

THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID

Part XIII. The Condensation of *o*-, *m*- and *p*- Chloro-benzaldehydes
and of *m*-Bromo-benzaldehyde: The Influence of Groups
and Comparison with Perkin's Reaction

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PERKIN'S reaction was probably first used by him (1868) for the preparation of the valuable perfume coumarine. Although cinnamic acid had actually been prepared from benzaldehyde a little earlier, namely, by Bertagini (1856) who had heated the aldehyde with sodium acetate and acetyl chloride in a sealed tube at 120–30°, and by Schiff (1870) who heated benzaldehyde with acetic acid and hydrochloric acid or zinc chloride in a sealed tube at 110–20°, and although controversies regarding the exact mechanism of Perkin's reaction started immediately, the method, with a little modification, soon became popular and attained a classical status in organic laboratory work (1877). It is still of very wide application.

The substitution of acetic acid by malonic acid was the next important step. Indeed it is interesting to realise that it was only in the course of the controversy about the mechanism of the reaction, going on between Perkin and Fittig, that the discovery was made by Stuart in Fittig's laboratory (1883), that the condensation of benzaldehyde to cinnamic acid took place equally well when sodium acetate was replaced by sodium malonate. Stuart also showed that instead of using acetic anhydride at 180°, if glacial acetic acid was used at 100°, better results were obtained. This method was then used by many workers, such as Komnenos (1883), Stuart, (1886), Fittig and Mackenzie (1894) and others. Satisfactory yields were also reported by Michael (1884) who merely heated the aldehyde with malonic acid alone in a sealed tube for several hours at 130–40°.

The next important change, so intimately associated with the name of Knoevenagel (1898), saw the introduction of a base, organic as well as inorganic, in place of acetic acid. His work was at first limited to aromatic aldehydes only (1896) : but it soon extended to aliphatic aldehydes also (1902), and is now well known to travel far beyond this simple aldehyde-malonic acid condensation. The inorganic base was ammonia, in the form

of alcoholic ammonia or ammonium malonate or chloride. The organic bases were either the primary bases like aniline and ethylamine, or the secondary ones like diethylamine and piperidine, or piperidine hydrochloride. The inorganic and the primary organic bases were employed in full molecular or even larger proportions, but the secondary bases were employed in small proportions only. Piperidine in a few drops, the "Knoevenagel's Reagent" is now a very useful ally of the synthetic chemist (1894–1904).

It is remarkable that Knoevenagel did not find much use of pyridine or of any tertiary organic base. It was Verley, according to Boxer and Linstead, who used it first (1899) ; this use was extended widely by Doebner (1900 and onwards) and others. A very important observation is that of Harding and Weizmann (1910), who specially recommended the use of a tertiary base in cases like the preparation of nonylenic acid from heptaldehyde, where Perkin's method gave poor yields of a mixed product and where Knoevenagel's bases gave small yields invariably mixed up with other condensation products (such as those formed from the usual Schiff's condensation of aldehydes with bases). For this and similar condensations, pyridine was generally used in full molecular proportions, or even in greater excess. Staudinger advised the use of anhydrous pyridine in dry ethereal solution: Florence (1927) also recommended the same method for the synthesis of α - β unsaturated aliphatic acids.

The present-day practice in fact favours the combination of pyridine with piperidine, as first recommended by Robinson to Perkin (1924). Haworth, Perkin and Raukin (1924) did not obtain more than a 30% yield of 3:4-methylenedioxcinnamic acid from piperonal by Perkin's method, but found that, following Robinson's suggestion, the yield became 'almost quantitative' when piperonal, malonic acid and pyridine were taken in 1:2.5:6 mol. proportions with a small amount of piperidine. [About ten years later, the same yield was obtained in this laboratory by Vahidy (1935) when the three were in the proportion of only 1:1:0.15 mol.] To-day the proportion of pyridine taken is about 3.5 mols. for 1 of the aldehyde, according to the method established by Robinsin and Shinoda (1925).

