GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS.

Part II.* *Cis* To *Trans*.

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IN discussing the mechanism of geometrical inversion in the acids derived from the coumarins (Seshadri, 1934) it was pointed out that *cis* to *trans* inversion takes place in an alkaline medium in which coumarins first form alkali salts of coumarinic acids and that addition of some addenda at the double bond is a requisite preliminary to the final inversion to the coumaric acids. In that connection mention was made that the results of the action of mercury compounds on coumarins (Sen and Chakravarti, 1929 and 1930) could be explained as due to the influence of substituent groups present in the benzene or pyrone ring. With a group of coumarins as exemplified by 6-nitro- and 6 : 8-dibromocoumarins they obtained coumaric acids whereas with others which contained alkyl and hydroxyl groups they obtained mercurated compounds.

According to the above-mentioned mechanism coumarin itself should give rise to coumaric acid or mercurated coumaric acid. By the action of sodium hydroxide and mercuric acetate in the cold Sen and Chakravarti (*loc. cit.*) reported the isolation of a diacetoxy-mercuri-coumaric acid where as Naik and Patel (1934), using apparently the same method, claimed to have obtained 6 : 8-bisacetoxy-mercuri-coumarin. By boiling, however, an alkaline solution of coumarin with mercuric oxide, the former authors stated, that they obtained mercurated coumarins. The reaction of alkali and mercuric acetate has now been investigated by us following Sen and Chakravarti's procedure and the product is found to be as they claimed a mercurated coumaric acid and not a mercurated coumarin (*cf.* Naik and Patel). By the mercuric oxide method of the same authors was obtained a compound which they believed to be 6-chloromercuri-coumarin and which is now found to be also a mercurated coumaric acid. It dissolves in aqueous sodium carbonate and bicarbonate and yields coumaric acid readily when hydrogen

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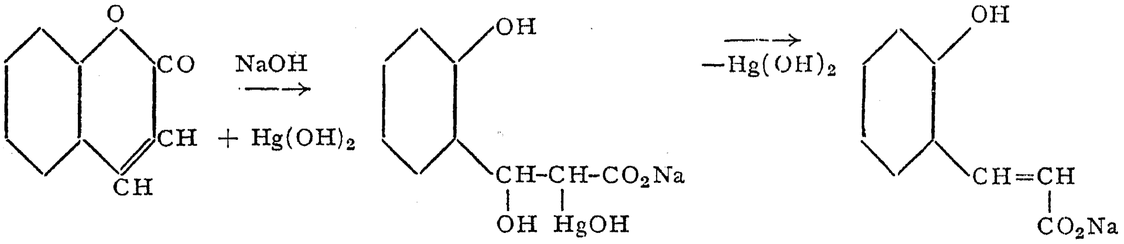
sulphide is passed into an alkaline solution of the compound in order to precipitate the mercury and subsequently the filtered solution is acidified. In the presence of cold caustic alkali and yellow mercuric oxide coumarin undergoes transformation into coumaric acid so easily that this inversion could not have failed to take place under the conditions mentioned above. Based upon this observation a very rapid and cheap method has been worked out for the preparation of pure coumaric acid from coumarin. 7-methylcoumarin behaves similarly and gives rise to a good yield of 4-methylcoumaric acid whereas 6-nitrocoumarin is unaffected in the cold even after treatment for several hours. Only the unstable nitro-coumarinic acid is produced which rapidly reverts to the nitrocoumarin. But at the boiling point the inversion takes place fairly easily giving rise to a good yield of 5-nitrocoumaric acid. Under these vigorous conditions coumarin and methylcoumarin undergo mercuration besides inversion and so produce mercurated coumaric acids.

The part played by mercuric oxide in effecting the inversion may be represented as below:



It adds on to the double bond in the *cis* stage and after the required rotation of the groups has taken place gets eliminated from the *trans* stage. In support of this may be mentioned (1) observations in which *cis* compounds add on mercury compounds readily whereas the corresponding *trans* compounds do not react or do so only slowly under the same conditions (Biilmann, 1912; Wright, 1935) and (2) the easy decomposition in the presence of alkali of addition compounds like methoxymelilotic acid and sodium dihydrocoumaric acid-β-sulphonate to give coumaric acid. The greater difficulty with which *trans* inversion takes place with 6-nitrocoumarin by the present method agrees with previous experience using other methods (Dey and Row, 1924; Dey, Rao and Seshadri, 1934). This may be attributed to the nature of the nitrogroup as an electron sink which diminishes the tendency to undergo inversion.

