CHAPTER IV

ION EXCHANGE RESINS AS CATALYSTS IN THE SYNTHESIS OF COUMARIN DERIVATIVES AND MICHAEL ADDITION TO SOME COUMARIN DERIVATIVES

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Ion exchange resins as catalysts in the synthesis of coumarin derivatives and Michael addition to some coumarin derivatives

The catalytic properties of ion-exchange materials have been known and have been employed commercially for many years. There are several apparent advantages in the use of the ion-exchangers, both inorganic substances and resins, as either acid or base catalysts. Several of the more important advantages are as follows: (1) By simple filtration step, catalyst free products can be obtained. (2) The catalysts can be recovered very easily and can be reused. (3) Continuous reactions can be obtained by passage of reactants through beds of ion-exchange resing catalysts. (4) Unusual selectivity effects are possible. (5) Side reactions can be kept at minimum . (6) Special corrosion-resistant equipment is not necessary as with some soluble catalysts. (7) In many reactions, either the products or reactants are damaged by acid or alkali catalysts. These effects are overcome by the use of resinous catalysts.

Ion-exchange resins have been used as catalysts for organic reactions since about 1939, but until 1946 only a few publications in this field were made. Since 1946, however, the availability of many new and improved resins, both cationic and anionic, has widened the scope of their application as catalysts and several types of organic reactions have been studied and they are reviewed by several authors (1,2,3) .

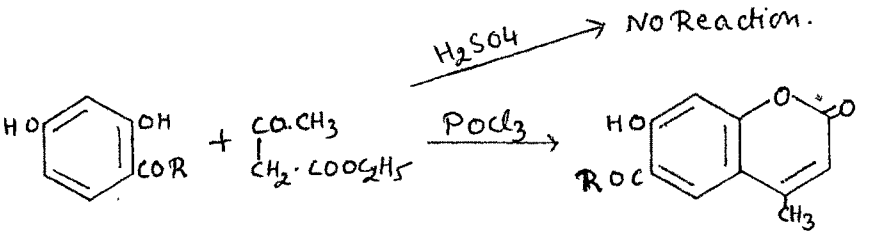
The present work deals with the use of Ion exchange resins as catalysts for the synthesis of coumarin derivatives by Pechmann reaction and Knoevenagel condensation. They are also tried as catalysts in bringing about the Michael reaction in which coumarin derivatives are used as acceptors.

Use of cation-exchange resins as catalysts in Pechmann reaction

The condensation of β-ketonic esters with phenols in the presence of different condensing agents leading to the formation of benzopyrone derivatives is known as the Pechmann reaction and has found extensive applications. It has been reviewed by Sethna and Phadke (4).

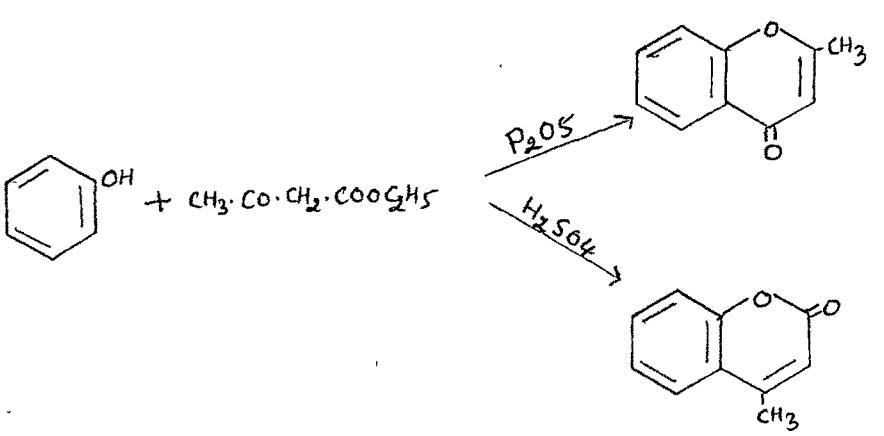
The condensing agent often plays an important role in the Pechmann reaction. One condensing agent may bring about condensation not brought about by another. The yields of the products with different condensing agents may also vary markedly. The orientation may also sometime change with a change in the condensing agent and sometimes the nature of the product also changes. A few examples are given below.

4-Acylresorcinols do not condense with ethyl acetoacetate in the presence of sulphuric acid but condense readily in the presence of phosphorus oxychloride to give 6-acyl-7-hydroxy-4-methylcoumarins (5).



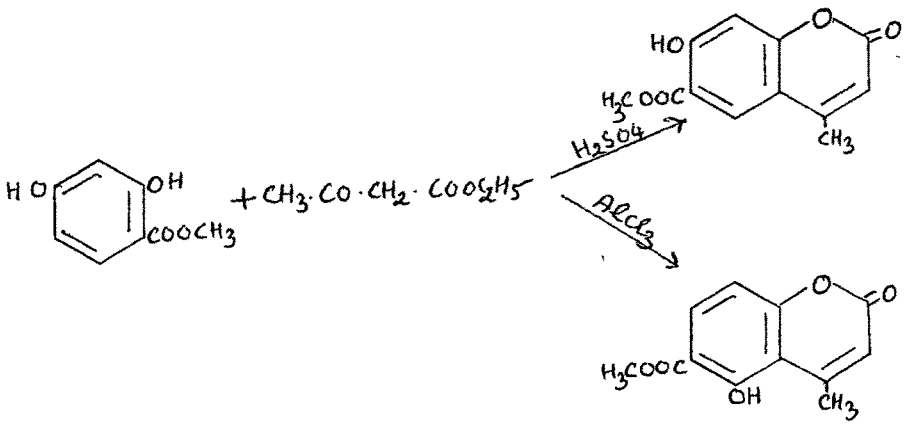
Phenol when condensed with ethyl acetoacetate in the presence of 73 % sulphuric acid gives 21 % yield of 4-methylcoumarin (6) but in the presence of anhydrous aluminium chloride the yield of 4-methylcoumarin is nearly doubled, 40-50% (7).

