List of Research Papers

1. Synthesis of Benzo-γ- pyrones by the condensation of β-ketonic esters with phenols without the use of a condensing agent. By K.B.Desai, K.N.Trivedi and Suresh Sethna. J.M.S.University of Baroda, Vol. IV No. 2 Page 1. (1955).
2. Silicon tetrachloride, a new condensing agent for Pechmann Reaction. By K.N.Trivedi. Current Science 28, 67 (1959).
3. Anion Exchange resins as catalysts in Knoevenagel Condensation: Synthesis of 3-substituted coumarins. By K.N.Trivedi. J.of Sci.and Ind.Res. 18B, 308 (1959).
4. Anion exchange resins as catalysts in Michael reaction J.Sci.Ind.Research, 18B, 397 (1959).
5. Anion exchange resins as catalysts in synthesis of pyridine derivatives. By K.N.Trivedi. Current Science, 28, 322 (1959).
6. 3-Hydroxycoumarin. By K.N.Trivedi and Suresh Sethna. J.Org.Chem., 25, 1817 (1960).
7. Synthesis of 4,5-dihydroxycoumarin; A rare observation of total γ- substitution in resorcinol. By K.N.Trivedi Current Science, 30, 54 (1960).
8. Formation of Malonmonoarylamides by partial hydrolysis of cyanacetarylamides by (a) Conc. Sulphuric acid and (b) Polyphosphoric acid. By G.H.Patel, K.N.Trivedi and C.M.Mehta, J.Sci.Ind.Research., 20B, 457 (1961).

SYNTHESIS OF BENZO γ-PYRONES BY THE CONDENSATION OF β-KETONIC ESTERS WITH PHENOLS WITHOUT THE USE OF A CONDENSING AGENT

By

K. B. Desai, K. N. Trivedi and Suresh Sethna

Department of Chemistry, M. S. University of Baroda, Baroda.

β-Ketonic esters condense with phenols in presence of sulphuric acid to give coumarin derivatives. When phosphorus pentoxide or phosphoryl chloride is substituted in place of sulphuric acid chromones may be formed instead of coumarins, especially in the case of less reactive phenols.[1]

It has been found recently by Mentzer and his coworkers[2], [3], [4] that when the condensation of β-ketonic esters with phenols is carried out at high temperatures (between 200-250°C), without using any condensing agent, chromones are exclusively formed.

It has been found by the present authors that if the above reaction is carried out in a high boiling inert solvent like diphenyl ether, at its boiling point, the reaction time in the case of reactive phenols is only about twenty minutes, the yield is improved in some cases and the product obtained is cleaner and does not require vacuum sublimation as was found necessary by Mentzer and his coworkers.

In the present work, resorcinol, pyrogallol, phloroglucinol, α-naphthol and β-naphthol have been found to condense with ethyl acetoacetate and ethyl benzoylacetate to give the corresponding chromone and flavone derivatives, (Table I). The yields in the condensations with ethyl acetoacetate have been found to be inferior in comparison with those obtained in the condensations with ethyl benzoylacetate, probably because a part of the ethyl acetoacetate decomposes at the reaction temperature. The latter was therefore selected for condensations with less reactive phenols. Attempts to condense phenol, p-hydroxy benzoic acid, methyl β-resorcylate, resacetophenone and hydroquinone, with ethyl benzoylacetate, did not succeed, only dehydrobenzoylacetic acid[5], [6] could be isolated. This was directly compared with an authentic specimen of the same prepared by heating ethyl benzoylacetate alone under the same conditions.

The reaction time was increased from 20 minutes to one hour in the condensations of resorcinol with ethyl acetoacetate and ethyl benzoylacetate

naphthol. The product obtained on removal of ether was crystallized from dilute alcohol.

