

## CONDENSATION OF ALDEHYDES WITH AMIDES

### Part XIV. Condensation of *n*-Heptaldehyde

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Received September 19, 1947

IN the papers so far published in this series, the condensation and the conditions of condensation of eighteen aldehydes with more or less common amides have been studied. Almost all the aldehydes have been aromatic: cinnamaldehyde and dihydrocinnamaldehyde being the only exceptions, in the sense that, though each contains a benzene ring, the aldehyde group is not situated on the ring but is on the side chain.

A straightforward study of the condensations of aliphatic aldehydes with amides has not so far been undertaken. Literature abounds in the condensations with amides of the three common aliphatic aldehydes, *viz.*, formaldehyde, acetaldehyde and chloral. In the present paper are included some condensation-studies of *n*-heptaldehyde ( $\alpha$ -n-anthaldehyde), a straight-chain aliphatic aldehyde, resembling benzaldehyde in so far as both contain C<sub>7</sub>.

Medicus (1871)<sup>1</sup> has reported *n*-heptylidene-*bis*benzamide and -*bis*-nitrobenzamide by following the method of Roth<sup>2</sup> and Schuster.<sup>3</sup> *n*-Heptaldehyde has also been reported to have been condensed with urea by Schiff<sup>4</sup> to give  $\alpha$ -n-anthylidene-diurea and di $\alpha$ -n-anthylideneurea, and also with thiourea (Schiff<sup>5</sup>). The yields have not been given.

It has been found in this laboratory that *n*-heptaldehyde condenses with acetamide, propionamide, urea, benzamide and cinnamamide, under varying conditions, giving different yields of the -*bis*amide type of product, and that it does not combine, under the same conditions, with formamide, *n*-butyramide and *n*-heptamide. Its failure to condense with formamide is not a surprise, because, of the 18 aldehydes so far examined, several have already failed to do this, but the other two amides had so far reacted very well.

As indicated by their properties and by analysis, the products of the condensation, wherever condensation did occur, were the heptylidene-*bis*-amides, the yields being generally below 50%, except in the case of propionamide which gave a 78% yield as the highest. Cinnamamide also reacted well, and gave slightly less than a 50% yield in a much shorter time (4 hours),

The conditions of the maximum yield were not identical in every case (*vide* Table). A comparison with the benzaldehyde-amide condensation (Bhatnagar and Pandya<sup>6</sup>) is also instructive, showing the differences in the yields when the condensation of the amide took place with an aromatic aldehyde and with an aliphatic aldehyde with the same number of carbon atoms (Table). It is noted that a pyridine-trace improves the yield, though in some cases only.

TABLE

Amides	From Benzaldehyde <sup>6</sup> maximum yield %	M.P.	Conditions	From <i>n</i> -heptal- dehyde yield %	M.P.	Conditions
Formamide	18	246°	Heated, small flame, 2 hrs alone	0	..	Under all conditions tried
Acetamide	55	245°	Alone, water-bath, 18 hrs.	43.9	176°	Alone, 14 hrs., at 120°-150°
Propionamide	30.7	220°	Alone, 8 hrs. 100-20°	78.1	150°	With pyridine and piperidine, both in traces, 100-12, 5 hrs.
<i>n</i> -Butyramide	86	170°	Alone, 8 hrs., 100-30°	..	..	..
<i>n</i> -Heptamide	48.2	124°	Alone, 9 hr. 100-30°	..	..	..
Benzamide	23	217.5°	Pyridine trace, 6 hrs, water-bath	35.9	128°	Alone, water-bath 10 hrs.
Cinnamamide	80	216°	130° 4 hrs., + 160° 5 hrs., alone	46.8	200°	Alone, 120-25°, 4 hrs.
Urea	Not tried	..	..	34.7	160°	Alone, 110-15° 15 hrs.

(Only maximum yields are given.)

Some of these condensations were first investigated here by Norman Phœnix David after he had studied the cœnanthaldehyde-malonic acid condensation (M.Sc. Thesis, 1946, unpublished).

#### EXPERIMENTAL

##### *Condensation with Acetamide without any Condensing Agent*

1. *n*-Heptaldehyde (1 g.) and acetamide (2 g.) (1 : 4 mol.) were heated in a 50 c.c. round-bottomed flask, fitted with an air-condenser, on water-bath, for six hours, when a homogeneous yellow solution remained. Copious steam vapours had come out. The next morning a cold yellow paste was observed; a test-portion on treatment with ether completely dissolved, showing that little or no reaction had taken place. The flask was again heated (water-bath) for eight more hours, when a yellow solid was formed. It was washed with cold distilled water, crushed in a mortar, first with cold

water and then with ether; a white product remained, which was recrystallised (cold absolute alcohol) into milk-white crystals. It did not decolorise bromine or Baeyer's reagent, suggesting absence of unsaturation. It also gave no colour with cold sulphuric acid. It melted at 166° C. and smelt very much like œnanthal, even after several recrystallisations. The yield was 0.63 g. or, as *bis*-acetamide, 33.7% of theory.

