

THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part IV. The Condensation of Piperonal.

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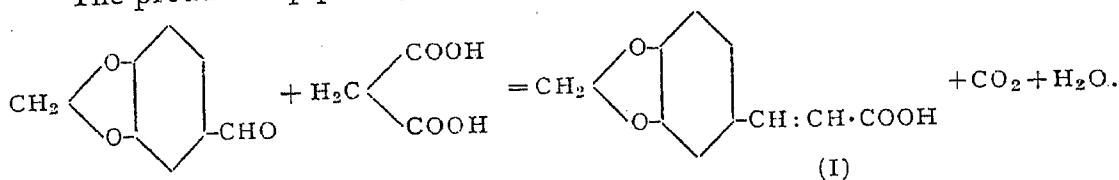
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IN the condensation of piperonal with malonic acid in the presence of a trace of pyridine,¹ it was found that the yield of the unsaturated acid was highest, *viz.*, 100%. A further study of this has revealed some interesting points.

The product is piperonyl-acrylic acid, (I)



It was first prepared by Lorenz² from piperonal, sodium acetate and acetic anhydride by Perkin's method. He gave the melting-point 232° C. Later on Perkin himself³ prepared it by a slightly different method, which, he says, "was found to give good yields". Somehow he does not state the actual yields, though he observes that his acid was in every respect identical with that of Lorenz, except in the melting-point, which he found to be higher, namely, 238° C. Dutt⁴ reports having prepared it from piperonal, malonic acid and pyridine-piperidine mixture. He, however, does not refer to Lorenz, refers only to Perkin's paper, says that he identified the acid according to Perkin, and yet gives not Perkin's, but Lorenz's figure for the melting-point, *i.e.*, not 238° C., but 232° C. He also reports an yield of 76% by his method. Later on Dutt prepared it again⁵ with a molecular proportion of another base, quinoline. The melting-point is not mentioned, but his "best possible yield" was now lower than before, *viz.*, only 60.9%. It was found by Kurien and one of us⁶ that with a trace only of pyridine, the yield was theoretical and that the product melted with decomposition at 240°C. In the present paper

it has been found that very careful and repeated purifications raise the melting-point still higher, *viz.*, to 242° C.

The condensations were carried out first with a trace of pyridine—0.15 mol. nearly, and the earlier good yield was confirmed. The following bases were then tried, usually in 0.15 molecular proportion, and the resulting yields varied from 40% to theoretic. In the cases of the lower yields, resinification was invariably noticed. It is possible that by varying some of the conditions improvements in the yield might have been seen. But uniform conditions were maintained to make comparisons fair. The bases were:

Lutidine, quinoline, iso-quinoline, quinaldine, diethylaniline, dimethyl-aniline; piperidine, methylaniline, ethylaniline, diphenylaniline; aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, α -naphthylamine, β -naphthylamine; ammonia and ammonium malonate.⁶ A very interesting peculiarity is shown by this aldehyde which may throw light on the specific catalytic influence of each of the bases used. Piperonal and malonic acid are found to undergo the same condensation even without the trace of any base. This has indeed been observed, in the case of benzaldehyde by Dutt, as well as by workers in this laboratory. But the product in this case was always the dibasic benzylidene malonic acid. Piperonal, on the other hand, gives the usual monobasic, piperonyl-acrylic acid in a straightforward way. Repeated experiments were made taking every precaution to exclude even a trace of any other substance. Yet the condensation proceeded as usual, and in four hours gave over 50% of piperonyl-acrylic acid. The yield increased on prolonging the heating on the water-bath, and reached the usual theoretical value, about 95% on eighteen hours' heating. Most of the organic bases bring about the same result in 4 hours, and a trace is more effective than a whole molecular proportion, as evidenced by the yields when quinoline and pyridine were used. In other cases resin-production probably not only clogs the reaction but certainly also makes separation less easy and thus diminishes the yield.

Experimental.