The less reactive phenols such as phenol and o-cresol condense with ethyl acetoacetate in the presence of sulphuric acid to give coumarin derivatives but when the reaction is carried out in the presence of phosphorus pentoxide, chromones are exclusively formed (8)



Sethna, Shah and Shah (9) found that anhydrous aluminium chloride dissolved in dry ether or nitrobenzene was not only an efficient condensing agent but also changed

the course of the reaction. If the 4-position in resorcinol is occupied by groups such as carboxyl, carbomethoxyl, acyl or nitro, the condensation with ethyl acetoacetate, instead of giving 7-hydroxycoumarin derivatives, gives either exclusively or mainly 5-hydroxycoumarin derivatives.



In view of this it was thought of interest to investigate the role of cation exchange resins in the condensation of β-ketonic esters with phenols.

Cation exchange resins used in this work were Duolite C-20 and Amberlite IR-120. These resins are polystyrene sulphonic acid type and are resistant to high temperature and can be used continuously at a temperature of 150° for short periods. The main advantages of the cation exchange resins over the usual condensing agents are that they can be recovered and can be reused.

The reactive phenols were first studied. When a mixture of resorcinol, ethyl acetoacetate and Duolite C-20 or Amberlite IR-120 was kept at room temperature for a week, only a negligible yield of 7-hydroxy-4-methylcoumarin was

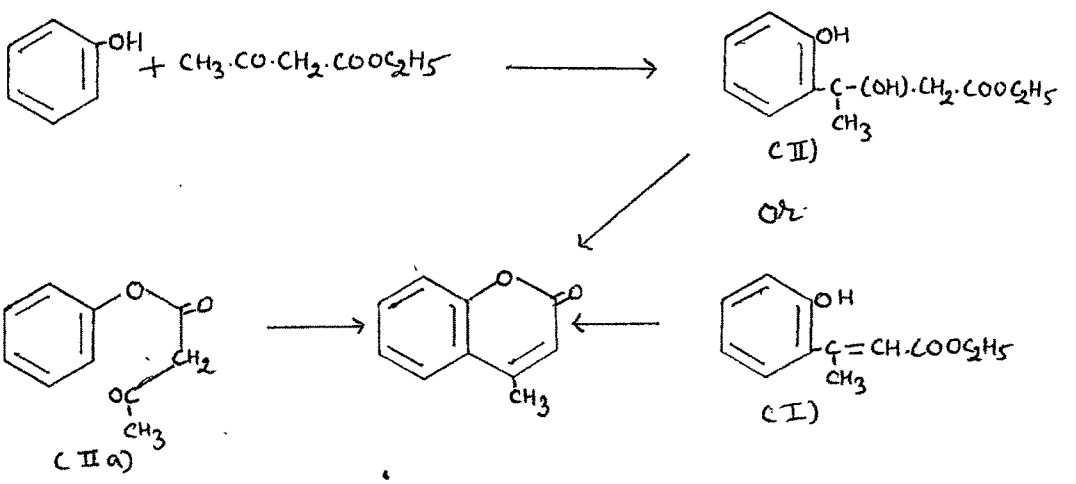
obtained. But when the reaction mixture was kept at room temperature for a month the yield of 7-hydroxy-4-methylcoumarin was improved. When the reaction was carried out by heating on a steam bath for 4 hr. poor yield of the coumarin derivative was obtained but when the reaction mixture was heated at 150° for 1 hr. 69 % yield of 7-hydroxy-4-methylcoumarin was obtained. When the other reactive phenols such as phloroglucinol, pyrogallol and α -naphthol were tried they also gave the corresponding coumarin derivatives in about 45 % yield. But when the reaction was tried with less reactive phenols such as phenol, β-naphthol or phenolic derivatives such as methyl-β-resorcylate no coumarin derivatives were obtained under the above conditions. Only the starting phenols were recovered. When ethyl-α-methylacetoacetate was used the yields were comparatively poor even with the reactive phenols.

The reaction between resorcinol and ethyl acetoacetate did not proceed when Duolite CS-101, a cation exchange resin with exchangeable hydrogen ion in a carboxyl group, was used as a condensing agent. It was observed by Chakravarti (10) that sodium ethoxide can be used as a condensing agent in the Pechmann reaction. It was therefore thought of interest to try a strong anion exchange resin as a condensing agent for the Pechmann reaction. The reaction between resorcinol and ethyl acetoacetate did not proceed under the above conditions when Amberlite IRA-400 was tried as a condensing agent.

While this work was in progress, there appeared two notes by John and Israelstam (11,12) on the use of cation exchange resins as condensing agents in the Pechmann reaction. In these notes the authors have described the condensation of reactive phenols with β -ketonic esters in the presence of Zeo Karb 225 and Amberlite IR-120 and have reported 50-79 % yields of the corresponding coumarin derivatives. They also carried out the reaction in n-hexane and obtained higher yields. They attributed this to the fact that β-ketonic ester enolises to 63 % in n-hexane as compared to the normal 7 %.