Procedure for the condensation of phenols with ethyl benzoylacetate :— The condensations were carried out as above (quantities and duration of heating as in Table 1). The products obtained after removal of the solvent by steam-distillation were treated as follows :

(i) In the condensation with resorcinol the product was treated with a few c. c. of 5% sodium carbonate solution to remove dehydrobenzoylacetic acid formed. It was then treated with more of 5% sodium carbonate solution to separate the mixture of 5-hydroxy and 7-hydroxy flavone. The 7-hydroxy flavone dissolved and was recovered on acidification. The 5-hydroxy flavone formed a sodium salt which was decomposed by treatment with dilute hydrochloric acid. The flavones were crystallized from dilute alcohol.

(ii) In the condensations with pyrogallol and phloroglucinol the products obtained after the removal of the solvent were directly crystallized from dilute alcohol.

(iii) In the condensations with α-naphthol and β-naphthol the pasty products obtained were treated with alkali to remove unreacted naphthols and then crystallized from dilute alcohol.

(iv) In the condensations with phenol, p-hydroxy benzoic acid, methyl β-resorcylate, reasacetophenone and hydroquinone the product obtained after the removal of the solvent by steam distillation was directly crystallized from alcohol when the dehydrobenzoylacetic acid crystallized out. Unreacted phenolic compound remained in the mother liquor.

1	2	3	4	5	6
Resorcinol	Ethyl benzoylacetate (5.2 g.)	Acetylene tetrachloride	2½ hr.	7-hydroxyflavone, m.p. 240°, (0.2 g.)	8
Methyl β-resorcylate	Ethyl benzoylacetate (3.5 g.)	Diphenyl ether	20 min.	Dehydrobenzoylacetic acid, m.p. 171-172°, (1.3 g.)	5,6
Resacetophenone	Ethyl benzoylacetate (3.8 g.)	Diphenyl ether	20 min.	Dehydrobenzoylacetic acid. m.p. 171-172°, (1 g.)	5,6
Hydroquinone	Ethyl benzoylacetate (5.2 g.)	Diphenyl ether	20 min.	Dehydrobenzoylacetic acid, m.p. 171-172 (1.1 g.)	5,6
Pyrogallol	Ethyl acetoacetate (3.1 g.)	Diphenyl ether	20 min.	7 : 8-dihydroxy-2-methylchromone, m.p. 241 242°, (0.75 g.)	10
Pyrogallol	Ethyl benzoylacetate (4 6 g.)	Diphenyl ether	20 min.	7 : 8-dihydroxyflavone, m.p. 246°, (1.7 g.)	10
Phloroglucinol	Ethyl acetoacetate (3.1 g.)	Diphenyl ether	20 min.	5 : 7-dihydroxy-2-methylchromone, m.p. 279°, (0.6 g.)	11
Phloroglucinol*	Ethyl benzoylacetate (1.52g.)	Diphenyl ether	20 min.	5 : 7 dihydroxyflavone, m.p. 275° (0.8 g.)	8
α-naphthol	Ethyl acetoacetate (2.7g.)	Diphenyl ether	20 min.	2-methyl-7:8-benzochromone, m.p. 174°, (1.0 g.)	12
α-naphthol	Ethyl benzoylacetate (4.0 g.)	Diphenyl ether	20 min.	7 : 8-benzoflavone, m.p. 155°, (1.6 g.)	12
β-naphthol	Ethyl acetoacetate (2.7 g.)	Diphenyl ether	20 min.	2-methyl-5 : 6-benzochromone, m.p. 168°, (0.25 g.)	13
β-naphthol	Ethyl benzoylacetate (4.0 g.)	Diphenyl ether	20 min.	5 : 6-benzoflavone, m.p. 164°, (1.3 g.)	14

* Only 1 g. taken for condensation.

