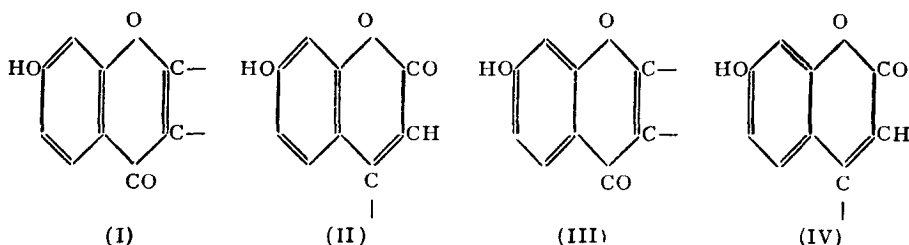


THE QUESTION OF THE FIXATION OF THE AROMATIC DOUBLE BONDS IN HYDROXY-CHROMONES AND COUMARINS. FORMATION OF AZO-DYES

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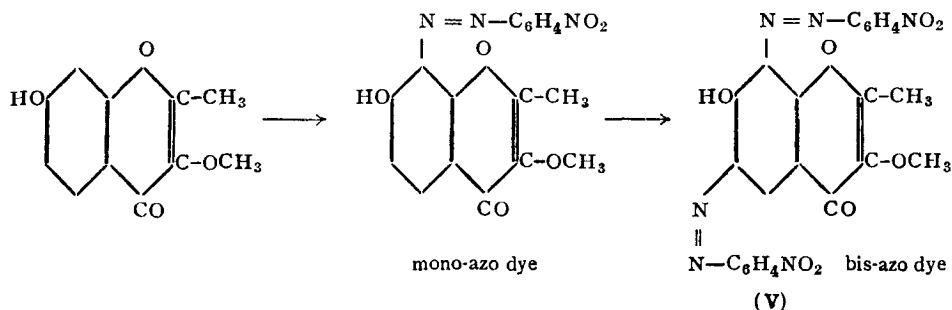
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FROM a detailed study of the properties of 7-hydroxy-chromones and coumarins with particular reference to the possibility of the fixation of the aromatic double bonds it was concluded that no rigid fixation exists.^{1, 2} It is true that the eighth position is predominantly reactive indicating a possible fixation of the aromatic double bonds as in (I) and (II) but the other alternatives (III) and (IV) promoting reactivity of position six do not seem to be altogether prohibited. It was noticed that when a fresh pyrone ring was sought to be introduced umbelliferone gave rise to two isomeric (7 : 8-) and (7 : 6-) compounds, the former being produced in a predominant proportion.³ In regard to Fries migration, allyl transformation and azo-dye formation, though position 8 is the one to react first, when it is protected by alkyl or allyl groups position six also exhibits reactivity.



Coupling with diazonium salts to form azo-dyes is a very facile reaction taking place energetically even at low temperatures. As a consequence of the results summed up in the above paragraph it was expected that when 7-hydroxy-chromones and coumarins were treated with diazonium salts bis-azo dyes would be produced due to reaction at the eighth and sixth positions in quick succession (V). As a matter of fact our early experiments carried out two years ago supported this expectation. In the meantime a paper

by Mahal and Venkataraman⁴ recorded that 6-hydroxyflavone forms only a mono-azo dye and the authors comparing this result with the observations



of Perkin⁵ who obtained bis-azo dyes from chrysin, apigenin, etc., expressed the opinion that this difference should be attributed to the existence of the fixation of the aromatic double bonds in the hydroxyflavones as in (I). The effect of this fixation should be the same whether the hydroxyl group is in the sixth or the seventh position so that 6-hydroxy- and 7-hydroxyflavones should behave alike. It was therefore felt necessary to examine in detail the behaviour of 7-hydroxy-chromones and coumarins in regard to the formation of azo-dyes. The following hydroxy-benzopyrones have been studied: (i) 2-methyl-3-methoxy-7-hydroxychromone, (2) 7-hydroxyflavone, (3) 7-hydroxycoumarin (umbelliferone) and (4) 4-methyl-7-hydroxycoumarin. In one series of experiments one molecular proportion of diazotised *p*-nitraniline has been employed and in another more than two molecular proportions. The products have been characterised by the melting point and nitrogen content and the results are presented in the form of a table.

In the case of (I) there is considerable formation of the bis-azo dye even when one molecular proportion of the diazonium salt is employed. With more than two molecular proportions the formation of the bis-azo dye is complete. On the other hand in the case of the hydroxyflavone (II) the mono-azo dye is obtained pure when one molecular proportion is employed and with a large excess of the diazonium salt only a small quantity of the bis-azo dye is produced along with a large amount of the mono-azo compound which is still the main component.

