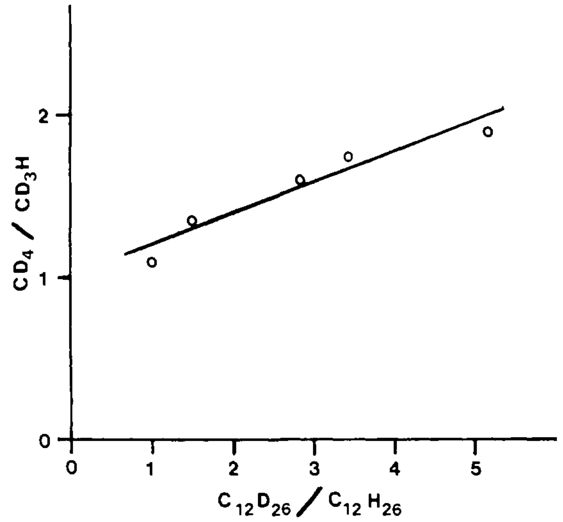

Figure 1. Plot of the CD_4/CD_3H ratio from the thermolysis of $Os(CO)_4(CD_3)_2$ in dodecane as a function of the n-$C_{12}D_{26}/n$-$C_{12}H_{26}$ ratio.

lated to 162.5 °C when necessary) have been reported for known methyl radicals attacking C_2H_6/C_2D_6 ($k_H/k_D = 5.6$)[17] and for the attack of deuteriomethyl radicals on secondary H and D in propane ($k_H/k_D = 5.2$).[18] Such isotope effects are known to be almost identical whether the reaction is conducted in solution or in the gas phase;[19] they are also virtually independent of the isotopic labeling of the methyl radical ($\cdot CD_3$ or $\cdot CH_3$).[17]

Although methane, via methyl radicals, is clearly the principal product (from 0.8 to 1.2 equiv, depending upon conditions) of the thermolysis of $Os(CO)_4(CH_3)_2$, small amounts of other products are formed. Acetone (0.2 equiv) can be detected from thermolysis in a sealed tube; the addition of 5.5 equiv of triphenylphosphine increases this yield (to 0.7 equiv) and acetone becomes the principal product. It is possible that this acetone results from simple intramolecular reductive elimination, and that the increase represents the accelerating effect of an external nucleophile,[20] but the dominance of the methyl radical path prevents investigation of this possibility: the acetone recovered from thermolysis of mixtures of $Os(CO)_4(CH_3)_2$ and $Os(CO)_4(CD_3)_2$ contains all possible combinations of hydrogen and deuterium.

In the presence of Ph_3P, as above, the principal inorganic product is $Os(CO)_3L_2$. Otherwise a number of clusters, unstable under the reaction conditions and therefore present in small steady-state concentrations, can be isolated in low yield,[21] along with some $Os_3(CO)_{12}$.

The fact that the primary process in the thermal decomposition[22] of $Os(CO)_4(CH_3)_2$ is Os–C bond cleavage contrasts with the smooth dinuclear elimination that we have observed in $Os(CO)_4H_2$[23] and $Os(CO)_4(H)CH_3$.[1] Together these results prompt the hypothesis that dinuclear elimination can only occur when hydride ligands are present or available. The fact that dinuclear elimination does not occur with the dimethyl compound $Os(CO)_4(CH_3)_2$ probably results from the inaccessibility of a methyl-bridged transition state—an inaccessibility also mirrored by the fact that methyl bridges between transition metals are extremely rare in stable compounds.[24] $Os(CO)_4(CH_3)_2$, in short, represents a case where both simple intramolecular reductive elimination and dinuclear elimination are so energetically unfavorable that the only decomposition pathway available under forcing conditions is metal-carbon bond homolysis.

Acknowledgment is made to Chevron Research Co. and to the National Science Foundation (Grant CHE76-09813) for support of this work and to Matthey-Bishop, Inc., for a generous loan of osmium tetroxide.

References and Notes

(1) Part 2: S. J. Okrasinski and J. R. Norton, *J. Am. Chem. Soc.* **99**, 295 (1977).

