Reactions of Ketenes with Peracids and Ozone[1a]

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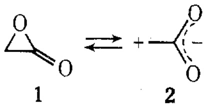
The oxidation of several ketenes with peracids has been examined. Di-*tert*-butylketene (**3**) reacts with peracetic acid to give carbon dioxide, di-*tert*-butyl ketone, β-lactone **4**, and α-acetoxy acid **6**. The formation of these products is rationalized by invoking α-lactone **9** as a key intermediate. It was independently demonstrated that peracid converts **9** to di-*tert*-butyl ketone. Ketene **14** yields α-acetoxy acid **17** upon reaction with peracetic acid and conjugated acid **18** when treated with MCPBA. Diphenylketene is oxidized by peracetic acid to benzophenone and benzhydryl acetate. The latter product appears to be formed by decomposition of intermediate diacyl peroxide **26**. Ketene **30** is unreactive to peracid oxidation but is converted to esters **31** and **32** by ozone, apparently in a normal oxidative cleavage process. The nature of these conversions is discussed.

The success of work directed toward the synthesis of allene oxides by peracid oxidation of allenes[2] has prompted us to examine the analogous reactions of ketenes with oxygen-transfer reagents as a possible synthetic pathway to the elusive α-lactone structure **1**. α-Lactones have long been proposed as reactive intermediates in reactions such as the solvolysis of α-halocarboxylate anions;[3] the interaction of appropriate ketenes, acid chlorides, and acid anhydrides with pyridine *N*-oxides;[4] the thermal and photochemical decomposition of certain diacyl peroxides,[5] peresters,[6] and cyclic peranhydrides;[7] the air oxidation of ketenes;[8] the addition of carbenes to CO_2;[9] and, in one instance, the peracid oxidation of diphenylketene.[10] During the course of the present investigation three reports of more substantial nature have appeared in the literature. Bartlett and Wheland presented evidence for oxygen transfer from ozone to ketenes, including low-temperature nmr characterization of the presumed α-lactone derived from di-*tert*-butylketene.[11] The most convincing demonstration for α-lactones comes from low-temperature infrared studies of the photolysis products from several malonyl peroxides. The intermediates thus generated show intense carbonyl bands at about 5.3 μ (~1900 cm^{-1}).[12] Most recently, bis(trifluoromethyl)acetolactone, a reasonably stable α-lactone, has been also prepared by this method.[13] In general, however, α-lactones are apparently extremely reactive, yielding predominantly polymers and products derived from nucleophilic attack at the α carbon. These reactions are readily understood in terms of a facile opening of **1** to the reactive zwitterionic intermediate **2**. Theoretical support has been gathered for this conjecture.[11]

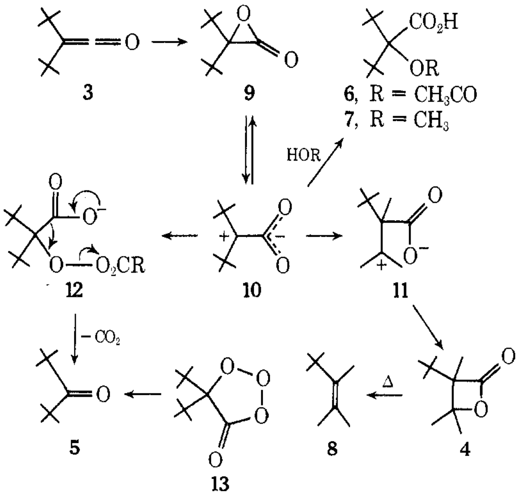


1 **2**

The oxidation of ketenes with peracids[14] was studied most extensively with di-*tert*-butylketene (**3**), a highly hindered, unreactive member of this class of compounds.[15] In principle, the bulky *tert*-butyl substituents should help to stabilize an α-lactone intermediate by shielding this species from attack by external reagents. Reaction of **3** with 2 equiv of peracetic acid in CH_2Cl_2 at 0° gave a 22% yield of β-lactone **4**, 33% of di-*tert*-butyl ketone (**5**) and 3% of α-acetoxy acid **6** in addition to uncharacterized polymeric material. A similar reaction in the presence of 8 equiv of methanol gave 5% of α-methoxy acid **7** in addition to 3% of **4** and 26% of **5**. Utilization of 1 equiv of *m*-chloroperbenzoic acid (MCPBA) as the oxidant gave a 31% yield of CO_2 as well as 34% of **4** and 31% of **5** (based on ketene consumed). Analysis of the effluent gases for CO demonstrated that only a trace (0.8%) was produced in this reaction. Product characterization was accomplished by glpc isolation and spectral examination, except for **4**, which was unstable to glpc and required careful vacuum distillation and column chromatography for purification. However, it was shown that **4** smoothly pyrolyzed to **8** under the glpc conditions and the latter was used as a quantitative measure of the amount of **4** present. The acidic products were isolated and characterized as their methyl esters.

