Determination of Nitrogen Yields in *tert*-Butyl Hypochlorite Oxidation. The 1,2-bis(hydroxylamine) and tributylamine were dissolved in toluene in the flask which was then cooled to −78 °C and flushed with argon. *tert*-Butyl hypochlorite was added via syringe to the stirred solution. The mixture was immediately allowed to warm to room temperature and was stirred for 10 min. Gas samples were taken and the percentage of nitrogen relative to argon was measured by GC (column B, 25 °C).[77] The yield of nitrogen was calculated from the percentage by using a calibration curve. Oxidation of **4** gave a 29 ± 1% yield of nitrogen (average of three injections on one sample). Oxidation of **5** gave a 21 ± 1% yield of nitrogen (average of four injections on one sample).

Determination of Nitrogen Yields in Nickel Peroxide Oxidations. To a suspension of nickel peroxide in tributylamine and toluene in a flask connected to a water-filled buret under argon was added a solution of the 1,2-bis(hydroxylamine) in toluene. The nitrogen yield was calculated from the displaced water in the buret. Qualitative analysis of the gas (GC, column B, 25 °C) showed the presence of nitrogen. Oxidation of **4** gave a 63% yield of nitrogen (single determination). Oxidation of **5** gave a 61% yield of nitrogen (single determination).

Acknowledgment. Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. The mass spectral facility was supported by NIH Grant. No. RR00954 from the Division of Research Resources.

Registry No. **1**, 6788-84-7; **2**, 91523-84-1; **3a**, 91523-85-2; **3b**, 91523-86-3; **4**, 5627-11-2; **4S** (supp), 91523-87-4; **5**, 91523-88-5; **5**·2HCl, 91523-89-6; **6**, 91523-90-9; **7**, 2425-28-7; **8**, 91523-91-0; **9**, 91523-92-1; **10**, 41252-83-9; **11**, 91523-93-2; **12**, 37110-02-4; **12S** (supp), 91523-94-3; **13**, 91523-95-4; **13S** (supp), 91523-96-5; **14**, 91523-97-6; **15**, 54722-79-1; **15S** (supp), 91523-98-7; **16**, 557-30-2; **16S** (supp), 54731-39-4; **17**, 93-56-1; **17S** (supp), 91523-99-8; **18**, 4589-97-3; **18S** (supp), 91524-00-4; **19**, 91524-01-5; **20**, 91524-02-6; **21**, 91524-03-7; **21S**, 91524-04-8; **22**, 91524-05-9; **22S**, 91524-06-0; **23**, 90005-59-7; **23S**, 91524-07-1; **24**, 25070-24-0; **24S**, 91524-08-2; **25**, 30842-07-0; **26**, 91524-09-3; **27**, 91524-10-6; **31**, 91524-11-7; **32**, 91524-12-8; 1,2-bis(phthalimidooxy)ethane, 6437-67-8; nickel peroxide, 12035-36-8; *tert*-butyl hypochlorite, 507-40-4; $C_6H_5CO_2SiMe_3$, 2078-12-8; $Me_3SiOCH_2CH_2OSiMe_3$, 7381-30-8.

Supplementary Material Available: Mass spectral data and the details of the assignments for the products from the oxidation of the 1,2-bis(hydroxylamines) (11 pages). Ordering information is given on any current masthead page.

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Reaction of Triplet Carbonyl Carbene with Olefins

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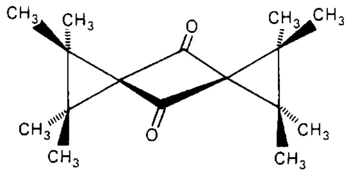
The gas-phase reaction of $C_2O(^3\Sigma)$ with 2,3-dimethyl-2-butene produces 1,1,2,2,6,6,7,7-octamethyldispiro[2.1.2.1]octane-4,8-dione and 2,2,3,3-tetramethylcyclopropanecarboxylic acid as major products rather than the allenic product characteristic of the reaction with simpler substrates. The positive identification of these molecules provides strong evidence for prior formation of the previously postulated cyclopropylideneketene. Further, the rate-determining step for reaction of $C_2O(^3\Sigma)$ with the substrate cannot be elimination of CO as has been postulated on the basis of calculations.

