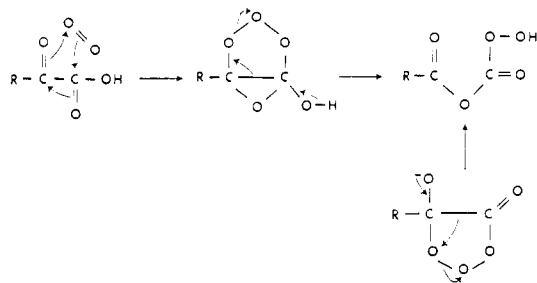


electrons to give back Fe<sup>II</sup> and hydroxylated substrate or the iron-bound oxene. The relationship between the reaction of <sup>1</sup>O<sub>2</sub> and α-ketoglutarate and the enzymic reaction is that in each the keto acid is the intermediary dioxygen acceptor. The oxygen-oxygen bond cleavage is coupled with loss of carbon dioxide. This mechanism assigns a role for the hitherto unexplained action of the keto acid in the enzymic reaction.<sup>11</sup>

**Acknowledgment.** We thank the National Science Foundation for support of this work under grant CHE-77-06617.

## References and Notes

- (1) V. Ullrich and H. Staudinger in K. Bloch and O. Hayaishi, "Biological and Chemical Aspects of Oxygenases", Maruzen, Tokyo, 1966, p 235.
- (2) G. A. Hamilton, *J. Am. Chem. Soc.*, **86**, 3391 (1964).
- (3) G. A. Hamilton in "Molecular Mechanism of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York, N.Y., 1974, p 405.
- (4) V. Ullrich, *Angew. Chem., Int. Ed. Engl.*, **11**, 701 (1972).
- (5) D. M. Jerina and J. W. Daly, *Science*, **185**, 573 (1974), and references cited therein.
- (6) D. M. Jerina, D. R. Boyd, and J. W. Daly, *Tetrahedron Lett.*, 457 (1970).
- (7) R. E. Keay and G. A. Hamilton, *J. Am. Chem. Soc.*, **98**, 6578 (1976).
- (8) F. Lichtenberger, W. Nastainczyk, and V. Ullrich, *Biochem. Biophys. Res. Commun.*, **70**, 939 (1976).
- (9) C. W. Jefford, A. F. Boschung, T. A. B. M. Bolsman, R. M. Moriarty, and B. Meilnick, *J. Am. Chem. Soc.*, **98**, 1017 (1976).
- (10) For an excellent review, see M. T. Abbott and S. Udenfriend, ref 3, p 167.
- (11) M. J. Barnes and E. Kodicek, *Vitamins Hormones*, **30**, 1 (1972).
- (12) R. S. Davidson, *Tetrahedron Lett.*, No. 46, 4181 (1976).
- (13) P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).
- (14) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **91**, 5358 (1969).
- (15) Singlet oxygen reacts with alkoxides (e.g., H. H. Wasserman and J. E. Van Werth, *J. Am. Chem. Soc.*, **96**, 585 (1974)). The reaction of the carboxylate anion would be analogous.
- (16) S. W. Benson and R. Shaw, *Org. Peroxides*, **1**, 105 (1970).
- (17) P. S. Bailey, J. A. Thompson, and B. A. Shoulders, *J. Am. Chem. Soc.*, **88**, 4098 (1966).
- (18) This was checked by treating TCNE with peroxy succinic acid at -100 °C.
- (19) R. Creigee and P. Günther, *Chem. Ber.*, **96**, 1546 (1963).
- (20) Epoxidation of olefins by <sup>1</sup>O<sub>2</sub> in the presence of α diketones has been observed by Bartlett and Shimizu.<sup>21</sup> Assuming that <sup>1</sup>O<sub>2</sub> adds to benzil in



these examples, a trioxide could form which is capable of yielding two atoms of oxygen. The trioxide proposed by us in the α-keto acid example could rearrange to a peroxy anhydride which could result from the bicyclic oxidotrioxide. We thank Professor H. H. Wasserman for calling our attention to the peroxy anhydride.

- (21) N. Shimizu and P. D. Bartlett, *J. Am. Chem. Soc.*, **98**, 4193 (1976).
- (22) C. W. Jefford, A. Exarchov, and P. A. Cadby, *Tetrahedron Lett.*, No. 23, 2053 (1978).

