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REMOVAL OF ACETIC ACID AS A VARIABLE IN THE PERKIN REACTION

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In the standard procedure for the Perkin synthesis of cinnamic acids, recently reviewed by Johnson (1), a mixture of an aromatic aldehyde, an aliphatic acid anhydride (usually acetic anhydride), and an alkaline catalyst (sodium or potassium acetate, potassium carbonate, triethylamine, etc.) is heated under an air condenser. When acetic anhydride is used, the by-product of the synthesis is acetic acid, which is removed to some extent by evaporation through the condenser.

Johnson and his students, or earlier workers, have made studies of most of the possible experimental variables in this synthesis. One of these, addition of free acetic acid to the reaction mixture, was studied by Kalnin (2); his work showed that the addition of progressively larger quantities of glacial acetic acid effected successive decreases in yield of cinnamic acid, with either sodium or potassium acetate as catalyst. From this, it would seem that continuous removal of all of the acetic acid from the reaction mixture might lead to improved yields. Of course, low-boiling by-products have often been removed in other reactions (esterifications, ester exchange reactions, etc.) in order to force the reactions more nearly to completion. Accordingly, it was thought desirable to conduct some Perkin syntheses in which all of the acetic acid is removed as it is formed, in place of the usual conditions under which there is a partial, uncontrolled removal of the acid through an air condenser.

In order to do this, a distillation set-up was assembled which permitted applying sufficient heat to the reaction mixture, so that the acetic acid by-product and the unchanged acetic anhydride were forced off. These were separated in a heated distilling column with a total-condensation still head, the acetic acid being removed at a take-off and the acetic anhydride returned to the reaction mixture. The distilling column was of the Vigreux type, and was electrically heated by an external wrapping of Nichrome wire, heating being controlled by a variable rheostat. The reaction flask and column were so heated that there was a steady reflux at the top of the column; whenever the vapor temperature at this location was near the boiling point of acetic acid, a stopcock in the still head was opened and the condensate removed. This procedure will be called the "heated-column" method in this paper to distinguish it from the standard or "air-condenser" method usually employed.

This variation in the usual experimental procedure was studied for syntheses catalyzed by three different materials, sodium acetate, potassium carbonate, and potassium acetate.

Several runs were made using the standard method and molal quantities recommended by Johnson (1). The results served both as a check on technique, since they could be compared to those obtained by other workers using this method, and also as a means of evaluating yield results obtained with the heated-column method.

EXPERIMENTAL

Sodium acetate as a catalyst. A mixture of benzaldehyde (0.4 mole), acetic anhydride (0.6 mole), and fused sodium acetate (0.24 mole) was refluxed in an oil-bath at 170–175° for 8 hours, using an air-cooled condenser. The reaction mixture was then steam distilled to remove unreacted benzaldehyde. After the residual mixture was filtered, acidified, and cooled, the cinnamic acid precipitated. The crystals were filtered, washed, and dried to a constant weight. The conversion of benzaldehyde into cinnamic acid was 34%; and the yield, considering that about 0.17 mole of benzaldehyde was recovered, was about 60%. The standard method was reported in Johnson's review to give about 40% yields (corresponding to the quantities termed "conversions" in this work).

TABLE I

Cinnamic Acid Produced when Sodium Acetate was Used as a Catalyst

RUN	MOLES USED			REACTION		CONVERSION	YIELD
	Aldehyde	Anhydride	Catalyst	Method[a]	Time		
					hrs.	*per cent*	*per cent*
1	0.4	0.6	0.24	A	8	34	60
2	.4	.6	.24	B	10	46	62
14	.4	.6	.24	B	9	50	62
7	.4	.6	.24	B	24	61	72
5	.4	.6	.4	B	10	28	38
6	.4	.8	.4	B	7	46	63
3	.4	.6	.24[b]	B	7	33	52

[a] Method A = air-cooled condenser; B = heated column.

[b] Eight drops of pyridine added.