(2) Examples of such studies are the thermolysis of $(C_5H_5)Pt(CH_3)_3$[3] and the photolysis of $(C_5H_5)_2M(CH_3)_2$ (M = Ti, Zr, Hf).[4] In a few cases, such as the thermolysis of $(C_5H_5)_2Ti(CH_3)_2$[5] and the photolysis of the monomethyl $CH_3Au(PPh_3)$,[6] spectroscopic evidence for the formation of odd-electron species has been obtained. For comments on the difficulty of providing definitive evidence of homolytic M–C bond cleavage, see in particular (a) R. R. Schrock and G. W. Parshall, *Chem. Rev.* **76**, 243 (1976), as well as the discussions of metal alkyls in other reviews such as (b) M. C. Baird, *J. Organomet. Chem.*, **64**, 289 (1974), and (c) P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, **76**, 219 (1976).

(3) K. W. Egger, *J. Organomet. Chem.*, **24**, 501 (1970).

(4) H. Alt and M. D. Rausch, *J. Am. Chem. Soc.*, **96**, 5936 (1974).

(5) G. A. Razuvaev, V. N. Latyaeva, and L. I. Vyshinskaya, *Dokl. Akad. Nauk SSSR*, **159**, 383 (1964).

(6) P. W. N. M. Van Leeuwen, R. Kaptein, R. Huis, and C. F. Roobek, *J. Organomet. Chem.*, **104**, C44 (1976).

(7) N. J. Cooper and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 208, 761 (1974).

(8) E. L. Muetterties and P. L. Watson, *J. Am. Chem. Soc.*, **98**, 4665 (1976).

(9) (a) F. L'Eplattenier, *Inorg. Chem.*, **8**, 965 (1969); (b) F. L'Eplattenier and C. Pelichet, *Helv. Chim. Acta*, **53**, 1091 (1970); (c) R. D. George, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 972 (1973). Although ref 9b states that ethane is formed on thermolysis of $Os(CO)_4(CH_3)_2$ under high CO pressure, we have been unable to detect ethane under any of the conditions that we have employed.

(10) We find the most convenient synthesis to be the treatment of a suspension of $Na_2Os(CO)_4$ in tetraglyme with excess methyl tosylate; the only component of significant volatility is the product $Os(CO)_4(CH_3)_2$. Use of methyl-d_3 tosylate permits easy preparation of $Os(CO)_4(CD_3)_2$.

(11) Confirmed by high-resolution mass spectrometry.

(12) The formation of CD_3H is noted as this is the most accurately measured isotopically mixed methane.

(13) Other interpretations of the gas phase data are certainly possible as considerable amounts of solid secondary products are formed. However, the reaction of methyl radicals with methane at this temperature and pressure is compatible with known rate constants.[14]

(14) See Table 3 in J. A. Kerr, "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 15.

(15) A control experiment (thermolysis of $Os(CO)_4(CH_3)_2$ in n-$C_{12}H_{26}$ under CD_4) demonstrates that methane is not attacked when the reaction is carried out in the liquid phase.

(16) This approach was suggested by that of W. A. Pryor, D. L. Fuller, and J. P. Stankey, *J. Am. Chem. Soc.*, **94**, 1632 (1972).

(17) J. R. McNesby, *J. Phys. Chem.*, **64**, 1671 (1962), and references therein.

(18) W. M. Jackson, J. R. McNesby, and B. deB. Darwent, *J. Chem. Phys.*, **37**, 1610 (1962).

(19) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, p 163.

(20) P. S. Braterman, R. J. Cross, and G. B. Young, *J. Chem. Soc., Chem. Commun.*, 627 (1975), and references therein.

(21) Mass spectrometry of these compounds and of their detuerated analogues, prepared from $Os(CO)_4(CD_3)_2$, tentatively shows their empirical formulas to be $Os_4(CO)_{12}C_3H_4$, $Os_4(CO)_{14}C_2H_4$, and $Os_4(CO)_{14}C_3H_6$.