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## Autoxidation of Ketenes.

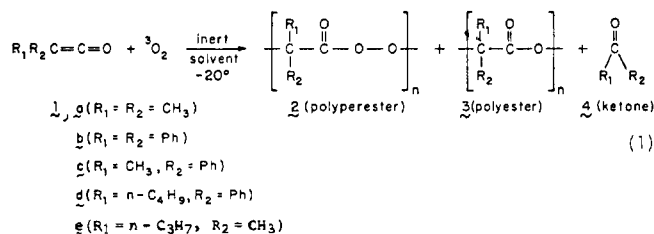
### Diradicaloid and Zwitterionic Mechanisms of Reactions of Triplet Molecular Oxygen and Ketenes

Sir:

The reaction of ketenes with singlet molecular oxygen has recently been shown to yield α-peroxylactones in addition to

other products derived from zwitterionic or perepoxy intermediates.<sup>1</sup> Over 60 years ago, the autoxidation of ketenes was reported to result in an unusual copolymerization to produce polyester (arylketenes) or polyperester<sup>2</sup> (alkylketenes) as the major products. We have reinvestigated these autoxidations. In addition to confirming and expanding the earlier studies,<sup>2</sup> we provide evidence (a) for the occurrence of two distinct mechanisms (zwitterionic and diradicaloid) in the reaction of triplet oxygen with ketenes, (b) for the occurrence of a novel (overall) cycloaddition of triplet molecular oxygen to ketenes to form α-peroxylactones, and (c) for the intermediacy of trappable diradicaloid and zwitterionic transients.

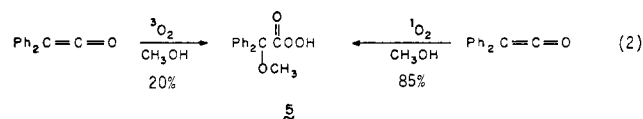
The autoxidation of dimethylketene<sup>3a</sup> (**1a**) was effected by bubbling oxygen gas through an ether solution (-20 °C) of **1a** (~0.1 M) for several hours. <sup>1</sup>H NMR analysis of the reaction demonstrated the formation of a major product (96%). A white precipitate developed which, after collection, washing with solvent and filtration (all manipulations at -20 °C), was assigned a polyperester structure (**2a**, eq 1) on the basis of the



following properties: (a) its tendency to undergo unpredictable, violent detonation as a dry solid; (b) its quantitative conversion<sup>4</sup> to acetone and CO<sub>2</sub> at temperatures >0 °C; (c) its spectral properties, especially <sup>1</sup>H NMR (δ<sup>Me<sub>4</sub>Si</sup>, CDCl<sub>3</sub>, -30 °C) 1.60 and IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 1775. The polyester **3a** is produced<sup>3b</sup> as a minor (~4%) product in the autoxidation of **1a**. No acetone is produced as a primary product of autoxidation of **1a** at temperatures below -20 °C. A similar course for autoxidation was found to occur for methyl-*n*-propylketene (**1e**).

The autoxidation of diphenylketene (**1b**)<sup>5</sup> leads to results that contrast sharply with those found for autoxidation of **1a**. The autoxidation of **1b** is much more sluggish and must be conducted at room temperature (benzene solvent) for over 3 days. The products of autoxidation of **1b** (~0.1 M, 1 atm of O<sub>2</sub>) are polyester<sup>6</sup> **3b** (~70%), **4b** (~30%), and CO<sub>2</sub> (~30%). No polyperester **2b** could be detected by IR analysis, even when the reaction was conducted at -78 °C (CS<sub>2</sub>). The infrared spectrum of polyester **3b** is experimentally indistinguishable from that of the polymer produced<sup>6a</sup> by reaction of **1b** with O<sub>3</sub>.

