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Reactions of sodium hypochlorite with some compounds having reactive methylene groups

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Summary Alkaline sodium hypochlorite solution oxidises a number of compounds having reactive methylene groups to the corresponding gem diols, but in some cases only decarboxylation occurs at room temperature.

During investigations into the use of sodium hypochlorite as a halogenating reagent in organic chemistry, the reaction between this compound and malonic acid was studied. In acidic solution, low yields of chloro- and dichloroacetic acids, and chloro- and dichloromalonic acids were obtained. In alkaline solution, the product, in 22% yield, was 2,2-dihydroxypropan-1,3-dioic acid, disodium salt (sodium mesoxalate). Previous syntheses of this compound had either been via diethyl 2-oxopropan-1,3-dioate¹; or 2,2dibromopropandioate².

It seems possible that the reaction producing the sodium mesoxalate is as follows:

$$CH_{2}(CO_{2}Na)_{2} \xrightarrow{NaOCl} Cl_{2}C(CO_{2}Na)_{2}$$

$$25^{\circ} \downarrow OH^{-}$$

$$(HO)_{2}C(CO_{2}Na)_{2}$$

We were able to show by gas chromatography that small amounts of dichloromalonate were present in the reaction mixture. Also, synthesis of sodium dichloromalonate² and reaction of the latter with sodium hydroxide yielded sodium mesoxalate.

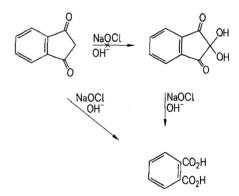
In an attempt to determine the scope of the reaction, we also carried out the following reactions:

$$CH_{3}COCH_{2}COCH_{3} \xrightarrow{OCl^{-}} CH_{3}COC(OH)_{2}COCH_{3}$$
$$HOOCCH_{2}COCH_{2}CO_{2}H \xrightarrow{OCl^{-}} CH_{3}COCH_{3}$$

HOOCCOCH₂CO₂H
$$\xrightarrow{\text{OCl}^-}$$
 CH₃COCO₂H

3,3-dihydroxypentan-2,4-dione for reference purposes was synthesised by the method of Calvin and Wood³,

We were hopeful that indan-1,3-dione could be converted to 2,2-dihydroxyindan-1,3-dione (ninhydrin) with alkaline hypochlorite. In the event we obtained an almost quantitative yield of phthalic acid. We found, however, that ninhydrin was also converted almost quantitatively to phthalic acid with alkaline hypochlorite:



All products have been characterized by comparison of melting points and spectra (UV, IR and NMR) with those obtained from authentic material.

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A possible biomimetic synthesis of fluoroacetic acid

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Summary. We propose that fluoroacetate may be formed in plants by fluorodecarboxylation of malonic acid.

Fluoroacetate and a number of related organofluorine compounds are biosynthesised in plants either naturally¹ or as the result of fluoride pollution². Fluorination of organic molecules generally takes place under fairly drastic conditions in the laboratory, and the fluorinating agent is nor-

mally hydrogen fluoride or some other inorganic fluoride, or elemental fluorine³. Since these conditions are not likely to obtain in a living plant cell, the precise method by which fluorine is introduced into organofluorine compounds in plants has so far remained unknown. A number of specula-