

CONDENSATION OF ALDEHYDES WITH MALONIC ACID

Part XVI. With *p*- and *m*-Methylbenzaldehydes : *p*- and *m*-Methyl-
benzylidenemalonic Acids

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IN this paper the influence of a methyl group on the aromatic ring of the aldehyde, in the aldehyde-malonic acid condensation, is investigated. The influence of such a methyl group on the yields in the Perkin's reaction has been reported by Lock and Bayer¹ under standard conditions to be as under:

Position of the Me group	<i>o</i>	<i>m</i>	<i>p</i>	2-4-6
% Yield	.. 15	33	15	0.5

as compared with 49% from the unsubstituted benzaldehyde. The depressing effect of the methyl group is very clearly shown. By increasing the heating time of the 2-4-6-tri-methylbenzaldehyde, from eight to fifty hours, the authors were able to raise up the yield from 0.5 to only 8%.

The first study of this in the aldehyde-malonic acid condensation, using pyridine in traces was made by Kurien and Pandya² (1934) who obtained 84% of *p*-methylcinnamic acid from *p*-tolylaldehyde. Later Mehra and Pandya³ (1936) obtained, on five hours' heating, 93% yield of the same product. In the present paper about 98% yield is reported, suggesting, therefore, that in the condensation by this method, the methyl group in the *p*-position did not depress, but possibly increased, the yield. On heating the *p*-tolylaldehyde alone with malonic acid on the water-bath for five hours, *p*-tolylidenemalonic acid, melting at 201° came out in 75% yield. No doubt longer heating might have increased the yield though decarboxylation also might have occurred. Heating the aldehyde and the acid with glacial acetic acid, following Stuart,⁴ gave only about 30% of the dibasic acid. The mono- and the dibasic acids had their melting-points very near, but the dibasic acid melted always with effervescence as one would expect. It was further confirmed by titration with standard alkali and by the silver salt, as well as by a mixed melting-point with the mono- or cinnamic acid.

In the condensation of the *m*-tolylaldehyde a peculiarity made its appearance which tended very greatly to restrict the yield of the pure product, though there was enough evidence to show that the condensation otherwise went very well. This peculiarity was that under the ordinary method of conducting the condensation with a trace of pyridine, the condensation product that came out was always a mixture of the mono- and the dibasic acids. It came out in good yields but it always melted from 92° to about 143°. About a dozen experiments with changes in the conditions of heating were made but they failed to secure only one pure product, though the proportions of the two among themselves varied. Separation of the two by means of solvents did not succeed. Increase of pyridine from 0·15 mol. to about 6 mols., with corresponding changes in the temperature and hours of heating gave the mono, the *m*-methylcinnamic acid, melting at 113–14°. The yield however was about 68%, probably on account of insufficient heating (*vide* Tables). Further increase took place when heating was abandoned and long time at room-temperature was given: thus by following the method of Vorsatz,⁵ an almost quantitative yield of the *m*-methylcinnamic acid was obtained. (The acid had been prepared by means of the Perkin's reaction by Bornemann⁶ and by Müller⁷. Lock and Bayer¹ also obtained it later. The first two do not mention yield.)

The *m*-methylbenzylidenemalonic acid does not seem to be mentioned in literature and is prepared for the first time. It was obtained here in a pure condition by the usual method of heating the aldehyde and the malonic acid alone on water-bath for six hours when about 30% yield was obtained. Stuart's method of using glacial acetic acid increased the yield to about 48%.

EXPERIMENTAL

Condensation of p-Tolylaldehyde in the presence of Glacial Acetic Acid.—1·2 g. *p*-tolylaldehyde, 1 g. malonic acid and 3 c.c. glacial acetic acid, heated on the water-bath for five hours, gave 0·6 g. of the *p*-tolylidenemalonic acid, *i.e.*, about 30%. The acid melted at 201°, was insoluble in cold, but soluble in hot water; it melted with effervescence, showed unsaturation and was soluble in ether, benzene and glacial acetic acid. Equivalent weight, by titration = 104·3, by silver salt = 105. $C_{11}H_{10}O_4$ requires 103.

Condensation in the absence of any Condensing Reagent.—The aldehyde and the acid were heated for two hours on water-bath and thereafter in an oil-bath, 110–120°, for 2·5 hours. The product was taken out as usual and weighed 1·5 g. (= 75% yield).