(22) Preliminary results suggest the same process occurs photochemically: photolysis (Hanovia 450W) of $Os(CO)_4(CH_3)_2$ in hexane through quartz yields methane and no ethane.

(23) J. Evans and J. R. Norton, *J. Am. Chem. Soc.*, **96**, 7577 (1974).

(24) See comments in J. Holton, M. F. Lappert, G. R. Scollary, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 425, 480 (1976). Substituted alkyl bridges have, however, recently been reported in paramagnetic Mn dimers: R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 2204 (1976).

(25) (a) Department of Chemistry, The University, Southampton S09 5NH England; (b) Camille and Henry Dreyfus Foundation Teacher-Scholar, 1976, and Alfred P. Sloan Fellow, 1977–1979.

John Evans,[25a] Stanley J. Okrasinski
Alan J. Pribula, Jack R. Norton*[25b]
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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Synthesis of α-Peroxylactones by Direct Oxygenation of Ketenes. Evidence for an Intermediate

Sir:

α-Peroxylactones possess inherent interest as high energy content molecules and importance as intermediates in chemiluminescent systems;[1] yet useful synthetic methods for pre-

Table I. Syntheses and Spectroscopic Properties of α-Peroxylactones

α-Peroxylactone	IR, cm^{-1} (solvent)	NMR, δ^{TMS} (m)	% yield[a] (solvent)
Dimethyl (**2a**)	1870 (CS_2)	1.81 (s)	7 (CH_2Cl_2) 14 ($CDCl_3$) 40 ($CFCl_3$)
Diphenyl (**2b**)	1870 ($CFCl_3$)		10 ($CFCl_3$)
tert-Butyl (**2c**)	1875 (CH_2Cl_2)	1.10 (s, 9H) 5.48 (s, 1 H)	50 (CH_2Cl_2)
Methylpropyl (**2d**)	1870 (CH_2Cl_2)	1.04 (t, 3 H) 1.55 (m, 2 H) 1.73 (s, 3 H) 1.82 (m, 2 H)	20 (CH_2Cl_2)
Phenylbutyl (**2e**)	1860 ($CFCl_3$)		14 ($CFCl_3$)
Bis(trifluoromethyl) (**2f**)	1940 (CH_2Cl_2)		*b* (CH_2Cl_2)

[a] Yields were based on initial ketene concentration, determined by quantitative NMR or IR of flash solutions. [b] Yield was too low to measure.

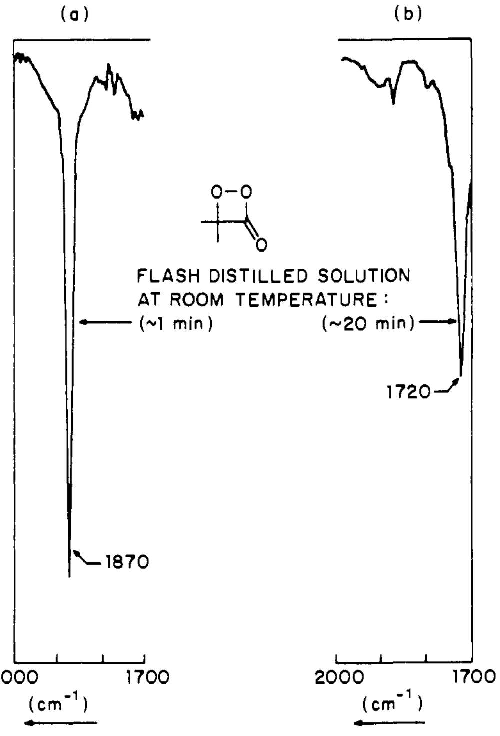
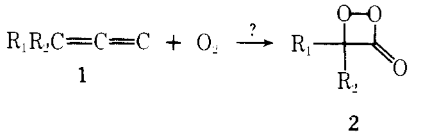


Figure 1. (a) Immediate room temperature infrared spectrum of flash distilled solution of dimethyl α-peroxylactone (**2a**) in CS_2. (b) Infrared spectrum of sample after 20 min at room temperature.

