THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part IV. Of *m*-Hydroxybenzaldehyde

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THE condensation of salicylaldehyde with amides has been already described[1] in which the products were all salicylideneamides, and possessed certain peculiar physical properties (*loc. cit.*). The use of pyridine in traces as a condensing agent gave excellent yields, which were often quantitative. Similar condensations with the isomeric *m*- and *p*-hydroxybenzaldehydes have, so far as is known to us, never been studied. These studies are described here and in the next paper.

m-Hydroxybenzaldehyde combines with amides to give products of a similar constitution, namely the *m*-hydroxybenzylideneamides, but there are certain peculiar features of the reaction which are in contrast with the behaviour observed in the case of salicylaldehyde. Since, in the case of all the condensations studied with salicylaldehyde, the yields were uniformly inferior both in quality and in quantity when sodium acetate was used as a condensing agent to those obtained by means of a trace of an organic base, in the present case the condensations were carried out exclusively by means of a trace of an organic base. Preliminary observations, however, showed definitely that the presence or absence of a trace of the base had not the same significance here that it had in the salicylaldehyde-condensations : in other words, the condensation readily took place even in the absence of any condensing agent (as in the case of salicylaldehyde), but the trace of pyridine or lutidine or so, when present, did not materially increase the yield, and was apparently responsible for some resinification (contrast).

Again, while salicylidene-formamide was obtainable in quantitative yields,[1] from formamide and salicylaldehyde, no pure product could be separated from *m*-hydroxy-benzaldehyde and formamide, even in the presence of a trace of pyridine or of lutidine under a variety of conditions of heating and of temperature. Acetamide also did not condense, though propionamide, benzamide and phenylacetamide gave the usual type of products. The yields in the three cases were materially improved by taking the aldehyde and the amide in 1 : 2 mol. proportions, which did not affect the nature of the product.

The products were, always, only the unsaturated benzylidene-amides and not the saturated bisamide in any case. The best yield did not exceed 58% of the theoretical.

The three products were either colourless or lightly coloured, were recrystallised easily and gave good melting-points as well as good analyses.

Experimental

m-*Hydroxybenzylidenepropionamide.*—*m*-Hydroxybenzaldehyde 3 g. and propionamide 1·8 g. (1 : 1 mol.) were heated on a boiling water-bath till fusion to a homogeneous liquid, when the heating was continued at 80–85° for six hours. The viscous mass, dark brown in colour, on cooling, partially solidified. It was washed with cold dilute alcohol, and the residue was crystallised from dilute alcohol. Pale yellow crystals, melted at 210° C., and weighed 0·7 g.

In another experiment the aldehyde 3 g. was heated with 3·6 g. of the amide (1 : 2 mol. proportions) and the product, taken out in the same way, weighed 1·2 g. (27·5%). Found: N = 7·79% ; $C_{10}H_{11}O_2N$ requires N = 7·91%.

m-*Hydroxybenzylidenebenzamide.*—The aldehyde 3 g. and benzamide 3 g. (1 : 1 mol.) were heated on an oil-bath at 110–15° for three hours. At 95° the mass fused to a homogeneous liquid and water vapours were given off. The colour gradually became dark brown. When cold, the mass was still plastic. It was treated with hot alcohol, when, on cooling, buff coloured crystals were obtained, which, on recrystallisation from hot alcohol, gave pure milk-white crystals, m.p. 205° (1·2 g.).

In another experiment, the initial heating was at 100° and, after fusion, at 80° for six hours. The reaction-product was slightly orange in colour, was cooled overnight, was found to be a hard solid orange mass next morning, and was crushed and purified by means of alcohol as before. The yield after this low-temperature and longer heating was higher, 1·8 g.

The substances were taken in 1 : 2 mol. proportions (3 g. aldehyde and 6 g. amide) and heated at first at 100° and then at 90° for eight hours. The mixture became brown, but on treating it as usual the yield increased to 3·2 g. (*i.e.*, 58% nearly). (Found: N = 5·79, 5·82%. $C_{14}H_{11}O_2N$ requires N = 6·22%.) Molecular weight by Rast's method, using camphor, gave M = 234 : *m*-hydroxybenzylidenebenzamide requires 225, while the bisamide requires 346.

m-*Hydroxybenzylidene-phenylacetamide.*—1·5 g. of the aldehyde and 3·4 g. of phenylacetamide (1 : 2 mol.) were heated on a water-bath for four hours. The mixture fused and gradually turned dark brown as heating went on. On cooling, the resinous mass was extracted with ether, and the residue was recrystallised from hot dilute alcohol or acetone. Buff-coloured needles melting at 190°. 1·2 g. or 40% yield. Found: N = 5·73% ; $C_{15}H_{13}O_2N$ requires N = 5·85%.

Condensations were attempted with acetamide, in the presence of a trace of pyridine or of lutidine, as well as in the absence of a condensing agent, and temperatures ranging from 50° to 130° C. were tried. In most cases much resinification was observed and some of the aldehyde was recovered unchanged. The same was observed when formamide was heated with *m*-hydroxybenzaldehyde.

The three condensation products obtained resembled the corresponding salicylidene-amides, in declolourising immediately Baeyer's reagent, in giving a colour with concentrated sulphuric acid and in being decomposed to the original aldehyde when heated with strong mineral acids.

Summary

m-Hydroxybenzaldehyde condenses when heated alone with propionamide, benzamide and phenylacetamide, giving corresponding *m*-hydroxybenzylideneamides, which have been described. No condensation product was obtained with acetamide or formamide.

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REFERENCE

1. Pandya and Sodhi .. *Proc. Ind. Acad. Sci.*, 1938, (A), 7, 361.