

CONDENSATION OF ALDEHYDES WITH MALONIC ACID

Part XXII. Condensation of 6-Bromo-Piperonal

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*6-BROMO-PIPERONAL has been condensed with malonic acid in the presence and absence of pyridine, in the presence of a pyridine-piperidine mixture and in the presence of glacial acetic acid. Two products have been obtained and identified: 6-bromo-piperonylacrylic acid and 6-bromo-piperonylmalonic acid. As in the case of piperonal-malonic acid condensation (Kurien and Pandya,³ 1934; Pandya and Vahidy, 1936⁶), the yield of bromopiperonyl-acrylic acid has been excellent, reaching up to the theoretical at best (in the pyridine-piperidine mixture, according to Robinson and Shinoda¹⁰).

Earlier workers above^{3, 6} did not succeed in obtaining from piperonal, piperonylmalonic acid, thought it was obtained earlier by Knoevenagel² and by Piccinini⁹ by other methods. The corresponding dibasic acid from 6-bromo-piperonal was not obtained, as was expected, in the condensation without any condensing agent; but it came out in the condensation in the presence of glacial acetic acid (Stuart's¹¹ method) in 72% yield.

The 6-bromo-piperonylmalonic acid melted with effervescence, like all malonic acids, and was thereby changed into the 6-bromo-piperonylacrylic acid.

Usually the dibasic acid melts at a higher temperature than does the monobasic acid obtained from it by the removal of carbon dioxide. In the present case, however, the opposite condition prevails: 6-bromopiperonylmalonic acid melts at 202–03°, while the 6-bromo-piperonylacrylic acid melts at 254°. The same is true with regard to the unbrominated piperonylacids; piperonylacrylic acid has the m.p. (according to various earlier workers^{4, 8}) varying from 232° to 242°. Piperonylmalonic acid is reported

* The condensation in the presence of pyridine-trace was first carried out by R. B. P. in 1942 and the product was identified. R. L. S. carried out the work independently in 1946–47.

to have the melting point at 187-89° (Piccinini⁹) and 190-95° (Knoevanagel²), but definitely lower.

EXPERIMENTAL

6-Bromo-piperonal.—It was prepared according to the method of Oelker melting at 128-29° (129°, Oelker⁵). The needle-shaped cream-coloured crystals were soluble in hot alcohol, hot benzene, and in excess of ether; readily soluble in chloroform and insoluble in water. The yield was about 56%. (37% reported by Parijs⁶ and 45% by Ittyerah¹; these last did not use iodine as a catalyst, as was done now.)

Condensation in the Presence of Pyridine

1. *A Trace of Pyridine*.—6-Bromo-piperonal (1.1 g.), malonic acid (0.5 g.) and pyridine (kept under alkali and fresh-distilled (0.15 g.) were heated together for three hours (1:1:0.35 mol.). As both the aldehyde and the acid had melting-points quite above the temperature of the water-bath, it was arranged that the heating was at 105-10° for two hours and at 120° for one hour. The mass became semisolid and gave out carbon dioxide, which slackened after 15 minutes. The reacting mass became yellow and hard and remained so all the time. This was then crushed and extracted with sodium carbonate solution (warm). It was filtered, the residue was again digested with sodium carbonate solution; the residue was the unreacted aldehyde (= 0.2 g.). The total filtrate and extract, when acidified gave a white precipitate, melting, after recrystallisation at 254°, and was identified as 6-bromo-piperonyl-acrylic acid. Yield 1.0 g., 1.1 g. (on the basis of the aldehyde taken = 77%—81% of theory: on the basis of the aldehyde actually used = 94% of theory.) Its properties and analysis are given below.

2. *In the Presence of Half a Molecule of Pyridine*.—The molecular proportion was 1:1:0.5, and the heating was at 115-20° for six hours. 0.15 g. aldehyde was recovered, and the yield was 1.1 g. (i.e., calculated on the aldehyde taken—81%, and on the aldehyde actually used over 98% of theory).