These results implicate α-lactone **9** as a reactive intermediate in this ketene oxidation. Reasonable transformations of **9** outlined in Scheme I account for the observed products, most likely *via* the intermediacy of zwitterion **10**. Reaction of acetate at the electrophilic site of **10** leads to the α-acetoxy acid, whereas the inclusion of methanol in the reaction mixture results in the diversion of **10** to α-methoxy acid **7**. Methyl migration transforms **10** into a new zwitterion **11**, the probable precursor of **4**.[16] Alternatively, **10** can react with additional peracid, ultimately producing **5** and CO_2, most likely by the indicated fragmentation of the nucleophilic adduct **12**.[17]

Scheme I



An opportunity to test this hypothesis was provided by the report that α-lactone **9** could be prepared by ozone treatment of **3**.[11] Firstly, the assigned structure **9** was conclusively demonstrated by a low-temperature ir spectrum which manifests an intense 5.29-μ (1889 cm^{-1}) carbonyl band. A solution of **9** in CH_2Cl_2 at −78° was prepared by the reaction of 1 equiv of O_3 with **3**. Warming a sample of this solution gave 35% of **4** and 6% of **5**. However, when the solution was treated with an excess of peracetic acid before warming, 9% of **4** and 18% of ketone **5** were obtained. The threefold increase in **5** demonstrates that **9** reacts with peracid to yield **5**. The diminution of the yield of **4** is likewise consistent with this explanation.

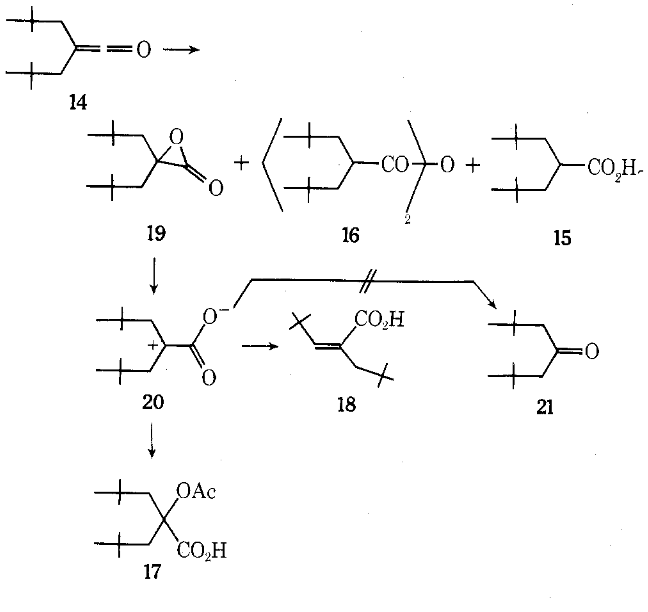
The source of the small amount of ketone **5** in the blank ozonolysis experiment was explored briefly. Although air oxidation of ketenes to ketones and CO_2 is known,[8,18] **3** did not react with O_2 under the reaction conditions nor does singlet O_2 react with **3**.[19] Oxidative decarbonylation[20] of the α-lactone by O_3 is also excluded by the observation that prolonged reaction with excess O_3 did not increase the amount of **5**. Spontaneous decarbonylation[21] of **9** is another potential pathway to **5** which appears to be excluded experimentally by the stability of the α-lactone over a long period of time at −78°. (However, it is possible that decomposition of **9** takes place during glpc analysis.) Addition of O_3 to **3** in a fashion analogous to that for simple olefins[22] should lead to **13** or its equivalent. The expected fragmentation of this primary ozonide would generate **5** and CO_3,[23] or CO_2 and the carbonyl oxide of **5**, decomposition of which could lead to **5** itself.[24]

The interaction of a second hindered ketene, dineopentylketene (**14**), with peracids was also studied briefly. Ketene **14** was synthesized by a similar route to that used for **3**,[15] but is a more typical ketene in regard to its reactivity. Although no evidence was obtained for dimerization, **14** does react readily with atmospheric moisture to give acid **15** and anhydride **16**.

The reaction of 2 equiv of peracetic acid with dineopentylketene gave anhydride **16** as the major product, but 4% of α-acetoxy acid **17** was also isolated. Utilization of 2 equiv of MCPBA as the oxidant resulted in the formation of 30% of α,β-unsaturated acid **18**. Assignment of the stereochemistry of **18** is based on the low extinction coefficient for its uv transition at 215 nm (ε 4090), which indicates steric inhibition of conjugation between the double bond and the carbonyl group.[25]

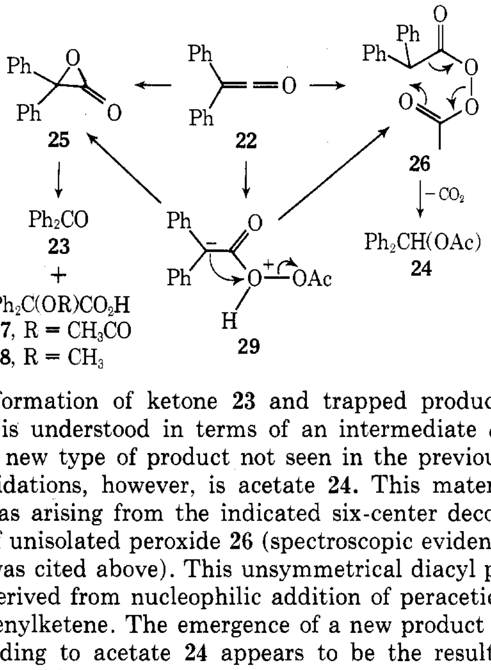
These results are best rationalized using α-lactone **19** as the key intermediate (Scheme II). Transformations of **19** *via* zwitterion **20** account for the observed products. Thus, attack of acetate leads to α-acetoxy acid **17**. Alternatively, zwitterion **20** can undergo loss of a proton (perhaps by a 1,4-hydrogen transfer to the carboxylate function) to generate α,β-unsaturated acid **18**. The fact that dineopentyl ketone (**21**) is not a product in these reactions is explained by this new reaction pathway which appears to compete successfully with peracid attack on **20**. This pathway is not available for di-*tert*-butylketene, which has no β hydrogens.

