THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part X. The Condensation of 2:4-Resorcylaldehyde.

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In the condensation of aromatic aldehydes with malonic acid in the presence of organic bases, attention has already been drawn to the remarkable influence which a hydroxy-group on the aromatic nucleus exerts on the condensation. It hinders or inhibits the reaction, reducing the yields to a very small amount or even to nil. Dutt, who also made the observation, tried to get over it by employing carbethoxy-derivatives of the hydroxy-aldehydes. The yields were still bad. Kurien and Pandya then found that yields of over 50% could be obtained in the case of salicylaldehyde, when pyridine was taken in a trace only: this observation was extended by Azhar, Kurien and Pandya who showed that traces of some other bases were equally or even more effective, while if the base was in larger proportions, the condensation altogether failed. The highest yield obtained from salicylaldehyde was 77%, and the p-hydroxybenzaldehyde gave 64%. The m-isomer showed, at least in this series, the least disturbance and no diminution, as it gave a theoretical yield. The yields in the cases of the o- and the p-hydroxybenzaldehydes approached even the quantitative, when the hydroxy group was replaced, not by the carbethoxy, but by the methoxy group: the o-, m- and p-methoxybenzaldehydes gave almost quantitative yields.

From this experience it would be expected that if the aromatic aldehyde contains more than one hydroxy-group on the nucleus, a further diminution of the yield might take place. In 2:4-resorcylaldehyde, the two hydroxy-groups are o- and p- to the aldehyde group, and the yields, under the best of conditions, are actually lower than were obtained with salicylaldehyde and p-hydroxybenzaldehyde, namely only 43% of umbelliferone. This was obtained with a trace of pyridine, the yield with a trace of piperidine being lower, namely 24%.

Perkin's reaction has also been applied to this aldehyde, by Tiemann and Lewy, who obtained first 7-acetoxycoumarin, which could be changed
into umbelliferone or umbellic acid by hydrolysis with alkali. This experiment was repeated and the yield of umbellic acid obtained was about 26%.

The condensation takes place even in the absence of any reagent, and is found to give umbellic acid, 33%. When a base is present the substance forms umbelliferone and not umbellic acid.

Robinson and Shinoda’s method* was applied, but it failed entirely, the mixture becoming black and tarry, and no umbelliferone could be taken out.

This led us to try Stuart’s method,10 of heating the aldehyde with malonic acid and glacial acetic acid, and this gave about 54% yield of umbellic acid.

It may be noted that Dey, Rao and Sheshadri11 have prepared umbelliferone from resorcinol and malic acid by means of Pechmann’s reaction. The yield of umbelliferone is, however, only 25% of theory.

The results of the condensation of protocatechuic aldehyde are in line with the above and will be included in the next part of the series.

**Experimental.**

*Condensation in the presence of a trace of piperidine.*—1.4 g. resorcyaldehyde, 1 g. malonic acid and 0.13 c.c. of piperidine were heated on the water-bath for about five hours. The colour of the mixture became soon dark brown and bubbling was seen. The whole mass, after cooling overnight, was extracted with sodium carbonate solution. The alkali extract showed a beautiful violet fluorescence. It was filtered, and the filtrate on acidification gave a brown solid, weighing 0.4 g.

The same experiment was repeated at 105-100°, but the yield remained the same.

*Condensation with a trace of pyridine.*—The same amounts with 0.12 c.c. of pyridine (1:1:0.15 mol.) treated in the same way, gave, on water-bath, 0.6-0.7 g.

Two other experiments, made so that the heating was carried out at 100 05°, and 105-10° respectively, made no improvement in the yield.

The umbelliferone so obtained, purified by methyl alcohol (animal charcoal) came out as colourless prisms, m.p. 225°. (Colour could not always be removed, as in the case of the products of the other condensations.) It gave a marked fluorescence with ammonia, as described by Sommer12 and Tiemann and Reimer.13 It reduced ammoniacal silver and gave a reddish brown colour with aqueous ferric chloride.

*Condensation without any reagent.*—2.8 g. resorcyaldehyde, and 2 g. malonic acid were heated alone as above. The product, after extraction,
was a light brown powder, umbellic acid. On purification, it became yellow, did not melt, but decomposed at 240° (cf. Posen). It weighed 1.2 g. or 33%.

Tiemann and Lewy's condensation.—2.8 g. resorcylaldehyde, 1.6 g. anhydrous sodium acetate and 6 c.c. acetic anhydride were heated in a flask, with a reflux condenser, at 160–80° for 8 hours. The colour of the mass changed to brown. The product extracted, as usual, weighed 1.4 g. It was 7-acetoxy coumarin, of a brown colour and melted at 140°. Hydrolysed by refluxing with 10% KOH solution, 3 g. gave 2 g. of umbellic acid.

Robinson and Shinoda's method.—1.3 g. aldehyde, 3 g. malonic acid, 2.8 c.c. pyridine with 3–4 drops of piperidine were heated on a water-bath for 90 minutes and on a wire-gauze for 20 minutes. The whole mass had become black, and gave nothing by the usual treatment.

Condensation by Stuart's method.—3 g. resorcylaldehyde, 3 g. malonic acid and 2 g. glacial acetic acid were heated on a water-bath for ten hours. The mass had become deep pink on the addition of the acetic acid and soon became liquid, which assumed a deep red, and finally a violet colour. Bubbling was continuous, and at the end, the umbellic acid was taken out as usual, and weighed 2.1 g. (53.6%).

Summary.

2:4 Resorcylaldehyde undergoes condensation with malonic acid giving umbelliferon or umbellic acid according to the conditions. The yield is as expected lower than the lowest obtained with mono-hydroxybenzaldehydes.

A trace of pyridine gives better yield than any method, except that the yield is slightly higher when glacial acetic acid is used in place of a base.

REFERENCES.
2. Dutt, *ibid.*, 1925, 1, 298.
6. ————, *ibid.*, 1936, 4, 144.
7. ————, *ibid.*, 1936, 4, 134; 1937, 5, 437.