Photodecarboxylation of Dicarboxylic Acids in the Presence of Iron(III) Chloride

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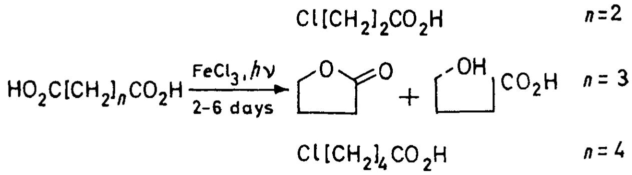
Summary The photo-oxidative decarboxylation of succinic, glutaric, and adipic acids with $FeCl_3$ yields as principal products, β-chloropropionic acid γ-butyrolactone, and δ-chlorovaleric acid, respectively.

THE photochemical reactions of various dicarboxylic acids in the presence of iron(III) chloride generally proceed by decarboxylation followed by hydrogen abstraction;[1,2] for example, tartaric acid gives CO_2[1] and formic acid, and citric acid gives CO_2 and acetone.[3] We now report that the photo-oxidative decarboxylation of the unsubstituted dicarboxylic acids, succinic, glutaric, and adipic, results in halogenation and hydroxylation to give β-chloropropionic acid, γ-butyrolactone, and δ-chlorovaleric acid, respectively.

The photochemical reactions were carried out with 0·02 M-solutions of $FeCl_3$ and dicarboxylic acid in open Pyrex tubes and irradiated in a Rayonet Photochemical Reactor† at 350 nm at 38° for 2—6 days. All products were purified by distillation or by preparative g.l.c. of their methyl esters.

The photolysis of succinic acid gave as principal products β-chloropropionic acid (78%, calculated with $FeCl_3$ as limiting agent), CO_2, and starting material. The isolated β-chloropropionic acid was identified by its i.r., ^1H n.m.r., and mass spectra which were identical to those of a known sample. Similarly, the photolysis of adipic acid yielded δ-chlorovaleric acid (70%) and CO_2. Unlike its 4-and 6-membered analogues, the photo-oxidation of glutaric acid with equimolar $FeCl_3$ produced only γ-butyrolactone, admixed with its corresponding hydroxy-acid (total yield 80%), CO_2, and starting material.



While a detailed mechanism has not yet been established, there is no doubt that these reactions are photolytic and that Fe^{3+} is the oxidant, since no reaction occurred in the dark or in the absence of Fe^{3+}. Also, the presence of

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oxygen did not alter either the nature or the yield of the products.

Irradiation of 3-hydroxypropionic acid with an equimolar amount of $FeCl_3$ did not produce the corresponding 3-chloro-derivative, indicating that 3-hydroxypropionic acid is not an intermediate in the photodecarboxylation of succinic acid. γ-Chlorobutyric acid was shown by experiment not to be an intermediate in the reaction.

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