SILICON TETRACHLORIDE, A NEW CONDENSING AGENT FOR PECHMANN REACTION

By
K. N. TRIVEDI

Reprinted from "Current Science," Feb. 1959, 28, 67

printed from "Curr. Sci.", Feb. 1959, 28, 67

SILICON TETRACHLORIDE, A NEW CONDENSING AGENT FOR PECHMANN REACTION

JT of several methods for synthesizing umarins,[1] the Pechmann reaction,[2] consisting condensation of a phenol with a β-ketonic ter, is considered to be the most convenient. this reaction, the choice of a proper condens-g agent plays a very important part. ılphuric acid, phosphorous pentoxide, phos-ıorous oxychloride, anhydrous aluminium loride and zinc chloride have been employed tensively to bring about the condensation.

In a search for a new condensing agent, it has en found that silicon tetrachloride serves as good condensing agent for the condensation of e more reactive phenols with β-ketonic ester. esorcinol and phloroglucinol condensed with hyl acetoacetate in presence of silicon tetra-loride to give the corresponding coumarin rivatives. But, it failed to bring about the ndensation in case of the less reactive phenols, ch as phenol and methyl-β-resorcylate. The perimental procedure is as follows:

Silicon tetrachloride (25 ml.) was added to solution of resorcinol (5·5 g.) in ethyl aceto-acetate (6·5 g.) with constant shaking. The reaction mixture was refluxed on water-bath for 4 hours with a calcium chloride guard tube. It was then poured into ice and water. The product with silica was collected on the filter and washed several times with water. The crude product was dissolved in a minimum quantity of alcohol and filtered to remove silica. It was finally crystallized from aqueous alcohol; yield 2·5 g., m.p. and mixed m.p. with an authentic sample of 7-hydroxy-4-methyl-coumarin[3] was 185° C.

I am thankful to Professor Suresh M. Sethna for suggesting the problem and also for guidance and help.

Chemistry Department, K. N. TRIVEDI.
Faculty of Science,
M.S. University of Baroda, Baroda-2,
September 22, 1958.

1. Sethna and Shah, *Chem. revs.*, 1945, **36**, 1
2. — and Phadake, *Organic Reactions*, 1953, **7**, 1.
3. Pechmann and Duisberg, *Ber.*, 1883, **16**, 2119.

Reprinted from the *Journal of Scientific & Industrial Research*, 1959, Vol. 18B, No. 7, pp. 308, 309

NION-EXCHANGE RESINS AS CATALYSTS IN :NOEVENAGEL CONDENSATION: SYNTHESIS OF 3-SUBSTITUTED COUMARINS

N-EXCHANGE RESINS, BOTH OF THE ACIDIC AND THE sic type, are used widely as catalysts in various ganic reactions. The synthesis of coumarin deritives by the condensation of *o*-hydroxyaldehydes th esters such as diethyl malonate, ethyl acetoace-:e, ethyl cyanoacetate by using an anion-exchange in has not been investigated so far. It has now en found that *o*-hydroxyaldehydes condense with e above esters in the presence of Amberlite IRA-0 to give the corresponding 3-substituted coumarin rivatives in varying yields. Thus salicylaldehyde idensed with diethyl malonate and ethyl aceto-etate in the presence of Amberlite IRA-400 to give arbethoxy and 3-acetyl coumarin respectively. the case of ethyl cyanoacetate, however, ethyl icylidine bis cyanoacetate was obtained instead the 3-cyanocoumarin. In the case of 2-hydroxy-aphthaldehyde, all the three esters condensed give corresponding 3-substituted 1,2,β,α-naphtha-rone derivatives. The properties and yields of the ubstituted coumarins thus synthesized are recorded Table 1.

The resin employed was Amberlite IRA-400 (A.G.). was regenerated by washing it with 5 per cent lium hydroxide solution (5 to 6 times its volume) a Buchner funnel. The resin was then rinsed with tilled water until the washings were neutral. The in was air dried before use. For reuse, the resin s rinsed with benzene and air dried.