The fact that pyridine is also such an excellent solvent for so many substances and should therefore be used in liberal proportions to help the condensation on, and the other fact that as a tertiary base it is less active and strong than piperidine, and may be taken as inert, are probably responsible for the omission, in investigation as well as in literature, of the observation of the catalytic activity of pyridine. The earliest suggestion to this property seems to be contained in the interesting account of Bacharach and Brogan (1928),

who report that a few drops of pyridine used in Perkin's synthesis of cinnamic acid increased the yield to an optimum value of 85%. (Had they used the pyridine alone, without the sodium acetate and acetic anhydride, they might have obtained the still higher yield of about 95%—*vide* Experimental.) A little later, Boxer and Linstead (1931) found that 'Tertiary bases as such have a definite catalytic activity.' A general and systematic study of this catalytic activity has still to be made.

The work of Florence (1927) led Surange in this laboratory in 1929 to apply the pyridine method to a synthesis of aromatic α - β unsaturated acids. When applied to aromatic aldehyde-malonic acid condensation, the original method had to be modified. Nearly quantitative yields were obtained of the corresponding cinnamic acids from benzaldehyde and from *o*-, *m*- and *p*-nitrobenzaldehydes, when the aldehyde, malonic acid and dry pure pyridine were heated together without any solvent on the water-bath for a few hours. Cinnamaldehyde also gave the same high yield, but of a mixture of cinnamylidene-malonic and phenylacrylic acids (unpublished). Surange's failure to obtain any condensation product from hydroxy-benzaldehydes seemed to have been shared by other workers, *viz.*, Dutt, who had used an indefinite pyridine-piperidine mixture (1925).

The problem of the hydroxy-benzaldehydes was reinvestigated by Kurien and Pandya in 1931, who found that only a few drops of pyridine instead of one molecule, were able to do the work, and that in this way pyridine was as good a catalyst as piperidine or other tertiary bases (1934). The work has thereafter been pursued, and most of it published, (i) with a large number of aromatic aldehydes, (ii) with traces of other organic bases as well, most of which were tertiary, and (iii) with not only malonic acid, but also with malonic ester (occasionally) and with malonanilic acid (Mehra, 1938, 1939; Ittyerah, 1941, and Miss Pandya, unpublished) and with the three malon-*o*-, *m*- and *p*-toluidic acids (Ittyerah, unpublished), all of which contain the same reactive methylene group.

In all the above cases pyridine has been found to be a very efficient catalytic agent. Other organic bases too show a similar ability in varying degrees, though one cannot say off-hand as to which base might give the maximum yield in a particular condensation. Thus with salicylaldehyde, it was methylacridine that gave the highest yield (Khan and Kurein, 1935), with piperonal piperidine (Vahidy, 1935), with anisaldehyde isoquinoline (Vahidy, 1936), with *m*-hydroxybenzaldehyde pyridine (Vahidy, 1936), and so on.

When no base and no other chemical agent is present and when the aldehyde and the acid are heated up alone, the condensation proceeds to take

place very slowly, the yield is very much smaller unless the heating is prolonged, and the condensation proceeds without the decarboxylation, the undecarboxylated product being isolable, under suitable conditions, in excellent yields and in a state of purity. In cases when on the aromatic ring the aldehyde has also other groups present, their nature and number have generally a very far-reaching influence on the whole reaction, particularly on its speed and on the yield.

This last point has already been made in an earlier paper by Pandya and Sodhi (1939). Recently Lock and Bayer (1939) have also made a study of the influence of groups on the yields obtained during Perkin's reaction under standardised conditions. A comparison can thus be made of the influence of groups in Perkin's reaction with the influence in the pyridine-trace condensation.