A series of careful experiments by Bayes et al.[1,2] has provided the basis for a recent detailed theoretical examination of the reaction of $C_2O(^3\Sigma)$ with olefins by Fukui and co-workers.[3] The Bayes group found that photolysis of C_3O_2 produced two distinct species depending upon whether or not radiation from a mercury lamp was filtered to eliminate radiation below 300 nm. The species produced with the filtered radiation was more discriminating than that made at shorter wavelengths, reacted rapidly with oxygen, and so was assigned as $C_2O(^3\Sigma)$. The less discriminating reactant was assigned as $C_2O(^1\Delta)$. Calculations[4] support the assignment of the triplet as the lower energy state, and further, Milligan and Jacox[5] have observed triplet C_2O in matrix experiments. While all available evidence supports $C_2O(^3\Sigma)$ as the species formed above 300 nm, the situation for shorter wavelength radiation is more clouded given recent work showing that $C_2O(^3\Sigma)$ is a product in multiphoton laser photolysis at 266 nm.[6] Since in this work we deal with photolysis above 300 nm, this need not concern us.

Bayes has shown that in the gas phase $C_2O(^3\Sigma)$ attacks ethylene at 150 torr to give allene as the most important end product (eq 1). In later work Willis and Bayes[2a] found

$$C_2O(^3\Sigma) + C_2H_4 \rightarrow C_3H_4 + CO \qquad (1)$$

that yields of allenes from olefins are pressure dependent, indicating existence of an intermediate which can be stabilized by loss of energy in collisions. In experiments with 2,3-dimethyl-2-butene (tetramethylethylene, TME) a solid material formed whose mass, infrared, and NMR spectra though not given were reported as consistent with those expected for 1,1,2,2,6,6,7,7-octamethyldispiro[2.1.2.1]octane-4,8-dione (ODOD), the dimer of (tetramethylcyclo-



ODOD

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0022-3263/84/1949-4494$01.50/0

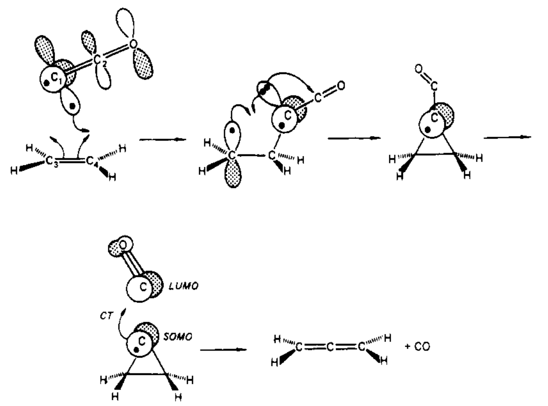


Figure 1. Schematic representation of calculated path for reaction of $C_2O(^3\Sigma)$ with C_2H_4. Adapted from Minato et al. (ref 3).

propylidene)ketene (TCPK), and so they proposed the following general mechanism for C_2O reactions, which we illustrate in eq 2–4 for ethylene. No structure proof was

$$C_2O + C_2H_4 \rightarrow \text{c-}C_3H_4{=}C{=}O^* \ (\text{CPK}^*) \qquad (2)$$

$$\text{CPK}^* + \text{M} \rightarrow \text{CPK} \qquad (3)$$

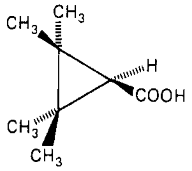
$$\text{CPK}^* \rightarrow C_3H_4 + CO \qquad (4)$$

provided for the proposed TCPK dimer formed from TME. Meanwhile, Mullen and Wolf[7] had demonstrated, using ^{14}C as a tracer, that the main reaction path to allene formation involves insertion of the terminal C of the C_2O between the two C atoms of ethylene.

