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.[12] 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 $^3D → Z$ conversion[10] was recently proposed to accommodate the apparent catalytic conversion of $^3O_2$ to $^1O_2$ by strained acetylenes. The same mechanism for the $^3D → Z$ 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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(7) 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 $^3O_2$ 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 $^1O_2$ 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.
(8) Phenylbutyl- and phenylmethylketene were prepared with the method modified from A. C. Duckworth, *J. Org. Chem.*, **27**, 3146 (1962).
(9) (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_2Cl_2). Instead, **7** is probably destroyed by reaction with ketene. In fact, **7a** (prepared by reaction of $^1O_2$ 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 $^3O_2$ to form dioxetenes have been proposed.[10] A formal [4 + 2] cycloaddition of $^3O_2$ 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).
(10) N. J. Turro, V. Ramamurthy, K. C. Liu, A. Krebs, and R. Kemper, *J. Am. Chem. Soc.*, **98**, 6758 (1976).
(11) No Me_2SO 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_2SO 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_2 pressure*; that for **1a** was done at 1 atm of O_2 pressure. For a pertinent analogy see C. S. Foote and J. W. Peters, *J. Am. Chem.*

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(13) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
(14) 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. Droescher, and A. Melzer, *Angew. Chem., Int. Ed. Engl.*, **3**, 650 (1964); *Helv. Chim. Acta*, **51**, 643 (1968).

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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.[1] In an accompanying paper, Turro et al. have obtained α-lactones in the reaction of triplet dioxygen with ketenes.[2] In our present investigation of the ketene-ozone reaction we confirm the results of earlier and subsequent work[3] and present evidence for intermediates in reaction 1.
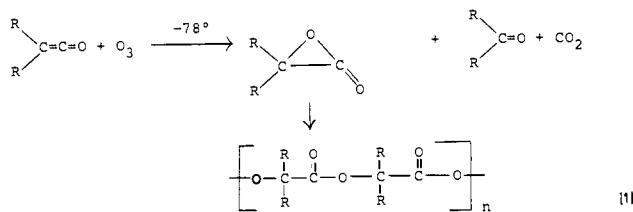
The mechanism of α-lactone formation was not dealt with in the previous study.[1,3] We now propose a pathway for this transformation which accounts for the products shown in eq 1 as well as other rearrangement products.[4] To separate the ozone reaction from the triplet dioxygen-ketene reaction we absorbed the ozone on silica gel and released it therefrom.[5,6] The central point in devising a mechanism for the reaction of ketenes with ozone is whether (a) ketene + O_3 → α-lactone + O_2 or (b) ketene + O_3 → 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-
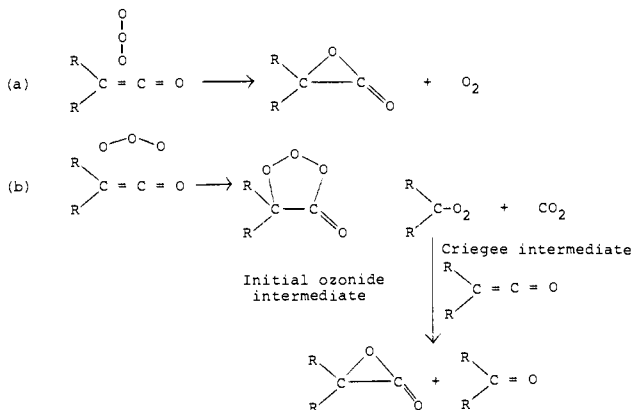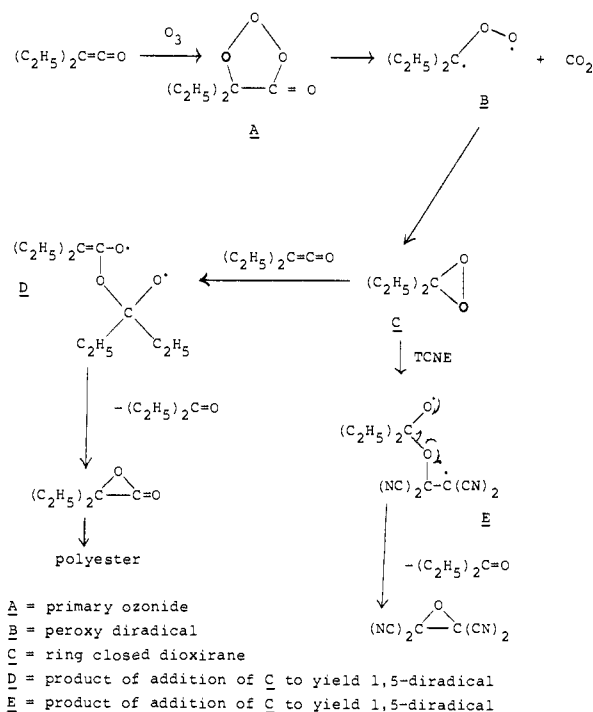
Scheme I