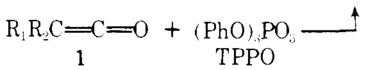
paring these compounds are quite limited in number and in scope.[2] The reaction of ketenes with molecular oxygen (eq 1) appears to be a most straightforward route to α-peroxylactones. Nevertheless, the literature indicates that reaction of singlet oxygen with ketenes does not yield α-peroxylactones[3] and that reaction of triplet oxygen with ketenes results in autoxidation and polymerization.[4] On the other hand, the reaction of triphenyl phosphite ozonide (TPPO) with diphenylketene produces a species capable of inducing the chemiluminescence of anthracenes.[5] The products of this reaction are benzophenone and (presumbably) benzilic acid polyester.[5] It was concluded that diphenyl-α-peroxylactone is the precursor of benzophenone and an energy source for inducing observed chemiluminescence. However, this conclusion is weakened by the fact that the reaction products are very similar to those obtained from autoxidation of diphenylketene with air[4] and the fact that numerous peroxy intermediates (e.g., polymeric peresters), which result from autoxidation, are also plausible energy sources for inducing chemiluminescence.

We report here that (1) the reaction of ketenes with TPPO at low temperatures provides a facile entry to α-peroxylactones, (2) this reaction involves $^1O_2$ as the reactive oxidizing species and does not result from direct reaction of TPPO and ketene or of reaction of triplet oxygen with ketene, and (3) an intermediate (presumably a perepoxide or zwitterion) occurs as precursor to α-peroxylactone formation.

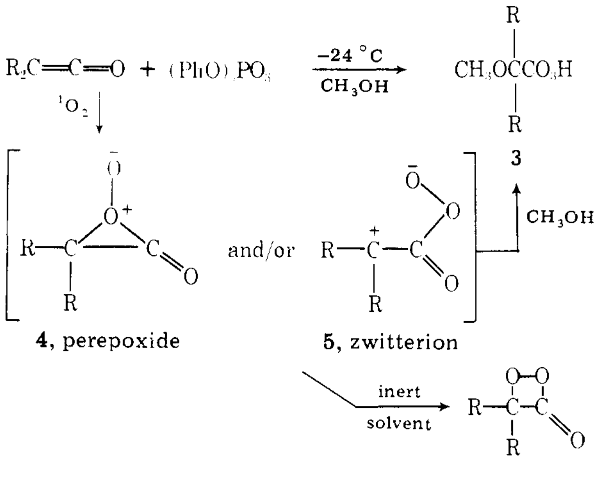
The α-peroxylactones synthesized by eq 2 are listed in Table I. A typical method of preparation is that for dimethyl-α-peroxylactone (**2a**, $R_1 = R_2 = CH_3$). A CS_2 solution (nitrogen purged) containing dimethylketene[6] was added to a stirred, nitrogen purged CS_2 solution of triphenyl phosphite ozonide,[7,8] the temperature of both solutions being maintained at ~−20 to −25 °C throughout the addition. After maintenance of the reaction mixture at −20 °C for 1 h and distillation at ~−30 to −40 °C (bath and column temperature) and ~0.1 mm, the distillate was shown by NMR and IR to contain acetone and dimethyl-α-peroxylactone (40% yield): ^{1}H NMR ($CDCl_3$, −40 °C) δ 1.81 (s): IR (CS_2, 25 °C) 1870 cm^{-1}. The acetone was removed by distillation at ~−78 °C (0.05 mm). The resulting solutions of dimethylperoxylactone were found to contain no other impurities that were detectable by IR (see Figure 1) or NMR analysis.



(1)



(2)



(3)

(4)

By a similar procedure diphenylperoxylactone (**2b**, $R_1 = R_2$

= Ph), *tert*-butylperoxylactone (**2c**, $R_1 = t\text{-}C_4H_9$; R_2 = H), methylpropylperoxylactone (**2d**, $R_1 = CH_3$; $R_2 = CH_3CH_2CH_2$), phenylbutylperoxylactone (**2e**, R_1 = Ph; $R_2 = CH_3CH_2CH_2CH_2$), and bis(trifluoromethyl)peroxylactone (**2f**, $R_1 = R_2 = CF_3$) were prepared. Although the formation of these α-peroxylactones by photooxygenation[9] at ~−78 °C could be established by spectroscopy (characteristic IR absorption ~1880 cm^{-1}), the yields were generally much lower[10] than those listed in Table I.

