to accommodate the biradical mechanism. However, the following procedures do allow this decision to be made. Equation 7 can be simplified if $k_{T_1} \gg k_{-ic}$ to give eq 9. With an estimated value for k_{S_0}, a range of values for

$$\frac{v_{T_1}}{v_{S_0}} \simeq \frac{k_{ic}}{k_{S_0}} \simeq 10^2 \text{ to } 10^{-1} \tag{9}$$

k_{ic} can be obtained, and with K_{ic}, values for k_{-ic} can be determined. Alternatively, eq 7 can be simplified if $k_{-ic} \gg k_{T_1}$ to give eq 10. With values for K_{ic} and k_{S_0}, a range of

$$\frac{v_{T_1}}{v_{S_0}} \simeq \frac{k_{T_1}K_{ic}}{k_{S_0}} \simeq 10^2 \text{ to } 10^{-1} \tag{10}$$

values for k_{T_1} can be obtained. The biradical mechanism can then be evaluated on the reasonableness of the deduced values for k_{ic}, k_{-ic}, and k_{T_1}.

It is apparent that a reasonably accurate value of k_{S_0} is basic to this examination of mechanisms. Since k_{S_0} has not been measured, a value must be deduced from other available data. We have estimated k_{S_0}, as described below, from the decomposition kinetics of the singlet tetramethylene 1,4-biradical (S_{RC}) and from relative rates of decomposition of singlet biradicals 3 and 4, produced in the photolysis of

$$(11)$$

$$(12)$$
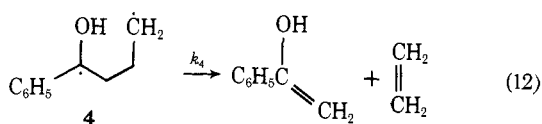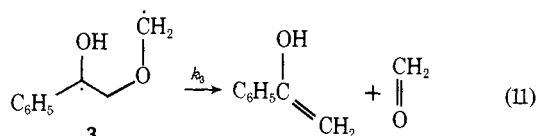
the corresponding ketones. From the reported quantum yields associated with these type II processes,[23] one obtains $k_3/k_4 \simeq 2.6$ by means of an iterative calculation. Since the A factors in eq 11 and 12 should be comparable, the difference between k_3 and k_4 can be attributed solely to differences in activation energies. Thus, the relative rate of decomposition of S_R to S_{RC}, due solely to differences in activation energies, is 5.2 (=2 × 2.6) or $10^{0.7}$. With the reported activation energy for ethylene production from S_{RC} of 5.9 kcal/mol,[4] it is deduced that E_a for decomposition of S_R is 5.2 kcal/mol (=5.9 − 0.7). The A factor for decomposition of S_R should be higher than the A factor for decomposition of tetramethylene ($A_{S_{RC}} = 10^{12.0}$ sec^{-1})[4] by about 6.0 eu. In moving to the transition state, S_{RC} loses entropy in the restriction of the two methylene end-group in-

ternal rotations (3 eu/rotor), while no such loss occurs for S_R. Thus, $A_{S_0} = 10^{1.3} \times A_{S_{RC}} = 10^{13.3}$ sec^{-1} and $k_{S_0} \simeq 10^{(13.3-5.2)/\theta}$ sec^{-1} or $k_{S_0} \simeq 10^{9.9}$ sec^{-1} (60°) for the decomposition of S_R. From eq 9, with $\alpha_{T_1} \to 1.0$ to 0.09, one obtains respectively $k_{ic} \simeq 10^{11.9}$ to $10^{8.9}$ sec^{-1} (60°), and $k_{-ic} \simeq 10^{9.7}$ to $10^{6.7}$ sec^{-1} (60°) with the value for K_{ic} ($=k_{ic}/k_{-ic} = 10^{2.2}$). From eq 10, with $\alpha_{T_1} \to 1.0$ to 0.09, one obtains $k_{T_1} \simeq 10^{9.7}$ to $10^{6.7}$ sec^{-1} (60°).