Table I. Ozonation of Ketene[a]

entry	ketene	solvent	coreactant	polyester, %	ketone, %	coproduct, %
I	$(CH_3CH_2)_2C{=}C{=}O$	EtOAc		43	57[b]	
II	$(CH_3CH_2)_2C{=}C{=}O$	EtOAc	TCNE[c]	6	80	40[d]
III	$(CH_3CH_2)_2C{=}C{=}O$	Freon II		40	55	
IV	$(C_6H_5)_2C{=}C{=}O$	Freon II		67	30[e]	
V	$(C_6H_5)_2C{=}C{=}O$	EtOAc		52	49	
VI	$(C_6H_5)_2C{=}C{=}O$	EtOAc	TCNE	18	75	79[d]
VII	$(C_6H_5)_2C{=}C{=}O$	EtOAc	propionaldehyde[f]	5	78	
VIII	$(tert\text{-}C_4H_9)_2C{=}C{=}O$	Freon II		91[g]	2	

[a] Ozonations were run at $-78\ °C$ until they were saturated as indicated by blue solution. The reaction time varied from 10 to 30 min. [b] Diethyl ketone was separated by distillation. [c] TCNE was 0.01 mol. No reaction between TCNE and the ketene occurred although a coloration of the solution was observed. [d] Determined by titration[26] and the oxide was separated from the polymer by sublimation. TCNE does not react with ozone under the conditions of the experiment. See also ref 19. [e] Separated by chromatography. [f] Fourfold excess. [g] As reported in ref 1.

Scheme II

A = primary ozonide
B = peroxy diradical
C = ring closed dioxirane
D = product of addition of C to yield 1,5-diradical
E = product of addition of C to yield 1,5-diradical

mation in the case of hindered olefins.[7-10] Route b is similar to the proposed mechanism for ozonation of carbon–carbon double bonds.[11-13] The primary ozonide intermediate cleaves to yield the Criegee intermediate and CO_2 as the carbonyl fragment. The Criegee intermediate may then transfer oxygen to a ketene molecule yielding the α-lactone and the derived ketone.[14] Ozone itself may be a singlet biradical as suggested by recent calculations[15] and the formation of the trioxalone may be concerted.[16]

Reference to Table I indicates that, at least from a stoichiometric viewpoint, both pathways appear to occur. Di-*tert*-butylketene (entry VIII) yields 91% polyester and <2% ketone. Thus a direct transfer of an oxygen atom from ozone apparently occurs. Whether $^1O_2$ plays a role in this reaction remains to be established. The reaction of ketenes with $^1O_2$ yields peroxylactones.[17]

Diethylketene (entry I) may follow route b upon ozonation. There is an approximate equivalence between the yields of polyester and ketone. Tetracyanoethylene (TCNE) suppresses polyester formation (entry II) to 6%, while the ketone yield is concomitantly increased to 80%, presumably owing to greater reactivity of the oxidizing agent toward the coreactant vs. the ketene. Furthermore, TCNE oxide is obtained in 40% yield.[18] We interpret these results in terms of interception of the

Criegee intermediate, either B or C, $(C_2H_5)_2CO_2$, by TCNE (Scheme II).

