

THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part VIII. The Condensations of 6-Nitropiperonal

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IN Part VII of the series have been described the condensations of piperonal with eight of the common acid amides, of which one formamide did not undergo condensation.¹ Wondering whether the introduction of any active group on the ring of the aromatic aldehyde would have any observable influence on the condensations of piperonal with these amides, simple derivatives of piperonal with an active substituent were considered desirable for a trial. Two of these are available and very easily prepared from the aldehyde itself, *viz.*, 6-nitro-piperonal and 6-bromopiperonal. In the present paper are described the experiments made to bring about the condensations of these eight amides with 6-nitropiperonal.

As in the case of unsubstituted piperonal,¹ nitropiperonal is found not to undergo any condensation with formamide, the simplest, and perhaps the most extraordinary, of the amides. Unexpectedly, the yields with propionamide, benzamide and phenylacetamide are poor, while the yields with the remaining amides are above 50%, the highest being with cinnamamide, which is found to be 83% of theory, which is indeed higher than any yield obtained also from piperonal and any of the amides. Chemically the products are of the same type, *viz.*, the 6-nitro-piperonyl-*bis*amide, and share the properties of the piperonal-analogues already described. Pyridine or any other organic base was not used.

Experimental

Preparation of 6-Nitropiperonal.—The following was found to be the best method of preparing it and gave nearly theoretical yields. 10 g. of piperonal were slowly added, in the course of 15 minutes, to 20 c.c. of nitric acid (density about 1.4), and left at room temperature for another ten minutes. (It is important that during the addition the temperature should not rise above 45°.) Water was then added, when solid nitro-piperonal came out in yellow crystals. Though described as 'colourless needles from water',

the substance is really very susceptible to the influence of light, and becomes yellow, as observed by Fittig and Remsen.² Indeed the description of F. M. Perkins³ is more true, as the compound changes from "pale yellow to intense, most brilliant yellow on the surface": m.p. 95°.

Attempted Condensation with Formamide.—The 6-nitropiperonal, 1.0 g. was mixed with 2 g. of formamide (1:2 mol.) and the mixture kept on a water-bath at 110–15° for 24 hours. Even then no solid separated and the whole mass remained liquid. On the addition of water, the aldehyde came out unchanged.

Condensation with Acetamide.—1.95 g. aldehyde and 1.2 g. acetamide were heated on an oil-bath at 110–15° for six hours. After two hours a solid began to set in. The product was taken out in the usual way and crystallised from alcohol-pyridine mixture as very pale yellow needles, melting at 235°. Yield 1.8 g. or 61% of theory. With concentrated sulphuric acid it gave a yellow coloration, which was changed to pale yellow on the addition of water.

Nitrogen, found 14.30%: the 6-nitropiperonyl-*bis*acetamide $C_{12}H_{13}O_6N_3$ requires 14.24%.

Condensation with Propionamide.—3 g. aldehyde and 2.2 g. propionamide (1:2 mol.) were heated at 110–15°. After six hours even the reacting mass remained liquid, showing that the condensation was taking place very slowly or not at all. Heating was continued for 18 hours when the mass solidified. The product was treated as usual, and after repeated crystallisations the melting-point rose to 212° and the substance came out as pale yellow micro-crystals. The yield was about 15%. With concentrated sulphuric acid it gave a yellow coloration, which became faint on the addition of water.

Nitrogen, found 12.96%: the 6-nitropiperonyl-*bis*propionamide $C_{14}H_{17}O_6N_3$ requires 13.00%.

Condensation with n-Butyramide.—1.95 g. the aldehyde and 1.74 g. *n*-butyramide were heated at 110–15° for 10 hours. The product was washed with ether to remove the unreacted aldehyde and then it melted at 190°. Recrystallised from alcohol, it came out in pale buff-coloured micro-needles, melting with decomposition at 209°. With concentrated sulphuric acid it gave a yellow coloration, but when water was added a little turbidity was seen and a fine violet ring formed at the surface of the mixture: on shaking and thoroughly mixing, both disappeared, leaving only a very pale yellow coloration. The yield was 2 g., or 57% of theory.

Nitrogen, found 12.33%: the 6:nitro-piperonyl-*bis-n*-butyramide $C_{16}H_{21}O_6N_3$ requires 11.96%.

Condensation with n-Heptamide.—0.98 g. of the nitropiperonal and 1.29 g. of *n*-heptamide (1:2 mol.) were heated at 110–15° for 10 hours. The mixture remained liquid for nearly six hours, after which solidifications set in. The product was washed with alcohol, and in the crude condition was brown in colour. Recrystallised from hot alcohol, it came out in pale lemon-coloured needles, melting at 185°. The yield was 1.2 g. or 55% of theory. It gave a reddish yellow coloration with concentrated sulphuric acid, which on the addition of water became turbid with a violet-coloured ring: all this disappeared on shaking when only a yellow coloured solution remained.

Nitrogen, found 9.80%: the nitropiperonyl-*bis*-heptamide $C_{22}H_{33}O_6N_3$ requires 9.65%.

Condensation with Benzamide.—0.98 g. of the aldehyde and 1.31 g. benzamide (1:2 mol.) were heated at 110–15°: after three hours the mass became solid, and the heating was continued for another three hours. The product was then taken out, well washed with alcohol and the bisamide crystallized from pyridine from which it came out in pale yellow needles, melting at 248°. The yield was only about 25% of theory: higher temperatures for the condensation were tried, but they produced resinous substances. With concentrated sulphuric acid, it gave an orange coloration, which deepened on keeping, but which, on the addition of water, changed to a pale yellow as usual.

Nitrogen found = 10.46%: the nitropiperonyl-*bis*-benzamide $C_{22}H_{17}O_6N_3$ requires 10.02%.

Condensation with Phenylacetamide.—1.95 g. of the aldehyde and 2.7 g. of phenylacetamide were heated together at 110–15° for six hours. The yield was poor about 10%. The product, crystallized from pyridine, was very pale yellow, in fine needles, and melted at 231°. With concentrated sulphuric acid it gave an orange-yellow coloration, which became yellow when water was added.

Nitrogen found = 9.8%: nitropiperonyl-*bis*-phenylacetamide $C_{24}H_{21}O_6N_3$ requires 9.4%.

Condensation with Cinnamamide.—2.0 g. nitropiperonal and 3.0 g. cinnamamide (1:2 mol.) were heated for six hours at 110–15°. The condensation was quicker than before, and the yield 3.9 g. or 82.7% of theory was the best so far obtained. Crystallised from pyridine, the product, which was pale

yellow needles, melted at 232°. With strong sulphuric acid it gave a very rich orange coloration, which changed into deep yellow, when water was added.

Nitrogen found = 9.32%: nitropiperonyl-*bis*-cinnamamide $C_{26}H_{21}O_6N_3$ requires 9.92%.

Summary

The condensations of 6-nitropiperonal with amides have been studied. The products are in their properties in a line with the products obtained from piperonal itself. In the case of acetamide and cinnamamide the yields were distinctly higher than they were with piperonal: in other cases the reaction was distinctly slower and gave lesser yields.

REFERENCES

1. Pandya and Varghese .. *Proc. Ind. Acad. Sci.*, (A), 1941.
2. Fittig and Remsen .. *Annal*, **159**, 134.
3. F. M. Perkin .. *J. C. S.*, 1891, **150**.