

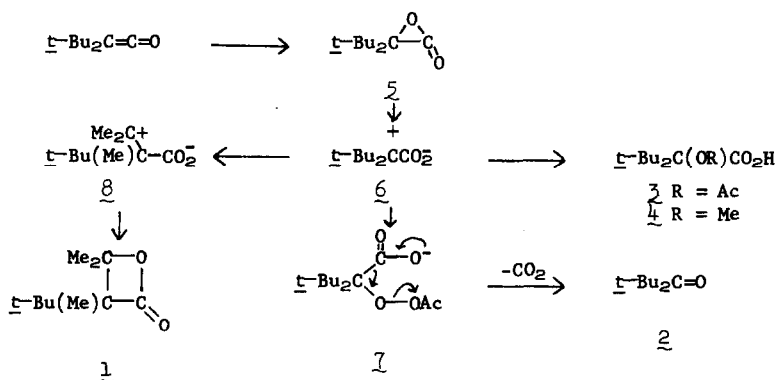
PERACID OXIDATION OF KETENES^{1a}
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α -Lactones have been implicated as reactive intermediates in several types of reactions: the solvolysis of α -halocarboxylate anions,² the decomposition of certain peresters,³ the interaction of ketenes, acid chlorides or anhydrides with pyridine N-oxides,⁴ and the reaction of methylene with CO₂.⁵ The speculation that such an intermediate was also involved in the reaction of peracids with ketenes,⁶ coupled with our interest in the epoxidation of cumulative double-bond systems,⁷ has prompted a detailed examination of this reaction. Recently, Wheland and Bartlett⁸ have found that ozone apparently serves as an oxygen-transfer reagent with ketenes at low temperatures leading to α -lactones as transient intermediates.

While the present studies have not resulted in the actual isolation of an α -lactone, firm evidence for their presence in the title reaction has been collected by the characterization of the subsequent chemistry of these reactive species. Thus, the reaction of 2 equiv of peracetic acid⁹ with hindered, unreactive di-*t*-butylketene gave a 33% yield of β -lactone 1,¹⁰ 22% of ketone 2 and 3% of α -acetoxyacid 3 in addition to polymeric material. A similar reaction in the presence of methanol gave 5% of α -methoxyacid 4 in addition to 3% 1 and 26% 2. Utilization of 1 equiv of *m*-chloroperbenzoic acid allowed for the demonstration of a 31% yield of CO₂ in addition to 31% 2 and 34% 1.

These results are best rationalized by postulating initial formation of α -lactone 5. Various reactions of this species, most likely via zwitterion 6, account for the observed products. Reaction of acetate with 6 gives 3, whereas in the presence of methanol 6 is preferentially converted to 4. Alternatively 6 can be attacked by excess peracid to give 2, possibly by the indicated fragmentation of intermediate 7. Methyl migration in 6 gives a new zwitterion 8 which can close to β -lactone 1.

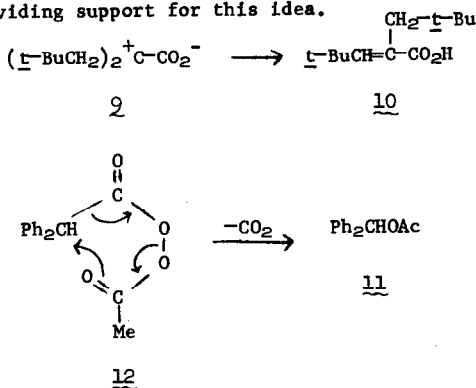


Since α -lactone 2 is the reactive species invoked by Wheland and Bartlett from the ozonolysis of di-t-butylketene, this scheme is subject to experimental verification. Firstly, we have conclusively established the structure assignment of 2 by a low-temperature ir experiment which showed a very intense 5.29μ carbonyl band as expected for 2.⁵ Reaction of 2 (prepared by ozonolysis in CH_2Cl_2) with excess peracetic acid gave a 9% yield of 1 and an 18% yield of 6. Warming the solution without peracid gave 35% of 1 and only 6% of 6.¹¹ In support of the suggested mechanism the amount of ketone 6 increased in the presence of peracid.

Reactions of other ketenes with peracids display similar chemistry. For example, the reaction of 2 equiv of peracetic acid with diisopentylketene gave a 4% yield of an α -acetoxyacid analogous to 3, whereas reaction with 2 equiv of m-chloroperbenzoic acid gave a 39% yield of α, β -unsaturated acid 10. In this case the corresponding zwitterion 9 can undergo 1,4-hydrogen transfer to yield 10. Interestingly, diisopentylketone was not a reaction product from this ketene. On the other hand, reaction of 1 equiv of peracetic acid with butylethylketene afforded a 19% yield of 3-heptanone and CO_2 as the only important volatile products.

Diphenylketene was converted by 1 equiv of peracetic acid to benzophenone and benzhydryl acetate (11) in a 20:80 ratio. The addition of methanol to this reaction led to the production of 3% of α -acetoxydiphenylacetic acid. Two competing processes appear to be important in this instance. The first leads to CO_2 and ketone in an analogous fashion to the ketenes discussed above. The second yields acetate 11 probably by spontaneous decomposition of diacyl peroxide 12 by the cyclic mechanism illustrated below. Compound 12 would be formed by normal nucleophilic addition of peracid to the ketene. Several attempts to prepare 12 by an independent

route led to 11 providing support for this idea.



In summation, the reasonably diverse chemical behavior of the intermediates formed in the oxidation of ketenes with peracids (namely oxidation to CO_2 and ketones, transformation to α -oxygenated or unsaturated acids, and formation of a rearranged β -lactone) matches the expected or demonstrated chemistry of α -lactones. Whether α -lactones are formed directly by the normal electrophilic attack of a peracid on a double-bond or by some more complicated mechanism is not clear at this time.

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- Supported by a research grant from the National Science Foundation.
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- It was demonstrated that under the glpc conditions β -lactone 1 pyrolyzed to 2,3,4,4-tetramethyl-2-pentene. Therefore the peak area of the latter was used as a measure of the amount of 1 present in the product.
- The mode of formation of the small amounts of 9 in this reaction is not clear. Loss of CO from 5 either spontaneously or induced by reaction with O_3 or O_2 is a possibility. However, the ketene does not give 9 by reaction with O_2 . Allowing 5 to react with excess ozone for a prolonged period at -78° appeared to increase the amount of 9.