Scheme II



Reaction of diphenylketene (**22**) with 1 equiv of peracetic acid in CH_2Cl_2 at 0° gave 14% of benzophenone (**23**) and 17% of benzhydryl acetate (**24**) (Scheme III) in addition to considerable polymeric material. Although the polymeric material was not analyzed in this particular experiment, it is undoubtedly the polyester of benzilic acid which was also obtained in the ozonolysis of diphenlyketene, presumably *via* α-lactone **25**.[11] The ir spectrum of the crude reaction mixture displayed additional absorption at 5.50 μ and the nmr spectrum had singlets at δ 1.88 and 6.79 which do not arise from characterized products of the reaction. These data are consistent with those expected for mixed diacyl peroxide **26**. Refluxing the crude reaction mixture in benzene for 8 hr resulted in the disappearance of the 5.50-μ ir absorption. Performing the epoxidation of **22** in the presence of 4 equiv of methanol gave **23** and **24** in addition to methyl diphenylacetate. Among the acidic products were small amounts of α-acetoxy acid **27** (0.3%) and α-methoxy acid **28** (3%), as well as diphenylacetic acid.

Scheme III



The formation of ketone **23** and trapped products **27** and **28** is understood in terms of an intermediate α-lactone. A new type of product not seen in the previous ketene oxidations, however, is acetate **24**. This material is viewed as arising from the indicated six-center decomposition of unisolated peroxide **26** (spectroscopic evidence for which was cited above). This unsymmetrical diacyl peroxide is derived from nucleophilic addition of peracetic acid to diphenylketene. The emergence of a new product pathway leading to acetate **24** appears to be the result of a more favorable conversion of **22** to diacyl peroxide **26**, relative to the related transformation for the dialkylketenes. This can be appreciated if α-lactone formation occurs by way of an intermediate such as **29**. Stabilization by phenyl groups should slow down ring closure of this species to the α-lactone, thereby allowing tautomerization of **29** to **26** to become an important competing process. Alternatively, the two competing processes may be between a one-step oxygen transfer from peracid to the ketene double bond and nucleophilic addition of peracid. The latter process should also be aided by phenyl substituents.

The lability of proposed intermediate **26** was corroborated by several attempts at its synthesis. Thus, treatment of diphenylperacetic acid with either acetyl chloride or ketene at low temperatures gave acetate **24** as the only isolable product. Likewise, reaction of peracetic acid with diphenylacetyl chloride also resulted in **24**. However, the crude reaction product of these reactions displayed ir and nmr absorptions appropriate for diacyl peroxide **26** in addition to those of **24**.

Treatment of butylethylketene[26] with 1 equiv of peracetic acid afforded 19% each of 3-heptanone and CO_2 as the only important volatile products. Examination of the acidic material revealed only acetic acid.

The oxidation of *tert*-butylcarbethoxyketene (**30**) was

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EXPERIMENTAL SECTION

General.--Nmr data were obtained on CCl_4 solutions using Varian A-60 and HR-220 spectrometers. Infrared (ir) spectra were obtained neat or on CCl_4 solutions with a Perkin Elmer IR-137. Analytical glpc was performed on an Aerograph 1200; preparative glpc on an Aerograph A700 instrument. Yields determined by glpc were obtained comparing peak areas against an internal standard and are corrected for compound response. Melting points are corrected. Anhyd $MgSO_4$ was used as a drying agent.

Peracetic Acid Solutions.--Typically, acetic acid was removed from 1.0 g of commercial 40% peracetic acid by slowly adding the peracid to an ice-cold slurry of excess anhyd Na_2CO_3 in 20 ml of CH_2Cl_2. After stirring at 0° for 45 min, the solid was removed by filtration and the peracetic acid solution was used immediately. This procedure resulted in a peracid solution without substantial loss of oxidizing agent.[30]

Oxidation of 3 with Peracetic Acid.--A. To 0.84 g of 3 and 1.2 g of anhyd Na_2CO_3 in 20 ml of CH_2Cl_2 at 0° was added dropwise one equiv of peracetic acid in 20 ml of CH_2Cl_2. After stirring at 0° for 2.5 hr the reaction mixture was filtered and the solvent was removed from the filtrate under reduced pressure: ir 4.79, 5.51, 5.72 and 5.92 μ. The volatile products were removed from the crude mixture by vacuum transfer. Glpc showed 8, 5, and 3 in a 13:43:44 ratio. Subjecting a sample to column chromatography on neutral alumina gave a small amount of 4:[11] ir 5.51 μ; nmr δ 1.11 (s, 9), 1.29 (s, 3), 1.45 (s, 3), and 1.68 (s, 3).

The residue from the vacuum transfer was dissolved in CH_2Cl_2 and extracted with Na_2CO_3 soln. The extract was acidified with conc HCl and extracted with ether. The ether extract was concentrated and the acidic products were esterified by the addition of ethereal diazomethane. Removal of the solvent and glpc isolation gave 70 mg of methyl 2-t-butyl-3,3-dimethylbutanoate: ir 5.78 μ; nmr δ 1.04 (s, 18), 2.09 (s, 1) and 3.53 (s, 3) and 39 mg (3%) of methyl 2-acetoxy-2-t-butyl-3,3-dimethylbutanoate mp 78.0-79.5°; ir 5.75, 7.96 and 8.08 μ; nmr δ 1.14 (s, 18), 2.00 (s, 3) and 3.61 (s, 3).

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Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 63.5; H, 9.8.