A mixture of salicylaldehyde, ester and Amberlite A-400 (30 per cent of the total weight) was shaken for 72 hr at room temperature. Benzene (60 ml.) was then added and refluxed with a water separator for 10 to 12 hr. The hot reaction mixture was filtered to remove the resin and the excess of benzene distilled off on a steam bath. The last traces of benzene were removed under vacuum. The viscous liquid was treated with petroleum ether (40-60°) when a solid product separated, which was crystallized from suitable solvent. In the case of ethyl cyanoacetate, ethyl salicylidine bis cyanoacetate separated when reaction mixture was shaken for 24 hr.

In the case of 2-hydroxy-1-naphthaldehyde, the reaction mixture was heated in an oil bath at 140° for 4 hr with occasional stirring. The reaction mixture was then cooled and treated with suitable hot solvent (Table 1) and filtered to remove the resin. The filtrate, on cooling, gave the 3-substituted 1,2, β,α-naphthapyrone derivatives.

TABLE 1—3-SUBSTITUTED COUMARINS SYNTHESIZED

ALDEHYDE	ESTER	PRODUCT OBTAINED	M P.* °C.	SOLVENT FOR CRYSTALLIZATION	YIELD g.
icylaldehyde 3 g.)	Diethyl malonate (4 g.)	3-Carbethoxy coumarin[1]	94	Alcohol	1·5
	Ethyl acetoacetate (3·3 g)	3-Acetyl coumarin[2]	120	Aqueous alcohol	2·5
	Ethyl cyanoacetate (2·75 g)	Ethyl salicylidine bis cyanoacetate[3]	139	Alcohol	3·0
ydroxy-1-phthaldehyde g.)	Diethyl malonate (2·9 g)	3-Carbethoxy-1,2,β,α-naphthapyrone[4]	102	Aqueous alcohol	1·3
	Ethyl acetoacetate (2·4 g.)	3-Aceto-1,2,β,α-naphthapyrone[5]	186	Acetic acid	2·7
	Ethyl cyanoacetate (2·1 g.)	3-Cyano-1,2,β,α-naphthapyrone[6]	283	Nitrobenzene	3·0

*Mixed melting point with the authentic sample was not depressed in all the cases.

The author's thanks are due to Prof. S. M. Sethna for his valuable guidance during the course of the investigation.

K. N. TRIVEDI

Chemistry Department
Faculty of Science
M.S. University of Baroda
Baroda

15 *April* 1959

1. KNOEVENAGEL, E., *Ber. dtsch. chem. Ges.*, **31** (1898), 2593.
2. KNOEVENAGEL, E., *Ber. dtsch. chem. Ges.*, **31** (1898), 732.
3. KNOEVENAGEL, E. & ARNOT, R., *Ber. dtsch. chem. Ges.*, **37** (1904), 4496.
4. KNOEVENAGEL, E & SCHROTER, F., *Ber. dtsch. chem. Ges.*, **37** (1904), 4486.
5. KNOEVENAGEL, E & SCHROTER, F., *Ber. dtsch. chem. Ges.*, **37** (1904), 4484.
6. KNOEVENAGEL, E. & SCHROTER, F., *Ber. dtsch. chem. Ges.*, **37** (1904), 4490.

Reprinted from the *Journal of Scientific & Industrial Research*, 1959, Vol. 18B, No. 9, p. 397

ANION-EXCHANGE RESINS AS CATALYSTS IN MICHAEL REACTION

HE USE OF ION-EXCHANGE RESINS, BOTH OF ACIDIC ıd basic type, as catalysts in various organic re-:tions is increasing rapidly. It was, therefore, of terest to investigate the applicability of the anion-:change resins in the Michael reaction in which ıumarin derivatives are used as acceptors. No work ems to have been carried out so far on this subject.

Coumarin, when condensed with cyanoacetamide presence of Amberlite IRA-400, gave 3,4-dihydro-ıumarin-4-cyanoacetamide in good yields. It also ndensed with diethyl malonate but the yield of the ndensation product was poor. Several other cou-arin derivatives such as 3-benzoylcoumarin and cyanocoumarin were found to be good acceptors as e negative group in 3-position enhances the reacti-ty of the double bond and also the rate of the re-:tion. The properties and yields of the 3,4-dihydro-umarin derivatives thus prepared are recorded in ıble 1.

