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PERACID OXIDATION OF CYCLOPROPENONES[1a]

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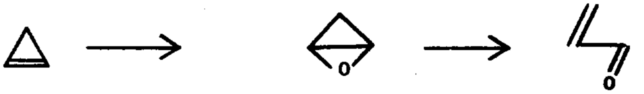
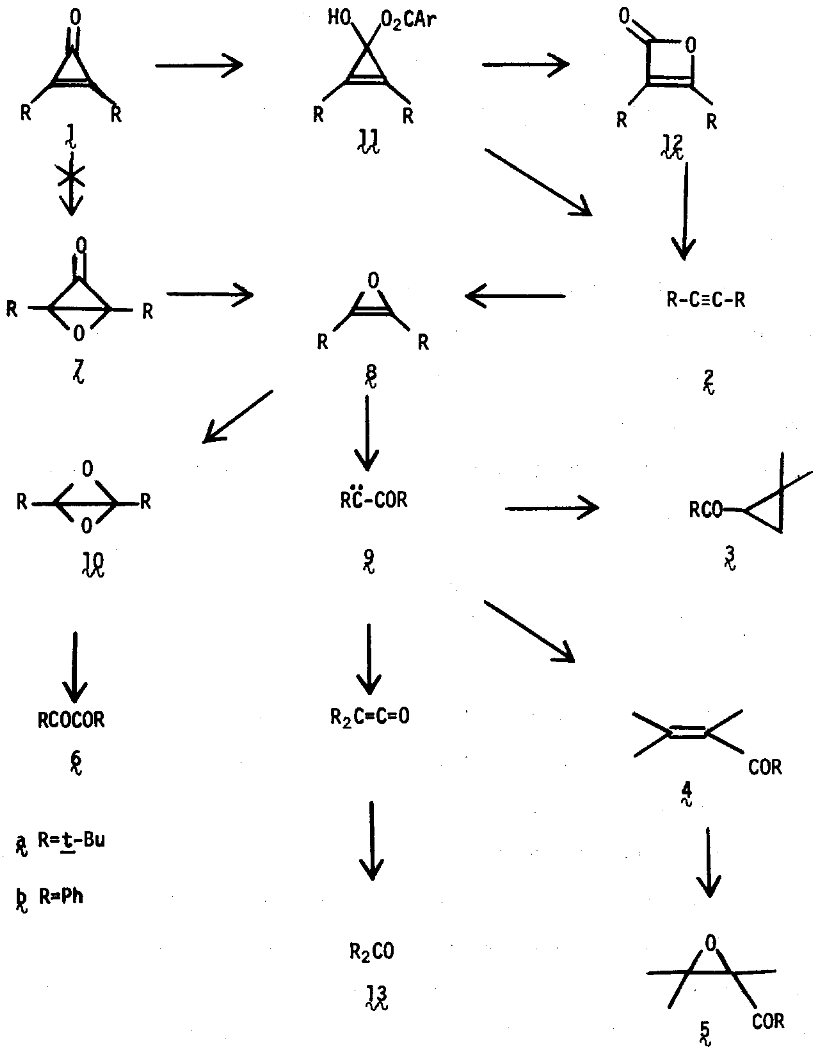
Recent reports describe peracid oxidation studies on cyclopropenes as a potential synthetic approach to an oxabicyclobutane derivative.[2] However, this heterocyclic system has not yet been obtained, apparently a result of its facile rearrangement to the isomeric conjugated carbonyl compound as indicated below. In the course of related work, we have examined the peracid oxidation of several cyclopropenones, a special class of electron-deficient cyclopropenes,[3] and in the present paper we report upon the novel transformation to acetylenes thus promoted.



Reaction of di-t-butylcyclopropenone (1a) with 5 equivalents of m-chloroperbenzoic acid in CH_2Cl_2 for 2 days resulted in the formation of di-t-butylacetylene (2a); ketones 3a, 4a and 5a; and dione 6a in the ratio of 1:2:5:90:2. The intermediacy of oxabicyclobutanone 7a was initially considered since this species could conceivably yield oxirene 8a by thermal[4] decarbonylation. A second route from 7a to 8a invokes the recently discovered "oxidative decarbonylation" which converts cyclopropanones to olefins with loss of the carbonyl group[5] as CO_2. Further tranformations of 8a, outlined in Chart I, account nicely for the observed ketonic products as recently discussed.[6] However, spontaneous decarbonylation of hypothetical intermediate 7a was contraindicated by the evolution of 88% of the theoretical amount of *carbon dioxide* during the course of the reaction. The oxidative pathway to the ketonic products via 8a is not categorically ruled out, but strong evidence against the intervention of 7a derives from its inability to rationalize the formation of di-t-butylacetylene *a demonstrated precursor of the other products* under epoxidation conditions.[6] This transfor-

Chart I



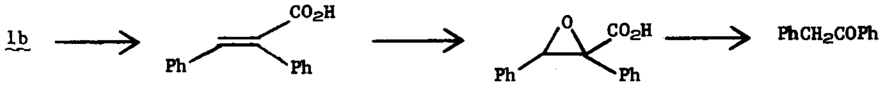
a R=t-Bu

b R=Ph

mation proceeds *via* oxirene 8a and subsequently generated intermediates 9a and 10a as outlined in Chart I. A more viable description of the oxidation of 1a invokes oxidative decarbonylation *of the cyclopropenone* as the initial phase of the reaction. Thus, addition of peracid to the carbonyl function of 1a gives adduct 11a which either collapses directly to CO_2 and the acetylene or proceeds through unstable β-lactone 12a which spontaneously decarboxylates.[7]

Similar peracid oxidation of diphenylcyclopropenone (1b) gave diphenylacetylene (2b), benzophenone (13b) and benzil (6b) in the ratio 40:10:50. Oxidation of 2b under these conditions gave 6b and 13b in accord with the literature.[8] These results fit into the same general pattern. Ketocarbene 9b apparently leads to benzophenone in this case, probably by peracid oxidation of its rearrangement product diphenylketene.[8a]

Comparison of these results with a report[9] describing the basic hydrogen peroxide oxidation of 1b prompted re-examination of the latter reaction which was reported to yield benzyl phenyl ketone (14) as the major product. Repetition of this reaction gave 2b, 13b and 6b in addition to 14, more in line with the anticipated similarity of the two oxidation reactions. The ratio of 2b:13b:6b:14 was 30:10:40:20. The observation of 14 only under the basic conditions suggested an alternative route to 14 from that originally proposed;[9] this entails base cleavage[10] of 1b to give acid 15 which leads to 14 by epoxidation and subsequent decarboxylation of glycidic acid 16 thus generated.[11] In fact, 1b was smoothly transformed to 15 under the reaction conditions minus hydrogen peroxide and resubmission of 15 to the original conditions readily effected the 15→14 conversion.



15 16 14

In conclusion, the oxidative decarboxylation reaction noted heretofore only for cyclopropanones is now extended to cyclopropenones. Similar transformations can probably be anticipated for other three-membered ring carbonyl compounds.

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   (b) Alfred P. Sloan Research Fellow 1968-70.
   (c) National Science Foundation Trainee 1969-70.

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