B. To a slurry of 0.41 g of 3 and 0.9 g of anhyd Na_2CO_3 in 10 ml of CH_2Cl_2 at 0° was added 2 equiv of peracetic acid in 30 ml of CH_2Cl_2. After stirring at 0° for 2.5 hr an aliquot analyzed by glpc showed a 33% yield of 5 and a 22% yield of 4. It was demonstrated that under the glpc conditions 4 pyrolyzed essentially quantitatively to 8; the peak area of the latter was used as a measure of the amount of 4 present.

Oxidation of 3 with Peracetic Acid in the Presence of Methanol.--To 0.46 g of 3 and 0.14 g of anhyd Na_2CO_3 in 10 ml of CH_2Cl_2 at 0° was added 2 equiv of peracetic acid in 23 ml of CH_2Cl_2 containing 5 equiv of methanol. The reaction mixture was stirred at 0° for 5 hr at which time a negative starch-iodide test was obtained. Glpc revealed the presence of 5 (26%) and 8 (3%).

The reaction mixture was diluted with water and the aqueous layer was separated, acidified and extracted with ether. The organic extract was dried and the solvent was removed to give 24 mg (5%) of 2-methoxy-2-t-butyl-3,3-dimethylbutanoic acid (7) as a gray solid: mp 125-135° (dec); ir 3-4 and 5.87 μ. This material was treated with ethereal diazomethane and the resulting ester was purified by glpc to give methyl 2-methoxy-2-t-butyl-3,3-dimethyl-butanoate: mp 63-4°; ir 5.78 μ; nmr δ 1.10 (s, 18), 3.54 (s, 3) and 3.68 (s, 3).

Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.18. Found: C, 66.3; H, 11.3.

Oxidation of 3 with MCPBA.--A. To 0.1 g of 3 in 10 ml of CH_2Cl_2 at 0° was added one equiv of MCPBA in 10 ml of CH_2Cl_2. The reaction mixture was stirred at 0° for 2 hr during which time a nitrogen stream was passed through the apparatus and then over Ascarite which absorbed a 31% yield of CO_2. Analysis of the reaction mixture by glpc gave 5 (31%) and 4 (34%). The reaction mixture was diluted with ether and extracted with a $NaHCO_3$ soln. The aqueous extract was acidified and extracted with ether. This extract was concentrated and esterfied with ethereal diazomethane. Evaporation of the solvent gave an oil which contained only methyl m-chlorobenzoate.

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B. To 265 mg of 3 in 20 ml of CH_2Cl_2 at 0° was added one equiv of MCPBA in 20 ml of CH_2Cl_2. The reaction mixture was allowed to stir at 0° for 2.5 hr while a nitrogen stream passed through the apparatus, through Ascarite to absorb CO_2, through a -41° trap to condense solvent vapor and then into I_2O_5 to detect CO;[31] a 24% yield of CO_2 and a 0.8% yield of CO were obtained. Glpc analysis gave 5 (30%) and 4 (24%).

C. To 0.33 g of MCPBA in 10 ml of CH_2Cl_2 at 0° was slowly added 0.09 g of 3 in 5 ml of CH_2Cl_2. The mixture was stirred at 0° for 2 hr while evolved gases were passed over Ascarite; a 32% yield of CO_2 was obtained. The excess peracid was destroyed by addition of 2-methyl-2-butene. Glpc showed 5 (23%) and 4 (18%).

Di-t-butylacetolactone (9).[11]--To a solution of 0.15 g of ketene 3 in 20 ml of $CFCl_3$ at -78° was bubbled in one equiv of O_3 from a Welsbach ozone generator. An aliquot was transferred to a low-temperature infrared cell at -78°. An intense absorption at 5.29 μ was observed upon ir examination of this cold reaction mixture. A white polymer developed upon warming the reaction mixture to room temperature. When CH_2Cl_2 was used as the solvent, the carbonyl band of 9 was again visible, but the addition of CH_3OH at -78° caused the 5.29 μ band to slowly disappear and the absorption bands of 4 to increase in intensity.

Reaction of 3 with Oxygen.--Oxygen was bubbled through a solution of 27 mg of 3 in 10 ml of CH_2Cl_2 for 6 hr at -78°. Evaporation of the solvent left only unreacted 3.

Reaction of 9 with Peracetic Acid.--Ozone was bubbled into a solution of 47 mg of 3 in 10 ml of CH_2Cl_2 at -78° until a blue color developed. After 10 min, at -78° a nitrogen stream was bubbled through the mixture until the blue color of excess O_3 had disappeared. An aliquot was allowed to warm to room temperature; glpc revealed 5 (6%) and 4 (35%). The remainder of the reaction mixture was treated with an excess of peracetic acid in CH_2Cl_2 at -78° and allowed to stand for 2.5 hr. After warming to room temperature, glpc showed 5 (18%) and 4 (9%).

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Reaction of 9 with Excess O_3.--To a solution of 0.2 g of 3 in 30 ml of CH_2Cl_2 was bubbled in excess O_3 at -78°. After 15 min, an aliquot was withdrawn and allowed to warm to room temperature. Glpc revealed 5 (3%) and 4 (43%). The remainder of the reaction mixture was held at -78° for 5 hr in the presence of excess ozone before warming to room temperature. Glpc analysis gave 5 (2%) and 4 (10%).