The recent calculations directed to a detailed analysis of this reaction[3] indicate, as outlined in Figure 1, that the reaction should proceed by a first step which involves joining of the terminal carbon (C_1) of triplet C_2O to one of the doubly bonded carbons (C_4) with the resulting intermediate being at a shallow minimum in the potential surface. This C_1 atom then bonds to the second olefinic carbon to give a triplet cyclopropylidene ketene. In effect in this step an electron moves from the C_3 atom of the olefin to the C_2 atom of C_2O. The next step, elimination of CO, is assigned as rate determining, and so its transition state is of particular interest. It is perhaps best understood by considering the interactions between a CO molecule and the cyclic triplet carbene diradical. In addition to an interaction between the highest occupied molecular orbital of the CO, centered on the carbon, and a singly occupied molecular orbital of the carbene, the theoretical work identifies two other charge-transfer (CT) interactions as particularly important. These involve electron donation from the two degenerate highest singly occupied molecular orbitals of the carbene to the two degenerate lowest unoccupied molecular orbitals of the CO. One of these is diagrammed in Figure 1. The other uses the two similar orbitals at right angles to those shown. It is to these charge-transfer interactions that initiation of the decomposition reaction is attributed, since they lower the energy of the transition state and so stabilize it. Thus electron-donating groups, such as methyl, on the C_3 and C_4 atoms should facilitate the stabilizing charge transfer, thereby lowering the activation energy for the decomposition. Since the theoretical analysis indicates that the decomposition is rate determining, we have, it was said, an explanation for the observed increased rate of reaction of C_2O with TME relative to ethylene. Also, according to the analysis, it is in this step that the system undergoes the required intersystem crossing so that singlet allene is produced without intermediacy of the triplet. In this work we reexamine the gas-phase reaction of $C_2O(^3\Sigma)$ with TME, provide evidence for the structure of the solid material formed in this reaction, and, in the light of this, comment on the mechanisms proposed for the reaction by others.

Results and Discussion

While at a pressure as low as 10 torr irradiation of gaseous mixtures of C_3O_2 and TME with a medium pressure mercury lamp well filtered by Pyrex yields about 10% of the allene, at 100 torr the upper limit for this yield is 2%.[8] The major products instead are solid. The solid residue when dissolved in carbon tetrachloride for ^1H NMR analysis gave evidence of two major constituents, one of which gave an NMR doublet, the other an NMR singlet. Together these accounted for at least 75% of the reacted C_2O. Their relative amounts varied markedly from irradiation to irradiation, indicating that at least one was formed in a heterogeneous reaction. These two compounds were separated on a silica gel column and identified as 2,2,3,3-tetramethylcyclopropanecarboxylic acid (TMCA)



TMCA

and ODOD. As part of the identification procedure TMCA was synthesized independently by using a modification of the methods of Mescheryakov and Dolgii[9] and Zimmerman and Pratt.[10] The NMR spectrum of the product agreed with that reported by Lavieties,[11] as did the melting point. In the mass spectrum we found the only two peaks previously reported[12] in addition to others which fit the proposed structure.

We had much less of the material from the photolytic reaction to work with than we had from the synthetic. However, as the data reported in the Experimental Section show, there is detailed agreement of the mass and infrared spectra of the synthesized and photolytic products, and the elemental analysis of the photolytic product agrees well with that calculated for TMCA. The NMR spectra, which are solvent dependent, show two groups of peaks in $CDCl_3$ at 360 MHz,[13] one indicating 7 H atoms, the other 6. We did not look for the acid proton in these experiments. At 60 MHz in CCl_4 we found the same distribution[14] but could not identify the acid proton as we did with the synthetic TMCA. We attribute this failure to the small size of our sample combined with limitations of the R12-B spectrometer. Overall the agreement in physical properties makes a compelling argument that the products of the photolytic and synthetic reactions are identical. We believe that in the C_2O system TMCA is formed by addition of water at

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(13) These spectra were provided by Dr. Charles Lerman whom we thank for them.

(14) In later work with an unseparated sample, F. Racke, a Haverford undergraduate, located the single proton on the C adjacent to the COOH at δ 1.130.

the walls of the reaction vessel to the TCPK formed by the addition of C_2O to TME (eq 5). This provides the

$$C_2O + TME \rightarrow TCPK \xrightarrow[\text{wall}]{H_2O} TMCA \qquad (5)$$

most convincing evidence to date for the existence of intermediates of the type represented by TCPK as originally postulated by Bayes and Willis.[2a]

Further evidence for the existence of TCPK comes from our identification of the second product as the previously uncharacterized ODOD. All of the physical measurements reported in the Experimental Section are consistent with this identification. The mass and infrared spectra are reasonable, and the NMR shows but a single proton resonance and four distinct ^{13}C peaks. The shifts for two of these ^{13}C peaks are in quite close agreement with two reported by Baxter et al.[15] for the C=O (δ 209.69) and spiro carbons (δ 50.65) in the related dispiro[2.1.2.1]octane-4,8-dione (DOD). ODOD presumably arises from the dimerization of TCPK as DOD was previously found to arise from the dimerization of CPK.[15] The other possible dimerization product, the less symmetric 4,5-dione with adjacent C=O groups, is also known, being the product of reactions other than ketene dimerization.[16] Were the analogous substituted 4,5-dione formed in our system, we would have expected to find two distinct groups of methyl hydrogens rather than one, and five rather than four ^{13}C resonances in the NMR.