Autoxidation of **1a** or **1b** in methanol solvent again leads to contrasting results.<sup>7</sup> In the case of **1a**, the only significant autoxidation product is α-hydroperoxy methyl isobutyrate. In the case of **1b**, in contrast, α-methoxydiphenylperacetic acid (**5**, eq 2) is a significant oxidation product. The latter is also

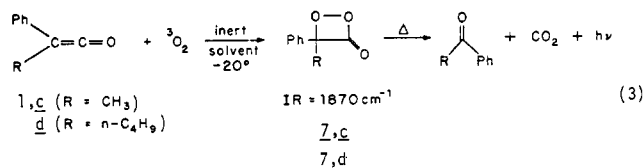


the major oxidation product of reaction of <sup>1</sup>O<sub>2</sub> with **1b** in methanol.<sup>1</sup>

The autoxidation of **1a** (CS<sub>2</sub> solvent, -20 °C) was found to be strongly inhibited (~98%) by 2,6-di-*tert*-butyl-4-methylphenol (**6**), but autoxidation of **1b** (CS<sub>2</sub> solvent) was only partially (~85%) inhibited by **6**. The formation of **5** (CH<sub>3</sub>OH solvent) was not inhibited at all by **6**.

Autoxidation of phenylalkylketenes (**1c** and **1d**, 0.1 M) in benzene at room temperature produces polyesters **3c** (65%) and **3d** (40%) and ketones **4c** (35%) and **4d** (60%) as the major

products. In both cases, a yield of  $\text{CO}_2$  equivalent to the yield of ketone is produced.<sup>4</sup> In addition to these products, low yields of peroxy lactones **7c** and **7d** are produced at  $-78^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ . **7c** and **7d** may be directly observed by infrared spectroscopy;<sup>9</sup> the yields of **7c** and **7d** are estimated as 1 and 5%, respectively. Support for these structures is provided by the observation that solutions containing **7c** or **7d** are chemiluminescent. The rate of disappearance of chemiluminescence of **7** is equal to the rate of disappearance of the characteristic peroxy lactone infrared band<sup>1</sup> at  $1870\text{ cm}^{-1}$  (eq 3), and acetophenone (0.1% detected by GC) is produced, presumably from excited valerophenone. Reaction of **1b** and **1c** with oxygen in dimethyl sulfide yields dimethyl sulfoxide (40 and 3%, respectively) in addition to polyester and ketone.<sup>11</sup>



The above results may be interpreted in terms of the pathways shown in Scheme I. We postulate that the autoxidation of a given ketene may proceed via two distinct intermediates: (1) a diradical D (produced by direct reaction of triplet oxygen and ketene) which may participate in a polymerization to form a polyperester and (2) a zwitterion Z (either produced directly from reaction of triplet oxygen and ketene or via D), which may rearrange to a peroxy lactone or be trapped (e.g., by a ketene, methanol, or dimethyl sulfide).

Thus, the autoxidation of **1a** is viewed as producing polyperester (~96%) via a copolymerization involving D (path a  $\rightarrow$  c) and polyester (~4%) via epoxidation of **1a** by Z thereby generating dimethyl- $\alpha$ -lactone. The latter then polymerizes to yield **3a** (path b (or a  $\rightarrow$  j)  $\rightarrow$  g  $\rightarrow$  h). The lack of significant formation of trapping products ( $\text{Me}_2\text{SO}$  and **5**) from Z support the postulate that the pathways involving Z are only of minor importance in the autoxidation of **1a**.

The autoxidation of **1b** (as well as **1c** and **1d**) is postulated to yield polyester **3b** (or **3c** and **3d**, respectively) via formation of Z, followed by epoxidation of **1b** by Z to form diphenyl- $\alpha$ -lactone and polymerization of the latter (path b (or a  $\rightarrow$  j)  $\rightarrow$  g  $\rightarrow$  h). Benzophenone is postulated to be produced via a copolymerization (involving D) to form a polyperester **2b** that decomposes under the reaction conditions to **4b** and  $\text{CO}_2$  (path a  $\rightarrow$  c  $\rightarrow$  d). The incomplete efficiency of **6** as an inhibitor of the autoxidation of **1b** relative to **1a** and the formations of **5**

Scheme I. Postulated Pathways for Diradicaloid and Zwitterionic Reactions of Ketenes and Molecular Oxygen