Amberlite IRA-400 (A.G.) was regenerated by ıshing with 5 per cent sodium hydroxide solution -6 times the volume of the resin) in a Buchner funnel and rinsed with distilled water until the washings were neutral. The resin was air dried before use. For reuse, the resin was rinsed with benzene and air dried.

To equimolecular quantities of the reactants dissolved in sufficient quantity of alcohol, Amberlite IRA-400 (30 per cent of the total weight) was added and the reaction mixture refluxed for specified periods and then filtered hot to remove the resin. The filtrate, on cooling, deposited a mass of crystals which were crystallized from a suitable solvent.

TABLE 1 — 3,4-DIHYDROCOUMARINS SYNTHESIZED

Reactants	Reaction period *hr*	Product	M.P.* °C.	Solvent for crystallization	Yield *g.*
ıumarin (3 g.)+cyanoacetamide (2 g.)	10-12	3,4-Dihydrocoumarin-4-cyanoacetamide[1]	219	Alcohol	4·0
ıumarin (3 g.)+diethyl malonate 3·2 g.)	48	Diethyl-3,4-dihydrocoumarin-4-malonate[2]	52	do	2·0
Benzoylcoumarin (2·4 g.)+cyano-cetamide (0·8 g.)	12	3-Benzoyl-3,4-dihydrocoumarin-4-cyanoacetamide[3]	314	Pyridine	1·2
Cyanocoumarin (3·4 g.)+cyano-cetamide (1·7 g.)	8	3-Cyano-3,4-dihydrocoumarin-4-cyanoacetamide[3]	>360	do	2·0
Cyanocoumarin (3·4 g.)+ethyl-yanoacetate (2·6 g.)	8	Ethyl-3-cyano-3,4-dihydrocoumarin-4-cyanoacetate[3]	247	Alcohol	2·5

*Mixed melting point with authentic sample was not depressed in all the cases.

The author's thanks are due to Prof. Suresh Sethna for his guidance and help.

K. N. Trivedi

Chemistry Department
Faculty of Science
M.S. University of Baroda
Baroda
30 *June* 1959

1. Seshadri, T. R., *J. chem. Soc.*, (1928), 166.
2. Connor, R. & McClellan, W. M. R., *J. org. Chem.*, **3** (1938), 570.
3. Sastry, V. D. N. & Seshadri, T. R., *Proc. Indian Acad. Sci.*, **16A** (1942), 29.

ANION EXCHANGE RESINS AS CATALYST IN THE SYNTHESIS OF PYRIDINE DERIVATIVES

BY

K. N. TRIVEDI

Reprinted from "Current Science", August 1959, 28, 322

eprinted from "Curr. Sci.", August 1959, 28, 322

ANION EXCHANGE RESINS AS CATALYST IN THE SYNTHESIS OF PYRIDINE DERIVATIVES

NION exchange resins are widely used as :talyst in numerous organic reactions. In the nthesis of pyridine derivatives, the use of ıion exchange resins as catalyst has not been :ported so far. It is now found that cyano-:etamide condenses with acetylacetone in pre-nce of Amberlite IRA-400 to give 3-cyano-: 6-dimethyl-2-pyridone in good yield. The :perimental procedure is as follows:—

Amberlite IRA-400 (A.G.) was washed with % sodium hydroxide solution (5 to 6 times e volume of the resin) in a Buchner funnel. ıe resin was rinsed with distilled water until e washings were neutral, and was air dried :fore use. Amberlite IRA-400 (4 g.) was lded to a saturated solution of cyano-etamide (4·2 g) and acetylacetone (5 g.) in cohol and the reaction mixture was refluxed r 3 to 4 hr. on steam bath. The reaction ixture was then filtered hot to remove the resin. The filtrate, on cooling, gave a crystalline product. This was collected on filter, washed with cold alcohol and crystallized from alcohol in white shining needles. M.p. and mixed m.p. with an authentic sample of 3-cyano-4 : 6-dimethyl-2-pyridone[1] was 289°. Yield 5 g.

