

CONDENSATION OF MALONANILIC ACID WITH ALDEHYDES

Part III. With *o*-, *m*- and *p*-Nitrobenzaldehydes

BY P. I. ITTYERAH AND KANTILAL C. PANDYA

(From the Department of Chemistry, St. John's College, Agra)

Received November 28, 1940

IN Part II¹ it has been shown that in the condensations of malonanilic acid with the hydroxybenzaldehydes, the reaction is not so rapid in the absence of any condensing reagent as when a trace of pyridine or of piperidine is present, and that the product was, entirely in the case of the *m*-isomer and mainly in the case of the *p*-, the corresponding hydroxybenzylidenemalonanilic acid, when no reagent was present, while it was mainly the decarboxylated hydroxycinnamanilide when the condensation was carried out in the presence of a base. The behaviour of the *o*-isomer, salicylaldehyde was peculiar.

Condensation of malonanilic acid with *o*-nitrobenzaldehyde, by Robinson's reagent, has been carried out by Ahluwalia, Haq and Ray,² and the condensations with the three, *o*-, *m*- and *p*-nitrobenzaldehydes, in the presence of a trace of pyridine or piperidine, have been already reported by Mehra and Pandya.³ The products in all the cases were the corresponding anilide.

The present work was started with the object of finding out whether the nitrobenzaldehydes would give the acid, as did the hydroxybenzaldehydes, when condensations were carried out in the absence of the base or of any other reagent. Moreover, the *m*- and *p*-acids do not appear to have been prepared so far.

The results are interesting. Here also the reaction in each case went very slowly in the absence of the base. The product in every case was a mixture of the acid and the anilide, with the acid product preponderating very largely in quantity. The behaviour of the *o*-isomer was again peculiar: it reacted with extreme slowness, and gave smaller yields of the mixture, even with longer heating (*vide* the Table). The behaviour of both the *o*-hydroxy- and the *o*-nitrobenzaldehydes must be due to what is now well recognized as the hydrogen bond, which gives greater stability and less reactivity to the aldehyde group.

Experimental

Condensation with p-Nitrobenzaldehyde.—0.75 g. of the aldehyde and 0.9 g. malonanilic acid were heated together on a water-bath. The solid mixture soon became a homogeneous liquid, but set to a green solid after about an hour's heating. Heating was continued for another hour. This was treated with 10% sodium carbonate solution, and the residue, *p*-nitrocinnamanilide was filtered off. This was recrystallised from dilute alcohol, when it melted at 208°, which is the same as reported by Mehra and Pandya.³ Yield 0.3 g. or 22.4% of theory.

p-Nitrobenzylidenemalonanilic Acid.—The filtrate containing the sodium salt was acidified and gave a yellow mass of crystals, which when recrystallised from dilute alcohol, came out as yellow needles, melting with decomposition at 240°. (Yield 1.2 g. or 76.9%.) (Found: Nitrogen 9.27%; $C_{16}H_{12}O_5N_2$ requires 8.94%.)

The acid gave a pale yellow silver salt which decomposed at 231°. (Found: Silver 26.08%; while $C_{16}H_{11}O_5N_2Ag$ requires 25.78%.)

Condensation with m-Nitrobenzaldehyde.—0.75 g. of *m*-nitrobenzaldehyde was condensed with 0.9 g. malonanilic acid as above. The solid soon fused to a homogeneous liquid which in two hours solidified to a green mass. After some more heating, it was cooled and extracted with sodium carbonate as above. The anilide as well as the acid were obtained separately.

The *m*-nitrocinnamanilide, on purification, melted at 194° (same as reported by Mehra and Pandya³). It weighed 0.4 g. (Yield 29.9%.)

m-Nitrobenzylidenemalonanilic Acid.—Recrystallised from dilute alcohol, the acid came out as tiny white needles, melting with decomposition at 226°. Weight 1.1 g. (Yield 70.7%.) (Found: Nitrogen 9.24%; Calc. 8.94%.)

The silver salt decomposed at 211°. (Found: Silver 25.9%; Calc. 25.78%.)

Condensation with o-Nitrobenzaldehyde.—0.75 g. of *o*-nitrobenzaldehyde was heated on the water-bath with 0.9 g. of malonanilic acid for six hours. There was a slight effervescence at first: the mass, which had fused to a green viscous liquid, remained so all through without becoming solid. On cooling and adding water, a solid was formed which was treated with sodium carbonate solution as usual. The undissolved anilide weighed 0.5 g. (37.3%), was recrystallised from alcohol and was separated by means of benzene into two fractions, one white, melting at 172° and the other yellow,

melting at 190°. These two isomers have also been reported by Mehra and Pandya.³

o-Nitrobenzylidenemalonanilic Acid.—The sodium carbonate extract on acidification gave a white precipitate, which on recrystallisation from alcohol, melted at 172° giving out carbon dioxide. This corresponds with the acid reported by Ahluwalia, Haq and Ray² as obtained by their method, though Mehra and Pandya (*loc. cit.*) did not obtain the acid when the condensation was carried out in the presence of a base, either according to the method of A., H. and R. or by the trace-method. The acid weighed 0.5 g., the yield being 32%.

As this acid as well as one form of the cinnamanilide had an identical melting-point, 172°, which is remarkable, a mixed melting-point of the two was taken: the mixture melted at 140–48°.

The following table, consolidating the results of Mehra and Pandya with the above results, gives a clear picture of (i) the influence of the base on these condensations and (ii) the influence of the nitro-group in different positions on the ring:—

TABLE

Aldehyde	Conditions of condensation		Products	
	Base	Hours of heating	Acid %	Anilide %
<i>p</i> -Nitrobenzaldehyde	Trace of pyridine	1.25	0	74.6
„	Nil	2	77.2	22.4
<i>m</i> -Nitrobenzaldehyde	Trace	1.25	0	67
„	Nil	2	70.7	30.2
<i>o</i> -Nitrobenzaldehyde	Trace	1.25	0	70.9
„	Nil	5	32.1	37.7

Summary

Condensations of the three nitrobenzaldehydes with malonanilic acid have been studied in the absence of any catalyst or condensing agent. The benzylidenemalonanilic acids are thus obtained. The *o*- gives both the acid and the anilide, but the yields are smaller and the reaction is much slower.

Our thanks are due to the Director of Public Instruction, United Provinces, for the grant of a research scholarship to one of us (P.I.) that has enabled him to take part in this work.

REFERENCES

1. Ittyerah and Pandya . . *Proc. Ind. Acad. Sci.*, (A), 1941, **13**, 119.
2. Ahluwalia, Haq and Ray . . *J.C.S.*, 1931, 2059.
3. Mehra and Pandya . . *Proc. Ind. Acad. Sci.*, (A), 1938, **7**, 369.