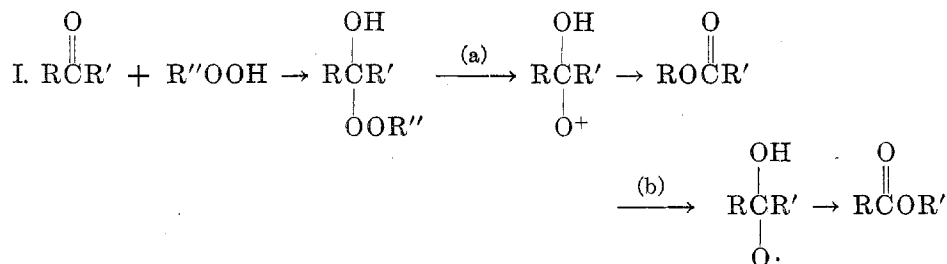


HYDROPEROXIDE OXIDATION OF α -DICARBONYL COMPOUNDSJOHN E. LEFFLER¹

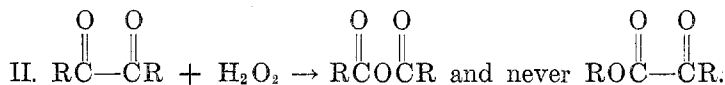
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The oxidation of simple ketones by hydrogen peroxide or by peroxy acids is generally believed to involve a preliminary addition of the peroxide to the carbonyl as in equation I (1-4). The next step is a decomposition of the compound thus formed into either (a) an oxygen cation or, possibly, (b) an oxygen radical, followed by migration of a group from carbon to oxygen.



Judging from experience with isolable peroxides either R or R' may migrate and the order of migration aptitudes in path (a) will usually be different from that in path (b) (5, 6).

The oxidation of α -dicarbonyl compounds might reasonably be expected to proceed by the same mechanism as that of simple ketones, but it will be seen that certain predictions of the mechanism are not realized. First of all, let it be noted that the product of oxidation of an α -dicarbonyl compound is *invariably* (or at least in all cases known to the author) the acid anhydride or solvolysis product thereof (Equation II) (8-11).



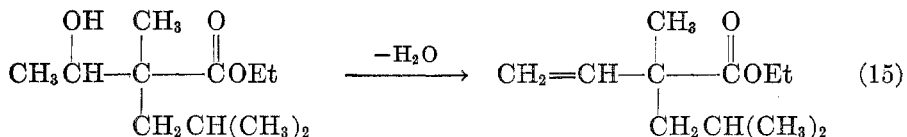
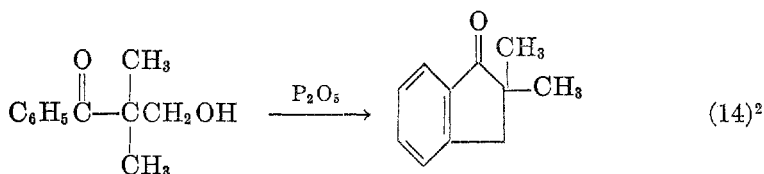
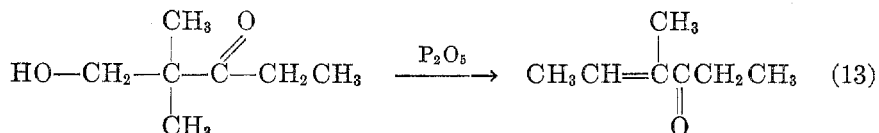
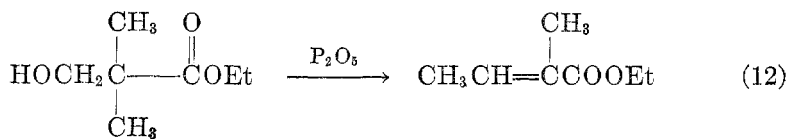
This is in contrast to the situation in the oxidation of the simple ketones, where a group R may migrate or not depending on the reaction conditions and the nature of the competing group R'. By operating in a polar solvent and in the presence of a strong acid it is possible to ensure, at least for hydroperoxides and some peroxy esters, that the decomposition of the peroxide goes by an ionic rather than a radical path (5-7). Under such conditions the diketones continue to give the same products. We may now say that the mechanism assumed above

requires the migration aptitude of the $\begin{array}{c} \text{O} \\ \parallel \\ \text{RC}- \end{array}$ group to be greater than that of any of the groups R even though R includes such groups of known high migration aptitude as anisyl and phenyl. In the ionic decomposition of hydroperoxides the