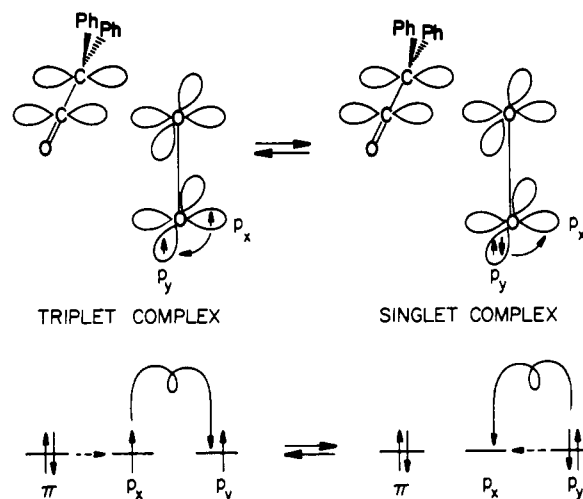
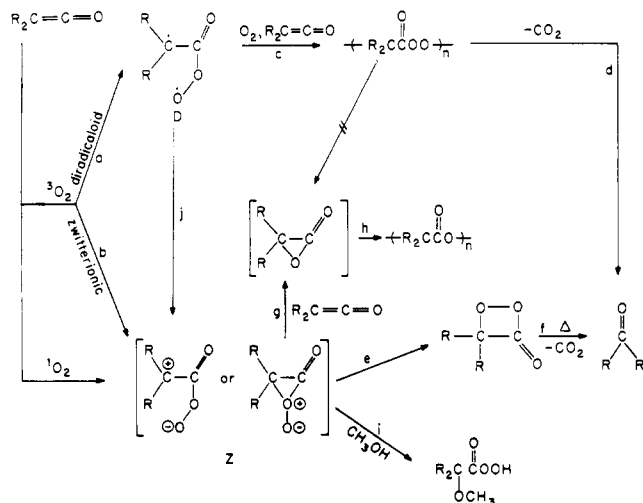


Figure 1. Schematic representation of the mechanism for generation of Z (Scheme I) by direct interaction of a ketene with triplet molecular oxygen.

and  $\text{Me}_2\text{SO}$  during autoxidation of **1b** (or reaction of **1b** with  ${}^1\text{O}_2$ ) in methanol and dimethyl sulfide support the occurrence of a significant zwitterionic pathway.

In the case of **1c** (or **1d**), Z may undergo rearrangement to a  $\alpha$ -peroxy lactone (path e) in competition with epoxidation of excess **1c** (or **1d**) and formation of polyester (path g  $\rightarrow$  h). In the case of **1b**, it is probable that some  $\alpha$ -peroxy lactone is also formed but that under our reaction conditions either its rate of destruction is too fast or its rate of formation is too slow to allow a detectable steady concentration of **7b** to be formed.

The autoxidation of **1a** differs from those of **1b**, **1c**, and **1d** in two major respects: (1) autoxidation of **1a** proceeds nearly exclusively via pathway a  $\rightarrow$  c, whereas autoxidations of **1b**, **1c**, and **1d** proceed comparably via pathway a  $\rightarrow$  c  $\rightarrow$  d and pathway b  $\rightarrow$  e or g; (2) The polyperester **2a** is isolable under our reaction conditions, whereas the polyperesters **2b-d** decompose into ketones and  $\text{CO}_2$  under the reactions conditions. The greater preponderance of the diradical pathway for **1a** could be due to a relatively slow rate of formation of Z via path b (or a  $\rightarrow$  j) or to a relatively faster rate of copolymerization via path c. We feel that the aryl group probably does not significantly influence the rate of conversion of D to Z. If this conversion is determined by intersystem crossing, its rate is probably determined by the spin-orbit coupling, generated by building odd-electron character on the oxygen atom.<sup>12</sup> Alternatively, Z may be formed relatively faster for aryl ketenes, as a result of a better interaction (Figure 1) leading to spin-orbit coupling.

The greater stability of **2a** relative to **2b**, **2c**, and **2d** is consistent with the relative rates of decomposition of structurally related *tert*-butyl peresters.<sup>13</sup>

It is possible that a radical mechanism may lead to formation of polyesters,<sup>6b</sup> ketones, and peroxy lactones even in the case of aryl ketenes. However, we suggest that the following observations are more suitably interpreted in terms of completing zwitterionic and diradicaloid mechanisms: (1) **2a** decomposes quantitatively to acetone and  $\text{CO}_2$  and does not even produce a trace of **3a**; (2) **3a** is only produced in trace amounts (~4%) from autoxidation of **1a**; (3) in methanol trapping experiments with **1b**, no polyester or trapping products derived from diphenyl- $\alpha$ -lactone are formed (but a substantial amount of benzophenone is produced (30%)); (4) at various pressures of  ${}^3\text{O}_2$ , the ratio of yields of ketone and polyester varies, as expected if ketone and polyester are produced via two independent pathways, each with different order in oxygen.<sup>14</sup> For example, for 0.15 M **1c** in benzene at room temperature the ratio of **3c/4c** decreases from 3.5 at 2 atm to 1.6 at 4 atm of oxygen.