Experimental.

Preparation of O-coumaric acid.—Finely powdered coumarin (8 g.) was treated with cold aqueous caustic soda (8 g. in 100 c.c.), yellow mercuric oxide (1 g.) added and the mixture shaken vigorously for ten minutes. Coumarin dissolved rapidly and the solution assumed a light yellow colour with a green fluorescence. It was then filtered through an ordinary filter without suction, the residue washed twice with small quantities of water and the collected filtrate acidified with concentrated hydrochloric acid. The colourless crystalline precipitate that was obtained was filtered at the pump and washed with small quantities of water. The yield was almost theoretical and the acid was pure melting at 208–10° (decomp.). When tested by passing hydrogen sulphide into an alkaline solution of the acid it gave no precipitate of mercuric sulphide thereby showing that it was free from mercury. Care should be taken that no rise of temperature takes place as otherwise some mercuration is effected.

4-*Methylcoumaric acid* was prepared from 7-Methylcoumarin (5 g.) by closely following the above procedure. The yield of the pure acid melting at 195–6° was 5 grams.

5-*Nitrocoumaric acid* could not be obtained by treatment in the cold as above. Only the unstable coumarinic acid was formed which reverted rapidly into the original nitrocoumarin. It was therefore made by following the method of Sen and Chakravarti (1930). The following modification of their method was found to give better yields. After boiling 6-nitrocoumarin in alkaline solution with mercuric oxide the crude nitrocoumaric acid was precipitated with hydrochloric acid and then purified by treatment with sodium bicarbonate instead of ammonia and by subsequent precipitation of the pure acid. This minimised contamination with unchanged nitrocoumarin which dissolved to a considerable extent in ammonia and only sparingly in sodium bicarbonate. Yield of the pure acid after crystallisation from alcohol was 4·5 grams from 5 grams of the nitrocoumarin.

Action of sodium hydroxide and mercuric acetate on coumarin.—By following the procedure of Sen and Chakravarti a compound (diacetoxymercuri-coumaric acid) was obtained which exhibited all the properties and reactions mentioned by them. It dissolved easily in cold aqueous sodium carbonate and bicarbonate and was therefore a diacetoxymercuri-coumaric acid and not a coumarin.

For obtaining pure coumaric acid from it the method of Sen and Chakravarti—boiling with dilute hydrochloric acid—was not found to be suitable. Removal of mercury was not always complete so that the product frequently melted low. A convenient method is to dissolve the mercurated compound in dilute ammonia and pass hydrogen sulphide till the precipitation of mercury sulphide is complete. It is then filtered and the clear filtrate acidified with hydrochloric acid. The crystalline precipitate melts with decomposition at 208-210° when filtered and washed with water and is found to be pure coumaric acid.

Action of hot sodium hydroxide and mercuric oxide on coumarin.—The product that was considered by Sen and Chakravarti to be 6-chloromercuricoumarin was prepared by their method (1929, p. 851). It was a colourless partly crystalline powder melting with decomposition at about 180° and was found to be soluble in aqueous sodium carbonate and sodium bicarbonate with evolution of carbon dioxide. Pure coumaric acid was obtained easily from it by the hydrogen sulphide method described above. It was therefore a mercurated coumaric acid and not a coumarin. It should be mentioned that these mercuration products underwent marked change when preserved over long periods and their solubility in aqueous sodium carbonate diminished.

Summary.

A rapid and efficient method has been found for preparing coumaric acid and 4-methylcoumaric acid from coumarin and 7-methylcoumarin respectively by treatment with mercuric oxide in the presence of cold alkali. 5-nitrocoumaric acid is not produced in the cold and is formed only by boiling the mixture of 6 nitrocoumarin, mercuric oxide and alkali. The action of cold alkali and mercuric acetate or of hot alkali and mercuric oxide on coumarin yields mercurated coumaric acids. From these pure coumaric acid can be produced by using ammonia and hydrogen sulphide.

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