In the case of the coumarins when caustic soda is employed the formation of the bis-azo dye takes place very easily even with one molecular proportion of the diazonium salt obviously due to the fact that the α -pyrone ring has been opened out by the caustic alkali. When this is prevented by using aqueous sodium carbonate mono-azo dyes alone are produced with one

Phenolic compound	Medium	No. of molr. proportions of diazotised nitraniline used	M.P.	% N found	% N Calc. for		Colour of the dye
					mono-azo dye	bis-azo dye	
I. 2-Me-3-MeO-7-hydroxy-chromone	Sodium hydroxide	1	> 360°	14.9	11.8	16.7	Deep violet
"	"	> 2	"	16.8			"
II. 7-Hydroxy-flavone	"	1	300° (d.)	10.9	10.9	15.7	Deep reddish brown
"	"	> 2	260-300° (d.)	12.2			"
III. 7-Hydroxy-coumarin	Sodium carbonate	1	283° (d.)	13.7	13.5	18.3	Deep brown
"	"	> 2	210-276° (d.)	15.3			"
IV. 4-Methyl-7-hydroxy-coumarin	"	1	251-252° (d.)	12.9	12.9	17.7	Brown
"	"	> 2	210-250° (d.)	13.7			"
V. "	Sodium hydroxide	1	220° (d.)	17.4	12.9	17.7	Pink brown
"	"	> 2	"	17.7			"

molecular proportion of the diazonium salt and with a large excess of the reagent only a partial formation of the bis-azo dyes takes place. The coumarins therefore behave like 7-hydroxy-flavone.

It is therefore clear that though in all cases the formation of the bis-azo dyes is possible it seems to take place with difficulty in a large number of examples. Our results recorded above indicate that they are formed in appreciable quantities though their isolation in the pure state has been possible in only one case. These are in support of the conclusion already expressed in our previous publications that the fixation of the aromatic double bonds in the benzo-pyrones is not a very rigid one. Further the composition of the dyes produced is obviously not controlled by the fixation of the double bonds, at any rate not entirely, and seems to depend on various other factors such as the reactivity of the components, the solubility of the mono-azo dye that may first be produced and its capacity to react further to form the bis-azo dye.

Experimental

The reactions were carried out under carefully controlled and standardised conditions so that the results obtained might be comparable. The following paragraph describes a typical experiment.

8-p-Nitrophenylazo-7-hydroxycoumarin—

p-Nitriline (2 g.) was dissolved in 50% hydrochloric acid (15 c.c.) and the solution after being cooled to 0° was treated in drops with an ice-cold solution of sodium nitrite (1.5 g. in 10 c.c. of water), the temperature being kept below 5° throughout the addition. The diazotised solution was then diluted to 50 c.c. using ice-cold water.

7-Hydroxycoumarin (0.7 g.) was dissolved in 10% aqueous sodium carbonate (60 c.c.) and treated with sodium acetate (6 g. dissolved in 20 c.c. of water) and then with the solution of the diazotised amine (16 c.c.—one molecular proportion) which was added slowly with stirring, the temperature not being allowed to exceed 5°. The mixture was well shaken and then left in in the ice-chest. The dye separated at the top as a foamy mass in the course of half-an-hour. After keeping for two days in the ice-chest during which period it was shaken now and then the solid was filtered with suction, drained well and crystallised from hot glacial acetic acid in which it was fairly soluble. Another crystallisation from the same solvent gave the dye in the form of a deep brown powder which had the appearance of small prisms under the microscope. It was then washed with a large volume of water and then with a little alcohol. The yield was almost quantitative.

In the case of the chromones a corresponding amount of sodium hydroxide was used. When the product could not be dissolved in hot acetic acid, purification was effected by boiling it twice with a large excess of the solvent and filtering hot. The yields were uniformly good, varying from 70–90% of the theoretical.

Summary

The formation of azo-dyes using one and more than two molecular proportions of diazotised *p*-nitriline and the following compounds has been investigated: (1) 2-methyl-3-methoxy-7-hydroxychromone, (2) 7-hydroxyflavone, (3) 7-hydroxycoumarin and (4) 4-methyl-7-hydroxycoumarin. (1) yielded a bis-azo dye with two molecules of the reagent and with one molecule of it a large proportion of the same bis-azo dye contaminated with the mono-azo compound. The other three behaved alike yielding mono-azo dyes with one molecule of the reagent and the same mono-azo compound predominantly mixed with considerable amounts of the bis-compounds when

more than two molecular proportions of the reagent were employed. The factors controlling the composition of the azo-dyes that are formed seem to be very complex.

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