These values appear to be in a reasonable range, and, under the conditions of the approximations made to obtain eq 9 and 10, the biradical mechanism accommodates the available data. Thus, the higher values of rate coefficients for reactions of S_R and T_R (i.e., k_{S_0}, k_{ic}, k_{-ic}, and k_{T_1}) are significantly less than the vibrational frequency of the C–C bond in the biradicals (900 cm$^{-1} \simeq 3 \times 10^{13}$ sec^{-1}).[24] This allows S_R and T_R to be defined as true reaction intermediates (i.e., a concerted decomposition of the dioxetane is not required). The value for k_{-ic} in carbon centered biradicals is in much dispute.[25] Bartlett and Porter's explanation of spin correlation effects[26] requires that rate coefficients for spin inversion of triplet 1,4-biradicals to singlet species be as low as 10^4 sec^{-1}. In contrast, Stephenson and Brauman[27] have argued that such slow rates are unreasonable. Our lower estimate of k_{-ic} ($10^{6.7}$ sec^{-1}), where $\alpha_{T_1} = 0.09$, is still larger than that proposed by Bartlett and Porter[26] for carbon centered biradicals. However, k_{-ic} will have lower values in dioxetane systems where low triplet efficiencies (α_{T_1}) are observed. In addition, an extrapolation of the intersystem crossing behavior of carbon centered 1,4-biradicals to 1,4-dioxybiradicals may not be valid. Salem and Rowland[28] have shown that intersystem crossing of carbon centered biradicals is dependent on the orientation of the carbon $2p_z$ orbitals. With 1,4-dioxybiradicals, the two lone pair electron orbitals on oxygen behave jointly in a nondirectional manner,[29] and this may appreciably increase their rates of intersystem crossing.

With the reported average $\%\phi(T_1) = 50\%$ and $\%\phi(S_1) = 0.2\%$ for excited state acetone production from TMD,[11] $v_{T_1}/v_{S_1} \simeq 2.5 \times 10^2$. From eq 8 and with $k_{T_1} \gg k_{-ic}$, one obtains eq 13. Setting $k_{ic} \simeq 10^{11.9}$ sec^{-1} (60°), as deduced

$$\frac{v_{T_1}}{v_{S_1}} = \frac{k_{ic}}{k_{S_1}} \simeq 2.5 \times 10^2 \tag{13}$$

from eq 9 for high excited state efficiencies, eq 13 gives $k_{S_1} \simeq 10^{9.5}$ sec^{-1} (60°). Values of the product determining rate coefficients then increase in what appears to be a reasonable order, i.e., at high efficiencies ($\alpha_{T_1} \to 1.0$), $k_{S_0} > k_{S_1} \gtrsim k_{T_1} = 10^{9.9} > 10^{9.5} \gtrsim 10^{6.7-9.7}$ sec^{-1}. Finally, an estimate of k_{-1} can be made from $\Delta S^*_{-1} = -5.8$ eu,[2c] $E_{-1} = 8.5$ kcal/mol, $k_{-1} = 10^{(12.0-8.5)/\theta} = 2.6 \times 10^6$ sec^{-1} (60°).

In summary, the available kinetic data and efficiencies of excited state carbonyl production from dioxetanes can be accommodated by Scheme I. A kinetic analysis of this scheme gives reasonable values for the rate coefficients and allows the biradicals S_R and T_R to be defined as true reaction intermediates. Scheme I also circumvents the problems of abnormally low dioxetane decomposition activation entropies, which although expected for a concerted, spin forbidden process, are not observed. The simplified mechanism (eq 1) can still be employed to predict reliable activation parameters, since the rate determining process is ring opening in both eq 1 and Scheme I. As yet, increased phenyl substitution of the dioxetane ring (to gem-diphenyl) has not resulted in a change to a concerted decomposition.

Experimental Section[30]

1,1-Diphenylethylene. This olefin was prepared by a previously reported method[31] in 88% yield by dehydration of 1,1-diphenyleth-

anol (Aldrich) with 20% sulfuric acid in acetic acid, bp 103–105° (2 mm) (lit.[31] bp 92–93° (0.8 mm)): nmr CH_2 (5.26, S, 2.0), C_6H_5 (7.13, S, 10.0).

