

THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part V. Of *p*-Hydroxybenzaldehyde

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p-HYDROXYBENZALDEHYDE condenses readily with formamide, acetamide, propionamide, benzamide and phenylacetamide, and the products are the corresponding *p*-hydroxybenzylidene-amides, as in the cases of the *o*- and *m*-hydroxybenzaldehydes^{1,2}. The condensations are brought about by heating the aldehyde with the amide for 4–5 hours at 130°–140°, in the presence or absence of a trace of organic bases like pyridine and piperidine. The presence of the base improved the yield only slightly (contrast salicylaldehyde,¹ and compare *m*-hydroxybenzaldehyde²). The yields, however, were uniformly very good, never being less than 60% of the theoretical, and reaching up to 92% as the highest, being in this respect more like those of the *o*- than those of the *m*-hydroxybenzylidene-amides.¹ In physical properties, too, they bore a very strong resemblance to them, being more or less yellow in colour, looking when cold in the reaction-flask, like 'organic glass' and having on the whole very limited solubilities in the usual organic solvents. They did not give a sharp melting point, but generally decomposed before reaching it. The constancy of this point, after repeated crystallisations or precipitations, and the agreement of the analytical figures showed the purity.

As before, they all instantly decolourised Baeyer's reagent, and gave a deep red coloration with concentrated sulphuric acid.^{1,2} They also gave a pink coloration with strong hydrochloric acid, which became deep rose on warming or on keeping. On heating, with strong mineral acids, they decomposed with the liberation of the original aldehyde.

Experimental

p-Hydroxybenzylidene-acetamide.—3 g. *p*-hydroxybenzaldehyde and 1.5 g. acetamide were taken, with 0.19 g. pyridine (1 : 1 : 0.1 mol.), and heated in an open flask in an oil-bath at 130–40°; the reacting mixture fused at 100–15° with liberation of water-vapours. After 4 hours, the

heating was stopped, and about 30 c.c. of alcohol were added to the cold flask, and the whole was left overnight. The insoluble portion was filtered off, the filtrate concentrated by evaporating the alcohol to half the bulk and cold water added which produced a precipitate. The whole was acidified with a little dilute hydrochloric acid; the precipitate collected and washed with water. When dry it weighed 3.7 g. (yield 92%).

It was a yellow powder, which was insoluble in hot or cold water, ether, chloroform or benzene, slightly soluble in acetone, and very easily soluble in alcohol, methyl alcohol and pyridine. It also dissolved readily in dilute alkali solution from which it could be reprecipitated by the addition of some dilute hydrochloric acid. It failed to come out in crystals from any one solvent or a mixture of solvents; it was purified by repeated precipitations (acetone and water) and washing with ether to remove any unchanged aldehyde that might have remained. It did not melt even till 340° but became dark brown showing decomposition had set in.

When piperidine was substituted (0.21 g.) in place of pyridine, and, also when no base was used, and the other conditions were unchanged, the yield in each case was 3.5 g. or 87.5%. Found nitrogen = 9.02%; $C_9H_9NO_2$ requires 8.59%.

p-Hydroxybenzylidene-formamide.—3 g. aldehyde, 1 g. formamide and 0.285 g. pyridine (1 : 1 : 0.15 mol.) were mixed in a flask. In a preliminary experiment, to avoid decomposition of formamide, which boils at 105°, the heating was done on a water-bath for 8 hours: but this gave the unchanged aldehyde only. The heating was, therefore, done in an oil-bath at the usual temperature of 130–40° for 4 hours, and when the contents were cold, methyl alcohol was added and the whole was left overnight. The product was taken out as before by partial concentration of the filtrate and subsequent addition of acidulated water. Yield 2.3 g. or 63%. The crude product was washed with ether and acetone, dissolved in aqueous acetone and reprecipitated by addition of excess of acetone. This was repeated several times, till the dark yellow product decomposed, without melting, at the constant temperature 216°. Its solubility was similar to that of the acetamide compound described above. It also gave the same reactions. With piperidine in place of pyridine, the yield was the same, 2.3 g., while in the absence of any base the yield was little less, 2.2 g. about 60%. Found N = 8.82%; $C_8H_7NO_2$ requires 9.30%.

p-Hydroxybenzylidene-propionamide.—The aldehyde (3 g.), propionamide (1.8 g.) and pyridine in a trace as before, were heated for 5 hours at 140°. The product was taken out in the usual way and weighed 3.6 g.

Yield 84%. It was dirty white, was purified by means of alcohol and water, washing at the end with ether and warm water. It decomposed at 195°.

Its behaviour was similar to that of the other derivatives described above. Piperidine in place of pyridine gave the same yield (84%), while in the absence of any base the yield was 3.5 g. or about 82%. (Found N = 7.898% ; C₁₀H₁₁O₂N requires 7.909%.)

p-Hydroxybenzylidene-benzamide.—3 g. aldehyde, 3 g. benzamide and pyridine in a trace (1 : 1 : 0.15 mol.) were heated at 140° for five hours, and the product was extracted with ethyl alcohol as before and precipitated by the addition of excess of water to the concentrated extract. The yield was 4.5 g. or 81%. With piperidine the yield was 4.6 g. or 83%. When no base was present, the yield was also 81%. Its solubilities, properties and reactions were similar to those described above. The crude product was yellow-brown, but the colour became lighter under the usual method of purification. It did not melt, but became dark red at 190° and swelled at about 215°. (Found N = 5.86% ; C₁₄H₁₁NO₂ requires 6.22%.)

p-Hydroxybenzylidene-phenylacetamide.—3 g. aldehyde, 3.3 g. phenylacetamide and pyridine (1 : 1 : 0.1 mol.) were heated in the usual way, and gave 4.8 g. or 81% yield. In the absence of any base the yield was 4.7 g. or 80%.

It was lemon-yellow in colour, did not melt even up to 340° though the colour was gradually darkening, indicating decomposition. (Found N = 6.07% ; C₁₅H₁₃NO₂ requires 5.86%.)

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Summary

p-Hydroxybenzaldehyde condenses with all the five amides easily, giving very good yields of the corresponding *p*-hydroxybenzylidene-amides, which resemble closely the products obtained from the condensation of salicylaldehyde (rather than those obtained from *m*-hydroxybenzaldehyde).

REFERENCES

1. Pandya and Sodhi .. *Proc. Ind. Acad. Sci.*, (A), 1938, 7, 361.
2. Mehra and Pandya .. *Ibid.*, (A), 1939, 10, 279.