N, found: 13.39%; *n*-heptylidene-*bis*acetamide  $C_{11}H_{11}N_2O_2$  requires 13.08%; *n*-heptylidene-*mono*-acetamide  $C_9H_{17}NO$  requires 9.52%.

2. *Condensation at 120–50°*.—The above experiment was repeated at the higher temperature (18 hours). The contents assumed a red colour. The product melted, after recrystallisation, at 166°. The yield was 0.82 g., or 43.9% of theory.

3. *Condensation on Water-bath in 1:2 mol. proportion*.—The total heating was for 18 hours, the product was identical, but the yield was only 0.19 g., or about 10.2% of theory.

4. *Condensation in the Presence of a Trace of Pyridine*.—*n*-Heptaldehyde (1 g.), acetamide (2 g.) and pyridine (2 drops) were heated (1:4:0.15 mol.) on water-bath, without a condenser for 18 hours. The yellowish-red solid on usual treatment gave the same product, yield = 0.6 g., or 32.1% of theory.

5. *Condensation in the Presence of Pyridine-acetate*.—The same amounts of the aldehyde and the amide were mixed with 2 drops of pyridine and 2 drops of glacial acetic acid, and the whole was heated on water-bath for 15 hours: when 0.34 g. of the same product was obtained (yield 18.2% of theory).

6. *In the Presence of Glacial Acetic Acid*.—*n*-Heptaldehyde (1 g.), acetamide (2 g.) and glacial acetic acid (2 g.) (1:4:4 mols.) were heated on an oil-bath at 120–25° for 15 hours; the same product came out, yield 0.4 g. (21.4% of theory).

*Condensation with Propionamide without any condensing Agent.*

1. *n*-Heptaldehyde (0.5 g.) and propionamide (0.75 g.) were heated together on water-bath for 5 hours (air-condenser). The product, after recrystallisations (absolute alcohol), came out in white needle crystals, melting sharply at 150°. Like the *bis*-acetamide, it was soluble in benzene, chloroform and acetone, and all other properties of the two were similar. N, found: 11.64%; *n*-heptylidene-*bis*propionamide  $C_{13}H_{26}N_2O_2$  requires 11.57%; the *mono*-amide  $C_{10}H_{19}NO$  requires 8.28%. The yield was 0.8 g., or 76.2% of theory.

2. *Condensation in the Presence of a Trace of Pyridine.*—*n*-Heptaldehyde (0.5 g.), propionamide (0.75 g.) and pyridine (2 drops) (1:2:0.15 mol.) were heated on water-bath (5 hours). The reaction was more quick and the product was identical with the earlier one. Yield 0.75 g. (71.4% of theory).

3. *Condensation in the Presence of a Pyridine-piperidine Mixture.*—To the same amounts of the aldehyde and the amide, one drop of pyridine and one drop of piperidine were added. The heating was on water-bath (3 hours) and on oil-bath (112°, 2 hours). The crude yellowish product was identical; yield 0.82 g. (78.1% of theory).

4. *Condensation in the Presence of a Trace of Pyridine at higher Temperature.*—The same experiment (No. 3) was repeated with pyridine alone at 112°, but did not prove satisfactory. 10 hours' heating gave some resin. The yield was less, 0.69 g. (64.8% of theory).

#### *Condensation with Formamide*

This did not take place, when (1) the aldehyde and the amide (one gram each) were heated alone on water-bath (16 hours) in the absence of any condensing agent, (2) they were heated on an oil bath (140–45° C.) for 4 hours, (3) they were heated for 4 hours in an alcoholic medium, (4) they were heated for 4 hours with sodium ethoxide, (5) they were heated on water-bath for 16 hours in the presence of glacial acetic acid. A few other conditions were also tried, but without success, the aldehyde and the amide being almost wholly recovered unchanged.

#### *Condensation with n-Butyrimide.*

*n*-Heptaldehyde (0.5 g.) and *n*-butyrimide (0.8 g.) were heated under different conditions: (1) heated on water-bath in the absence of any condensing agent for 16 hours, (2) heated with a trace of pyridine on water-bath for 16 hours, (3) heated for over 6 hours in the presence of pyridine-acetate: but no product could be isolated, the reactants being recovered unchanged.