4,4-Dimethyl-2-neopentylpentanol.[32]--To a flame-dried apparatus flushed with nitrogen was added 4.4 g of $NaBH_4$ to 250 ml of THF containing 18 g of 4,4-dimethyl-2-neopentyl-1-pentene. To this stirred suspension was added 20 ml of distilled BF_3 etherate during 1 hr, maintaining the temperature at approximately 30°. The resultant reaction mixture was heated for 3 hr at 40° after which excess hydride was destroyed by the addition of 50 ml of water. The organoborane was oxidized by the addition of 40 ml of 3 N NaOH followed by dropwise addition of 40 ml of 30% hydrogen peroxide. The reaction mixture was saturated with NaCl and the organic layer was separated, washed with satd NaCl soln, dried over anhyd Na_2SO_4 and concentrated. The resultant yellow paste was redissolved in ether, and dried again over anhyd Na_2SO_4. Removal of the solvent gave an oil which crystallized upon cooling to give 10.6 g (97%) of 4,4-dimethyl-2-neopentylpentanol: mp 36-41°; ir 3.09 and 9.71 μ; nmr δ 0.82 (s, 18), 1.35 (m, 5), 3.60 (m, 2) and 5.95 (s, 1).

4,4-Dimethyl-2-neopentylpentanoic Acid (15).[32]--To a cooled, stirred solution of 10.6 g of 4,4-dimethyl-2-neopentylpentanol in 100 ml of acetone was added 52 ml of 8 N chromic acid over a period of 30 min. The reaction mixture was heated at 60° for 2 hr and then allowed to stand for 12 hr at room temperature. After the addition of 225 ml of water, the mixture was extracted four times with ether. The combined layers were dried and concentrated. Recrystallization from 3:1 methanol-water gave 9.2 g (81%) of 15, mp 85-86°. Recrystallization and sublimation gave a pure sample: mp 86.8-87.2°; ir 3-4 and 5.88 μ; nmr δ 0.93 (s, 18), 1.30 (m, 4), 2.35 (m, 1) and 12.11 (s, 1).

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4,4-Dimethyl-2-neopentylpentanoyl Chloride.[32]--To a cooled, stirred solution of 8.3 g of 15 in 120 ml of anhydrous benzene was added 8.8 ml of oxalyl chloride over a period of 15 min. The reaction was allowed to stand at room temperature until gas evolution ceased (2 hr). After 4 hr at reflux, the brown liquid was vacuum distilled to give 7.8 g (86%) of 4,4-dimethyl-2-neopentylpentanoyl chloride as a clear colorless liquid: bp 73° (1.6 mm); ir 5.58 μ; nmr δ 0.95 (s, 18), 1.51 (m, 4) and 2.89 (m, 1).

Dineopentylketene (14).--To a flame-dried apparatus flushed with nitrogen was added 2.0 g of 4,4-dimethyl-2-neopentylpentanoyl chloride and 1.7 g of triethylenediamine in 60 ml of dry benzene. The reaction mixture was refluxed for 70 hr during which time a yellow color and a gray precipitate developed. The reaction mixture was filtered through a sintered glass funnel under a nitrogen blanket and the filtrate was vacuum transferred twice to remove solid material and residual solvent. Nmr analysis of the resulting yellow distillate revealed triethylenediamine, benzene, and 14: ir 4.79 μ; nmr δ 0.89 (s, 18) and 1.80 (s, 4). The yield of 14 was estimated to be 40% by addition of a known amount of CH_2Cl_2 as an nmr standard.

Oxidation of 14 with Peracetic Acid.--To a slurry consisting of 2 equiv of peracetic acid and 3.5 g of anhyd Na_2CO_3 in 30 ml of CH_2Cl_2 at 0° was added 3.0 g of 14. After 17 hr at room temperature, the mixture was filtered and the solvent was removed from the filtrate to give 387 mg of a paste. This material was subjected to column chromatography on silica gel. In addition to the major product 16: ir 5.73, 5.86 and 9.68 μ; nmr δ 0.95 (s, 18), 1.65 (m, 4) and 2.50 (m, 1); there was 150 mg (4%) of 2-acetoxy-2-neopentyl-4,4-dimethylpentanoic acid (17) as a white solid: mp 123.5-124.4°; ir 5.74 and 5.82 μ; 220 MHz nmr δ 0.93 (s, 18), 1.83 (d, 2, J = 15 Hz), 2.00 (s, 3) and 2.58 (d, 2, J = 15 Hz).

Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.09; H, 10.14. Found: C, 65.2; H, 9.9.

Oxidation of 14 with MCPBA.--To 110 mg of 14 in 20 ml of CH_2Cl_2 was added 2 equiv of MCPBA in 30 ml of CH_2Cl_2. The reaction mixture

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was stirred at room temperature for 24 hr at which time a negative starch-iodide test was obtained. The mixture was concentrated and the residue was subjected to column chromatography on silica gel. Fractions containing m-chlorobenzoic acid, 15 and 16 were obtained in addition to 46 mg (30%) of 2-neopentyl-4,4-dimethyl-2-pentenoic acid (18) as a white solid: mp 74.1-74.9°; ir 3-4, 5.90 μ; nmr δ 0.90 (s, 9), 1.16 (s, 9), 2.18 (s, 2), 5.52 (s, 1) and 12.22 (s, 1); uv (hexane) 215 nm (ε 4090).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 73.0, H, 11.2.