Synthesis of other pyridine derivatives using the anion exchange resins as catalyst is in progress.

I am thankful to Prof. Suresh M. Sethna for his guidance and help.

Chemistry Department, K. N. TRIVEDI.
Faculty of Science,
M.S. University of Baroda,
Baroda-2, *April* 6, 1959.

1. Bardhan, J. C., *J. Chem. Soc.*, 1929, 2223.

[Reprinted from the Journal of Organic Chemistry, 25, 1817 (1960)]

3-Hydroxycoumarins

K. N. Trivedi and Suresh Sethna

Received March 30, 1960

3-Hydroxycoumarin has an inhibiting effect on the growth of *avena* roots[1] and 3-aminocoumarins, which are intermediates in the synthesis of 3-hydroxycoumarins, are found to have antibacterial properties.[2] The present work deals with the synthesis of some substituted 3-hydroxycoumarins and a study of the pattern of substitution in 3-hydroxycoumarin.

5-Bromo-, 3,5-dibromo-, 3-nitro-, 5-nitro-, and 3,5-dinitrosalicylaldehyde, methyl 2,4-dihydroxy-3-formylbenzoate and 2,4-dihydroxy-3-formylacetophenone were condensed according to Shaw, McMillen, and Armstrong[3] with acetylglycine in the presence of sodium acetate and acetic anhydride and the 3-acetamidocoumarins formed hydrolyzed with alcoholic 3*N*-hydrochloric acid to the 3-hydroxycoumarins. The intermediate 3-aminocoumarins could not be isolated even under controlled hydrolysis with acid or alkali.

The ketonic character of the 3-hydroxycoumarin has been shown by the formation of a phenylhydrazone and a quinoxaline derivative with *o*-phenylenediamine.[4] It is now found that 3-hydroxycoumarin gives the isonitroso derivative with nitrous acid. With bromine in acetic acid it gave the 4-bromoderivative and with iodine and iodic acid the 4-iodo derivative, both of which gave the original coumarin on reduction with zinc and acetic acid. Further bromination did not succeed, but the 6-bromo- and 6,8-dibromo-3-hydroxycoumarin were brominated in the 4-position. 3-Acetoxycoumarin underwent Fries migration to give the 4-acetyl derivative which was also obtained in the Friedel-Crafts acetylation of 3-hydroxycoumarin. On oxidation it gave salicylic acid. 3-Hydroxycoumarin when treated with formaldehyde gave 4-4′-methylenebis(3-hydroxycoumarin).

EXPERIMENTAL

Synthesis of 3-hydroxycoumarins. An equimolecular mixture of the salicylaldehyde derivative, acetylglycine, and anhydrous sodium acetate and acetic anhydride (2 moles) was heated on a steam bath for 1 hr. The 3-acetamidocoumarin derivative obtained on dilution with water was crystallized from acetic acid (Table I).

The acetamidocoumarin was dissolved in a minimum quantity of alcohol and refluxed with 3*N* hydrochloric acid for 3 to 4 hr. The 3-hydroxycoumarin obtained on cooling was crystallized from alcohol (Table II). All the 3-hydroxycoumarins gave a characteristic green coloration with alcoholic ferric chloride, and were soluble in sodium hydroxide solution in the cold on standing.

4-Isonitroso-2,3-diketochroman. A mixture of 3-hydroxy coumarin (1 g.) in a minimum quantity of acetic acid and 5 ml. concd. hydrochloric acid was kept in an ice bath and sodium nitrite solution (0.5 g. in 5 ml. of water) was added dropwise. Sodium bicarbonate solution was added to neutralize the solution, which was then extracted with ether. The product obtained from ether crystallized from a benzene-ligroin mixture in stout yellow needles, m.p. 185° dec.