We chose to represent the Criegee intermediate $(C_2H_5)_2$-CO_2 as initially a 1,3 diradical (B) which converts to the dioxirane (C) and reacts as a 1,3-singlet diradical. This representation is supported by calculation[15] and recent observations on CH_2O_2.[20]

As far as the mechanism of α-lactone formation is concerned, the essence of our proposal is that $(CH_3CH_2)_2CO_2$ is the oxygen transfer agent which converts the ketene into the α-lactone. It is interesting to note that this mechanism was anticipated by Eaton et al.[21] The conversion of a ketene into a ketone by ozonolysis was a key step in the synthesis of the [2.2.2]propellane system. To obtain a high yield of ketone, however, propionaldehyde[22] was required as a coreactant. This may be understood in terms of the R_2CO_2 species transferring an oxygen atom to propionaldehyde in preference to α-lactone formation and polymerization. In the present work we also observed the analogous effect with propionaldehyde (Table I, entry VII). Djerassi et al. have studied the reaction of aldehydes with O_3 in basic media.[24]

This mechanism also offers a rationale for some recent results on the ozonation of other ketenes. Brady and Saidi[4] reported that ozonation of trimethyl- and triethylsilylketenes proceed with rearrangement to yield the silylformates (eq 2).
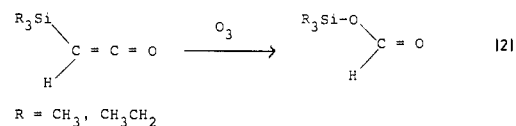

We would propose the pathway shown in Scheme III.

Crandall et al. report that carboethoxy-*tert*-butylketene upon ozonolysis yields ethyl *tert*-butyloxalate and the keto ester[25] (Scheme IV).

Entry VI shows an even stronger effect of TCNE upon the ozonation of diphenylketene. Ozonation of diphenylketene at $-78\ °C$ in the absence of TCNE gives an immediate precipitate of polyester although the lactone is stable at $-100\ °C$.
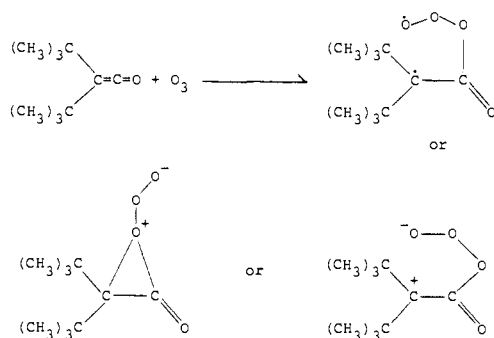
Scheme III
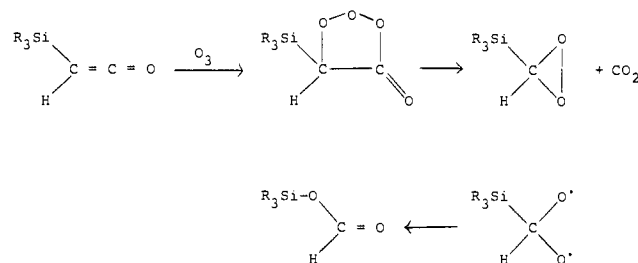
Scheme IV
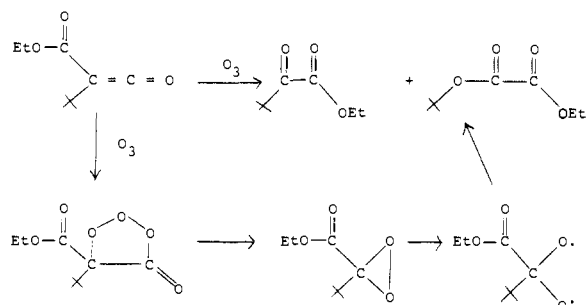
Scheme V

Oxygen transfer from $(C_6H_5)_2CO_2$ to diphenylketene can be readily diverted by TCNE or propionaldehyde.