The strong evidence provided for the existence of TCPK as an intermediate by the identification of two of its plausible reaction products provides an opportunity for comment on the detailed mechanism proposed for $C_2O(^3\Sigma)$ reactions on the basis of the potential surface calculations for the ethylene system.[3] As indicated earlier, the transition state for CO elimination from triplet CPK was calculated to be the highest point on the surface, and so this was assigned as the rate-determining step both for allene formation and for the overall reaction. While the transition state for loss of CO may be the highest in the reaction sequence which produces allene, and so may well be rate determining for production of *this* compound, it does not follow that it is rate determining for attack on *any* olefin to product *all* products, i.e., the total rate of reaction. It was this total rate rather than the rate of allene production which was actually measured by Bayes et al.[1,2] Intermediates which are formed with too little energy to cross the barrier for CO elimination, or, which lose energy by collision with other molecules before that fraction of the energy required for bond rupture can collect in the C=CO bond, will be trapped and must either revert to reactants or go to stable products via processes requiring less energy than the C=CO rupture. This is clearly what happens to the TCPK precursor formed by C_2O addition to TME. Before it can decompose it loses its excess energy and is stabilized as TCPK. The evidence that TCPK is the major product of the reaction of $C_2O(^3\Sigma)$ with TME thus places the rate-determining step for the reaction of triplet C_2O with TME earlier than the CO elimination. The assertion that CO elimination in the ethylene reaction itself is overall rate determining may be valid at low pressures where allene and its isomer, methylacetylene, account for 95% of the reacting C_2O, but we note that Willis and Bayes[2a] found that these yields too dropped off with an increase in pressure, indicating that in ethylene stabilization of the intermediate can also compete with CO elimination.

There are two results of the theoretical model on which our work sheds little light. It may indeed be true that methyl groups stabilize the transition state for CO elimination, but if so their effect as an energy sink in excited TME, lengthening its lifetime against CO elimination and thus allowing time for energy loss, is more important. Finally, definitive location of the intersystem crossing is difficult. In the sequence producing allene one possibility is the CO elimination step as is postulated on the basis of the calculations. However, even if we accept this, we must still deal with the question of the location of that crossing in the sequences leading to other products. At this point we have no basis for asserting that it occurs before TCPK formation since both the dimerization of TCPK and its reaction at the wall could involve either singlet or triplet allene. We will have further comments on these points in reports on studies of the reactions of $C_2O(^3\Sigma)$ with halogenated olefins.

Experimental Section

C_3O_2 was prepared by dehydration of Fisher reagent grade malonic acid with P_2O_5 in a manner similar to that of Long, Murfin, and Williams.[17] It was purified gas chromatographically using a 25-ft column containing 15% GESF 96 silicone oil on fire brick. Analysis with a GC–mass spectrometer showed it to be 99.5% pure, with CO and CO_2 as the major impurities. This level of impurity would not affect our results. The 2,3-dimethyl-2-butene was Aldrich "Gold Label", analyzed gas chromatographically by us, and found to be 99.4% pure. Two C_6H_{12} isomers accounted for over 80% of the 0.6% impurity. It was used without further purification.

Irradiations were done in Pyrex vessels with a Pyrex filter in order to block out the short-wavelength radiation which produces $C_2O(^1\Delta)$ from C_3O_2. C_3O_2 pressures ranged from 4.4 to 10.9 torr and TME pressures from 78 to 115 torr for these experiments. A 400-W medium-pressure Hanovia mercury lamp (679a 36) was the light source. Nonvolatile products were separated on a silica gel column starting with high boiling petroleum ether, switching to high boiling petroleum ether/carbon tetrachloride, then pure carbon tetrachloride, carbon tetrachloride/diethyl ether, and finally pure diethyl ether. Two minor and two major products eluted, the first major material (ODOD) eluting with a 4/1 mixture of carbon tetrachloride/diethyl ether, the second (TMCA) in pure diethyl ether.