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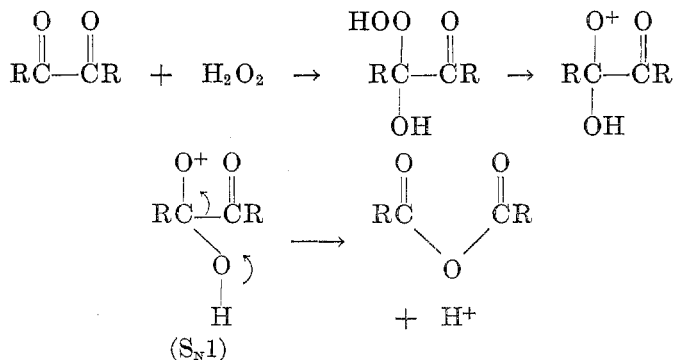
migration aptitude of the various groups parallels that found in carbonium ion rearrangements (4-6). On the other hand, it will be seen from the examples

below that the group $\text{RC}=\text{O}$ has very little tendency to migrate in carbonium ions, its migration aptitude apparently being less than that of CH_3 .



In view of the unsatisfactory state of affairs as described above it seems desirable to modify the theory of ketone oxidation for the special case of α -dicar-

bonyl compounds in such a way as to dispense with the migration of $\text{RC}=\text{O}$ to cationic oxygen. Such a mechanism might be



² Blaise and Herman, *Ann. Chim.*, [8] **23**, 527 (1911), probably obtained the same compound although they considered it to be the at that time unknown 1-benzoyl-1-methylcyclopropane.

The oxidations of benzoyldiphenylcarbinol and its methyl ether to benzophenone and benzoic acid were studied in the hope of throwing further light on the general problem of ketone oxidation. Since the ether was readily cleaved to the carbinol under the conditions used and since the carbinol could be attacked either at the hydroxyl or at the carbonyl group, the result is of no theoretical significance.

EXPERIMENTAL

A solution of 1.02 g. of benzil, 1 cc. of 70% HClO_4 , and 1 cc. of 95% H_2O_2 in 25 cc. of acetic acid was refluxed for 15 minutes, becoming almost colorless in the first five minutes. The solution on dilution to ca. 100 cc. with H_2O and extraction with CHCl_3 gave 0.97 g. of $\text{C}_6\text{H}_5\text{COOH}$, m.p. 119–121°. Under these conditions benzoic anhydride is hydrolyzed to benzoic acid.

A solution of 1.0 g. of benzil in 10 cc. of benzene was let stand with 10 cc. of 95% H_2O_2 for one week at the end of which time the color of benzil had been discharged. The benzene layer, washed with NaHCO_3 , dried over MgSO_4 , and evaporated to dryness, gave an oil (0.7 g.) which on saponification gave 0.6 g. of benzoic acid, m.p. 120–122°.

A solution of 0.74 g. of anisil and 0.5 cc. of 95% H_2O_2 in 20 cc. of acetic acid, refluxed for 5.5 hours, diluted with water, and worked up in the usual way gave 0.55 g. of anisic acid and a small amount of unchanged anisil. A solution of 1.01 g. of anisil, 0.16 g. of 95% H_2O_2 , and 1 cc. of 70% HClO_4 in 25 cc. of acetic acid was allowed to stand at room temperature for 17 hours. The black solution, diluted with water and worked up in the usual way gave 0.23 g. of anisic acid and 0.29 g. of crude anisil.

A solution of 1.4 g. of benzoyldiphenylcarbinol, 0.2 g. of 90% H_2O_2 , and 0.1 cc. of 70% HClO_4 in 15 cc. of acetic acid was refluxed for 80 min., diluted with water, and extracted with CH_2Cl_2 . The extract contained 0.41 g. of benzoic acid and 0.6 g. of benzophenone. A similar experiment with benzoyldiphenylcarbinol methyl ether gave a small amount of benzoic acid and benzophenone. Under milder conditions (room temperature for 50 hours), 0.48 g. of the ether gave 0.06 g. of the starting material; a small amount of the acetate of the carbinol, m.p. 143–145°, cleaved to benzoic acid and benzhydrol by aqueous alcoholic alkali; and 0.26 g. of the free carbinol.

SUMMARY

A cyclic mechanism is proposed for the oxidation of α -dicarbonyl compounds. This mechanism avoids the necessity of assigning a high migration aptitude to the acyl group.

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