In addition to the spectral evidence for the assigned structures, the chemistry of the compounds listed in Table I is also consistent with the α-peroxylactone structure. For example, warming of solution of dimethylperoxylactone results in the quantitative formation of CO_2 and acetone. Furthermore, the thermolyzed solutions exhibit an intense chemiluminescence which was established as acetone phosphorescence.[11]

Given the structural assignments, let us now turn to the mechanism of reaction of ketenes with TPPO. Is there a direct, bimolecular reaction[12] between a ketene and TPPO, or does the latter first decompose to release a reactive form of oxygen (or its equivalent) which then reacts with the ketene?

To test whether or not ketenes enter into a direct, bimolecular reaction with the ozonide, the kinetics of decomposition of TPPO were determined. At −24 °C, the disappearance of TPPO is strictly first order and occurs at the same rate in the presence and absence of diphenylketene (first-order rate constants of $4.1 \pm 0.4 \times 10^{-4}\ s^{-1}$ and $4.5 \pm 0.1 \times 10^{-4}\ s^{-1}$, respectively).[13] Thus, a direct bimolecular reaction between TPPO and diphenylketene does not occur. The ozonide instead undergoes a unimolecular decomposition which produces an oxidizing agent. That this active species is singlet oxygen is required by the following observations: (a) reaction between TPPO and ketenes occurs at a significant rate only at or above temperatures (~≥−30 °C) for which TPPO is known to undergo decomposition to yield $^1O_2$; (b) the α-peroxylactones listed in Table I are also produced at −78 °C by photooxygenation; (c) the formation of 9,10-dimethylanthracene *endo*-peroxide (by reaction of 9,10-dimethylanthracene with TPPO) is strongly quenched by diphenylketene;[14] (d) the yields of α-peroxylactones parallel the order based on singlet oxygen lifetimes;[15] (e) reaction of ketenes with $^3O_2$ is negligible under our reaction conditions.[16]

The reaction of singlet oxygen and ethylenes to form dioxetanes is often viewed as proceeding via a perepoxide and/or zwitterion precursor.[17] In an attempt to establish whether reaction 1 (where O_2 is now understood to imply $^1O_2$) proceeds via trappable intermediates, the reactions of dimethylketene and of diphenylketene with TPPO in the presence of CH_3OH were studied. Indeed, when CH_3OH is present, α-peroxylactone formation is completely suppressed[18] and α-methoxyperacetic acids (eq 3) are produced. The same situation obtains for photooxygenation of dimethyl- or diphenylketenes at −78 °C. Since it was found that the α-peroxylactones (and the peresters formed from autoxidation) are stable to methanol under the reaction conditions, we conclude that methanol has intercepted a precursor to the α-peroxylactone (e.g., the perepoxide **4** or zwitterion **5** in eq 4).

In conclusion, the reaction of ketenes and TPPO represents a novel and direct synthesis of α-peroxylactones which may be conveniently purified by distillation and studied in inert solvents systems. The reaction mechanism involves generation of $^1O_2$ from TPPO followed by attack of $^1O_2$ on the ketene to produce a perepoxide **4** (and/or zwitterion **5**) intermediate that collapses to α-peroxylactone in inert solvents or may be trapped by methanol to yield α-methoxyperacetic acid derivatives.

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References and Notes

(1) Review: W. Adam, *J. Chem. Educ.*, **52**, 138 (1975).

(2) To date, only the cyclization of α-hydroperoxy acids has been shown to be a viable method for synthesis of α-peroxylactones: W. Adam and J.-C. Liu, *J. Am. Chem. Soc.*, **94**, 2894 (1972); W. Adam and H.-C Steinmetzer, *Angew. Chem., Int. ed. Engl.*, **6**, 540 (1972).

(3) See ref 1, p 141, and R. Wheland, Ph.D. Dissertation, Harvard University, 1970, p 261.