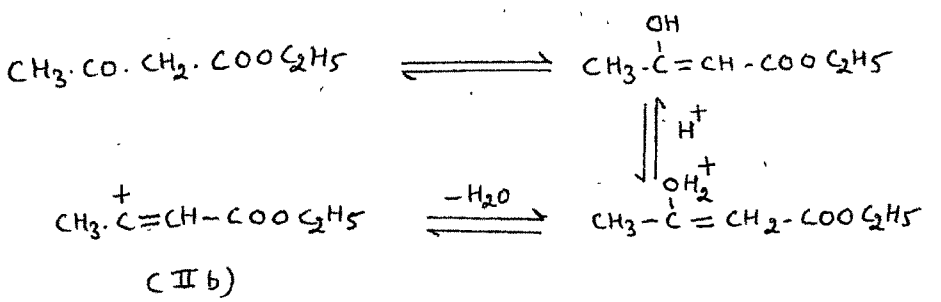
Mechanism of Pechmann reaction

Two essentially similar views have been put forward regarding the mechanism of Pechmann reaction of coumarins from phenols and β-ketonic esters (13,14). Robertson, Waters and Jones (15) suggested a substituted cinnamic acid derivative (I) as an intermediate, while Ahmed and Desai (16) believed that the intermediate is a β-hydroxy- β-phenyl butyric ester derivative (II)

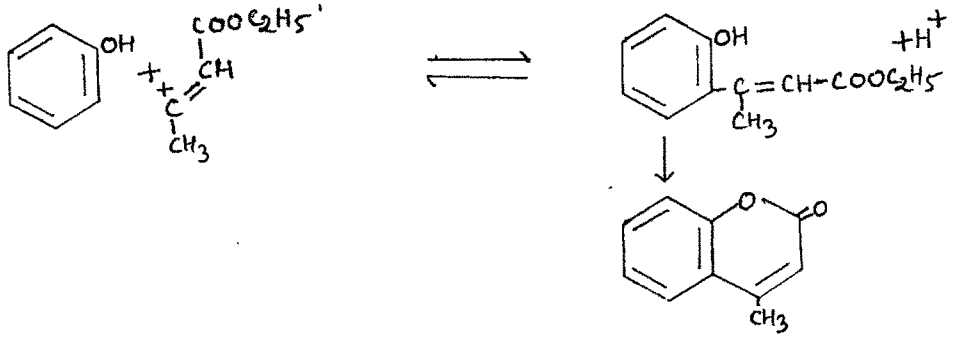


Of the two similar views described above regarding coumarin formation, that of Robertson and coworkers is simpler and plausible and also based on the experimental evidences, while that of Ahmed and Desai, whose assumption of additive compound though ingenious, is not based on any experimental evidence.

Lacey (17) obtained coumarin derivatives by treating different arylacetoacetates (II a) with sulphuric acid and found that the yields of coumarin derivatives were comparable to the corresponding Pechmann reaction. From this observation he has put forward the following mechanism for the Pechmann reaction ~~and~~ which is not contrary to the mechanism put forward by Robertson and coworkers (15) although the possibility that the Pechmann reaction may proceed via., arylacetoacetate has been demonstrated. In either case, the controlling step is the condensation of esters on the ortho position of the phenol and it is suggested that for the Pechmann reaction these involves first the formation of the carbonium ion (II b) which may then attack the nucleus in the usual manner in aromatic cationoid reactions.



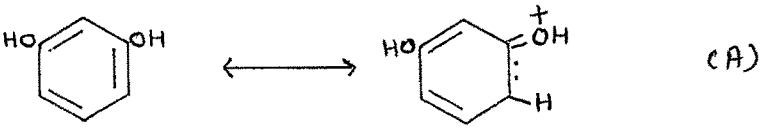
(II b)



Such alkylations are reversible and condensation would proceed only if the substitution takes place in the ortho position so that coumarin formation follows.

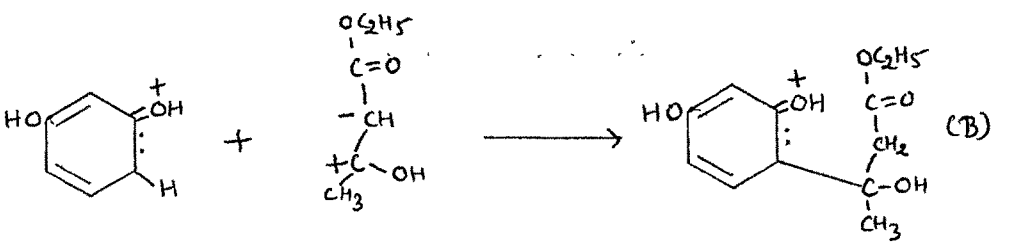
Recently John and Israelstam (12) have proposed the following mechanism for the Pechmann reaction.

Resorcinol as a result of resonance (A) has a centre of high electron density at the position ortho to the hydroxyl groups. Addition then takes place across the



(A)

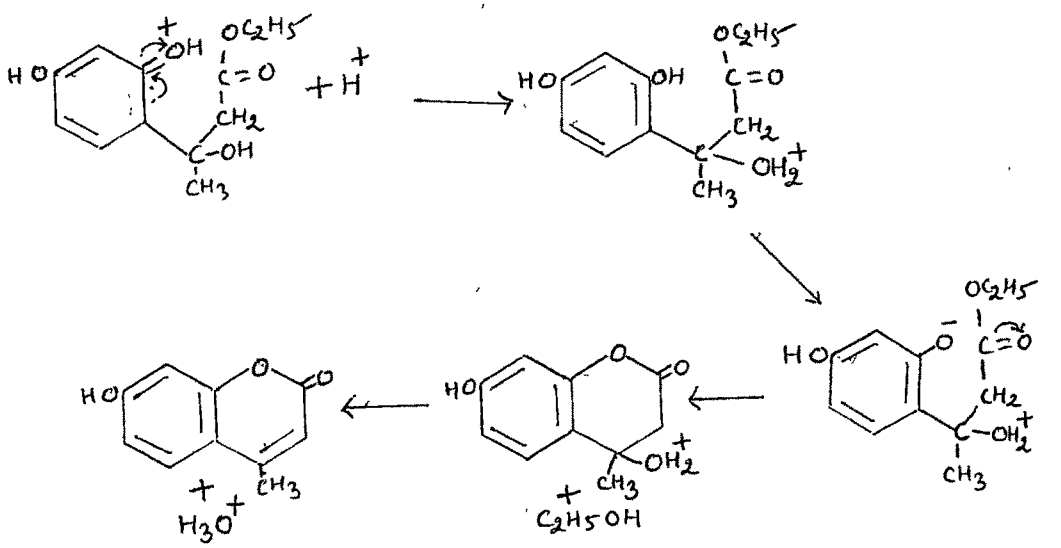
double bond in the enolic form of the β-ketonic ester as in (B)



(B)

The hydrogen ions produced by the resin (or from ~~the~~ any acid for that matter) would cause dehydration and produce an olefinic bond, at the same time ethylalcohol

would be eliminated with ring closure.