Oxidation of 22[29] with Peracetic Acid.--To 0.97 g of 22 and 1.0 g of anhyd Na_2CO_3 in 10 ml of CH_2Cl_2 at 0° was added one equiv of peracetic acid in 20 ml of CH_2Cl_2. The peracetic acid was added dropwise until the bright yellow color of 22 disappeared. After stirring at 0° for 25 min, the ir of an aliquot showed the absence of 22. Since the reaction mixture gave a positive starch-iodide test, 2-methyl-2-butene was added to destroy excess peracetic acid. The mixture was filtered, diluted with CH_2Cl_2 and washed with $NaHCO_3$ soln. The aqueous layer was extracted with CH_2Cl_2 and the combined extracts were dried and concentrated to give 0.83 g of paste: ir 5.50, 5.75 and 6.02 μ; nmr singlets at δ 1.88, 1.94, 4.97, 6.79, 7.07, and 7.16. Calibrated glpc analysis revealed 23 (14%) and 24 (17%). Refluxing a portion of the crude reaction product in benzene for 8 hr resulted in the disappearance of the 5.50 μ absorption. The product distribution was essentially the same when the reaction was performed at -23° and at room temperature.

Oxidation of 22 with Peracetic Acid in the Presence of Methanol.--To 0.68 g of 22 and 1.0 g of anhyd Na_2CO_3 in 10 ml of CH_2Cl_2 at 0° was added one equiv of peracetic acid in 10 ml of CH_2Cl_2 and 4 equiv of anhyd methanol. After stirring for 35 min. at 0°, ir revealed the complete disappearance of 22. Excess peracid was destroyed by the addition of 2-methyl-2-butene and the reaction mixture was filtered and diluted with CH_2Cl_2. The organic layer was washed with satd $NaHCO_3$ soln, dried and concentrated to leave 0.59 g of a cloudy glass. Three volatile products in the ratio of 35:51:14 were identified as 23, 24 and methyl diphenylacetate.

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The aqueous layer was acidified and extracted with ether. The extract was dried and concentrated to give 58 mg of a clear oil which was esterified by treatment with ethereal diazomethane. Three peaks in the ratio 53:43:3 were identified as methyl diphenylacetate and the methyl esters of 28 (3%): ir 5.74 μ; nmr δ 3.12 (s, 3), 3.70 (s, 3) and 7.24 (m, 10); and 27 (0.3%): ir 5.72 μ; nmr δ 2.08 (s, 3), 3.88 (s, 3) and 7.15 (s, 10).

Diphenylperacetic Acid.--To a beaker containing 3.0 g of diphenylacetic acid was added 10 g of methanesulfonic acid. The mixture was cooled to 5° and stirred vigorously with a high-speed stirrer while 3.0 g of 50% H_2O_2 was added dropwise. The addition took 20 min. and the temperature was not allowed to exceed 11°. The resulting slurry was warmed slowly to 25° over 4 hr by letting the surrounding ice bath melt. (Removal of the ice bath caused decomposition as did higher temperatures or prolonged standing at 25°.) The slurry turned gray during this time. After cooling back to 5°, ice (10 g) was carefully added (exothermic !) followed by 10 ml of cold satd $(NH_4)_2SO_4$ soln. The contents of the beaker were transferred to a separatory funnel and extracted three times with benzene. The extract was washed twice with cold satd $(NH_4)_2SO_4$ soln, dried over anhyd Na_2SO_4, and the solvent was cautiously removed on the flash evaporator at less than 30°. The resulting yellow solid was recrystallized twice from 3:1 pentane-ether to give 2.0 g (60%) of diphenylperacetic acid as a light yellow solid: mp 87.0-88.1° (dec); ir 5.71 and 8.97 μ; nmr δ 5.11 (s, 1) and 7.30 (s, 10). Analysis gave a peracid content of 98.9%.[30]

Attempted Synthesis of Acetyl Diphenylacetyl Peroxide (26).--A. To 0.41 g of diphenylperacetic acid in 8 ml of ether at 0° was added 0.14 g of acetyl chloride in 10 ml of ether. Addition of 0.14 g of pyridine caused the instantaneous formation of a white precipitate. After stirring 45 min. at 0° the mixture was diluted with ether, washed with cold water, dried, and concentrated to give 0.45 g of a cloudy glass: ir 5.49 and 5.75 μ; nmr singlets at δ 1.83, 1.91, 4.98, 5.59, 6.83, 7.09 and 7.19. Attempted purification of the diacyl peroxide by column chromatography gave only 24.

B. A ketene generator[34] was used to obtain a ketene solution in CH_2Cl_2 at -78° which was added to 0.3 g of diphenylperacetic acid in

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5 ml of CH_2Cl_2 at -78°. The resulting mixture was stirred for 2 hr and then solvent and excess ketene were removed under vacuum at 0°. The residue was dissolved in ether, washed with satd $NaHCO_3$, dried, and concentrated to give 0.18 g of a glass: ir 5.51 and 5.75 μ. Only 24 was obtained upon column chromatography.

C. To one equiv of peracetic acid in 15 ml of ether at 0° was added 2.5 g of diphenylacetyl chloride in 20 ml of ether, followed by 0.9 g of pyridine. After stirring for 45 min. at 0°, the reaction mixture was washed twice with water, dried and concentrated to give 2.4 g of a yellow oil: ir 5.55 and 5.75 μ. Column chromatography gave only 24.

Diethyl t-Butylmalonate.[35]--To a flame-dried apparatus was added 25.2 g of CuI and 24.2 g of diethyl isopropylidenemalonate in 165 ml of anhyd ether under N_2. The stirred mixture was cooled to 0° and 2 equiv of methyllithium in ether was added. After stirring at 0° for 1 hr and room temperature for 2 hr, the reaction mixture was quenched with cold NH_4Cl soln and filtered. The filtrate was washed with water, dried, and the solvent was removed to give 21.7 g (83%) of essentially pure diethyl t-butylmalonate as a clear, colorless liquid.