Although each piece of evidence is circumstantial, we feel that the weight of the data argue against **2b** as a precursor to **3b**.

Since triplet oxygen is a "textbook example" of a conventional diradical, it is perhaps surprising that this species becomes involved in "zwitterionic" reactions with ketenes.<sup>12</sup> However, the problem of a D → Z conversion and the problem of triplet-singlet intersystem crossing are probably strongly coupled in the systems studied here. Indeed, a <sup>3</sup>D → Z conversion<sup>10</sup> was recently proposed to accommodate the apparent catalytic conversion of <sup>3</sup>O<sub>2</sub> to <sup>1</sup>O<sub>2</sub> by strained acetylenes. The same mechanism for the <sup>3</sup>D → Z conversion can be put forth (Figure 1) to explain the zwitterionic reactions of ketenes; i.e., an interaction of the C=C bond of a ketene with one atom of triplet oxygen induces a strong spin-orbit interaction of the distal oxygen atom and facilitates collapse to Z.

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## References and Notes

- N. J. Turro, Y. Ito, M. F. Chow, W. Adam, O. Rodriguez, and F. Yany, *J. Am. Chem. Soc.*, **99**, 5836 (1977).
- H. Staudinger, "Die Ketene", Verlag F. Enck, Stuttgart, Germany, 1912, Chapter 3; H. Staudinger, K. Dyckerhoff, H. W. Klever, and L. Ruzicka, *Chem. Ber.*, **58**, 1079 (1925).
- (a) W. E. Harford and J. C. Sauer, *Org. React.*, **3**, 136 (1946). (b) This material possessed an infrared spectrum experimentally identical with that of **3a** prepared by decomposition of di-*tert*-butylperoxy dimethylmalonate: L. B. Gortler and M. D. Saltzman, *J. Org. Chem.*, **31**, 3821 (1966).
- Oxygen consumption was analyzed with a gas-uptake apparatus, by volume change. The CO<sub>2</sub> produced was analyzed with "Ascarite" (Arthur H. Thomas Co.).
- L. I. Smith and H. H. Hoehn, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 356.
- Polyester **2b** has been reported to result from the reaction of ozone with diphenylketene: (a) R. Wheland and P. D. Bartlett, *J. Am. Chem. Soc.*, **92**, 6057 (1970). It is also produced in the (decomposition) of di-*tert*-butylperoxy diphenylmalonate: (b) P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963).
- The direct addition of methanol to ketenes to form methyl esters is the major reaction pathway under these conditions (74 and 88% for **1a** and **1b**, respectively, based on ketene consumed). A competing oxidation reaction is the formation of *α*-hydroperoxy methyl esters. Since these products are those expected of reaction of <sup>3</sup>O<sub>2</sub> with enol (or a related species) produced by addition of methanol to ketenes, we cannot at this time assess the mechanistic significance of this product relative to the trapping of Z (Scheme I). However, the observation that *α*-peroxy esters are formed only in trace amounts relative to **5** when <sup>1</sup>O<sub>2</sub> reacts with **2b** in methanol is support for the irrelevancy of these oxidation products to the Z intermediates of Scheme I. The yields of **5**, benzophenone, and *α*-hydroperoxy methyl ester (20, 30, and 50%, respectively) are based on the oxidation products.
- Phenylbutyl- and phenylmethylketene were prepared with the method modified from A. C. Duckworth, *J. Org. Chem.*, **27**, 3146 (1962).
- (a) The formation of **7** is enhanced by increasing oxygen pressure (10 atm). The detection of *α*-peroxylactone requires that its rate of formation be considerably greater than its rate of destruction. We do not feel that the destruction is a unimolecular thermal decomposition of **7** under the experimental conditions (-78 °C, CH<sub>2</sub>Cl<sub>2</sub>). Instead, **7** is probably destroyed by reaction with ketene. In fact, **7a** (prepared by reaction of <sup>1</sup>O<sub>2</sub> and **1a**) was found to react with **1b** in Freon-11 at ≤ -40 °C. The products were a mixture of polymeric materials. It is assumed that an increase in oxygen concentration enhances the rate of formation of **7** without influencing its rate of destruction. (b) Formal [2 + 2] cycloadditions of <sup>3</sup>O<sub>2</sub> to form dioxetenes have been proposed.<sup>10</sup> A formal [4 + 2] cycloaddition of <sup>3</sup>O<sub>2</sub> to cyclic dienes has been reported to be catalyzed by electrophilic reagents: D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus, and I. D. Menzies, *J. Chem. Soc., Perkin Trans 1*, 2055 (1975).
- N. J. Turro, V. Ramamurthy, K. C. Liu, A. Krebs, and R. Kemper, *J. Am. Chem. Soc.*, **98**, 6758 (1976).
- No Me<sub>2</sub>SO can be detected when **1a** is autoxidized in the presence of dimethyl sulfide or when **2a** is decomposed in the presence of dimethyl sulfide. This result and the formation of Me<sub>2</sub>SO during the autoxidation of **1b** and **1c** are consistent with the selective trapping of Z rather than D (Scheme I). The trapping experiments for **1b** and **1c** were undertaken at 80–100 atm of O<sub>2</sub> pressure; that for **1a** was done at 1 atm of O<sub>2</sub> pressure. For a pertinent analogy see C. S. Foote and J. W. Peters, *J. Am. Chem.*

