THE CONDENSATION OF ALDEHYDES

Part III. Of *p*-Tolylaldehyde with Amides

Part XI. Of *p*-Tolylaldehyde with Malonic Acid and Malonanilic Acid

By Rup Kishore Mehra and Kantilal C. Pandya

(From the Chemistry Laboratory, St. John's College, Agra)

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p-Tolylaldehyde when heated with one of the amides described below combines to give compounds of the type of *p*-tolylidene-bisamides, very like the benzylidenebisamides obtained from benzaldehyde by Bülow and others.[1] It is found that acetamide, propionamide, benzamide and phenylacetamide undergo this condensation merely by heating the two alone, the presence of pyridine not having any appreciable influence on the yields. Formamide, however, remained unaffected even after prolonged heating, but the condensation was effected in the presence of a trace of pyridine. The yields were not high, being below 50% of theory. All the condensation-products were saturated, and did not affect Baeyer's reagent.

Experimental

Condensation with Formamide.—*p*-Tolylaldehyde 3 g., formamide 2·2 g. and pyridine (0·3 c.c.) (1 : 2 : 0·15 mol.) were heated together at 175–80° for three hours. Longer or higher heating gave a dark brown colour, and lower temperatures were ineffective. The flask was taken out of the oils bath when the colour showed signs of darkening. On cooling, pale yellow crystals separated, which were filtered out and washed well with water and boiling alcohol or boiling acetone, respectively. The crystals were insoluble in the usual solvents. Repeated washing as above gave a sample melting at 287° C.

Nitrogen found : 14·54%; *p*-tolylidene-bisformamide $C_{10}H_{12}O_2N_2$ require 14·59%.

The product weighed 0·7 g. and the yield was 14·6% of theory.

Condensation with Acetamide.—3 g. Aldehyde and 3 g. acetamide (1 : 2 mol.) were heated for 4 hours at 120–125°. The whole became a homogeneous mass at about 105° and gave out water vapours. After 1·5 hours' heating, a solid began to separate, which increased in amount after the heating was stopped and the flask was cooled. The unaffected aldehyde was removed

by extraction with ether, and the solid was crushed with cold water to remove the acetamide. The crude product on recrystallisation from hot dilute alcohol came out in milk-white silky needles, melting at 274° C. It weighed 1·5 g. and the yield was 27·3% of theory.

Nitrogen found : 12·90% ; *p*-tolylidene-bisacetamide $C_{12}H_{16}O_2N_2$ requires 12·73%.

Condensation with Propionamide.—The aldehyde 3 g. and the amide 3·6 g. (1 : 2 mol.) were heated at 120° for 4 hours ; the mixture behaved as in the acetamide condensation, and the product was taken out in the same way, being recrystallised from hot alcohol or hot acetone. Milk-white silky needles melted at 232° C. Yield = 1·5 g. or 24·2%.

Nitrogen found : 11·35% ; the *p*-tolylidene-bispropionamide $C_{14}H_{20}O_2N_2$ requires 11·29%.

Condensation with Benzamide.—The aldehyde 3 g. and the amide 6 g. (1 : 2 mol.) were heated together at 120–125° for 3 hours. Within half-an-hour a crystalline white solid began to make its appearance. It was taken out in the same way and the same was purified as before. Milk-white needles, m.p. 230° C. Weighed 3·5 g. or 40·7% of theory.

Nitrogen found : 8·67% ; the bisbenzamide $C_{22}H_2O_2N_2$ requires 8·14%.

Condensation with Phenylacetamide.—1·5 g. of the aldehyde and 3·4 g. of the amide (1 : 2 mol.) were heated for 3 hours at 125–130°. The mixture fused to a homogeneous mass and gave out water vapours at 120°, and solid particles began to come out after 1·5 hours. The product was taken out and purified as before, but was found to be very little soluble in cold alcohol or acetone. Recrystallized from the hot solvent it came out as white silky needles, m.p. 238° C. Weight 2 g. = yield 43% of theory.

Nitrogen found : 7·93% ; the bisphenylacetamide $C_{24}H_{24}O_2N_2$ requires 7·53%.

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Condensation with Malonic Acid and Malonanilic Acid

In our paper on the condensation of aromatic aldehydes with malonanilic acid, it was stated that this acid condenses with *p*-tolylaldehyde giving about 71% yield of the cinnamanilide. The work, however, was not described further as sufficient amount of the aldehyde or of the condensation-product was not in hand for analytical purposes.[2] This work is now concluded and confirmed, the details are given below. The condensation was brought about by a trace of pyridine and the product did not contain any acid.

The condensation with malonic acid was carried out as usual, the yield of the *p*-methylcinnamic acid being quantitative when a trace of pyridine was used and only slightly less in the absence of any condensing agent.

Condensation was found to take place similarly with ethyl malonate.

Condensation with Malonanilic Acid.—1·2 g. *p*-Tolylaldehyde, 1·8 g. malonanilic acid and a trace of pyridine (1 : 1 : 0·15 mol.) were heated on a water-bath for 5 hours. In the course of an hour, fusion to a homogeneous mass took place and gas was liberated. After 5 hours' heating, it was left overnight, when most of it had solidified leaving a little of the unused liquid aldehyde. This was removed by means of ether, and the solid treated as usual with sodium bicarbonate solution. The bicarbonate extract did not give any acid product on acidification. The anilide which did not dissolve was purified by crystallisation from hot dilute alcohol. It came out in tiny white shining needles, melted at 184° C. and weighed 1·7 g. (yield 71·7%).

Nitrogen found : 5·86%; the *p*-methylcinnamanilide $C_{16}H_{15}ON$ requires N = 5·93%.

Condensation with Malonic Acid.—The aldehyde, malonic acid and pyridine were taken as 1 : 1 : 0·15 mol. and heated on the water-bath for 5 hours. The methylcinnamic acid was taken out in the usual way. The yield was about 93% : with acid malonic in 1·5 mol. proportion, the yield was about 99%. When no pryidine was used, the yield came up to about 91%, but the product was less pure and the heating was for 5·5 hours.

It melted at 197–198° C. (It has been prepared before by Perkin's reaction by several workers.[3])

Summary

The condensation of *p*-tolylaldehyde with five different amides, and with malonic acid and malonanilic acid have been described. The amides give bisamide products, and malonanilic acid the cinnamamilide. The yield with malonic acid is almost quantitative.

REFERENCES

1. Bülow, *Ber.*, **26**, 1972–74 ; Roth, *Annal.*, 1870, **154**, 72 ; Hoffmann and Victor, Meyer, *Ber.*, **25**, 212, etc.
2. Mehra and Pandya, *Proc. Ind. Acad. Sci.*, 1938, **7**, 370.
3. *Vide* Beilstein, Band **9**, 617.