This material was transformed into 30 by the literature preparation.[27]

Oxidation of 30 with Ozone.--O_3 was bubbled into a solution of 60 mg of 30 in 6 ml of CH_2Cl_2 at 0° for 15 min. After warming the mixture to room temperature, glpc analysis showed a 26% yield of ethyl trimethylpyruvate (31) and 59% of t-butyl ethyl oxalate (32). Ozone did not react appreciably with 30 at -78°. Compound 31 showed: ir 5.75, 5.80 and 9.30 μ; nmr δ 1.22 (s, 9), 1.36 (t, 3, J = 7 Hz) and 4.25 (q, 2, J = 7 Hz).

t-Butyl Ethyl Oxalate (32).--To a stirred solution of 4.4 g of oxalyl chloride in 30 ml of anhyd ether at 0° was added 1 equiv of t-butanol. After stirring at room temperature for 1 hr, 1 equiv of absolute ethanol was added and the reaction mixture was stirred for an additional hour. The reaction mixture was poured onto ice and the organic layer was washed with satd $NaHCO_3$ soln, dried, and concentrated to give 3.5 g (52%) of essentially pure 32 as a clear, colorless liquid: ir 5.66, 5.73 and 8.73 μ; nmr δ 1.33 (t, 3, J = 7 Hz) 1.57 (s, 9) and 4.30 (q, 2, J = 7 Hz).

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Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.5; H, 8.2.

Oxidation of Butylethylketene with Peracetic Acid.--To a slurry consisting of 0.5 g of butylethylketene and 0.6 g of Na_2CO_3 in 12 ml of CH_2Cl_2 at 0° was added 1 equiv of peracetic acid in 12 ml of CH_2Cl_2. A nitrogen stream was bubbled through the reaction mixture into an Ascarite absorption bulb. Over the 5 hr reaction period 19% of CO_2 was absorbed. Excess peracid was destroyed by the addition of 2-methyl-2-butene and the reaction mixture was filtered and carefully concentrated. Glpc analysis gave a 19% yield of 3-heptanone.

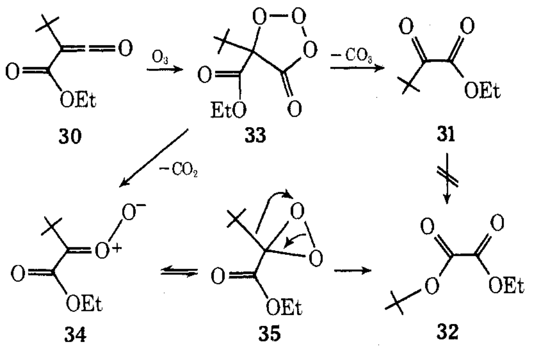
The residual salts were dissolved in water, acidified and extracted with ether. The extract was dried and the solvent was removed to give acetic acid as the only important product.

Oxidation of Ketene with Ozone.--A solution of ketene was ozonized at -78° until a deep blue color developed. After standing at -78° for 5 hr the reaction mixture was brought slowly to room temperature. Solvent was removed at reduced pressure to yield a thick brown oil which gave a positive starch-iodide test. White crystals of succinic anhydride (5%) sublimed from the crude reaction mixture upon attempted vacuum transfer.

Oxidation of Dimethylketene with Ozone.--Dimethylketene was synthesized by pyrolysis of tetramethyl-1,3-cyclobutanedione at 600° and trapped at -78°. Methylene chloride was added to the cold trap and the solution was ozonized at -78°. The solution became green but did not turn the typical blue color even after lengthy ozonization. The green solution was allowed to stand at -78° for 12 hr and then brought slowly to room temperature. The green color faded to yellow accompanied by gas evolution: ir 3.0-4.0, 4.29 (CO_2) and 5.8 μ; nmr δ 2.14 (s), 2.06 (s) and 1.1-1.6 (numerous absorptions). After a few hours at room temperature, the reaction mixture became colorless and gas evolution ceased. The nmr showed new signals at δ 8.58 and 8.09 in addition to the above. The reaction mixture was dissolved in ether and washed three times with cold $NaHCO_3$ soln. The organic layer was shown to contain a 20% yield of acetone by glpc.

examined, since this readily available,[27,28] stable ketene should give an α-lactone intermediate whose zwitterionic form is destabilized by the electron-withdrawing carbethoxy group. However, this substituent also retards electrophilic attack on the ketene. Thus, treating 30 with peracids resulted in the slow formation of very complex product mixtures which could not be effectively examined. However, reaction with an excess of O_3 at 0° (no appreciable reaction occurred at −78°) resulted in a 26% yield of α-keto ester 31 and 59% of oxalate ester 32 (Scheme IV).

Scheme IV



Keto ester **31** was not converted to **32** under the ozonolysis conditions.

These products can be adequately explained by a normal 1,3-addition of O_3 across the carbon–carbon double bond of **30** and do not require an α-lactone intermediate. The resulting ozonide **33** can decompose to α-keto ester **31** and CO_3. Alternatively, fragmentation in another manner gives carbonyl oxide **34**, which may lose oxygen to give **31**.[24] This species can also lead to **32**, since it is conceivable that charged species **34** is in equilibrium with its closed form **35**, rearrangement of which (in a fashion analogous to that of a Baeyer–Villiger oxidation) gives **32**. A bimolecular reaction between **31** and **34** could also result in **32**.

Oxidation of ketene itself with excess O_3 resulted in an extremely complex mixture. Nonetheless, the isolation of about 5% of succinic anhydride from this reaction is of interest. The formation of this unexpected product could be the result of a 1,3-dipolar addition of the α-lactone zwitterion to ketene.[29] (However, the production of succinic anhydride can be explained without postulating an α-lactone intermediate.)[29] Finally, the only characterized product of the reaction of dimethylketene with O_3 was acetone.

