

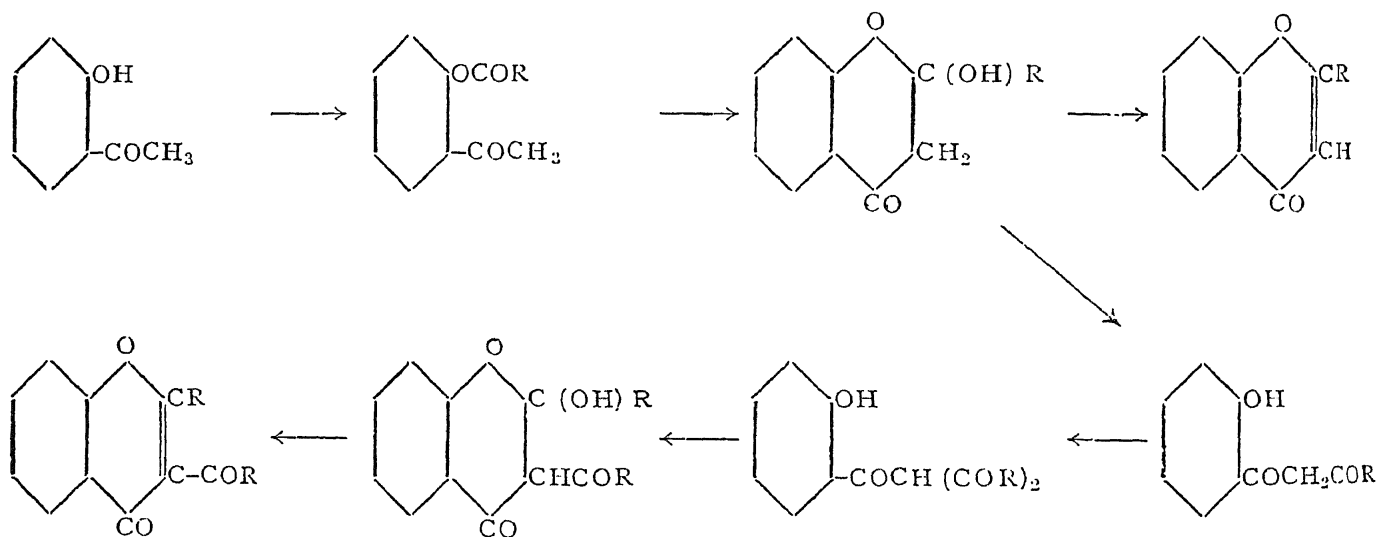
## 3-BENZOYL-7-HYDROXYFLAVONE

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THE formation of 3-acetylchromones when an *ortho*-hydroxy-acetophenone is heated with acetic anhydride and sodium acetate is of common occurrence and several 3-acetyl derivatives have been isolated and described.<sup>1</sup> The corresponding series of 3-benzoylflavones when Allan and Robinson's method is employed is not so well known probably due to the ease with which the 3-benzoyl group gets eliminated during the treatment with alkali. Starting from res-diacetophenone Algar *et al*<sup>2</sup> obtained 3 : 3'-dibenzoyl-diflavone. During the course of a detailed study of the mechanism of 3-acylation Baker<sup>3</sup> obtained a mixture of 7-benzoyloxyflavone and 7-benzoyloxy-3-benzoylflavone by heating resacetophenone with sodium benzoate and benzoic anhydride. He postulated the following general mechanism for such reactions.



Employing 2 : 6-dihydroxyacetophenone Sugasawa<sup>4</sup> was able to isolate 3-benzoyl-5-hydroxyflavone and he expressed the opinion that a higher temperature than the one ordinarily employed for the condensation is essential for effecting 3-benzoylation.

While repeating the preparation of 7-hydroxyflavone by the procedure adopted by Robinson and Venkataraman<sup>5</sup> it was frequently found by us that

the product after hydrolysis was very sparingly soluble in alcohol and acetic acid from which 7-hydroxyflavone can be conveniently crystallised. By careful fractionation it could be easily separated into two components, the more soluble one being 7-hydroxyflavone. The less soluble fraction which could be crystallised from pyridine melted at 264–65° and had the composition  $C_{22}H_{14}O_4$ . On further hydrolysis by boiling with aqueous sodium carbonate it gave rise to benzoic acid and 7-hydroxyflavone. It could readily be distinguished from its isomer, 7-benzoyloxyflavone because it had a much higher melting point, dissolved readily in cold dilute alkali and formed an acetyl derivative. It is therefore given the constitution of 3-benzoyl-7-hydroxyflavone.

Our experience shows that 3-benzoylation takes place to a very high degree under the ordinary conditions of the synthesis of the flavones. Using the difference in the ease with which the benzoyloxy and the C-benzoyl groups undergo hydrolysis, by suitable modification of the treatment with alkali it is possible to obtain either the free hydroxyflavones, or their 3-benzoyl derivatives. In some experiments as high as 80 per cent. of the product was found to be 3-benzoyl-7-hydroxyflavone. It should however be noted that the same conditions do not work satisfactorily in all cases, since using phloracetophenone we could obtain only chrysin and failed to isolate the corresponding 3-benzoyl compound.

#### *Experimental*

*3-Benzoyl-7-hydroxyflavone.*—An intimate mixture of resacetophenone (10 g.), sodium benzoate (12 g.) and benzoic anhydride (40 g.) was heated for 4–5 hours in an oil-bath at 180–190°. The residue was then boiled with 10 per cent. alcoholic potash (250 c.c.) until complete solution was effected (about 20 min.) Most of the alcohol was then distilled off (15–20 min.), the residual liquid diluted with water and saturated with carbon dioxide. The precipitate obtained was filtered, washed with water and then boiled with a large volume of glacial acetic acid. The portion insoluble in acetic acid was crystallised from pyridine in which it was moderately soluble whereby the 3-benzoyl compound was obtained as narrow rectangular rods and prisms melting at 264–65°. (Found : C, 77.5 ; H, 4.1 ;  $C_{22}H_{14}O_4$  requires C, 77.2 ; H, 4.1 per cent.)

The compound dissolved readily in cold dilute sodium hydroxide giving a pale yellow solution from which it was re-precipitated by acids. The yellow solution in concentrated sulphuric acid exhibited no marked fluorescence and a solution in alcohol showed no ferric chloride colouration. The acetate prepared by the action of boiling acetic anhydride and fused sodium acetate

crystallised from an alcohol-acetic acid mixture as rectangular prisms and tablets melting at 192–94°. (Found: C, 75.0; H, 4.5;  $C_{24}H_{16}O_5$  requires C, 75.0; H, 4.2 per cent.)

*Hydrolysis to 7-hydroxyflavone.*—The above compound (1 g.) was boiled with 5 per cent. aqueous sodium carbonate (40 c.c.). The substance went into solution within the first 10 minutes. After boiling for 2 hours the resulting solution was cooled and acidified when a precipitate was formed. This was filtered and boiled with a little water and filtered hot. Subsequent crystallisation from alcohol yielded colourless rectangular prisms of 7-hydroxyflavone melting at 244–45°. From the mixed aqueous filtrates benzoic acid was obtained by ether-extraction.

#### Summary

3-Benzoyl-7-hydroxyflavone has been prepared and its properties have been studied.

#### REFERENCES

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