3. *In the Presence of Pyridine-Piperidine* (according to Robinson and Shinoda¹⁰).—The aldehyde (1.15 g.), malonic acid (1.30 g.), pyridine (1.20 g.) and piperidine (two drops) were treated by the above method. The mass fused within fifteen minutes, then became semi-solid, and there was a brisk effervescence: when the latter slackened, a homogeneous liquid was left, which changed to a semi-solid first and then to a light orange coloured solid. The unreacted aldehyde recovered was only 0.05 g.; and the yield of the purified product was 98.5-100%.

The 6-bromo-piperonyl-acrylic acid was crystallised from hot alcohol, and melted finally at 254°. It was almost insoluble in acetone, chloroform, carbon tetrachloride and benzene. Though when freshly crystallised it had a white colour, it always became slightly yellowish on keeping even in a corked tube. It immediately decolourised Baeyer's reagent as well as bromine water in the cold. [Equivalent weight found = 270.1, 271.9 by titration (in hot alcohol against standard sodium hydroxide solution). $C_{10}H_7O_4Br$ requires equivalent weight = 271.0. Found: Br, 29.54, 29.23%. $C_{10}H_7O_4Br$ requires Br, 29.52%.]

In the Absence of Any Condensing Agent

The aldehyde and malonic acid were heated alone (in 1 : 1 mol.) on water-bath; even after 2 hours, no fusion and no condensation took place. The same thing happened when the heating was carried out at 105–10°. The aldehyde sublimed away.

In the Presence of Glacial Acetic Acid (according to Stuart¹¹)

(1) The same amounts of the aldehyde and malonic acid were heated on water-bath with 2 c.c. of glacial acetic acid (1 : 1 : 3.5 mol.) for 11 hours. Within 10 minutes, a clear liquid was formed, and a yellowish red colour appeared. 0.2 g. of unreacted aldehyde was recovered, and a product recovered in the usual way: it was a yellowish solid, which on shaking with ether and on evaporation of the ether later, gave fine yellow crystals (needles): the melting-point, after purification, was 202–03°. This was the 6-bromo-piperonyl-malonic acid. It weighed 0.9 g. (*i.e.*, 59.6% on the aldehyde taken or 72.6% on the aldehyde used).

(2) In another experiment more of glacial acetic acid was taken (1 : 1 : 5 mol.). The heating was for 13 hours at 100–105°. The yield however was lower (50.6%).

(3) The quantities were as in (1), the temperature was 100–05° and the heating was for only 6½ hours. The yield was still less (29.7%).

When absolute alcohol was taken, instead of the acetic acid, in sufficient quantity (7 c.c.), and the reactants were refluxed on water-bath for 14½ hours, resinification was found to have taken place and nothing could be separated.

The 6-bromo-piperonyl-malonic acid had a bright yellow colour: various methods of purification left the melting-point unchanged (202–03°, with effervescence and decomposition). It was soluble in alcohol, but less so in chloroform and benzene (warm). After melting at 202–03°, and after

the effervescence had stopped, a solid was left behind, which melted only at 250° (without effervescence), showing that the dibasic acid had changed into the mono-basic 6-bromo-piperonyl-acrylic acid (m.p. 254°). This was confirmed by means of the identical mixed melting-point with a specimen of the monobasic acid. Equivalent weight found (by titration of alcoholic solution) 158.3; $C_{11}H_7O_6Br$ requires equivalent weight = 157.5. Found: Br, 24.93. $C_{11}H_7O_6Br$ requires Br, 25.39%.

SUMMARY

6-Bromo-piperonal has been condensed with malonic acid and gives two different products; 6-bromo-piperonyl-acrylic acid (the highest yield being quantitative) and 6-bromo-piperonyl-malonic acid (the highest yield being 72%). The presence of pyridine gives the first, that of glacial acetic acid gives the second.

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