THE CONDENSATION OF ALDEHYDES WITH AMIDES.

Part II. The Condensation of Cinnamaldehyde.

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As far as we are aware, there has been only one such condensation reported, and that is by Gupta,[1] of cinnamaldehyde with phenylacetamide, brought about without any condensing or catalytic agent, by merely heating the two together, and resulting in the production of cinnamylidene-bisphenylacetamide. In the present paper, the condensations of this aldehyde are studied with four amides, namely, phenylacetamide, acetamide, propionamide and benzamide, under several different conditions of temperature, molecular proportions and catalytic influences. The condensations in all cases take place and produce the cinnamylidene-bisamides. The yields are fair and at times good, but are not generally as good as were noted with salicylaldehyde in Part I.[2] The bisamides have always to be freed from unused cinnamaldehyde and resinous products: this, though obviously lowering the yield, is easily accomplished by means of alcohol.

The yields have often increased considerably by judicious variations in the period of heating or the temperature, or even by taking an excess of the amide. Indeed, it is clear that, in the present case at least, the improvement in the yield is dependent more on the suitable observation of these conditions than on the presence or the absence of an organic base as a catalyst. The best yield has at times been obtained in the absence of any base. It is not improbable that the presence of even a trace of a base may promote side-reactions such as polymerisation, or condensation-polymerisation, which must be particularly likely in the case of an unsaturated aldehyde like this. The cinnamaldehyde recovered from these condensations was deeply coloured and could not well be used again.

As Gupta[1] does not mention any yield, his condensation has been repeated and the yield is found to be only about 15 %. This improves only slightly to 18 %, by an alteration in the heating.

The cinnamylidene-bisacetamide, m.p. 234°, is obtainable in the maximum yield of over 50 %. Many alterations in the conditions of the condensation had to be tried before this result was arrived at (*vide* tables).

Cinnamylidene-bisbenzamide was a little more readily obtained, in the maximum yield of 55 %, m.p. 250°.

The aldehyde condensed also with propionamide, when the corresponding bisamide was obtained in yields of about 50 %.

The condensation of cinnamaldehyde with formamide also takes place and has been studied, but has not been mentioned in the experiments, because the solid amorphous substance obtained could not be very well purified in so far as a good melting-point has not been obtained. Curiously, however, several N-determinations give very consistent values. These values, however, are much lower than those calculated for possible condensation-products. The substance has, therefore, to be investigated further.

Under the expectation that hydrocinnamaldehyde being saturated, might give a better yield, one experiment on its condensation was performed and is recorded. It is found to condense with benzamide, when the two are heated together, but some benzamide and some aldehyde are recovered unchanged, and the yield of the dihydrocinnamylidene-bisbenzamide is about 40 %.

Experimental.

Condensation of cinnamaldehyde with phenylacetamide.—

Gupta's experiment being repeated, 3·5 g. of cinnamaldehyde and 6·9 g. phenylacetamide (1 : 2 mol.) on heating under reflux at 160–70° for two hours gave 1·5 g. of the bisamide, melting at 238°.

Other experiments were tried as described in the Table below : the maximum yield of 18·7 % was obtained by a modification in the conditions as under :—

TABLE I.

Molecular Proportions Aldehyde : Amide : Pyridine	Temperature	Time of Heating	Yield	
			Weight	Per cent.
1 : 1 : 0·0	160–70°	2 hours	0·6 g.	6·2
1 : 2 : 0·0	,,	,,	1·5 g.	15·6
1 : 2 : 0·05	,,	,,	,,	,,
,,	130–40°	3 hours	,,	,,
1 : 2 : 0·0	,,	,,	1·8 g.	18·7

As the presence of pyridine did not influence the yield in the ordinary way, other bases and different conditions were not tried in this case.

Condensation of cinnamaldehyde with acetamide.—

3·5 g. cinnamaldehyde and 1·5 g. dry powdered acetamide (1 : 1 mol.) were heated in a small flask on the water-bath for six hours. The product separated in fine crystals even when the flask was still warm. On cooling the mixture was taken out in a mortar and ground well with hot alcohol to dissolve the unchanged aldehyde. It was filtered on cooling, washed with cold alcohol, and recrystallised from hot alcohol. Fine milk-white needle crystals, of cinnamylidene-bisacetamide, m.p. 234°, were obtained. Yield 0·8 g. (13·8 %). (Found : N = 11·7, 11·6 %. $C_{13}H_{16}N_2O_2$ requires N = 12·07 %.)

Various modifications in the conditions were tried to improve the yield, the most important of which are given in the Table below. On the addition of a trace of pyridine, as well as with other changes in the manner of heating, the yield increased only to 0·9 g. or to 15·5 %. It was obvious that for obtaining the bisacetamide, the molar proportions should be 1 : 2. This change was made, and the yield improved, under different conditions and ranged from 25 to 43 % of theory. It was observed that some acetamide

TABLE II.