Under the conditions chosen, these workers obtain a yield of 49% of cinnamic acid from benzaldehyde. The influence of the halogen atom is stated to produce higher yields of the corresponding cinnamic acids, the position and the number of the halogens making an evident difference. Thus chlorine is stated to give the following yields, which are all higher than that given by the unsubstituted benzaldehyde, *i.e.*, higher than 49% :

Position of chlorine	..	2	3	4	2-3	2-5	2-6	2-3-6	nil
Yield %	..	71	63	52	62	78	82	66	49

That the yields are higher than those obtained from ordinary unsubstituted benzaldehyde is undoubtedly true, but no other generalisation regarding the influence of number and position would be safe as the figures are so irregular.

In the present paper the condensations of benzaldehyde, of the three chlorobenzaldehydes and of *m*-bromobenzaldehyde with malonic acid and with a trace of pyridine, as well as in the absence of any condensing agent, have been studied. In all the cases, the reactions go very well under the conditions described. Benzaldehyde with only four hours' heating on the water-bath, in the presence of a few drops of pyridine, gave a 95% yield of cinnamic acid. With the entree of a halogen, the reaction was very obviously quickened, so that in the case of the four haloid-benzaldehydes, the reaction was often completed in one hour, the yields were quantitative and the products, therefore, unusually pure. There is no doubt about the accelerating influence of chlorine and bromine here, nor any about this being the best of all the methods found in literature for the preparation of *o*-, *m*- and *p*-chloro- and *m*-bromocinnamic acids.

Originally all these four acids were first prepared by Gabriel (1882) and Gabriel and Herzberg (1883) by a roundabout process of preparing first

the desired nitrocinnamic acid, which was then reduced to the corresponding aminocinnamic acid, which was then diazotized to the diazonium nitrate or sulphate, and then this was warmed with fuming hydrogen chloride or with ten parts of strong hydrobromic acid. *o*-Chlorocinnamic acid was obtained a little later by Stuart (1888) from *o*-chloro-benzalmalonic acid, itself prepared by the 'Stuart-method' of heating *o*-chlorobenzaldehyde with malonic acid and glacial acetic acid. Perkin's method was first applied to *m*-bromobenzaldehyde by Miller and Rohde (1890) who, after heating the Perkin mixture at 140–50° for as many as twenty hours, obtained a 73% yield of *m*-bromocinnamic acid. Perkin's method was applied to the three chlorobenzaldehydes by Meyer and Beer (1913) and by Meyer, Beer and Lasch (1913); these have been confirmed by Lock and Bayer (1939) and have been stated above. Neither this nor any other group of workers has referred to the condensation of *m*-bromobenzaldehyde by Perkin's method under the standardised conditions, though they make a comparison of all the *p*-haloid-benzaldehydes: thus the yields of *p*-bromocinnamic acid from *p*-bromobenzaldehyde in two experiments (Perkin) are given as 48·6 and 52·6% respectively. This is about the same as their yield of the *p*-chlorocinnamic acid. Could we thus assume that the yield of the *m*-chlorocinnamic acid would be about the same as the yield of the *m*-bromocinnamic acid, their yield of the latter might then be about 63%. Against this, the yields of these four haloid-cinnamic acids obtained by our pyridine method range between 97 and 99%.

All the four haloid-benzaldehydes also condense with malonic acid when heated alone with them, giving, under carefully controlled conditions, nearly quantitative yields of the corresponding haloid-benzalidene-malonic acid: of these only one, the *o*-chlorobenzalmalonic acid, has been previously described (Stuart, 1888).

The halogen undoubtedly increases the yield in the Perkin as well as in the pyridine-trace condensations, but the influence of the position of the halogen does not seem to coincide in both. The *p*-chlorine which seems to be most helpful in the pyridine-trace condensation appears to be the reverse in the Perkin condensation.

The three chlorobenzaldehydes undergo a similar condensation with malonanilic acid, but the details of this must find place in a separate paper.

