

REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED α - β UNSATURATED CARBONYL COMPOUNDS.

Part IV. Action of Bromine on Coumaric Acids.

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IN connection with the elucidation of the constitution of certain mercury compounds derived from the coumarins,¹ the tribromo derivatives of coumarin and 7-methylcoumarin were required. There existed some difficulty in preparing them, since coumarin requires to be brominated in a sealed tube at about 150°² and since under the same conditions 7-methylcoumarin yields complex products. The action of bromine on coumaric acid was expected to solve this difficulty and as the preparation of the coumaric acids from the coumarins has been rendered simple by recent work in these laboratories, the method described in this paper should make the brominated coumarins readily available.

Simonis and Wenzel³ treated coumaric acid with two molecular proportions of bromine in carbon disulphide solution and noticed that besides addition at the double bond, substitution in the ring in a position *para* to the hydroxyl group took place. The bromocoumaric acid dibromide thereby formed closed up the ring with the elimination of water and at the same time the unstable dibromide lost one molecule of hydrogen bromide to produce 3 : 6-dibromocoumarin.

In the experiments described in this paper, coumaric, 5-nitrocoumaric and 4-methylcoumaric acids have been treated with excess of bromine in boiling glacial acetic acid solution for 1 to 2 hours. The primary products of the reaction are found to be the dibromides of the coumarins with further bromine atoms, in the 6- and 8-positions if they are available for substitution. No free carboxylic acid is detected, complete conversion into the coumarins having taken place. This is obviously due to the addition of bromine at the double bond, thus facilitating the rotation of groups to enable ring closure.

The dibromides of the bromocoumarins undergo partial decomposition even during the preparation and the subsequent crystallisation and the brominated coumarins can be isolated pure by repeated crystallisations

alone. However, the readiest method is to treat the dibromides with cold alcoholic potash, when potassium bromide separates rapidly and the corresponding bromocoumarins are formed. Though the main products are 3:6:8-trisubstituted compounds, small quantities of partially brominated compounds are also isolated by working up the mother liquors. Thus coumaric acid yields 3:6:8-tribromocoumarin as the main product and 3:6-dibromo and 3-bromocoumarins as minor products. 5-nitrocoumaric acid gives as the main product 3:8-dibromo-6-nitrocoumarin and as byproduct 3-bromo-6-nitrocoumarin in a small yield. 4-methylcoumaric acid readily produces a good yield of 3:6:8-tribromo-7-methylcoumarin which is found to be the same as the one obtained from the mercury compound of 7-methylcoumarin.¹

For purposes of comparison the action of bromine on 6-nitrocoumarin⁴ has been reinvestigated and it has now been found that the initial product is 6-nitro-8-bromocoumarin dibromide which slowly decomposes during the process of heating and the subsequent repeated crystallisations to yield the required 3:8-dibromo-6-nitrocoumarin. Purification by repeated recrystallisations is rather tedious, since the decomposition of this dibromide is slow. With cold alcoholic potash, however, removal of the hydrogen bromide takes place very easily and hence the pure 3:8-dibromo derivative is obtained readily.

Experimental.

Action of bromine on coumaric acid. Preparation of 3:6:8-tribromocoumarin.—Coumaric acid (2 g.) was dissolved in boiling glacial acetic acid (15 c.c.) and a little over three molecular proportions of bromine (2.5 c.c.) dissolved in the same solvent (10 c.c.) was added. The mixture was boiled gently under reflux using a water condenser. There was a rapid absorption of bromine and a copious evolution of hydrogen bromide. The reaction was almost complete within an hour. The yield, however, increased by 0.5 g. on continuing the boiling for one hour more and further heating did not produce any improvement. When the solution was cooled at the end of the heating a pale brown solid separated out (3.5 g.). It was insoluble in aqueous sodium bicarbonate indicating that it was not an acid. It melted rather indefinitely between 180–93° C. After two crystallisations from glacial acetic acid using animal charcoal, it was obtained in the form of colourless thin needles melting at 199–200° C. (Found: Br, 63.0; $C_9H_3O_2Br_3$ required Br, 62.6%.) The melting point was unaffected when it was mixed with a sample of tribromocoumarin obtained by the method of Simonis and Wenzel.²

The crude product of bromination (2 g.) was suspended in ethyl alcohol (6 c.c.) and treated with alcoholic potash (1 g. in 4 c.c. of alcohol). The

suspension went into solution rapidly and potassium bromide separated out. After shaking for a few minutes the mixture was allowed to stand for about an hour with occasional agitation. It was then diluted with water and acidified. The colourless solid that separated out was rendered quite pure by one crystallisation from alcohol or acetic acid and was found to be identical with 3:6:8-tribromocoumarin. It was therefore, clear that the crude product contained considerable amount of dibromides which decomposed in cold alcoholic potash or in boiling acetic acid.