Proportions Mol. Aldehyde : Amide : Pyridine	Temperature	Time of Heating	Yield	
			Weight	Per cent.
1 : 1 : 0·0	Water-bath	6 hours	0·8 g.	13·8
1 : 1 : 0·15	,,	,,	0·9 g.	15·5
1 : 1 : 0·0	120–25°	2 ,,	,,	,,
1 : 2 : 0·0	Water-bath	8 ,,	1·5 g.	25·3
,,	110–15°	4 ,,	,,	,,
,,	120–25°	2 ,,	1·7 g.	28·8
1 : 2 : 0·15	,,	4 ,,	,,	,,
1 : 2 : 0·0	100–10°	24 ,,	2·5 g.	43·1
1 : 3 : 0·0	110–15°	10 ,,	2·7 g.	46·5
1 : 4 : 0·0	120–25°	2 ,,	,,	,,
1 : 4 : 0·15	,,	4 ,,	3·0 g.	51·7

used to volatilise away and that some was left behind and could be recovered with some of the aldehyde. Temperatures higher than 125° induced charring: so did much prolonged heating. The next experiments were tried with 3 mols. of the amide for one of the aldehydes and the yield slightly increased, ranging from 38 to 46 %. With 4 mols. of acetamide, the yield went up to 51·7 %.

Condensation of cinnamaldehyde with benzamide.—

The condensation was carried out in the usual manner. It was necessary to use higher temperatures. The highest yield with 1 : 1 mol. proportions was 40 % and with 1 : 2 mol. 55 %. Cinnamylidene-bisbenzamide, recrystallised from hot alcohol, came out as a white micro-crystalline substance with a m.p. at 250°. It was insoluble not only in water but also in methyl alcohol, acetone, benzene and carbon bisulphide: very slightly soluble in cold alcohol, and a little more in hot.

Nitrogen, Found: 8·5 %. $C_{23}H_{20}N_2O_2$ requires N = 7·9 %.

TABLE III.

Molar Proportions Aldehyde : Amide : Pyridine 3·3 g.	Temperature	Time of Heating	Yield	
			Weight	Per cent.
1 : 1 : 0·0	110°	8 hours	1·5 g.	16·9
1 : 1 : 0·15	,,	,,	,,	,,
,,	115–120°	10 ,,	1·7 g.	19·1
1 : 1 : 0·0	140–145°	2 ,,	2·1 g.	23·6
1 : 1 : 0·15	110–120°	9 ,,	2·9 g.	32·6
1 : 1 : 0·0	115–120°	9 ,,	3·6 g.	40·4
1 : 2 : 0·0	100–110°	8 ,,	1·7 g.	19·1
,,	140–145°	2 ,,	2·5 g.	28·1
,,	115–120°	9 ,,	4·5 g.	50·5
,,	140° and 110°	2 ,, 6 ,,	4·5 g.	50·5
1 : 2 : 0·15	,,	,,	4·9 g.	55

Condensation of cinnamaldehyde with propionamide.—

3·3 g. aldehyde, 3·6 g. propionamide and 0·2 c.c. pyridine were heated on the water-bath for 8 hours. The product was extracted and purified as usual. Milk-white needles, m.p. 220–21°. Yield 3·0 g. (46 %).

The same heated in the same way but without pyridine, gave a slightly greater yield, 3·3 g. (50·9 %).

Cinnamylidene-bisprop onamide gave N = 10·5 %. $C_{15}H_{20}N_2O_2$ requires N = 10·8 %.

Condensation of hydrocinnamaldehyde with benzamide.—

3·2 g. of the hydrocinnamaldehyde and 6 g. of benzamide (1 : 2 mol.) were heated alone without pyridine for 2½ hours at 140–50°. The product extracted and purified as usual came out as a white micro-crystalline powder, m.p. 244–45°. Yield 3·5 g. (39·1 %).

The bisbenzamide gave N = 7·9 %. $C_{23}H_{22}N_2O_2$ requires N = 7·8 %.

Summary.

1. Cinnamaldehyde has been condensed with four amides, in the presence of a trace of pyridine as well as in the absence of any reagent. The yields are on the whole good. The presence of the base does not very much affect the yield.

2. The product in all cases is the cinnamylidenebisamide.

3. Similarly hydrocinnamaldehyde is also condensed with benzamide and gives a fair yield of the bisamide.

REFERENCES.

1. Gupta, *J.C.S.*, 1921, **119**, 298.
2. Pandya and Sodhi, *Proc. Ind. Acad. Sci.*, 1938, **7**, 361.