The above mechanism put forward by John and Israelstam (12) is untenable for following reasons. Firstly there is no experimental evidence for the existence of the hypothetical compound as visualised in reaction(B). It is the same compound as suggested by Ahmed and Desai (16) but with a modern electronic structure. Secondly this hypothetical compound, which is formed in the absence of hydrogen ions, does not account for the recent observation by Mentzer and his coworkers (18) and ~~later on modified~~ by Desai,Trivei and Sethna (19) that substituted phenols which in Pechmann reaction give coumarins in high yields when condensed with β-ketonic esters, ~~afforded~~ chromones simply when heated or refluxed in an inert solvent like diphenyl ether without any condensing agent.

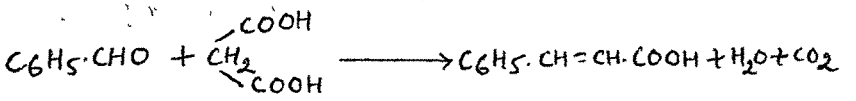
So it seems ~~for~~ from the above disscussion, that the mechanism put forward by Robertson and coworkers and later

on modified by Lacey seems to be the appropriate mechanism for the Pechmann reaction. But it was observed in the present work that the Pechmann reaction took place when resorcinol and ethyl acetoacetate were condensed in the presence of cation exchange resins at room temperature for a month giving a good yield of the coumarin derivative. At a higher temperatures, better yield of the coumarin derivative was obtained. This indicates that temperature and the presence of a proton donated from the condensing agent play an important role in the Pechmann reaction, former controlling the rate of reaction. The higher temperature is either obtained by the heat of the reaction or by means of external application of heat. It has been also observed by Barris and Israelstam (20)that it is not necessary to have a large quantities of condensing agents for the reaction to proceed. They have condensed resorcinol (0.2 mole) with ethyl acetoacetate (0.2 mole) at 120^{0} and obtained 94 % yield of the 7-hydroxy-4-methylcoumarin even though only 0.1 g. of the sulphuric acid was used as a condensing agent.

Use of Anion-exchange resins as catalysts in the Knoevenagel condensation : Synthesis of 3-substituted coumarins

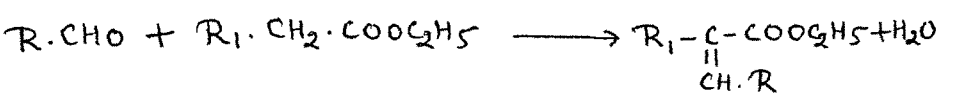
The reaction between a carbonyl compound and a compound containing a reactive methylene group in molecular proportions in the presence of basic catalysts is generally referred to as Knoevenagel condensation. Thus benzaldehyde condenses with malonic acid to form cinnamic acid in the

presence of pyridine.



Except in a few isolated cases, the reaction between carbonyl compounds and compounds containing a reactive methylene group proceeds only in the presence of catalysts. Alkali metal alcoholates may serve as catalysts, but as a general rule, the reaction is best catalysed with secondary bases, especially piperidine. Ammonia and primary amines may also serve the purpose. Small quantities of acid added to the base have beneficial effect. In many cases a mixture of equivalent quantities of piperidine and acetic acid to which a little alcohol has been added or piperidine acetate is particularly a good catalyst.

Astle and Zaslowasky (21) investigated the use of anion exchange resins as catalysts for Knoevenagel condensation. A series of aldehydes were reacted with ethyl acetoacetate, ethyl cyano acetate and diethyl malonate according to the following equation.

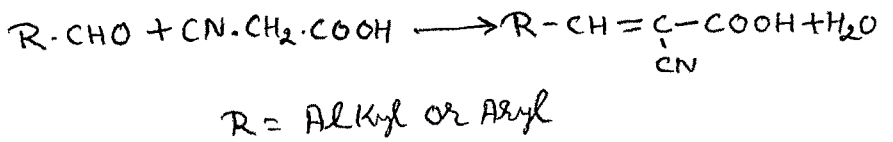


R = Alkyl or Aryl

R_1 = $COCH_3$, CN or $COOC_2H_5$.

Strongly basic resins do catalyse the reaction, but weekly basic resins either in free amine forms or as the acetate give better yields.

Astle and Gergel (22) condensed cyano acetic acid with aliphatic aldehydes and ketones and aromatic aldehydes using organic salts of weekly basic anion exchange resin such as Amberlite IR-4B.



R = Alkyl or Aryl

The present work deals with the synthesis of 3-substituted coumarins from o-hydroxy aromatic aldehydes and substances with a reactive methylene group, such as diethylmalonate, ethyl acetoacetate and ethyl cyanoacetate using anion exchange resins such as Amberlite IRA-400 as catalyst. It is a strongly basic anion exchange resin with exchangeable hydroxyl ions.

Condensation of salicylaldehyde with diethyl malonate, ethyl acetoacetate and ethyl cyanoacetate

Salicylaldehyde when condensed with diethyl malonate in the presence of Amberlite IRA-400 in boiling benzene gave 3-carboethoxycoumarin (III a) as seen by direct comparison with a sample prepared according to Knoevenagel (23).