The mother liquor left after the separation of the above-mentioned pale-brown solid was diluted with water. This time a more deeply coloured solid was obtained. When this was treated with cold alcoholic potash as mentioned above potassium bromide separated out and the final product was a colourless solid from which by fractional crystallisation using alcohol small quantities of 3:6-dibromocoumarin melting at 183° C. and 3-bromocoumarin melting at 110° C. were isolated. If the treatment with alcoholic potash were omitted a rather prolonged series of crystallisations from alcohol using animal charcoal were necessary to obtain the compounds in a pure condition.

Treatment of coumaric acid with a large excess of bromine for about four hours did not appreciably increase the yield of the main product and in this case there was some complex decomposition and the lower bromination compounds could not be obtained.

On 5-nitrocoumaric acid. Preparation of 3:8-dibromo-6-nitrocoumarin.—In the methods described till now⁵ for the preparation of 5-nitrocoumaric acid, red oxide of mercury was employed. It has now been found that by using the yellow oxide the yield is appreciably improved.

5-Nitrocoumaric acid (2 g.) was dissolved in sufficient quantity of boiling glacial acetic acid, a little over two molecular proportions of bromine added and the whole boiled for 2 hours. On cooling the solution, no solid separated out owing to the large volume of the solvent used. To the hot solution therefore water was added till it became cloudy and on cooling this time about 3 g. of a brown solid was formed. When subjected to the treatment with cold alcoholic potash as already described it gave a pale yellow solid, which after crystallisation from glacial acetic acid, melted at 218–19° C. and was found to be identical with 3:8-dibromo-6-nitrocoumarin obtained by the method of Dey and Row.⁴ (Found: Br, 45.0; $C_9H_3O_4NBr_2$ required Br, 45.8 %.) The dibromo-nitrocoumarin could also be obtained from the crude product by repeated recrystallisations from glacial acetic acid using animal charcoal.

From the mother liquor after the isolation of the crude bromo-nitrocoumarin dibromide a somewhat resinous solid was obtained on adding water. On treatment with alcoholic potash it yielded a small amount of 3-bromo-6-nitrocoumarin melting at 215° C. after repeated crystallisations from acetic acid.

On 6-nitrocoumarin.—The procedure of Dey and Row⁴ was adopted and the product was found to contain a considerable amount of the dibromide which decomposed during crystallisations comparatively slowly. A large number of recrystallisations from boiling glacial acetic acid (about 6) were therefore necessary to get a pure sample of 3:8-dibromo-6-nitrocoumarin melting at 218–19° C. This was, however, readily obtained from the crude material by the treatment with cold alcoholic potash for one hour and subsequent acidification after dilution with water. It crystallised from glacial acetic acid as prisms melting at 218–19° C. and was found to be identical with the specimen obtained from nitrocoumaric acid. By working up the mother liquor 3-bromo-6-nitrocoumarin melting at 215° C. was obtained in a small yield.

On 4-methylcoumaric acid. Preparation of 3:6:8-tribromo-7-methylcoumarin.—This acid (2 g.) in glacial acetic acid (15 c.c.) was treated with bromine (2.5 c.c.) in the same solvent (10 c.c.) and boiled for 2 hours. The crude product (yield 4 g.) readily gave 3:6:8-tribromo-7-methylcoumarin on treatment with cold alcoholic potash and this was found to be identical with the sample obtained from 7-methylcoumarin through mercuration and subsequent treatment with bromine.¹ It could not be obtained by the method of Simonis and Wenzel in which the methyl coumarin was treated in a sealed tube with bromine and water using a little iodine as a catalyst. Several experiments using temperatures between 120° and 150° C. yielded only indefinitely melting mixtures from which the tribromo derivative could not be isolated.

The pure tribromo-methylcoumarin which was easily obtained from the methylcoumaric acid crystallised from glacial acetic acid as colourless long narrow plates melting at 207–8° C. (Found: Br, 60.6; $C_{10}H_5O_2Br_3$ required Br, 60.4 %.) The coumarilic acid obtained by treatment with hot alcoholic potash crystallised from glacial acetic acid in the form of flat needles and melted at 270° C.

Summary.

By the action of bromine on coumaric, 4-methylcoumaric and 5-nitrocoumaric acids in boiling glacial acetic acid solution 3:6:8-tribromocoumarin, 3:6:8-tribromo-7-methylcoumarin and 3:8-dibromo-6-nitrocoumarin have been obtained in good yield. The primary products are the

dibromides of the bromo-compounds produced by the addition at the double bond, subsequent substitution in the nucleus and final ring closure. Hydrogen bromide gets slowly removed during the boiling and during the subsequent crystallisations so as to yield the above-mentioned bromo-coumarins. The best method for this however is to use cold alcoholic potash. Small quantities of the lower bromination products are also produced as by-products.

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