

## CONDENSATION OF ALDEHYDES WITH AMIDES

### Part XVII. Of 5-Chloro- and 3:5-Dichlorosalicylaldehyde

#### ADDENDUM

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To Part XVII already published,<sup>19</sup> four more condensations are to be added, viz., two more condensations of each of the two aldehydes with phenylacetamide and cinnamamide. In all the four cases the products have been of the *-bis* form, and the yields have generally increased on conducting the condensations a little above the water-bath temperature: indeed quantitative yields were obtained in the 3:5-dichlorosalicylaldehyde-cinnamamide condensation conducted at 100–110°. Cinnamamide, in fact, condensed more quickly than most of the other amides. The influence of the chlorine on the aldehyde was most marked in the case of the dichlorosalicylaldehyde, which often gave higher yields than were given by salicylaldehyde. The general conclusions drawn earlier<sup>19</sup> are thus confirmed.

#### EXPERIMENTAL

##### *Condensation with Phenylacetamide*

5-Chlorosalicylaldehyde (0.40 g.) and phenylacetamide (0.675 g.) (1:2 mol.) were heated together on water-bath (98°) for ten hours. A homogeneous liquid was soon formed but it changed into a solid after six hours' heating. It was a hard yellow mass difficult to break. After standing overnight, it was extracted with water, washed with ether and then with hot water, when a crude product melting at 190–195° was obtained. It was white and was crystallised from alcohol in needle crystals: m.p. 201°. It weighed 0.35 g. Cl, found: 9.010 per cent. Chlorosalicylidene-*mono*-phenylacetamide C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>NCl requires 12.18%; Chlorosalicylidene-*bis*-phenylacetamide C<sub>23</sub>H<sub>21</sub>O<sub>3</sub>N<sub>2</sub>Cl requires 8.69%. The product was thus the *bis*-compound, and the yield was 35.5% of theory.

When the experiment was repeated at 100–110°, the yield increased to 57.46%. It decolourised potassium permanganate (alkaline), gave no red colour with concentrated sulphuric acid and had the usual solubility.

3:5-Dichlorosalicylaldehyde (0.5 g.) and phenylacetamide (0.675 g.), (1:2 mol.), were heated on water-bath for ten hours and, as before, gave

after six hours a hard yellow solid. After the same treatment as above a crude product was obtained melting at 180–190°; on recrystallisation from alcohol it came out in white needle crystals melting at 195°. It weighed 0.30 g.

Cl, found: 16.16%; dichlorosalicylidene-*monophenylacetamide*  $C_{15}H_{11}O_2NCl_2$  requires 23.05%; dichlorosalicylidene-*bisphenylacetamide*  $C_{23}H_{20}O_3N_2Cl_2$  requires 16.03%. The product was thus the *bis*-compound and the yield was 25.86%.

Heating in the same way at 100–110° raised up the yield to 86.24%.

In the other properties it completely resembled the first compound above.

#### Condensation with cinnamamide

5-Chlorosalicylaldehyde (0.40 g.) and cinnamamide (0.735 g.) were heated as usual for ten hours on water-bath. A hard solid came out with an orange tinge. After washing as above, a white crude product was obtained melting at 165–170°, with a change into an orange colour and a slight melting at 125–130° and resolidification. Recrystallised from methyl alcohol it came out quite white, but again developed on orange colour and a slight melting appearance at 135–137°, solidifying above 137° and finally melting completely at 181°. Repeated recrystallisations from methyl alcohol and from acetone failed to do away with this phenomena which continued. It weighed 0.80 g.

Cl, found 7.902%: chlorosalicylidene-*monocinnamamide*  $C_{16}H_{12}O_2NCl$  requires 12.44%, and chlorosalicylidene-*biscinnamamide*  $C_{25}H_{21}O_3N_2Cl$  requires 8.208%. The yield of the *bis*compound was 72.36%.

Heating at 100–110° gave only a resinous mass. The compound was soluble in methyl alcohol, acetone and glacial acetic acid. It decolourised alkaline permanganate but did not give a pink colour with concentrated sulphuric acid.

3:5-Dichlorosalicylaldehyde (0.50 g.) and cinnamamide (0.735 g., 1:2 mol.) were heated on water-bath for ten hours; the homogeneous liquid which formed very soon solidified also quickly, in one hour. It had an orange yellow colour. Taken out as before, the white crude product melted at 200–204°: recrystallised from acetone, it finally melted at 205° and weighed 1.1 g.

Cl, found 15.23%; dichlorosalicylidene-*monocinnamamide*  $C_{16}H_{11}O_2NCl_2$  requires 22.19%, while dichlorosalicylidene-*biscinnamamide*  $C_{25}H_{20}O_3N_2Cl_2$  requires 15.20%. The yield was about 90%.

When the heating was at 100–110°, the yield was about quantitative. It had the same properties as those described above, except that it was soluble in acetone and in glacial acetic acid and was only sparingly soluble in methyl alcohol.

To the table on page 63<sup>19</sup> the following addition is made:—

Phenylacetamide	..	85.7 <i>mono</i>	57.46 <i>bis</i>	86.24	<i>bis</i>
Cinnamamide	..	Not done	72.36 ,,	Quantitative	,,

#### SUMMARY

Salicylaldehyde-amide condensations always produced the salicylidene-*mono*amides and the highest yield was always obtained in the presence of pyridine.<sup>7</sup> The 5-chlorosalicylaldehyde and the 3:5-dichlorosalicylaldehyde gave the best yield usually when heated alone; the product was almost always the *-bis* in the case of the latter, and generally so in the case of the former. The condensations with cinnamamide gave a quicker and a higher yield, it being quantitative in the case of the dichlorosalicylaldehyde. As before a temperature slightly higher than that of the water-bath produced generally a better yield in the last two amide condensations.

#### REFERENCE

19. Nigam and Pandya .. *Proc. Ind. Acad. Sci.*, 1949, 29, 56.