Anal. Calcd. for $C_9H_5O_4N$: N, 7.3. Found: N, 7.1.

Brominations. To 3-hydroxycoumarin or its derivative in acetic acid a molecular quantity of bromine in acetic acid was added and the reaction mixture stirred for 0.5 hr. The product which separated was crystallized from acetic acid (Table II).

4-Iodo-3-hydroxycoumarin. To 3-hydroxycoumarin (1.72 g.) and iodine (1.16 g.) dissolved in a minimum quantity of alcohol, iodic acid (0.4 g.) was added with stirring. The product which separated was filtered and crystallized from alcohol as pale yellow needles, m.p. 223° dec.

Anal. Calcd. for $C_9H_5O_3I$: I, 44.06. Found: I, 43.74.

Reductions. 4-Bromo- or 4-iodo-3-hydroxycoumarin (0.5 g.) was dissolved in acetic acid (25 ml.) and zinc dust (1 g.) was added. The reaction mixture was refluxed for 2 hr. It was filtered hot and diluted with water. The product which separated was crystallized from alcohol; melting point and mixed melting point with 3-hydroxycoumarin was 151°.

3-Acetoxycoumarin was obtained by heating 3-hydroxycoumarin with pyridine and acetic anhydride. It crystallized from benzene in colorless needles; m.p. 105–106°. It did not give any coloration with alcoholic ferric chloride.

Anal. Calcd. for $C_{11}H_8O_4$: C, 64.71; H, 3.93. Found: C, 64.81; H, 4.3.

4-Acetyl-3-hydroxycoumarin. A mixture of 3-acetoxycoumarin (1 mole) and anhydrous aluminum chloride (2 moles) was heated in an oil bath at 140° for 2 hr. The reaction mixture was worked up as usual. The product obtained was dried and extracted with hot petroleum ether (b.p. 60–80°). The product obtained on repeated crystallization from the same solvent gave colorless needles, m.p. 85°. The same product was obtained in the Friedel-Crafts acetylation of 3-hydroxycoumarin (1.6 g.) by heating it with anhydrous aluminum chloride (2.5 g.) and acetic anhydride (4 ml.) on a steam bath for 3 hr. It gave a green coloration with alcoholic ferric chloride.

Anal. Calcd. for $C_{11}H_8O_4$: C, 64.71; H, 3.93. Found: C, 64.84; H, 3.88.

The 2:4-dinitrophenylhydrazone, prepared as usual, melted at 236–238° dec.

Anal. Calcd. for $C_{17}H_{11}O_7N_4$: N, 11.59. Found: N, 11.7.

Oxidation. 4-Acetyl-3-hydroxycoumarin (1 g.) was dissolved in sodium hydroxide (10%; 10 cc.) and heated with potassium permanganate (0.5 g.) on a steam bath for 3 hr.

(1) R. H. Goodwin and G. Taves, *Am. J. Botany*, **37**, 224 (1950).

(2) G. Rodighiero and C. Antonello, *Bull. Chim. Farm.*, **97**, 592 (1958).

(3) K. N. F. Shaw, A. McMillen, and M. D. Armstrong, *J. Org. Chem.*, **21**, 601 (1956).

(4) E. Erlenmeyer, Jr., and W. Stadlin, *Ann.*, **337**, 283 (1904).