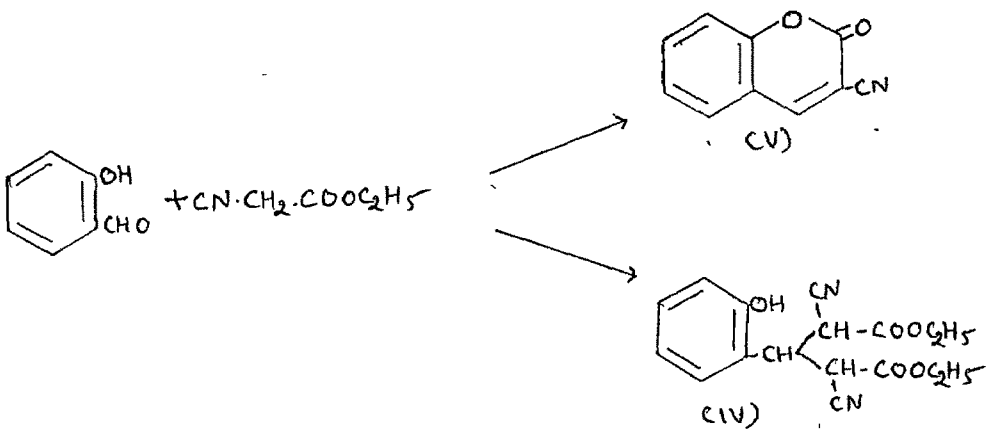
C(III)

(a) R = $COOC_2H_5$

(b) R = $COCH_3$

Salicylaldehyde on a similar condensation with ethyl acetoacetate in the presence of Amberlite IRA-400 gave 3-acetylcoumarin (IIIb) as seen by direct comparison with an authentic sample prepared according to Knoevenagel (24).

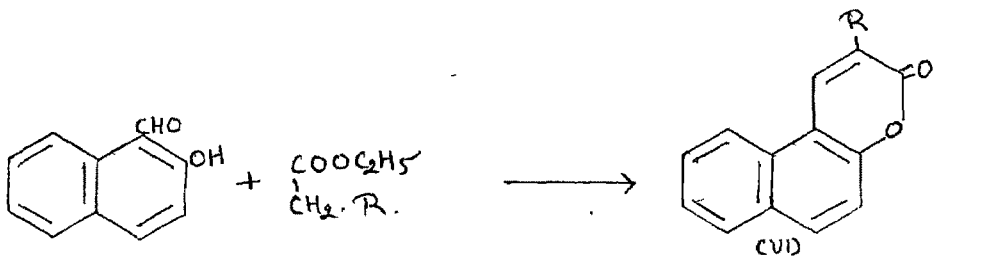
The Knoevenagel condensation of salicylaldehyde with ethyl cyanoacetate has been previously observed to give two different products (a) ethyl salicylidin bis cyanoacetate (IV)(25) and (b) 3-cyanocoumarin (V) (26) under different experimental conditions. In the present case when salicylaldehyde was condensed with ethyl cyanoacetate in the presence of Amberlite IRA-400 by shaking the reaction mixture at room temperature, ethyl salicylidin bis cyanoacetate was obtained. The structure was confirmed by direct comparison with an authentic specimen prepared according to Knoevenagel and Arnot (25).



Condensation of 2-hydroxy-1-naphthaldehyde with diethyl malonate, ethyl acetoacetate and ethyl cyanoacetate

2-Hydroxy-1-naphthaldehyde when condensed with

ethyl acetoacetate, ethyl cyanoacetate and diethyl malonate in the presence of Amberlite IRA-400 gave 3-acetyl-(VI a), 3-cyano-(VI b) and 3-carboethoxy-5,6-benzocoumarin (VI c) respectively. In all the cases the reaction did not proceed at room temperature. The coumarin derivatives were obtained only when the reaction was carried out at 140°. The structure of these compounds were confirmed by direct comparison with the authentic specimens prepared according to Knoevenegal and Schröter (28)



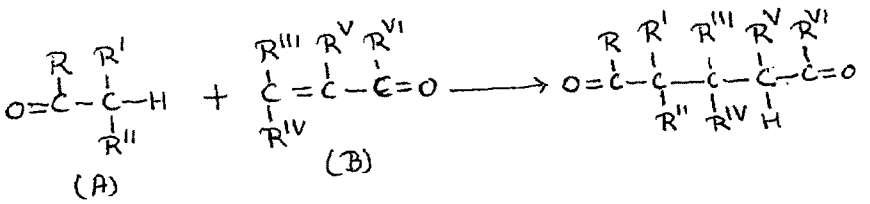
(VI)

(a) R = $COCH_3$ (b) R = CN

(c) R = $COOC_2H_5$

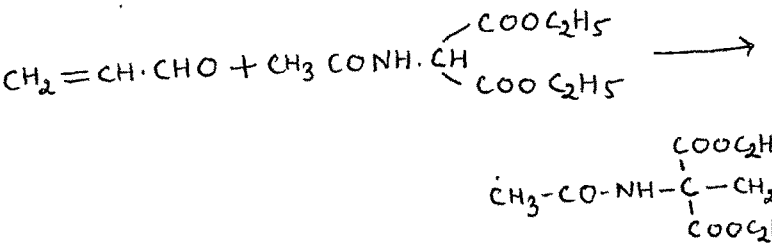
Use of Anion exchange resins as catalysts in Michael reaction

Michael reaction in its original scope is the condensation of a donor (A) containing an α-hydrogen in the system O=C-CH to a carbon-carbon bond that forms a part of this conjugated system of the general formulation C=C-C=O in an acceptor (B)

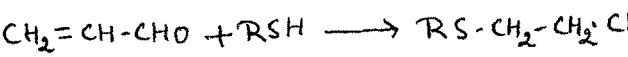


The condensation takes place under the influence of alkaline reagents, such as sodium methoxide, potassium methoxide, sodium hydroxide, ammonia, sodamide, diethylamine, piperidine and pyridine. The reaction has been reviewed by Bergmann, Ginsburg and Pappo (29).

Yamada, Chibata and Tsurui (30) investigated the Michael reaction of acrolein with ethyl acetamido malonate and ethyl nitro malonate using Amberlite IRA-400 as a catalyst.



They also prepared a series of β-thio-propionaldehyde derivatives by the addition of mercaptans to acrolein using Amberlite IRA-400.