In summary, it appears that certain ketenes react with peracids and with O_3 to give products which apparently are derived from intermediate α-lactones. In other cases, more classical processes are sufficient to explain the experimental results.

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Registry No.—**3**, 19824-34-1; **4**, 30436-15-8; **6** methyl ester, 51552-66-0; **7**, 51705-84-1; **7** methyl ester, 51552-56-8; **9**, 30436-13-6; **14**, 51552-57-9; **15**, 30667-81-3; **16**, 51552-58-0; **17**, 51552-59-1; **18**, 51552-60-4; **22**, 525-06-4; **23**, 119-61-9; **24**, 954-67-6; **26**, 51552-61-5; **28** methyl ester, 51552-62-6; **30**, 51552-63-7; **31**, 5333-74-4; **32**, 50624-94-7; MCPBA, 937-14-4; peracetic acid, 79-21-0; methyl 2-*tert*-butyl-3,3-dimethylbutanoate, 10250-50-7; ozone, 10028-15-6; 4,4-dimethyl-2-neopentylpentanol, 51552-64-8; 4,4-dimethyl-2-neopentyl-1-pentene, 141-70-8; 4,4-dimethyl-2-neopentylpentanoyl chloride, 38591-84-3; methyl diphenylacetate, 3469-00-9; diphenylperacetic acid, 51552-65-9; diphenylacetic acid, 117-34-0; oxalyl chloride, 79-32-8; *tert*-butyl alcohol, 75-65-0; butylethylketene, 17139-73-0; dimethylketene, 598-26-5; ketene, 463-51-4.

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References and Notes

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(2) J. K. Crandall, W. H. Machleder, and S. A. Sojka, *J. Org. Chem.*, **38**, 1149 (1973), and references cited therein.

(3) F. G. Bordwell and A. C. Knipe, *J. Org. Chem.*, **35**, 2956 (1970), and references cited therein.

(4) R. N. Pratt and G. A. Taylor, *J. Chem. Soc. C*, 1653 (1968), and references cited therein.

(5) J. E. Leffler and R. G. Zepp, *J. Amer. Chem. Soc.*, **92**, 3713 (1970), and references cited therein.

(6) L. B. Gortler and M. D. Saltzman, *J. Org. Chem.*, **31**, 3821 (1966).

(7) W. Adam and R. Rucktaschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971).

(8) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963).

(9) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **36**, 2911 (1962).

(10) J. K. Stille and D. D. Whitehurst, *J. Amer. Chem. Soc.*, **86**, 4871 (1964).

(11) R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 6057 (1970).

(12) O. L. Chapman, P. W. Wojtkowski, W. Adam, O. Rodriguez, and R. Rucktaschel, *J. Amer. Chem. Soc.*, **94**, 1365 (1972).

(13) W. Adam, J. Liu, and O. Rodriguez, *J. Org. Chem.*, **38**, 2269 (1973).

(14) For a preliminary report, see J. K. Crandall and S. A. Sojka, *Tetrahedron Lett.*, 1641 (1972).

(15) M. S. Newman and A. Leegwater, *J. Org. Chem.*, **33**, 2144 (1968).

(16) For a similar rearrangement, see J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, **90**, 7347 (1968).

(17) W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **89**, 2230 (1967).

(18) H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p 49.

(19) W. Adam and J. Liu, *J. Amer. Chem. Soc.*, **94**, 2894 (1972).

(20) J. E. Baldwin and J. H. I. Cardellina, *Chem. Commun.*, 558 (1968); J. K. Crandall and W. W. Conover, *Tetrahedron Lett.*, 583 (1971).

(21) Cyclopropanones can be thermally decarbonylated: N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(22) R. W. Murray, *Accounts Chem. Res.*, **1**, 313 (1968).

(23) P. R. Jones and H. Taube, *J. Phys. Chem.*, **75**, 2991 (1971).

(24) The spontaneous reduction of carbonyl oxide intermediates in ozonolysis reactions to the corresponding carbonyl compound is an often observed, if not a well-understood process. It is particularly prevalent with α-ketocarbonyl oxides such as formed from acetylenes: W. B. DeMore and C.-L. Lin, *J. Org. Chem.*, **38**, 985 (1973).

(25) A. I. Scott, "Ultraviolet Spectra of Natural Products," Macmillan, New York, N. Y., 1964, pp 79–81.

(26) This sample was kindly provided by Eastman Chemical Products, Inc., Kingsport, Tenn.

(27) M. S. Newman and E. A. Zuech, *J. Org. Chem.*, **27**, 1436 (1962).

(28) An improved procedure for the preparation of diethyl *tert*-butylmalonate (the precursor of **30**) from diethyl isopropylidenemalonate and lithium dimethylcuprate is described in the Experimental Section.

(29) An analogous transformation has been observed in the reaction of pyridine *N*-oxide with a diarylketene: T. Koenig and T. Barklow, *Tetrahedron*, **25**, 4875 (1969).

(30) F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

(31) P. W. Mullen, "Modern Gas Analysis," Interscience, New York, N. Y., 1955, p 143.

(32) F. C. Whitmore, *et al.*, *J. Amer. Chem. Soc.*, **63**, 643 (1941).

(33) L. Smith and H. Hoehn, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 356.

(34) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

(35) S. Wideqvist, *Ark. Kemi*, **23B**, No. 4 (1946).