1-Bromo-2,2-diphenyl-2-hydroperoxyethane (2c). 1,3-Dibromo-5,5-dimethylhydantoin (MCB) (5.32 g, 18.7 mmol) was added in portions to a stirred solution of 1,1-diphenylethylene (5.18 g, 28.7 mmol), 98% hydrogen peroxide (FMC) (3.26 ml, 144 mmol), and sodium acetate (0.153 g, 1.87 mmol) in anhydrous monoglyme (52 ml) at −40° under a nitrogen atmosphere. The temperature was maintained at −30° for an additional 0.5 hr and then the reaction mixture was allowed to warm to room temperature over a 1-hr period. Ice-cold water (100 ml) was slowly added with stirring and the organic phase was separated. The aqueous phase was extracted with ether, and the combined organic phases were washed with ice-water and dried over sodium sulfate. Concentration of the organic phase under reduced pressure (final pressure was 2 mm) with a 30° bath gave 8.13 g of a yellow oil. *Caution—this oil may decompose exothermically.* It was estimated that the oil contained approximately 50% **2c** from its nmr spectrum. Column chromatography on silica gel (40/60 mesh, MCB) was used to purify **2c** by elution with hexane, 50% hexane–50% benzene, and finally benzene. Decomposition of **2c** occurred on the column, so that **2c** was obtained in 27% yield based on diphenylethylene after purification: nmr: CH_2 (4.27, S, 2.0), OOH (7.64, S, 0.87), C_6H_5 (7.28, S, 10.4). Amperometric iodometric analysis[32] indicates 98.7 ±0.5% purity.

2-Benzyl-3-phenyl-1-propene. Methylenetriphenylphosphorane was prepared from methyltriphenylphosphonium bromide (Aldrich) and the methylsulfinyl carbanion[33] in dimethyl sulfoxide (DMSO) solvent.[34] To the Wittig reagent (69.4 mmol, based on the phosphonium bromide) in 105 ml of DMSO was added 16.0 g (76.3 mmol) of dibenzyl ketone (MCB) in 38 ml of DMSO over 20 min at room temperature. The red solution was stirred for 1 hr at this temperature and then for an additional 3 hr at 80°, at which time the solution was yellow-brown. Glc analysis (5 ft × 1/8 in. 3% SE-30 on Chromosorb W column at 120°, nitrogen flow 28 ml/ min) during the course of the reaction at 80° indicated a constant olefin/ketone area ratio after about 2.5 hr. Water (100 ml) was added to the reaction mixture (exothermic) and the mixture was extracted with three 100-ml portions of ether. The combined ether phases were washed with three 40-ml portions of water, dried over magnesium sulfate, and concentrated on a rotary evaporator to give 23.4 g of an oil-solid mixture. This mixture was filtered and the solid was washed with pentane. The solid (6.10 g) was recrystallized from cyclohexane–benzene and identified as triphenylphosphine oxide, mp 155–156° (lit.[35] mp 156°): nmr C_6H_5, 7.52–7.75, multiplet. The filtrate was concentrated and then chromatographed on acid washed alumina (Merck). Elution with pentane gave 8.78 g of the olefin. Subsequent elution with benzene gave 8.79 g of recovered ketone. This corresponds to 81% yield of the olefin, accounting for recovered ketone: nmr $C_6H_5CH_2$ (3.15, S, 4.0), =CH_2 (4.73, S, 2.0), C_6H_5 (7.08, m, 10.7); ir 3030 (Ar–H), 3065, 3085 (=CH_2), 2910, 2830 ($C_6H_5CH_2$), 1641 (C=C) cm^{-1}; mass spectral $M\cdot^+$, 208, $C_6H_5CH_2$, 91 m/e.

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.53; H, 7.44.