Experimental

Condensation of Benzaldehyde:

In the Presence of a Trace of Pyridine.—1·06 g. benzaldehyde, 1·04 g. dry malonic acid and 0·13 g. pyridine, purified in the usual way, (1:1:0·15 mol.) were heated together on water-bath for four hours; the mixture

soon became a homogeneous liquid and effervescence commenced within ten minutes of the heating and continued for about an hour. Cinnamic acid came out at the end in white crystals, which were extracted as usual and which then melted at 133° and weighed 1.4 g. or 94.6% of theory. In another experiment the heating was stopped after two hours only; the yield was 1.3 g. or 87.8%. This is considerably greater than that of Bayer and Lock, and is higher than the highest yield claimed under Perkin's method under the most favourable conditions.

Without any Condensing Agent.—The same amounts of benzaldehyde and malonic acid were heated alone separately on water-bath in three different flasks that were heated respectively for four, six and eight hours. The mixture did not become a homogeneous liquid and no effervescence was observed. After about ten minutes a pinkish colour began to make its appearance and after one hour the whole mixture had become a pinkish solid mass. At the end of the heating, the benzalmalonic acid was extracted as usual by means of sodium carbonate and hydrochloric acid. It melted at 195–96° and weighed 1.5, 1.5 and 1.3 g. respectively, the yield thus being 78, 78 and 73% respectively.

The Condensation of p-Chlorobenzaldehyde with Malonic Acid

(i) *In the Presence of a Trace of Pyridine:*

The Materials.—The *p*-chlorobenzaldehyde was very pure and melted at 47°. (Literature gives 47°, 48°, 49°, Beilstein.) The malonic acid, Merck, Pure for Scientific Purposes, was powdered, dried at 100° and kept in a desiccator. Pyridine, Extra Pure, Merck, or Purest, Schering-Kahlbaum, was kept over sticks of pure caustic potash for several days and fresh-distilled (b.p. 114–115°).

p-Chlorocinnamic Acid.—1.04 g. malonic acid, 1.4 g. *p*-chlorobenzaldehyde and 0.14 c.c. pyridine (1 : 1 : 0.16 mol. proportions, 1/100th mol.wt.) were mixed in a flask and heated on water-bath without a condenser for four hours. The reaction started very quickly: in two minutes the whole fused to a homogeneous liquid and effervescence commenced. In another five minutes, a cream-coloured solid mass made its appearance, and the whole mass had become perfectly solid long before the heating was stopped. It was allowed to cool, treated with 10% sodium carbonate solution and the small amount of the residue was removed by filtration. As the residue, however, gave the same high melting-point as the crude product, namely, 235°, it was clear that it was not the unreacted aldehyde, melting at 47°: in fact treatment with hot sodium carbonate solution dissolved it completely, and, on acidification of both the extracts, the same white precipitate was obtained.

On washing with water it melted at 245°. This must be highly pure as its melting-point, even before recrystallisation, was higher than that given in literature (240–42°, Gabriel and Herzberg, *loc. cit.*).

The *p*-chlorocinnamic acid was a cream-coloured indistinct crystalline mass, very slightly soluble in water, alcohol, benzene, chloroform or carbon tetrachloride in the cold, slightly soluble in hot water or hot benzene, and soluble in acetone or in hot alcohol. Recrystallisation raised its melting-point to 246–47°, and it came out in long silky needles. It at once decolourized Baeyer's reagent. Yield 1.8 g. (theoretical yield = 1.825 g.).

In another experiment, the reaction mixture, of the same composition as above, was kept on the water-bath for only one hour instead of four, as the reaction seemed then to be complete. No aldehyde was recovered back, the *p*-chlorocinnamic acid was sufficiently pure, as, after a washing with water, it melted at 244–245°, and it was not necessary to extract it with sodium carbonate solution or to prepare the not very soluble sodium salt. The yield was again quantitative, and the melting-point, after recrystallisation, 247°. (Lock and Bayer give the same.)