#### *Condensation with n-Heptamide*

*In the Absence of a condensing Agent.*—No condensation took place when *n*-heptaldehyde (0.5 g.) and *n*-heptamide (1.2 g.) were heated (a) up to 16 hours on water-bath, or (b) up to 10 hours at 120–25° C. None took place also (c) in the presence of a trace of pyridine, (d) in the presence of pyridine-acetate, (e) in the presence of glacial acetic acid (130–35° C.), resinous material being sometimes obtained.

*Condensation with Benzamide*

1. *On a free flame with no condensing agent.*—*n*-Heptaldehyde (0.5 g.) and benzamide (1.2 g.) (1:2 mol.) were heated under reflux on a free flame for about 5 hours. The mixture melted, became deep yellow and syrupy but solidified on cooling. It was dissolved in boiling alcohol, and white crystalline flakes came out from the solution which were recrystallised (hot alcohol). They had the properties described by Medicus, and melted without decomposition at 128° (Medicus, 128°). N, found = 8.4, 7.96%: *n*-heptylidene-*bis*benzamide  $C_{21}H_{26}N_2O_2$  required 8.28%. The yield was 0.4 g. (27.6% of theory). Medicus does not state his yield.

2. *Condensation on Water-bath without any Agent.*—Water-bath and an air-condenser were used, the heating being for 10 hours; the product was identical. The yield was slightly higher, 0.52 g. (35.9% of theory).

3. *Condensation in the Presence of a Trace of Pyridine.*—Exp. 2 was repeated with 2 drops of pyridine. Some resinification took place: the yield = 0.47 g. (32.4% of theory).

4. *Condensation at 120–25° without any Agent.*—Here also resinification occurred, and the yield was slightly less being 0.35 g. (24.2% of theory).

*Condensation with Cinnamamide*

1. *On Water-bath without any condensing Agent.*—*n*-Heptaldehyde (0.5 g.) and cinnamamide (1.5 g.) were heated without a condenser for 4 hours. The product was taken out as usual and recrystallised (hot 60% alcohol): it melted finally at 200° C. N, found: 7.3%; *n*-heptylidene-*bis*cinnamamide  $C_{25}H_{30}N_2O_2$  requires 7.18%; the *mono*-amide requires 5.78%. Its properties were similar to those of the other products described above. Yield 0.75 g. (43.9% of theory).

2. *At 120–25°, without any condensing Agent.*—The reaction was a little quicker. Yield = 0.8 g. (46.8% of theory).

3. *In the Presence of a Trace of Pyridine.*—The three were heated (1:2:0.15 mol.) on water-bath for 10 hours; the reaction was slower and the yield less: = 0.5 g. (29.2% of theory).

*Condensation with Urea*

1. *On Water-bath, without a condensing Agent.*—*n*-Heptaldehyde (1.1 g.) and urea (1.3 g.) (1:2 mol.) were heated for 14 hours. The cold mass was crushed and washed with cold water and ether separately. The white product, having the usual properties, and recrystallised from 60% alcohol,

melted at 160°. N, found 25.8%; *n*-heptylidene-bisurea  $C_9H_{20}N_4O_2$  requires 25.9%. The yield was 0.5 g. (or 26.3%).

2. *On Water-bath in the Presence of a Trace of Pyridine.*—The usual mol. proportions were taken. The heating was for 15 hours. The product was identical, and weighed 0.51 g. (26.8% of theory).

3. *At 110–15° without a condensing agent.*—After 15 hours' heating, the same product came out. Yield 0.66 g. (34.7% of theory).

4. *At 110–15° with a trace of pyridine.*—The yield in this case was 0.4 g. (21% of theory).

#### SUMMARY

*n*-Heptaldehyde or œnanthaldehyde condenses with acetamide, propionamide, benzamide, cinnamamide and urea, giving fair to very good yields under particular conditions. All the products are *bis*-amides. It does not undergo condensation with formamide, *n*-butyramide and *n*-heptamide. The yields from *n*-heptaldehyde and from benzaldehyde are compared in the table above, the former giving higher yields with prioponamide and benzamide.

#### REFERENCES

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| 3. Schuster             | .. <i>Ibid.</i> , 154, 89.                         |
| 4. Schiff               | .. <i>c. r.</i> , 65, 801.                         |
| 5. _____                | .. <i>Ber.</i> , 11, 883.                          |
| 6. Bhatnagar and Pandya | .. <i>Proc. Ind. Acad. Sci.</i> , 1946, A 24, 487. |