

LETTERS TO THE EDITOR.

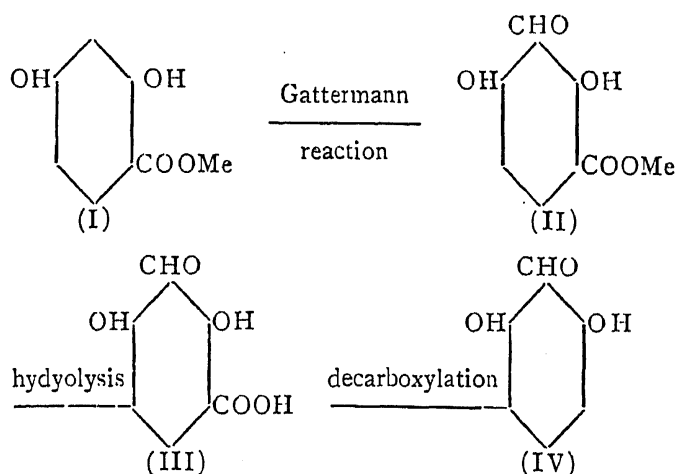
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A Synthesis of γ -Resorcyaldehyde.

METHYL β -resorcyate (I) does not undergo the Gattermann reaction under the usual conditions. It is found, however, that under special conditions, *viz.*, in the presence of anhydrous aluminium chloride dissolved in dry ether¹ the reaction proceeds very smoothly and a high yield of the aldehyde-ester (II) is obtained. The aldehyde group is found unexpectedly to enter exclusively the usually inaccessible γ -position in the resorcinol nucleus. This welcome observation has made possible a simple synthesis of γ -resorcyaldehyde, which has been synthesised in the following manner:—

Methyl 2 : 4-dihydroxy-3-aldehyde-benzoate (II), the product of the Gattermann reaction on methyl β -resorcyate (I) was hydrolysed almost quantitatively under properly regulated conditions by cold dilute alkali (48 hrs.) to the free acid (III). The acid (III) on decarboxylation by heating with water in a sealed tube at 100–110° gave γ -resorcyaldehyde (IV), m.p. 155–156° in a fair yield (30%).



γ -resorcyaldehyde has been very recently synthesised by a different method from 2-acetyl resorcinol through a number of stages.²

The constitution of the aldehyde ester (II) was conclusively established by Clemmensen-reduction followed by partial methylation, when known methyl 2-hydroxy-3-methyl-4-methoxy benzoate of proved constitution³ was obtained. A number of derivatives and related compounds have also been prepared

A detailed account of this investigation will shortly be published elsewhere.

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¹ Shah, *Curr. Sci.*, 1934, 157.

² Limaye, *Rasayanam*, 1936, 1, 13.

³ Cf. Jones and Robertson, *J.*, 1932, 1689.

Action of Thionyl Chloride on Esters of Salicylic Acid in the Presence of Catalysers.

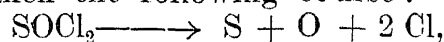
COPPER or its chlorides work as catalysers for the interaction between sulphur mono- or di-chloride and esters of salicylic acid but fail to behave similarly when thionyl chloride is used. In the latter case they (*i.e.*, copper or its chlorides) are required in molecular proportions. These reactions were studied by Hirve, Jadhav and Chakradeo¹ and products of the type $(C_6H_3OH.COOR)_2S$ were obtained, where R represents CH_3 , C_2H_5 , etc. The explanation given by these authors was that thionyl chloride was first converted into sulphur monochloride, sulphur dichloride and sulphur dioxide, copper also taking part in the reaction. The former two then reacted with the esters of salicylic acid as mentioned in the beginning.

In search of catalysers for the interaction between thionyl chloride and esters of salicylic acid, almost all the metals or their chlorides were tried. Out of them zinc dust, iron dust and the chlorides of zinc, iron, tin, bismuth and antimony work satisfactorily, 0.1 to 0.2 g. being sufficient.

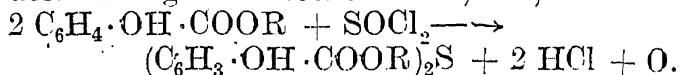
The most suitable proportion for the reaction was found to be two molecules of thionyl chloride to two molecules of the ester, though it was found that out of the two molecules of thionyl chloride, only one was actually used up, the second one being swept away by the hydrochloric acid gas evolved.

The reaction took place with copious evolution of hydrochloric acid gas and was over within about six hours at room temperature. The resulting products were identical with the thioethers obtained by Hirve, Jadhav and Chakradeo. In no case did any sulphur precipitate.

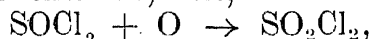
As only one molecule of thionyl chloride is required in the reaction for every two molecules of the ester and as hydrochloric acid gas is evolved, the reaction seems to have taken the following course:



the two chlorine atoms going with the two hydrogen atoms from the two benzene rings, the sulphur atom taking the place of these two hydrogen atoms and the oxygen atom being liberated as such, *i.e.*,



The oxygen atom was searched for in the form of oxygen gas or in the form of sulphur chloride, *i.e.*,



but it could not be detected in any of these forms. Hence it is possible that it is used up in oxidising the organic substances whereby the yields were always found to be not more than 73 per cent.

The above explanation amounts to the same thing as saying that the catalysers act as double catalysers; firstly they convert thionyl chloride into sulphur dichloride and oxygen, and then bring about the condensation between sulphur dichloride and the esters of salicylic acid. The action of sulphur dichloride on the methyl, ethyl and phenyl esters of salicylic acid as well as free salicylic acid was tried in the presence of these very catalysers and the same products were obtained also with evolution of hydrochloric acid. This proves the correctness of the view mentioned in the beginning of this paragraph.

Free salicylic acid does not react with thionyl chloride in the same way as with sulphur dichloride, perhaps because thionyl chloride exerts a dehydrating action on the hydroxy and carboxylic groups which are in ortho position to each other. For this reason the carboxylic group requires to be protected by esterification. As no dehydrating action is exerted by sulphur dichloride, such a protection becomes unnecessary in its case.

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¹ *J. Univ. Bomb.*, 1933, 128; *J. Ind. Chem. Soc.*, 1934, 551; and *J. Am. Chem. Soc.*, 1935, 101.