IR spectra were recorded with a Perkin-Elmer 237B spectrometer. Routine NMR spectra were taken with a Perkin-Elmer R-12B spectrometer; high-resolution proton and ^{13}C spectra were recorded with a Brucker 360 instrument.[13] Shifts are relative to Me_4Si. Visible and UV spectra were measured with a Cary 118 instrument, fluorescence spectra with a Perkin-Elmer MPF-3L spectrometer, and mass spectra with an Hitachi-Perkin-Elmer RM-50 machine.

1,1,2,2,6,6,7,7-Octamethyldispiro[2.1.2.1]octane-4,8-dione (ODOD): crystals were pale yellow; mass spectrum (70 eV), *m/e* (relative intensity) 249 (7), 248 (M^+, 36), 233 (100), 177 (25), 96 (25), 81 (52), 55 (26), 41 (53), 39 (21); ^1H NMR (360 MHz, $CDCl_3$) δ 1.390; ^{13}C NMR (360 MHz, $CDCl_3$ (intensity, 30 s delay)) δ 17.9 (100.0), 49.7 (33.23), 65.4 (10.25), 207.7 (9.09); IR (KBr pellet) ν (cm^{-1}) 659 (m), 737 (w), 999 (s), 1075 (s), 1197 (s), 1226 (m), 1323 (w), 1378 (m), 1421 (m), 1443 (m), 1468 (m), 1699 (s), 2740 (w), 2924 (m), 2950 (m); UV–vis λ (ε (M^{-1} cm^{-1})) 240 (15000), 270 (1500), 310 (680); fluorescence, excitation λ_{max} 368 nm, emission λ_{max} 418 nm.

2,2,3,3-Tetramethylcyclopropanecarboxylic Acid (TMCA): crystals were colorless; mass spectrum (40 eV), *m/e* (relative intensity) 142 (M^+, 6), 127 (100), 109 (31), 97 (83), 81 (40), 69 (20), 59 (30), 53 (77); ^1H NMR (360 MHz, $CDCl_3$ (integral)) δ 1.198 (917.0), 1.254 (794.8); ^1H NMR (60 MHz, CCl_4 (integral)) δ 1.225

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(7), 1.280 (6);[14] ^{13}C NMR (360 MHz, $CDCl_3$ (intensity, 30-s delay)) δ 16.6 (92.2), 23.6 (100.0), 31.4 (78.8), 35.7 (54.1), 178.3 (38.7); IR (KBr pellet) ν (cm^{-1}) 667 (m), 716 (m), 844 (m), 927 (s), 972 (m), 1113 (s), 1233 (s), 1322 (m), 1383 (m), 1450 (s), 1666 (s), 2933 (s). Anal. (Galbraith Laboratories, Knoxville, TN) C, H. Found: 67.7, 9.7. Calcd 67.6, 9.85.

Synthesis of 2,2,3,3-Tetramethylcyclopropanecarboxylic Acid. This synthesis combined the methods of Meshcheryakov and Dolgii[9] with the separation procedures of Zimmerman and Pratt.[10] Ethyl diazoacetate and 2,3-dimethyl-2-butene (DMB) were mixed in a 2/1 molar ratio and added dropwise to a mixture containing the same amount of DMB and cupric sulfate in a 20/1 molar ratio. After 2 h of refluxing, the mixture was distilled and ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate was collected at 52–53 °C and 2 torr. This was refluxed in methanol containing 15% KOH for 3 h, washed with diethyl ether, and acidified, and the ether layer was collected and dried with magnesium sulfate. After removal of the ether, the white crystals were collected and recrystallized from benzene: mass spectrum (40 eV), m/e (relative intensity) 142 (M^+, 8), 127 (100), 109 (36), 97 (97), 81 (67), 69 (35), 59 (50), 53 (24); ^{1}H NMR (60 MHz, CCl_4 (integral)) δ 1.125 (1), 1.175 (6), 1.225 (6); IR ν (cm^{-1}) (KBr pellet) 672 (m), 716 (m), 850 (m), 933 (m), 978 (m), 1117 (s), 1327 (m), 1388 (m), 1405 (m), 1450 (m), 1694 (s), 2955 (s).