SYNTHESIS OF 4:5-DIHYDROXY-COUMARIN : A RARE OBSERVATION OF TOTAL γ-SUBSTITUTION IN RESORCINOL

By

K. N. TRIVEDI

Reprinted from "Current Science," February 1961, 30, 54-55

Reprinted from "Curr. Sci.", February 1961, 30, 54-55

SYNTHESIS OF 4:5-DIHYDROXY-COUMARIN: A RARE OBSERVATION OF TOTAL γ-SUBSTITUTION IN RESORCINOL

MENTZER and Vercier[1] carried out the thermal condensation of phenols with substituted malonic esters and obtained 3-substituted-4-hydroxy-coumarin derivatives. It is now observed that when the same reaction is carried out in refluxing diphenyl ether corresponding 3-substituted-4-hydroxy-coumarin derivatives are obtained in good yields.

When resorcinol is condensed with ethyl methylmalonate it furnishes 3-methyl-4 : 7-dihydroxycoumarin as obtained by Mentzer *et al.* But when it is condensed with ethyl benzylmalonate in refluxing diphenyl ether, 3-benzyl-4 : 5-dihydroxycoumarin, m.p. 259-60°C. (Found : C = 71·99, H = 4·56 ; $C_{16}H_{12}O_4$ requires C, 71·64, H, 4·48%) is obtained in good yield. This compound underwent debenzylation when heated with anhydrous aluminium chloride at 200° C. for 15 min. to give 4 : 5-dihydroxycoumarin, m.p. 221°C. The structure of this compound was confirmed by direct comparison with an authentic sample of 4 : 5-dihydroxycoumarin prepared according to the method of Desai and Sethna.[2] Recently Vallet and Mentzer[3] carried out the above condensation and obtained 3-benzyl-4 : 7-dihydroxycoumarin, m.p. 245° C. This is a rare observation in which total γ-substitution in resorcinol has taken place without the use of condensing agent and furnishes an easier method for the synthesis of 4 : 5-dihydroxy-coumarin. Details of the condensation of phenols with substituted malonic esters in refluxing diphenyl ether will be published elsewhere.

Author's thanks are due to Prof. S. M. Sethna for his valuable guidance and help and also to Shri S. S. Lele for carrying out the micro-analysis.

Chemistry Department, K. N. TRIVEDI:
Faculty of Science,
Baroda-2, *October* 21, 1960.

1. Mentzer, C. and Vercier, P., *Compt. rend.*, **1951, 232, 1674.**
2. Desai, N. J. and Sethna, *J. Org. Chem.*, **1957, 22, 388.**
3. Mentzer, C. and Vallet, *Compt. rend.*, **1959, 248, 184.**

Reprinted from the *Journal of Scientific & Industrial Research*, 1961, Vol 20B, No 9, pp. 457, 458

Formation of Malon Monoarylamides on Partial Hydrolysis of Cyanacetarylamides using Polyphosphoric Acid & Sulphuric Acid

G. H. PATEL, K N. TRIVEDI & C. M. MEHTA
Faculty of Science, M S. University of Baroda, Baroda

Manuscript received 6 *July* 1961

A number of cyanacetarylamides have been partially hydrolysed to corresponding malon monoarylamides by means of polyphosphoric acid or 75 per cent sulphuric acid; the yields of the amides are quantitative.

IN the hydrolysis of nitriles to acids, the use of 100 per cent phosphoric acid has been known for some time. Recently, it has been observed that the amides obtained by Beckmann's rearrangement and acylation of amines are stable in polyphosphoric acid and do not undergo hydrolysis[1,2]. The reaction of polyphosphoric acid has, therefore, been investigated with various cyanacetarylamides with a view to preparing with ease malon monoarylamides, which are used as intermediates in the synthesis of 2,4-dihydroxyquinolines[3].

It has been found that simple nitriles can be hydrolysed to amides by polyphosphoric acid[4]. However, the method was not found to be suitable for the hydrolysis of sterically hindered nitriles. Sperber *et al.*[5] carried out the conversion of tributyl acetonitrile to tributyl acetamide on a steam bath using 80 per cent sulphuric acid. These workers tried different concentrations of sulphuric acid and also other reagents, viz. polyphosphoric acid, concentrated hydrochloric acid, etc., and found that the expected tributyl acetic acid from the corresponding amide was not