1-Bromo-2-benzyl-3-phenyl-2-hydroperoxypropane (2d). This hydroperoxide was prepared by a method similar to that used for **2c**, except that the solvent was ether and sodium acetate was omitted. From 1.04 g (5.00 mmol) of 2-benzyl-3-phenyl-1-propene, 0.57 ml (25 mmol) of 98% hydrogen peroxide, and 0.715 g (2.50 mmol) of 1,3-dibromo-5,5-dimethylhydantoin in 13 ml of ether, crude **2d** (1.66 g) was obtained as a clear colorless oil. Iodometric titration[36] indicated that the crude product was 64% **2d**, which corresponds to a 66% yield. The crude product was chromatographed on 24 g of silica gel (40/60 mesh, MCB). Elution was begun with pentane, then 20% benzene–80% pentane, and finally with benzene. The latter solvent eluted **2d**, which was recrystallized from pentane containing a small amount of ether, to give white needles, mp 91.5–92.5°, 90% pure by iodometric analysis,[36] 51% yield. Further recrystallization from cyclohexane gave **2d** in 99% purity[36]: mp 92.7–93.5°; nmr $C_6H_5CH_2$ (2.98, S, 4.0), CH_2Br (3.30, S, 2.0), OOH (7.38, S, 1.0), C_6H_5 (7.23, S, 9.9); ir (KBr) 3450 (OOH), 3030, 3065, 3085 (C_6H_5), 2940, 2965, 1433, 1455 (CH_2), 538 (C–Br) cm^{-1}.

3,3-Diphenyl-1,2-dioxetane (1c). A 0.63 M solution of sodium

methoxide in methanol, containing 2 mol % EDTA (based on sodium methoxide) was prepared from sodium and anhydrous methanol.[37] A 6.5-ml portion of this solution was added dropwise over 20 min to a stirred solution of 0.174 g (2.43 mmol) of **2c** in 5 ml of methanol at −30° under a nitrogen atmosphere. The solution was stirred for an additional 1.5 hr at −30°, during which time the solution became more intensely yellow. Now the reaction mixture was poured onto 5 ml of ice-cold water and then rapidly extracted with seven 2-ml portions of ice-cold carbon tetrachloride. The yellow organic extract was washed with four 2-ml portions of ice-cold water and then dried over sodium sulfate in a freezer (ca. −20°). A measured amount of methylene chloride was added to the solution and a nmr spectrum was measured. From this, a 21% yield of **1c** was calculated. The solution of **1c** was purified first by recrystallization. The carbon tetrachloride was progressively replaced with hexane. The solution was partially concentrated under reduced pressure at low temperature and then hexane was added. *Caution—upon complete removal of solvent, a vigorous exothermic reaction was observed.* This was repeated until hexane was the predominant solvent, at which time a solid precipitated and was filtered. The structure of the solid was tentatively assigned as 1,1-diphenyl-1,2-ethanediol: nmr ($CDCl_3$, saturated solution) C_6H_5 (7.37, S, 10.5), CH_2 (4.13, S, 2.0), OH (3.25, S, 0.94 and 2.00 S, 0.88). The filtrate was treated by the partial concentration method to replace hexane with carbon tetrachloride. The carbon tetrachloride solution was rapidly chromatographed three times on silica gel (40/60 mesh, MCB) with carbon tetrachloride as the eluent. A measured amount of methylene chloride was added to the partially concentrated carbon tetrachloride fractions and the nmr spectrum indicated 63% **1c**, 32% benzophenone, and 5.5% 1,1-diphenylethylene oxide. The analysis for benzophenone was based on the ortho protons (7.75 ppm, m) and the analysis for the epoxide on the methylene protons (3.05 ppm, s). Correcting for benzophenone para and meta protons and the aromatic proton of the epoxide, the nmr of **1c** was CH_2 (5.63, S, 2.0), and C_6H_5 (7.39, S, 10.3). Iodometric analysis[32] of a solution of known concentration of **1** as determined by nmr *vs.* methylene chloride internal standard, indicated 102 ± 3% purity of **1c**. After thermal decomposition of this sample, the nmr absorptions assigned to benzophenone ortho protons (7.75 ppm) increased in intensity, while those assigned to the methylene of **1c** (5.63 ppm) disappeared. The epoxide methylene absorption (3.05 ppm) remained unchanged.