Yield Measurements. For the quantitative measurements $^{14}C(CO)_2$ was prepared from $^{14}C(COOH)_2$ supplied by New England Nuclear. It has been shown previously[18] that ^{14}CO and $^{14}CO_2$ are the only products of the reaction with oxygen, and we have shown that the allene and methylacetylene products from ethylene at 100 torr account for 95% of the ^{14}CCO produced by photolysis using the oxygen reaction as a standard. Yields are based on comparison of TME products to the yield of allene and methylacetylene from ethylene. A window flow counter[19] was used for measurement of radioactivity in the flow stream from the gas chromatograph.

Acknowledgment. This work was supported by the Research Corporation under a Cottrell Grant. G.P. was a DuPont Summer Fellow.

Registry No. ODOD, 81359-25-3; TMCA, 15641-58-4; C_3O_2, 504-64-3; C_2O, 12071-23-7; $(CH_3)_2C{=}C(CH_3)_2$, 563-79-1; $N_2{=}CHC(O)OEt$, 623-73-4; ethyl 2,2,3,3-tetramethylcyclopropanecarboxylate, 771-10-8.

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Thermolysis of Alkyldioxetanes: Effect of 3,3-Cyclic Substituents and Conformation on the Activation Parameters

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3,3-Tetramethylene-1,2-dioxetane (**1**), 3,3-pentamethylene-1,2-dioxetane (**2**), 3,3-hexamethylene-1,2-dioxetane (**3**), *cis*-4-*tert*-butylcyclohexanespiro-3′-(1′,2′-dioxetane) (**4**), and 4-methylcyclohexanespiro-3′-(1′,2′-dioxetanes) **5a** and **5e** were synthesized in ~10% yield by closure of the β-bromo hydroperoxides with base at low temperature. The dioxetanes were purified by low-temperature (−78 °C) column chromatography on silica gel. The configurations of **4** and **5a** were shown to have oxygen-2 in an axial position while that of **5e** was found to have oxygen-2 in an equatorial position (relative to the equatorial 4-alkyl groups). Thermal decomposition of **1**–**5** produced the expected cleavage products. Thermolysis of the compounds produced (directly) high yields of excited triplet carbonyl products. The activation parameters for the thermal decomposition of **1**–**5** in xylenes were determined by the Arrhenius method: for **1**, E_a = 23.4 kcal/mol, log A = 13.1, $k_{60\,°C} = 5.8 \times 10^{-3}\ s^{-1}$; for **2**, E_a = 24.6 kcal/mol, log A = 13.2, $k_{60\,°C} = 1.2 \times 10^{-3}\ s^{-1}$; for **3**, E_a = 24.7 kcal/mol, log A = 13.2, $k_{60\,°C} = 1.3 \times 10^{-3}\ s^{-1}$; for **4**, E_a = 24.5 kcal/mol, log A = 13.1, $k_{60\,°C} = 1.0 \times 10^{-3}\ s^{-1}$; for **5a**, E_a = 24.9 kcal/mol, log A = 13.3, $k_{60\,°C} = 1.1 \times 10^{-3}\ s^{-1}$; and for **5e**, E_a = 24.1 kcal/mol, log A = 13.0, $k_{60\,°C} = 1.4 \times 10^{-3}\ s^{-1}$. The data for **2**–**4** and **5a** are similar to those for 3,3-diethyl-1,2-dioxetane. The data for **5e** show that the "equatorial" dioxetane is less stable than the "axial" dioxetane due to lower steric interactions. An interpretation of the data for **1** suggests that the lowest steric interactions occur in **1**, resulting in the lowest E_a. The results are consistent with a diradical mechanism of dioxetane thermolysis.

The unique, chemiluminescent thermolysis of alkyl and other simply substituted 1,2-dioxetanes to carbonyl fragments has been shown[2] to produce (directly) high yields of excited triplet carbonyls (Scheme I). For alkyldioxetanes, most experimental evidence[3] has been interpreted[2] in favor of a two-step (diradical) mechanism rather than a concerted process. Recent work has shown[4] that

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[1] Fellow of the Camille and Henry Dreyfus Foundation, 1981–86.

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