Bergmann and Corett (31) carried out the Michael reaction with methyl vinyl ketone, octyl acrylate, acrylonitrile and methyl methacrylate as accepters with nitro propane, ethyl acetoacetate, diethyl malonate, acetyl acetone and benzyl cyanide as donors using Amberlite IRA-400 and Amberlite IRA-410 as catalysts.

$CH_3.CO.CH_2.COOC_2H_5 + CH_2=CH.CO.CH_3 \longrightarrow$

$CH_3.CO.\underset{\underset{COOC_2H_5}{|}}{CH}.CH_2.CH_2.CO.CH_3$

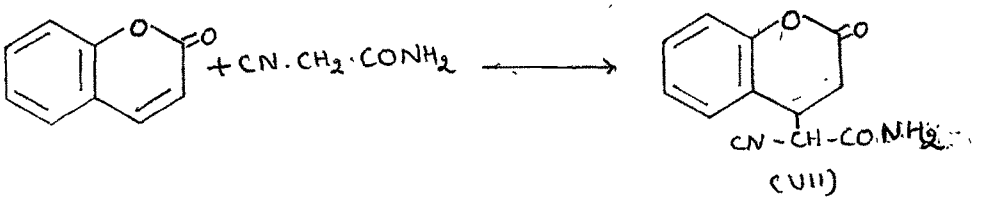
$CH_3.CO\ CH_2.COOC_2H_5 + CH_2=CH.COOC_8H_{17} \longrightarrow$

$CH_3.CO.\underset{\underset{COOC_2H_5}{|}}{CH}-CH_2.CH_2.COOC_8H_{17}$

$CH_3.CO.CH_2.CO.CH_3 + CH_2=CH.CN \longrightarrow$

$CH_3.CO-\underset{\underset{COCH_3}{|}}{CH}-CH_2-CH_2.CN$

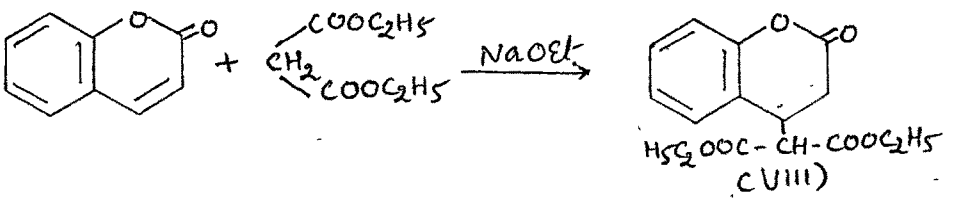
Seshadri (32) in order to test the reactivity of the double bond in the pyrone part of the coumarin molecule, carried out the Michael reaction on coumarin with cyano acetamide using piperidine as catalyst and obtained 3,4-dihydrocoumarin-4-cyanoacetamide (VII).



(VII)

Sastry and Seshadri (26) observed that the presence of a negative group such as benzoyl or cyano in the 3-position, enhances the reactivity of the double bond and also the rate of Michael reaction. Thus they condensed 3-benzoylcoumarin and 3-cyanocoumarin with cyanoacetamide and ethyl cyanoacetate and obtained the corresponding 3,4-dihydrocoumarin derivatives.

Connor and McClellan (33) also obtained a 3,4-dihydrocoumarin derivative when coumarin was condensed with diethyl malonate in the presence of sodium ethoxide.

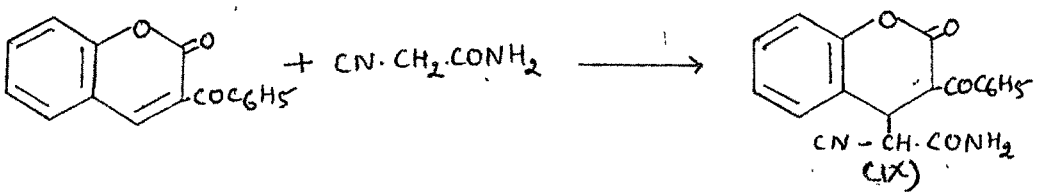


(VIII)

It was therefore thought of interest to investigate the applicability of the anion exchange resins as catalysts in the Michael reaction in which coumarin derivatives are used as acceptors and cyano acetamide, diethyl malonate and ethyl cyanoacetate as donor.

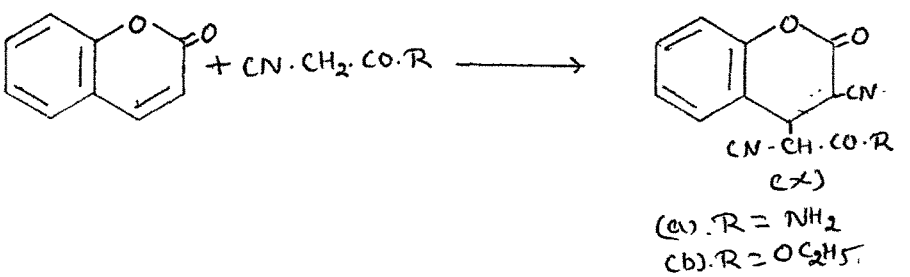
Coumarin was condensed with cyanoacetamide and diethyl malonate using Amberlite IRA-400 by refluxing the reaction mixture in alcohol and 3,4-dihydrocoumarin-4-cyano-acetamide and diethyl-3,4-dihydrocoumarin-4-malonate(VIII) were obtained respectively. In the latter case the product could be isolated with difficulty and more time was required for the reaction.

The condensation of 3-benzoylcoumarin with cyanoacetamide in the presence of Amberlite IRA-400 was quite smooth and gave 3-benzoyl-3,4-dihydro-4-cyanoacetamide. (IX).



(IX)

3-Cyanocoumarin on a similar condensation with cyanoacetamide and ethyl cyanoacetate in the presence of Amberlite IRA-400 gave 3-cyano-3,4-dihydrocoumarin-4-cyanoacetamide (X a) and ethyl-3-cyano-3,4-dihydrocoumarin-4-cyanoacetate respectively. (X b).