Condensation with a trace of Pyridine (1 : 1 : 0·2 mol.).—The aldehyde, the acid and pyridine, taken as above, were heated (compare Mehra and

Pandya³) as usual: about 98% yield was obtained. The *p*-methylcinnamic acid melting at 195° (pure m.p. 197–98°), when mixed with the dibasic *p*-tolylidenemalonic acid, m.p. 201°, melted at 180°.

Condensation of m-Tolylaldehyde, in the presence of Pyridine.—The³ table gives the details. Aldehyde taken was 1.2 g.

Condensing Agent	Proportion mol.	Temperature	Time hrs.	Product m.p.	Yield	
Pyridine	0.15	Waterbath	5	98–139°	1.66 g.	
"	"	"	8	98–140°		
"	"	"	12	"		
"	"	"	18	98–143°		
"	"	100–105°	5	"		
"	"	"	10	"		
"	"	"	16	"		
"	0.2	105–110°	17	95–139°		
"	0.5	Waterbath	6.5	96–133°		
"	1	Then 110–115°	6	98–141°		
"	2	110–115°	18	94–139°		
"	3	115–120°	17	95–143°		
The mixture of the acids was heated with pyridine, 1.0 g. with						
"	0.3	Waterbath	2			
"		Then 110–120°	2	98–143°		
"	3.0	as above	6			
"			4			
"	3	Refluxed over wire-gauze	2	110–111°	60%	

This product on recrystallization (alcohol and ligroin) melted at 113–114°, which remained constant after further crystallisation. The yield was over 60%. Its properties coincided with those described by Heilbron. Oxidation with potassium permanganate gave *m*-toluic acid, m.p. 110–111°. Bromine water gave an acid, dibrom derivative, m.p. 164–67°.

The cinnamic acid was also obtained pure when the aldehyde, the acid and pyridine in 1:1:4 mol. proportion were heated on waterbath for 2.5 hours and then refluxed on wire-gauze for half an hour. Yield = 62%. m.p. 114°.

Long time and room temperature condensations were also tried. The best yield was nearly quantitative yield obtained by the application of Vorsatz's method of keeping the aldehyde and the acid in a flask with about 6 mols. of pyridine and a few drops of piperidine for three months.

Condensation in the Absence of Pyridine: m-Tolylidenemalonic Acid.—The aldehyde and malonic acid were heated alone on waterbath for varying periods: the product in the crude form melted between 160–68° and, after recrystallization, at 172–74° with effervescence. The yield varied, according

to the heating time, from 20 to 32%. Less than five hours' heating gave little sign of the condensation having occurred, while longer heating or higher temperature produced the mixture of the di- and the mono-acids referred to above.

Condensation in the presence of Glacial Acetic Acid.—The aldehyde, malonic acid and glacial acetic acid (1:1:3 mol.), were heated on water-bath for about six hours, the dibasic acid was obtained, m.p. 172°, in 48% yield. The dibasic acid *m*-tolylidenemalonic acid was soluble in alcohol. Repeated recrystallisations from benzene-alcohol mixture raised the melting point to 173–74°, effervescence always accompanying the melting. It was also soluble in ether, chloroform and ethyl acetate: it was almost insoluble in cold water, benzene and glacial acetic acid. It readily decolourised in the cold Baeyer's reagent, and also bromine water. Rast's method of determining the molecular weight was not applicable as it decomposed on melting with camphor. Equivalent weight found by alkaline titration was = 103·9, the acid $C_{11}H_{10}O_4$ requires 103. The molecular weight by the silver salt method was 206·7: required 206.

TABLE
The influence of the methyl group on the yield

	Benzaldehyde	Position of Me group		
		<i>o</i>	<i>m</i>	<i>p</i>
By Perkin's Reaction	49%	15	33	15
.. Pyridine Trace	95	..	68	98
.. Vorsatz's Method	98	..

SUMMARY

The condensation of *p*-tolylaldehyde with malonic acid by the pyridine-trace method gave, on repetition, a nearly quantitative yield of the *p*-tolylidene-acrylic (*p*-methylcinnamic) acid. *p*-Tolylidenemalonic acid has been isolated for the first time in this condensation, in the absence of pyridine, in 75% yield.

m-Tolylaldehyde, on condensation with malonic acid in the presence of pyridine in traces, gave up to 68% of the *m*-methylcinnamic acid. By a long-time-room-temperature condensation in the presence of both pyridine and piperidine, the yield came up to the theoretical. The *m*-tolylidenemalonic acid came out best in the presence of glacial acetic acid, but the yield was not great, being = 48%.

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