Finally returning to the case of di-*tert*-butylketene (entry VIII) the question remains as to why a mechanism different from that observed in the ozonations of diphenylketene and diethylketene occurs. It may be that the initial ozonide is an open diradicaloid or zwitterionic intermediate due to the stabilizing influence of two *tert*-butyl groups. Singlet diradical and zwitterionic character represent a continuum which is affected by substituents.[27] Rearrangement of these species to α-lactones via a peroxy oxide may be favored.[2] Also the di-*tert*-butyl groups may hinder trioxalone formation.[28] (See Scheme V.)
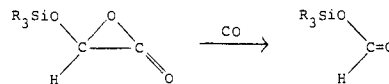
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(14) Alternatively the primary ozonide could cleave to yield R_2CO and CO_3. We prefer R_2CO_2 to CO_3 as the oxygen atom donor because of variations in the overall reaction as a function of differences in the nature of R (Table I). Were CO_3 the common oxidizing agent, a greater uniformity in the yield of ketone would be expected.
(15) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975).
(16) R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976), and the discussion therein.
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(23) Reference 4. These workers propose a basically different mechanism which involves a key step loss of carbon monoxide from an α-lactone. The gas-

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Photoelectron Spectra of the Ozonides of Ethylene, Cyclopentene, and Cyclohexene. Experimental Evidence for the Magnitude of the "Pure" Inductive Effect of an Ether Oxygen on Ionization Energy

Sir:

While ozonides have been used as valuable synthetic intermediates for some time, relatively little structural information is available about them except in the case of ethylene ozonide (**1a**),[1a] propylene ozonide (**1b**),[1b] and *trans*-2-butene ozonide (**1c**).[1b]

<u>1</u> <u>a</u>   R = R' = H

   <u>b</u>   R = H; R' = CH_3

   <u>c</u>   R = R' = CH_3 (<u>cis</u> and <u>trans</u>)
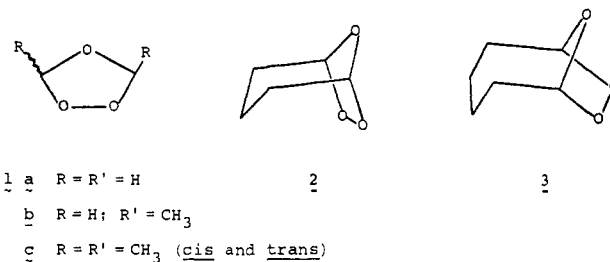
As part of our continuing effort[2] to determine the effects of remote substituents on ionization energies (IP), we have prepared and determined the photoelectron spectra (PES) of the ozonides of ethylene (**1a**),[3] cyclopentene (**2**),[4] and cyclohexene (**3**).[5] From microwave data **1** exists in the gas phase in a half-chair conformation having C_2 symmetry.[1] Importantly, however, the symmetry characteristics of the component oxygen orbitals of **1a** offer a unique opportunity to assess the inductive effects of the peroxide and ether oxygens on each other in the absence of interferring conjugative effects.

From an analysis of the PES of tetrahydrofuran ($n_0 = 9.47$ eV),[6] cyclopentene ($\pi = 9.18$ eV),[7] and 2,5-dihydrofuran (**4**)

<u>4</u>
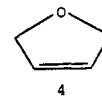
($n_0 = 10.59$ eV, $\pi = 9.14$ eV),[6] Bain et al.[6] concluded that, in the latter compound, the inductive stabilization of the π bond by the electronegative allylic oxygen (assumed to be 0.8 eV)