(X)

(a) R = NH_2

(b) R = OC_2H_5

EXPERIMENTAL

Pechmann condensations

The resins were allowed to soak for 10 min. in 5 % hydrochloric acid and washed with dilstilled water until the washings were neutral. The resins were air dried before used. For re-use the resins were rinsed several times with benzene and alcohol and air dried. The weight of the resin used was generally 30 % of the total weight of the reacting material.

7-Hydroxy-4-methylcoumarin

A mixture of resorcinol (3.3 g. ; 0.03 mole) ethyl acetoacetate (3.9 g. ; 0.03 mole) and Duolite C-20 (3 g.) was heated in an oil bath at 150° with occassional stirring. In the first 15 minutes the reaction product started solidifying. The reaction mixture was further heated for 45 minutes, to complete the reaction. To the cooled reaction mixture sufficient alcohol was added and the mixture refluxed. It was then filtered hot to remove the resin. The filtrate on cooling gave the product which crystallised from alcohol in whitish yellow needles, m.p. 185°. Yield 3.65 g. (69.2 %). Russell and Frye (34) have reported 82-90% yield of 7-hydroxy-4-methylcoumarin when concentrated sulphuric acid is used as condensing agent. Mixed m.p. with an authentic specimen prepared according to Pechmann and Duisberg (35) was not depressed.

When the above reaction was carried out on a steam bath the yield of the coumarin derivative was 2.8 g.

and it was 1.5 g. when the reaction mixture was kept at room temperature for a month.

The reaction did not proceed when resorcinol and ethyl acetoacetate were condensed in the presence of Duolite CS-101 or Amberlite IRA-400 under above conditions. But when it was carried out in the presence of Amberlite IR-120 as catalysts at 150° the yield of the coumarin derivative was 3.8 g.(72 %).

7-Hydroxy-3,4-dimethylcoumarin

A mixture of resorcinol (3.3 g. ; 0.01 mole) ethyl α-methyl acetoacetate (4.2 g. ; 0.03 mole) and Duolite C-20 (3 g.) was heated in an oil bath at 150° with occasional stirring for one hour. The reaction mixture was worked up as above and the product crystallised from alcohol in whitish yellow needles, m.p. 256°. Yield 2.8 g. (50 %). Mixed m.p. with an authentic specimen of 7-hydroxy-3,4-dimethylcoumarin prepared according to Chakravarti (10) was not depressed. When the above reaction was carried out in the presence of Amberlite IR-120 as catalyst, the yield of the coumarin derivative was 2.9 g. (51.7 %).

5,7-Dihydroxy-4-methylcoumarin

A mixture of phloroglucinol (3.78 g. ; 0.03 mole) ethyl acetoacetate (3.9 g. ; 0.03 mole) and Duolite C-20 (3 g.) was heated in an oil bath at 150° with occassional stirring for one hour. The coumarin obtained on working up as before crystallised from alcohol in colourless needles, m.p. 282°. Yield 2.8 g. (48 %) Mixed m.p. with

an authentic specimen prepared according to Pechmann and Cohen (36) was not depressed. When the above reaction was carried out in the presence of Amberlite IR-120 the yield of 5,7-dihydroxy-4-methylcoumarin was 3 g. (52 %).

7,8-Dihydroxy-4-methylcoumarin

A mixture of pyrogallol (3.78 g. ; 0.03 mole), ethyl acetoacetate (3.9 g. ; 0.03 mole) and Duolite C-20 (3 g.) was heated in an oil bath at 150° with occassional stirring for 1 hr. The product obtained on working up as before crystallised from alcohol in colourless needles, m.p.232°. Yield 2.1 g. Mixed m.p. with an authentic specimen of 7,8-dihydroxy-4-methylcoumarin, prepared according to Canter, Martin and Robertson (37) was not depressed.

When the above reaction was carried out in the presence of Amberlite IR-120 the yield of 7,8-dihydroxy-4-methylcoumarin was 2.3 g.

4-Methyl-7,8-benzocoumarin

A mixture of α-naphthol (4.32 g. ; 0.03 mole) ethyl acetoacetate (3.9 g. ; 0.03 mole) and Duolite C-20 (2.7 g.) was heated in an oil bath at 150° for 1 hr. The product obtained on working up as before crystallised from alcohol in colourless needles, m.p. 170°. Yield 3.7 g.(58.7 %). Mixed m.p. with an authentic specimen of 4-methyl-7,8-benzocoumarin, prepared according to Robertson et al. (27) was not depressed.

When the above reaction was carried out in the presence of Amberlite IR-120 the yield of 4-methyl-7,8-

benzocoumarin was 3.8 g.(60.3 %).

Knoevenagel condensations

The resin employed was Amberlite IRA-400 (61). It was regenerated by washing it with 5 % sodium hydroxide solution (5 to 6 times its volume) in a Buchner funnel. The resin was then rinsed with distilled water until the washings were neutral. The resin was air dried before the use. For re-use the resin was rinsed with benzene and air dried. Weight of the resin used was generally 30 % of the total weight of the reacting material.

3-Acetylcoumarin

A mixture of salicylaldehyde (3.05 g.; 0.025 mole) ethyl acetoacetate (3.15 g. ; 0.025 mole) and Amberlite IRA-400 (3 g.) was shaken for 72 hr. at room temperature. Benzene (60 ml.) was then added and the reaction mixture refluxed with water separator for 10 to 12 hr. The hot reaction mixture was filtered to remove the resin and the excess of benzene was removed by distillation. The last traces of benzene were removed under vacuum. The viscous liquid was treated with petroleum ether (40-60^{o}) when a solid separated which crystallised from alcohol in colourless needles, m.p. 120^{o}. Yield 2.5 g. Mixed m.p. with an authentic specimen prepared according to Knoevenagel (24) was not depressed.