(4) H. Standinger, K. Dycherhoff, H. W. Klever, and L. Ruzeka, *Chem. Ber.*, **58**, 1079 (1925).

(5) L. J. Bollyky, *J. Am. Chem. Soc.*, **92**, 3230 (1970).

(6) W. E. Hanford and J. C. Sauer, *Org. React.*, **3**, 136 (1946); J. M. Witzel, "Dimethyl Ketene and Its Reaction with Cyclopentadiene", Ph.D. Thesis, Cornell University, 1941.

(7) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **91**, 5358 (1969).

(8) Other solvents which have been employed are $CFCl_3$ (Freon 11) and CH_2Cl_2.

(9) For a review of photooxidations, see R. W. Denny and A. Nickon, *Org. React.*, **20**, 133 (1973).

(10) For example, employing polymer-bound rose bengal as photosensitizer, ~5–10% yield of **2a** was observed, the major products being acetone and the autooxidation product of dimethylketene (a polyperester).[4] It appears that the generally lower yields obtained by photooxidation are due to competing autooxidation of the ketene and possibly by instability of α-peroxylactones to the reaction conditions.

(11) N. J. Turro, H. C. Steinmetzer, and A. Yekta, *J. Am. Chem. Soc.*, **95**, 6468 (1973), and references therein.

(12) The direct reaction of TPPO with olefins has been observed to occur at temperatures (−70 °C) below that for unimolecular decomposition (−20 °C): P. D. Bartlett and G. D. Mendenhall, *J. Am. Chem. Soc.*, **92**, 210 (1970).

(13) The initial concentrations of ketene and ozonide in CH_2Cl_2 were 4.5×10^{-2} M and 1.5×10^{-2} M, respectively. For a higher concentration of ozonide, a literature value[7] for decomposition of TPPO is $\sim 6 \times 10^{-4}\ s^{-1}$ at −24 °C. It appears that a direct bimolecular reaction between TPPO and ketenes is important at low temperatures (−78 °C). For example, reaction of **1a** and TPPO at −78 °C yields *acetone* as the exclusive product. In the case of *tert*-butylketene, reaction at −78 °C produces α-peroxylactone in good yield.

(14) From literature rate constants and competitive quenching with 9,10-dimethylanthracene, the rate of quenching of diphenyl ketene is estimated to be $\sim 1 \times 10^7\ M^{-1}\ s^{-1}$ at −15 °C in CH_2Cl_2.

(15) P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, **94**, 1029 (1972).

(16) Reaction of ketenes and TPPO are generally complete in ~1 h at −20 °C. In contrast, 90% reaction of diphenylketene, phenylbutylketene, and dimethylketene with $^3O_2$ (autoxidation) requires ~4 days, 2 days, and 10 h, respectively. Except for diphenylketene, the autoxidation products are quite different from the products produced from ketenes and TPPO.

(17) For a recent discussion, see (theory) M. J. S. Dewar, A. C. Griffin, W. Thiel, and I. J. Turchi, *J. Am. Chem. Soc.*, **97**, 4439 (1975), and S. Inagaki and K. Fukui, *ibid.*, **97**, 7480 (1975); (experimental) I. Saito, M. Imuta, Y. Takahashi, S. Matsugo, and T. Matsura, *ibid.*, **99**, 2005 (1977).

(18) Substantial amounts of methyl dimethylacetate and methyl diphenylacetate are produced in these reactions. The yields derived from reaction of molecular oxygen with the ketenes are 40% for dimethylketene and 100% for diphenylketene.

Nicholas J. Turro,* Yoshikatsu Ito, Ming-Fea Chow
Chemistry Department, Columbia University
New York, New York 10027

Waldemar Adam, Osvaldo Rodriquez, Faris Yany
Chemistry Department, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

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Electrochemistry of Some Surface-Bonded Pyrazoline Derivatives

Sir:

Since the first report by Murray et al.[1] on the success of chemically modifying a metal oxide electrode by covalently attaching reagents, other laboratories,[2,3] have shown interest