The procedure was in all cases very similar to what was found good in earlier condensations. The bases were all purified and generally freshly distilled. The aldehyde was also recrystallised and dried. The malonic acid was Scherring-Kahlbaum's, "pure for scientific purposes," and dried at 100° C. 3 grams piperonal, 2 grams malonic acid and the base in traces as in the Tables, were mixed in a dry flask and heated on a water-bath for about four hours. The aldehyde melted immediately (m.p. 37° C) and the acid gradually dissolved in it. This took about half an hour, after which an evolution of carbon dioxide was

observed, and after about an hour the whole mass in the flask became solid. Heating was continued for three hours more, when it was stopped. On cooling, the mass was taken out, crushed, treated with sodium carbonate solution and warmed. If there was any resinous mass, it was filtered out, and the acid piperonyl-acrylic was separated by the addition of dilute hydrochloric acid. In every case the crude acid was slightly coloured, dirty white, grey or yellow, as was found in earlier cases, by Dutt and by others in this laboratory.

The acid recrystallised from alcohol or acetone melted with decomposition at 242°C. Recrystallisation from glacial acetic acid, or changing into sodium and barium salts and re-precipitating the acid by dilute HCl made no change in the melting-point. The acid was found to be able to undergo sublimation on warming: crystals obtained on sublimation also melted at 242°C.

The equivalent weight of the acid was found

(1) by titration with standard baryta = 193,

(2) by the silver salt method = 192.4,

while the formula $\text{CH}_2 : \text{O}_2 : \text{C}_6\text{H}_5\text{CH} : \text{CH.COOH}$ requires 192.

Determination of carbon and hydrogen gave:

Carbon found = 62.26%, hydrogen found = 4.19%.

The formula $\text{C}_{10}\text{H}_8\text{O}_4$ requires C = 62.50%, H = 4.16%.

The exact yields with the different bases used are given in the Table at the end.

Condensation without a base.—Malonic acid (2 grams) and piperonal (3 grams) were taken in a flask that was very carefully cleaned and dried. The mixture was heated on the water-bath for different periods, and the product treated as before to separate the acid formed. It was found that with the usual four hours' heating, piperonyl-acrylic acid was formed with 52% yield, and when the heating was prolonged to eighteen hours, the almost theoretical yield of 95% was obtained. The acid was identical in its melting-point to the one obtained before.

REFERENCES.

1. Kurien and Pandya, *Jour. Ind. Chem. Soc.*, 1934, **IX**, Part I, 825.
2. Lorenz, *Ber.*, 13, 757.
3. Perkin, *J. C. S.*, 1891, Trans. 152.
4. Dutt, *Jour. Ind. Chem. Soc.*, 1925, **I**, 300.
5. Dalal and Dutt, *Jour. Ind. Chem. Soc.*, 1932, **IX**, 313.
6. According to Knovenagel.

TABLE.

Base	Quantity in c.c.	Approximate in molar proportion	Yield		Remarks : Colour, etc.
			in grams	in %	
<i>Tertiary.</i>					
Pyridine ..	0.24	0.15	3.4	92	White.
Lutidine ..	0.34	"	"	"	"
Quinoline ..	0.35	"	3.5	93	Yellowish.
Iso-quinoline ..	"	"	3.6	95	White.
Quinaldine ..	0.4	"	3.4	92	Grey, resin.
Diethylaniline ..	0.48	"	3.2	87	Yellowish, resin.
Dimethylaniline ..	0.37	"	2.5	67.5	"
<i>Secondary.</i>					
Piperidine ..	0.25	0.15	2.5	67.5	White, no resin.
Piperidine ..	0.5	0.25	3.6	96	"
Methylaniline ..	0.33	0.15	1.5	40.5	Grey, " much resin.
Ethylaniline ..	0.37	"	1.7	46	"
Diphenylamine ..	0.5	"	2.0	52.6	White, " much resin.
<i>Primary.</i>					
Aniline ..	0.27	0.15	2.1	56.7	Grey, some resin.
<i>o</i> -Toluidine ..	0.32	"	2.9	78.0	"
<i>p</i> -Toluidine ..	"	"	"	"	"
<i>m</i> -Toluidine ..	"	"	2.8	75.6	"
<i>α</i> -Naphthylamine ..	0.43	"	3.0	80.0	Yellowish, resin.
<i>β</i> -Naphthylamine ..	gram.	"	3.2	87.0	"
Ammonium hydroxide ..	0.1	"	2.7	73.0	White, " no resin.
Ammonium malonate ..	0.4 c.c. gram.	"	"	"	"