(ii) *In the Absence of any Condensing Agent:*

p-Chlorobenzalmalonic Acid.—The aldehyde and the acid (1/100th mol.) were heated alone, as before, on water-bath. The reaction was much slower; it required an hour's heating to change the whole to a clear liquid and there was no effervescence, even during eight hours' heating. Slowly a solid began to be formed and took several hours to be completed. The crude product was treated with cold 10% sodium carbonate solution which dissolved the whole and left no residue. Acidification with hydrochloric acid yielded a slightly cream-coloured solid, which was filtered and washed with cold water. The acid immediately decolourised Bayer's reagent, was very little soluble in cold water, moderately soluble in excess of hot water and easily soluble in alcohol or acetone even in the cold. Recrystallised from dilute alcohol, or dissolved in minimum quantity of alcohol and precipitated on scratching after the addition of a large amount of water, it came out in white needles, and after drying in the desiccator for 24 hours, it melted with effervescence at 197–98°. The yield was 1.8 g. or about 80% of theory.

In a second experiment it was observed that the reaction was really completed in four hours and the yield then—2.25 g.—was quantitative. Further confirmation of its identity was obtained from analysis. (Cl, found, by Piria and Schiff's method: 15.63%; $C_{10}H_7O_4Cl$ requires 15.67%. Equivalent weight by titration, found = 113.2; *p*-chlorobenzalmalonic acid requires 113–25. Molecular weight, silver salt, found 226.4; theory requires 226.5.)

(iii) *Condensation with Ethyl Malonate :*

3.2 g. Ethyl malonate, Schering, Extra Pure, fresh redistilled, 2.8 g. *p*-chlorobenzaldehyde and 0.28 c.c. pyridine (1/50th mol., 1 : 1 : 0.16) were mixed and heated together on water-bath for 26 hours. White needle crystals separated out of the liquid on cooling. They were filtered off from the mother-liquid, washed, dried on a porous plate, washed on the porous plate with a little water and dried : m.p. 235°. Insoluble in water and easily soluble in alcohol, the substance had the characteristic fragrant smell of esters. Yield 1.0 g. (18% of theory). Recrystallised from alcohol, it melted at 237°. It instantly decolorised Baeyer's reagent. (Cl, Found : 12.09%; Ethyl *p*-chlorobenzylidenemalonate, C₁₄H₅O₄Cl requires 12.56%.)

The Condensation of m-Chlorobenzaldehyde with Malonic Acid

(i) *In the Presence of a Trace of Pyridine :—*

m-Chlorocinnamic Acid.—The aldehyde, the acid and pyridine were taken in the same proportion as above and heated on the water-bath. The reaction was slower distinctly than was observed with the *p*-isomer. It took ten minutes to liquefy completely and the effervescence continued much longer. In half an hour, the whole became solid again and the heating was stopped after one hour. The crude product was white and melted at 159°. It dissolved in sodium carbonate solution without leaving a residue, and *m*-chlorocinnamic acid was easily recovered on acidification of the sodium salt solution. After filtration and washing with water, it melted at 160°. It was readily soluble in cold acetone, soluble in alcohol and in hot benzene, less in hot water, still less in cold benzene. Recrystallised from alcohol repeatedly, the melting point remained stationary at 163°. Gabriel and Herzberg describe it as indistinct yellow, melting at 176°, which is not confirmed: other workers, however, give the melting point at 165° (Heilbron, *Dictionary of Organic Chemistry*, 1, 276). It decolorised Baeyer's reagent. Yield 1.8 g. (theoretical 1.825 g. from 1.4 g. of the aldehyde).

(ii) *Condensation without any Condensing Agent :*

m-Chlorobenzylidenemalonic Acid.—1.04 g. Malonic acid and 1.4 g. *m*-chlorobenzaldehyde were heated alone on the water-bath for four hours. A solid with a pale pink tint had been formed at the end, which dissolved completely in sodium carbonate solution ; from this, on acidification, a cream-coloured solid was obtained which decolorised Baeyer's reagent, and which, on recrystallisation from alcohol, melted at 184–86°. It weighed 2.2 g. (theoretical yield = 2.25 g.). (Equivalent weight, found by titration with standard alkali, 113.6; the dibasic acid C₁₀H₇O₄Cl requires 113.25. Cl, found: 15.29%; the chlorobenzylidene-malonic acid requires 15.67%.)

