

CONDENSATION OF MALONANILIC ACID WITH ALDEHYDES

Part II. With *o*-, *m*- and *p*-Hydroxybenzaldehydes

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IN an earlier paper, Mehra and Pandya have reported on the condensation of malonanilic acid with aromatic aldehydes, making a comparative study of the yields and the products obtained by two different methods, *viz.*, (i) by Robinson's method of pyridine-excess with piperidine-trace and (ii) by the trace method, *i.e.*, by the use of only a trace of pyridine or of piperidine.¹ It was shown that the comparison of the results clearly pointed out that the advantage lay with the trace method, and that this was only an extension of the observations recorded about the trace-method in connection with condensations of various aromatic aldehydes with plain malonic acid.²

In the case of some of the aldehydes the product was a mixture of the corresponding benzylidenemalonanilic acid and the decarboxylation product cinnamanilide, *e.g.*, piperonal gave piperonylidenemalonanilic acid and 3 : 4-methylenedioxcinnamanilide.¹ The three hydroxybenzaldehydes, however, gave, by both the methods, only the decarboxylated anilide. Similarly the unsubstituted benzaldehyde itself gave only the cinnamanilide. In these four cases the trace-method, while giving a higher yield, gave the same anilide as did the other pyridine-excess-piperidine-trace method, and no acid.

The decarboxylation to the anilide may be due to the temperature employed, or to the base used, or to both. In the present paper are included the results obtained when either or both of these conditions were controlled. It appears that the base, even in a small trace, induced decarboxylation. In the absence of a base or any reagent, benzaldehyde, *m*-hydroxybenzaldehyde and *p*-hydroxybenzaldehyde gave the corresponding benzylidenemalonanilic acid and the *m*- and *p*-hydroxybenzylidenemalonanilic acids respectively. But the *o*-isomer, salicylaldehyde, even under these conditions, gave only the same coumarin-3-carboxyanilide, showing that even in the absence of any base, the coumarined ring formation took place. When a much lower temperature was employed, no condensation took place at all,

even after 20 hours. The *p*-isomer gave a low yield (18%), the *m*- gave a fair yield of over 50% and the unsubstituted benzaldehyde gave up to 87%. This is but another illustration of the influence of the hydroxy group in these condensations.³

Experimental

Condensation with Salicylaldehyde.—3.5 g. malonanilic acid and 2.4 g. salicylaldehyde were mixed in a flask and heated on a water-bath for three hours, when the reactants became a solid mass. It was then extracted with sodium carbonate solution and filtered. The filtrate was acidified but no acid separated out. The pale yellow residue weighed 1.6 g. and, on recrystallisation, melted at 246–47°. (The coumarin-carboxyanilide melts at 247°, Ahluwalia, Haq and Ray⁴, Mehra and Pandya¹.) The yield was thus 30.2%.

Another condensation was attempted at 60° with the same quantities. There was no effervescence observed during 20 hours' heating. On treatment with sodium carbonate and then hydrochloric acid, no acid came out. Extraction with ether gave some unchanged malonanilic acid.

Condensation with m-Hydroxybenzaldehyde.—The aldehyde and the acid were heated together as before, in molecular proportions, on the water-bath, for five hours. The mass was still a brown viscous liquid. After treatment with sodium carbonate solution, extraction of the unused aldehyde with ether, and acidification of the alkali extract, *m*-hydroxybenzylidenemalonanilic acid came out, which on recrystallisation was obtained as white needles, melting at 209°. The yield was 2.4 g. (52% of theory). The acid was insoluble in water, but soluble in alcohol, ether, etc. With ferric chloride it gave no colouration. (N, Found : 4.95% ; C₁₆H₁₂O₄ N requires 4.96%).

Condensation with p-Hydroxybenzaldehyde.—1.8 g. of malonanilic acid and 1.2 g. of the aldehyde were heated on the water-bath for five hours. The mass became greenish and remained semi-solid. On treatment with sodium carbonate solution it became pink, again becoming greenish on acidification. *p*-Hydroxybenzylidenemalonanilic acid was obtained in a small quantity (0.5 g., *i.e.*, 18% of theory). On recrystallisation it became colourless, and melted at 239–40°. A small quantity of the anilide was also separated, m.p. 208°. (N, Found: 5.08% ; C₁₆H₁₂O₄N requires 4.96%.) With alcoholic ferric chloride the acid gave a deep red colour.

Condensation with Benzaldehyde.—1.1 g. benzaldehyde and 1.8 g. malonanilic acid were heated alone on a water-bath. In ten minutes the mixture was a homogenous liquid, and in half an hour it became a solid with a bluish tinge. After 45 minutes' heating, the heating was stopped, and

when cold the product was extracted as usual. It had a bluish tinge. Recrystallised from hot alcohol, benzylidenemalonanilic acid came out in fine white needles, melting at 238°. The acid weighed 1.8 g. (65% of theory) with 0.2 g. of the anilide, m.p. 149°.

In another experiment, the heating was continued for five hours, when the yield increased to about 86%. The acid was insoluble in water but soluble in the common organic solvents. It decolourized Baeyer's reagent in the cold (N, Found : 5.38%; $C_{16}H_{13}O_3N$ requires 5.24%).

Summary

The condensations of *o*-, *m*- and *p*-hydroxybenzaldehydes with malonanilic acid in the absence of any condensing agent have been studied. The *o*-isomer gives the same coumarin-3-carboxyanilide as it does with a base, but the *m*- and the *p*-hydroxybenzaldehydes give the corresponding benzylidenemalonanilic acids: so does the unsubstituted benzaldehyde also. The last gives very good yields, while the para gives low yields.

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