TABLE II

Cinnamic Acid Produced when Potassium Carbonate was Used as a Catalyst, Heated-column Method

RUN	MOLES USED			REACTION TIME	CONVERSION YIELD	
	Aldehyde	Anhydride	Catalyst			
				hrs.	*per cent*	*per cent*
18	0.4	0.6	0.24	4S4[a]	51	67
8	.4	.6	.24	24	58	58[b]
9	.4	.6	.24	8	54	54[b]
10	.4	.72	.12	8	59	59[b]

[a] 4S4 = Reacted 4 hrs., stood overnight, reacted 4 hrs.

[b] Styrene formed and recovered rather than benzaldehyde.

Reactions similar to the above were then carried out with the heated-column method. The temperature of the oil-bath was maintained at 180–190° and all liquid distilling between 117° and 125° was removed. (Acetic acid boils at 118.1°; acetic anhydride at 139.6°.) The total reaction times, molal quantities of reactants, and results are shown in Table I.

Potassium carbonate as catalyst. When potassium carbonate was used as a catalyst in the heated-column method, the conversions of cinnamic acid were slightly better than those obtained with sodium acetate, but were only about the same as the yields reported in the literature for reactions run for similar lengths of time by the standard method with potassium carbonate. A summary of runs in which this catalyst was used appears in Table II.

Potassium acetate as a catalyst. The standard method was applied with potassium acetate as catalyst, using both the fused and the nonfused salt. Both conversion and yield values were appreciably higher with the fused catalyst, and only the latter material was used for subsequent runs with the heated-column procedure. The results of these experiments are shown in Table III.

TABLE III

CINNAMIC ACID PRODUCED WHEN POTASSIUM ACETATE WAS USED AS A CATALYST

RUN	MOLES USED			REACTION		CONVERSION YIELD	
	Aldehyde	Anhydride	Catalyst[a]	Method	Time		
					hrs.	*per cent*	*per cent*
11	0.4	0.6	0.24	A[b]	5	36	36[d]
12	.4	.6	.24	A	5	56	63[e]
13	.4	.6	.24	B[c]	4	59	59[d]
16	.4	.6	.24	B	8	58	80
17	.4	.6	.24	B	4S4[g]	57	57[f]

[a] Fused potassium acetate used in all but Run 11.

[b] A = air condenser used.

[c] B = Heated-column.

[d] Styrene formed.

[e] Styrene and benzaldehyde formed.

[f] No benzaldehyde or styrene obtained from reacted mixture.

[g] 4S4 = Reacted 4 hours, stood overnight with no heat, reacted 4 hours.

DISCUSSION

The heated-column method with sodium acetate catalyst gave higher conversions and about equal yields, compared to results obtained from the standard method (runs 2 and 14 *vs.* run 1). The addition of more catalyst gave poorer results (run 5) unless more anhydride was also present (run 6). The higher conversion and yield in run 7, compared to runs 2 and 14, were due to the longer time of heating, an observation frequently made by previous workers. One earlier investigator (3) claimed that a small amount of pyridine enhanced the yield materially. Neither this work (run 3) nor that by Johnson's group (1), substantiated this claim.

As was expected, syntheses catalyzed with potassium carbonate gave somewhat higher conversions (51–59%) than did runs of equal duration using sodium acetate. However, the material volatile with steam from these runs was frequently found to be styrene, or styrene mixed with a little benzaldehyde. In these cases a zero recovery of benzaldehyde was assumed, and hence, the yield was set equal to the conversion. Perhaps due to decarboxylation of part of the cinnamic acid already formed, the conversion and yield of acid were not increased by a long time of heating (run 8 *versus* runs 9 and 18). A change of proportions of anhydride and catalyst produced a slightly better conversion and yield (run 10 *versus* run 9). The standard method, using this catalyst, gave a 59% conversion for 8 hours reaction time, according to Johnson's review.

For syntheses catalyzed with fused potassium acetate, the standard method gave a conversion which was equal to that reported in Johnson's laboratory procedure, using the same reactants and conditions. Conversions were slightly higher when the heated-column method was used; the yields were erratic since benzaldehyde was not recovered regularly.

SUMMARY

Continuous removal by distillation of the acetic acid formed in the Perkin reaction enhanced the conversion, but not the yield, of cinnamic acid over those obtained by application of the standard method (in which no controlled removal of acetic acid is made) when sodium acetate was the catalyst, but did not significantly improve either conversion or yield when potassium carbonate or potassium acetate was the catalyst.

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