3-Carboethoxycoumarin

A mixture of salicylaldehyde (3.05 g.; 0.025 mole), diethyl malonate (4.05 g. ; 0.025 mole) and Amberlite IRA-400 (3 g.) was shaken for 72 hr. at room

temperature. The product obtained on working up as before crystallised from aqueous alcohol in colourless needles, m.p. 94°. Yield 1.5 g. Mixed m.p. with an authentic specimen of 3-carboethoxycoumarin prepared according to Knoevenagel (23) was not depressed.

Ethyl salicylidine bis cyanoacetate

A mixture of salicylaldehyde (3.05 g.; 0.025 mole), ethyl cyanoacetate (2.8 g. ; 0.025 mole) and Amberlite IRA-400 (3 g.) was shaken for 24 hr. when a product separated. The reaction mixture was refluxed with alcohol (20 ml.) and filtered hot to remove the resin. The product which separated crystallised from alcohol in colourless needles, m.p. 139°. Yield 3 g. Mixed m.p. with an authentic specimen of ethyl salicylidine bis cyanoacetate prepared according to Knoevenagel and Arnot (25) was not depressed.

3-Acetyl-5,6-benzocoumarin

A mixture of 2-hydroxy-1-naphthaldehyde (3.4 g.; 0.02 mole),ethyl acetoacetate (2.52 g. ; 0.02 mole) and Amberlite IRA-400 (3 g.) was heated in an oil bath at 140° for 4 hr. To the cooled reaction mixture acetic acid (10 ml.) was added and refluxed. The product obtained on working up as before crystallised from acetic acid in colourless needles, m.p. 186°. Yield 2.7 g. Mixed m.p. with an authentic specimen prepared according to Knoevenagel and Schroter (28) was not depressed.

3-Carboethoxy-5,6-benzocoumarin

A mixture of 2-hydroxy-1-naphthaldehyde (3.4 g.; 0.02 mole), diethyl malonate (3.2 g. ; 0.02 mole) and

Amberlite IRA-400 (3 g.)' was heated in an oil bath at 140° for 4 hr. The product obtained on working as before crystallised from alcohol in colourless needles, m.p.102°. Yield 1.3 g. Mixed m.p. with an authentic specimen prepared according to Knoevenagel and Schroter (28)was not depressed.

3-Cyano-5,6-benzocoumarin

A mixture of 2-hydroxy-1-naphthaldehyde (3.4 g.; 0.02 mole), ethyl cyanoacetate (2.2 g. ; 0.02 mole) and Amberlite IRA-400 (2.5 g.) was heated in an oil bath at 140° for 4 hr. To the cooled reaction mixture,nitrobenzene (10 ml.) was added and refluxed. The product crystallised from nitrobenzene in yellow needles, m.p.283°. Yield 3 g. Mixed m.p. with an authentic specimen prepared according to Knoevenagel and Shroter (28) was not depressed.

Michael condensations

3,4-Dihydrocoumarin-4-cyanoacetamide

Coumarin (2.92 g. ; 0.02 mole) and cyanoacetamide (1.6 g. ; 0.02 mole) were dissolved in sufficient quantity of alcohol. Amberlite IRA-400 (2 g.) was added and the reaction mixture was refluxed for 10 to 12 hr. It was then filtered hot to remove the resin. The product which separated crystallised from alcohol as colourless needles, m.p. 219°. Yield 4 g. Mixed m.p.with an authentic specimen of 3,4-dihydrocoumarin-4-cyanoacetamide prepared according to Seshadri (32) was not depressed.

Diethyl-3,4-dihydrocoumarin-4-malonate

Coumarin (2.92 g. ; 0.02 mole) and diethyl malonate

(3.2 g. ; 0.02 mole) were dissolved in sufficient quantity of alcohol. Amberlite IRA-400 (3 g.) was added and the reaction mixture was refluxed for 48 hr. It was then fultered hot to remove the resin. The product from the filtrate was crystallised several times from alcohol in colourless needles, m.p. 52°. Yield 2 g. Mixed m.p. with an authentic specimen of diethyl-3,4-dihydrocoumarin-4-malonate prepared according to Connor and McClellan (33) was not depressed.

3-Benzoyl-3,4-dihydrocoumarin-4-cyanoacetamide

3-Benzoylcoumarin (2.5 g. ; 0.01 mole) and cyano acetamide (0.8 g. ; 0.01 mole) were dissolved in minimum quantity of alcohol. Amberlite IRA-400 (1.5 g.) was added and the reaction mixture refluxed for 12 hr. The product obtained on working up as usual crystallised from pyridine gave colourless needles, m.p. 314°. Yield 1.2 g. Mixed m.p. with an authentic specimen of 3-benzoyl-3,4-dihydrocoumarin-4-cyanoacetamide according to Sastry and Seshadri (26) was not depressed.

3-Cyano-3,4-dihydrocoumarin-4-cyanoacetamide

3-Cyanocoumarin (3.4 g. ; 0.02 mole) and cyanoacetamide (1.6 g. ; 0.02 mole) were dissolved in the minimum quantity of alcohol. Amberlite IRA-400 was added in the reaction mixture was refluxed for 8 hr. The product obtained on working up as usual crystallised from pyridine in colourless needles, m.p. >360°. Yield 2 g. The authentic specimen prepared according to Sastry and

Seshadri (26) gave m.p. > 360°.

Ethyl-3-cyano-3,4-dihydrocoumarin-4-cyanoacetate

3-Cyanocoumarin (3.4 g. ; 0.02 mole) and ethyl cyanoacetate (2.26 g. ; 0.02 mole) were dissolved in minimum quantity of alcohol. Amberlite IRA-400 (2 g.) was added and the reaction mixture refluxed for 8 hr. The product obtained crystallised from alcohol in colourless needles, m.p. 247°. Yield 2 g. Mixed m.p. with an authentic specimen of ethyl 3-cyano-3.4-dihydrocoumarin-4-cyanoacetate prepared according to Sastry and Seshadri (26) was not depressed.

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