*Soc.*, **93**, 3796 (1971).

- L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).
- P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
- The autoxidation of diarylketenes has been found to proceed with an increasing yield of ketone relative to polyester as the solutions become more dilute in ketene: E. F. Jenny, H. Droscher, and A. Melzer, *Angew. Chem., Int. Ed. Engl.*, **3**, 650 (1964); *Helv. Chim. Acta*, **51**, 643 (1968).

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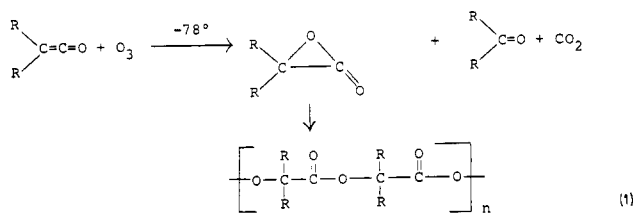
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## Ozonation of Ketenes. Nature of Intermediates

Sir:

In 1970 Wheland and Bartlett reported that ozonation of diphenylketene and di-*tert*-butylketene at -78 °C yielded the related *α*-lactones which underwent rapid polymerization to the polyesters.<sup>1</sup> In an accompanying paper, Turro et al. have obtained *α*-lactones in the reaction of triplet dioxygen with ketenes.<sup>2</sup> In our present investigation of the ketene-ozone reaction we confirm the results of earlier and subsequent work<sup>3</sup> and present evidence for intermediates in reaction 1.



The mechanism of *α*-lactone formation was not dealt with in the previous study.<sup>1,3</sup> We now propose a pathway for this transformation which accounts for the products shown in eq 1 as well as other rearrangement products.<sup>4</sup> To separate the ozone reaction from the triplet dioxygen-ketene reaction we absorbed the ozone on silica gel and released it therefrom.<sup>5,6</sup> The central point in devising a mechanism for the reaction of ketenes with ozone is whether (a) ketene + O<sub>3</sub> → *α*-lactone + O<sub>2</sub> or (b) ketene + O<sub>3</sub> → an oxidizing agent → (ketene) *α*-lactone + other products derived from the oxidizing agent. If route a prevails a 100% yield of *α*-lactone is theoretically possible, while route b leads to a maximum yield of 50% of *α*-lactone because 1 equiv of ketene is consumed in generating the oxidizing agent (assuming the oxidizing agent cannot decompose unimolecularly to either *α*-lactone or ketene). Routes a and b may be exemplified by the expressions in Scheme I.

Route a resembles the suggested pathway for epoxide for-

## Scheme I