3,3-Dibenzyl-1,2-dioxetane (1d). This peroxide was prepared by the same method as employed for **1c** from 0.963 g (3.00 mmol) of **2d** in 5 ml of methanol and 9.0 ml of 0.592 M sodium methoxide in methanol (containing 2 mol % EDTA). Nmr analysis indicated a 38% yield (0.274 g) of **1d** in the carbon tetrachloride extract. The peroxide was purified by chromatography on silica gel (40/60 mesh, MCB) contained in a jacketed column, through which methanol was circulated at −20°. The carbon tetrachloride solvent in the sample of **1d** was replaced with pentane by the partial concentration technique that was used with **1c** and the column was eluted with pentane. Concentration of the pentane fractions under reduced pressure at low temperature gave a 33% recovery of crystalline **1d**. Recrystallization in pentane at about −20° was used to further purify **1d**, to give a light yellow solid, mp 60–61°. *Caution, occasionally solid **1d** will decompose exothermically;* however, solutions of **1d** were stable in solution for long periods at about −20°. Nmr analysis in carbon tetrachloride, relative to a known amount of toluene, showed that the peroxide was approximately 100% pure. Iodometric analysis[36] indicated 91% purity. The nmr spectrum of **1d** indicated: $C_6H_5CH_2$, (3.06, S, 4.0), CH_2 (4.85, S, 2.00), and C_6H_5 (7.16, S, 10.2).

Product Studies. Decomposition of **1c** (6.00 × 10^{-2} M) in carbon tetrachloride at 60° in a sealed tube gave a 99.5% yield of benzophenone by glc analysis (5 ft × 1/8 in. 10% XF-1150 on Varaport-30 column, 28 ml/min nitrogen flow, column temperature 150°, fluorene internal standard *vs.* a standard mixture of benzophenone and fluorene in carbon tetrachloride). A similar analysis, but with a 5 ft × 1/8 in. 3% SE-30 on Varaport column at 115°, indicated a 102% yield of benzophenone with **1c** at 1.80 × 10^{-2} M in carbon tetrachloride. With **1c** (9.80 × 10^{-4} M) in benzene solution, a 93% yield of benzophenone was calculated where the analysis was carried out on the XF-1150 column at 160° with biphenyl as the internal standard. Decomposition of **1d** (1.04 × 10^{-3} M) in degassed benzene gave an 88% yield of dibenzyl ketone and a 2.2%

yield of bibenzyl by analysis on a 5 ft × ⅛ in. 3% SE-30 on Varaport column at 130° with 28 ml/min nitrogen flow. Reaction of **1d** in carbon tetrachloride was observed to give an 83% yield of dibenzyl ketone by nmr analysis.

Kinetic Methods. Stock solutions of **1c** and **1d** were prepared in benzene or carbon tetrachloride and stored in a freezer (ca. −20°). The stock solutions were prepared from concentrated solutions of the peroxides, whose concentrations were determined by nmr vs. methylene chloride internal standard, by volumetric means. 9,10-Diphenylanthracene was included in the stock solutions when rate measurements were made by light emission. By this method, about 3 ml of the peroxide solution was placed in a 1-cm stoppered Pyrex cell, which was previously swept with nitrogen. The solutions were not purged with nitrogen or degassed. The cell was placed in a thermostated bath controlled to ±0.05°, which was part of an apparatus that was previously described.[38] Output from a R374 Hamamatsu photomultiplier tube, in nanoamps, was recorded vs. time as well as the dark current. The data were processed by a least-squares first-order computer program. Kinetic data were also determined by nmr in sealed tubes under a nitrogen atmosphere. The tubes were heated in a thermostated bath, and the nmr spectrum was periodically recorded. Areas of the absorptions were measured relative to methylene chloride internal standard vs. time and were processed by a least-squares first-order computer program. The disappearance of the 1,2-dioxetane methylene group was followed for **1c** and **1d**, as well as the appearance of the benzylic protons of dibenzyl ketone for **1d**. Iodometric kinetic measurements were carried out on solutions that were purged with nitrogen and kept under a nitrogen atmosphere. Aliquots were removed and analyzed by the biamperometric method.[32]

Reference and Notes

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(14) In this event, $k_{exptl} = K_{1,-1}k_{ic}$. With $E_{exptl} = \Delta H_{1,-1}° + E_{ic}$, and since $E_{ic} \simeq 0$; $E_{exptl} \simeq \Delta H_{1,-1}°$.
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