*The Condensation of o-Chlorobenzaldehyde with Malonic Acid**(i) In the Presence of a Trace of Pyridine:*

o-Chlorocinnamic Acid.—The three were heated in the usual proportions on a water-bath. In ten minutes the reaction mixture became a clear liquid and effervescence started. Within half an hour a white solid began to be formed. After four hours' heating, the cold product was treated with a little cold water and a little ether. The remaining crude product melted at 207° and, when recrystallised from alcohol, melted at 210°. Further recrystallisations raised the melting point to 211–212°. The *o*-chlorocinnamic acid was then in the form of colourless needles. In literature Gabriel and Herzberg (1883) have described it as indistinct yellow, melting at 200°; Stoermer (1911) gives 205° as the m.p. and Lasch (1913) gives 211°. The yield was 1.8 g. (the theoretical is 1.825 g.).

Condensation without any Condensing Agent: o-Chloro-benzalmalonic Acid.—1.4 g. *o*-chlorobenzaldehyde and 1.04 g. malonic acid were heated alone on a water-bath for six hours. There was no effervescence, but the reacting mass began to solidify after only one hour's heating. The product was washed with water and dried: it melted at 185°, and, when crystallised from hot alcohol, it came out in white crystals, melting at 192°: Stuart also gives 192°. It weighed 2.1 g. (93% of theory).

Condensation of m-Bromobenzaldehyde:

In the Presence of Pyridine.—0.925 g. *m*-Bromobenzaldehyde, 0.52 g. malonic acid and 0.07 g. pyridine were heated together on a water-bath. The mixture immediately became a clear liquid and effervescence started within five minutes. Within half an hour a pale yellow solid began to come out in the liquid. In two concordant experiments, the total heating was two and four hours respectively. The solid dissolved completely in sodium carbonate solution, and the addition of concentrated hydrochloric acid drop by drop brought about the separation of white crystals of *m*-bromocinnamic acid. The yields were 1.0 and 1.1 g. respectively, corresponding to 88.5 and 97% of the theoretical. The crude product melted at 170°, the recrystallised at 174°.

Condensation in the Absence of a Condensing Agent: m-Bromobenzalmalonic Acid.—1.04 g. malonic acid and 1.85 g. *m*-bromobenzaldehyde were heated alone on a water-bath in two separate flasks for four and eight hours respectively. The reacting mass did not liquefy nor effervesced, but in about 45 minutes a pale yellow solid began to emerge in view, till, as usual, the whole mass set as a solid. This was treated with cold sodium carbonate solution, the residual resinous matter filtered off and *m*-bromobenzalmalonic

acid precipitated as a white shining crystalline mass by careful treatment with strong hydrochloric acid. The acid was very soluble in cold alcohol and acetone, and was recrystallised from benzene or dilute alcohol or a benzene-alcohol mixture. It melted with effervescence at 192°. The yields were 2.4 and 2.7 g. or 87 and 99% of theory, respectively.

[Bromine found = 29.86%: bromobenzalmalonic acid $C_{10}H_7O_4Br$ requires 29.52%. Equivalent weight found by titration = 135.4; required = 135.5.]

Summary

1. Benzaldehyde and four haloid-benzaldehydes have been condensed with malonic acid, in the presence of a trace of pyridine as well as in the entire absence of any condensing agent.

2. The yields in all cases have been excellent, in some cases almost quantitative.

3. Chlorine and bromine have undoubtedly accelerated the condensation and increased the yields.

4. Compared to the yields obtained by Perkin's method, these yields are very superior, the condensations quicker and the products cleaner.

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