CHAPTER IV

ROSENMUND-VON BRAUN REACTION ON IODOCOUMARINS : SYNTHESIS OF CYANOCOUMARINS

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Aryl nitriles can be prepared by many methods. A survey of all the methods has been made by Mowry (Chem. Revs., 1948, 42, 189). The first synthesis of nitriles was reported by Wöhler and Liebig (Ann. 1832, 3, 249, 267) who prepared benzoyl cyanide and benzonitrile by distillation of benzoyl chloride over mercuric cyanide.

The synthesis of benzonitrile by the fusion of alkali metal salts of benzene sulphonic acid with potassium cyanide was discovered by Merz, (Z. Chem., 1868, 4, 33, 396). Further study of this reaction revealed that a good yield of β-naphthonitrile can be obtained from sodium-β-naphthalene-sulphonate by treatment with an excess of sodium cyanide. Witt (Ber., 1873, 6, 448) showed that the less toxic potassium ferrocyanide gave somewhat better results.

In general the yields of purified aromatic nitriles vary from traces to 60-80 % depending on the structure of the reacting compound. Dry reagents, intimate mixing and uniform heating of reaction mass to high temperatures appear desirable. The use of sand in the reaction mixture is recommended to increase the yield by modifying the exothermic reaction and the introduction of a small quantity of iron fillings to aid the distribution of heat (Wahl and co-workers, Bull. Soc. Chim., 1939, 5 6, 533)

A smoother reaction and increased yields are also obtained by heating the reagents in an inert diluent such as mineral oil (British Patent, 1944,7565647).

A number of dicyano derivatives of benzene, biphenyl, naphthalene and higher condensed ring systems have been prepared from the corresponding disulphonates. Yields are usually less than 20 % and the product is contaminated with mononitrile.

Rosenmund and Struck (Ber., 1919, 52, 1749) found that the replacement of aryl halogen atom by the cyano group can also be accomplished by the action of anhydrous cuprous cyanide. The use of cuprous cyanide dissolved in cyclic aromatic amines was described in the German patent literature (German Patent 1920, 327049).

Later, Diesbach et al. (Helv. Chim, Acta., 1923, 6, 548) extended the cuprous cyanide reaction and reported the conversion of a mixture of dibromo xylenes to the dinitriles in good yields. This technique has proved very popular with later workers. The arylbromide and slight excess of dry cuprous cyanide are added to sufficiently dry quinoline or pyridine to form homogeneous complex at reaction temperatures of 150-250°. Thus Newman (J. Am. Chem. Soc., 1937, 59, 2473) converted α-bromonaphthalene to α-naphthonitrile with cuprous cyanide in pyridine solution in 93 % yield.

It was observed by von Braun and Manz (Ann., 1931, 488, 111) that the bromo derivatives of high boiling aromatic hydrocarbons are smoothly converted into nitriles in a very high yield by treatment with a slight excess of cuprous cyanide at 260° without using any solvent or promoter. This method, later called the Rosenmund-von Braun synthesis, has been studied in detail by Koelsch and Whitney (J. Am. Chem. Soc., 1936, 58, 1328) who found that the reaction is auto catalytic and that addition of small amount of nitrile from a previous run shortens the reaction time and copper sulphate in small amounts has a marked catalytic effect while hydroquinone retards the reaction. They recommended the addition of 0.01 mole of copper sulphate per 0.1 mole of iodo derivative and gradual addition of the halide to the mixture of cuprous cyanide and catalysts. This observation led to the hypothesis that only the divalent copper ion can react with aryl halide to form a stable complex. The following mechanism has been proposed by Koelsch and Whitney (J. Org. Chem., 1941, 6, 795)

$$\mathrm{Arx} + \mathrm{Cu}^{++} \longrightarrow \left[\mathrm{Arx} \rightarrow \mathrm{Cu}\right]^{++}$$

$$\overset{+}{\mathrm{Cu}} + \left[\mathrm{Arx} \rightarrow \mathrm{Cu}\right]^{++} \qquad \mathrm{Cu}^{++} + \left[\mathrm{Arx} \rightarrow \mathrm{Cu}\right]^{+}$$

$$\left[\mathrm{Arx} \rightarrow \mathrm{Cu}\right]^{+} \longrightarrow \mathrm{Ar}^{+} + \mathrm{Cux}$$

$$\mathrm{Ar}^{+} + \overset{-}{\mathrm{C}}\mathrm{N} \longrightarrow \mathrm{ArCN}$$

The gradual addition of the halide to the cuprous cyanide and catalysts promotes rapid conversion. For large scale runs, as in commercial practice, the use of a solvent or an inert diluent is desirable to assist the dissipation of heat of reaction. This may be either a solvent for the cuprous cyanide such as pyridine, quinoline, or phenyl acetonitrile or a diluent such as nitrobenzene, dichlorobenzene or naphthalene. In general the use of solvents enables the reaction to be effected at lower temperatures.

An anomalous reaction was observed by Diesbach et al. (Helv. Chim. Acta., 1927, 10, 886) who obtained a highly coloured insoluble mass when o-dibromoxylene was reacted with copper cyanide in pyridine solution. The nature of these materials was elucidated by Linstead and Lowe (U.S. Patent 1936, 2,054,088) who showed them to be phthalocyanines or tetrabenzotetraazaporphins, a class of blue organic pigments which now have acquired considerable commercial importance.

Though various chloro and bomocoumarins are known this reaction has not been applied to such compounds. Some cyanocoumarins have been synthesised by other methods. For examples Dey and Kutti (Proc. Natl. Insti. Sci., India, 1940, 6, 641) obtained 5-cyano-8-methoxycoumarin from 5-amino-8-methoxycoumarin by diazotization and treatment with potassium cyanide. Link and co-workers (J. Am. Chem. Soc., 1953, 75, 1886) obtained 3-cyano-4-methylcoumarin from ethyl cyanoacetate and o-hydroxy acetophenone in presence of sodium ethoxide. 3-Cyano-4-alkylcoumarins were obtained, by the condensation of ethyl cyanoacetate and various o-hydroxy acyl phenones in presence of ammonium acetate and using benzene-acetic acid mixture as solvent, by Link and co-workers

(J. Am chem. Soc., 1957, 79, 5301). Baker and Howes (J. Chem. Soc., 1953, 119) obtained 3-cyanocoumarin and 7-methoxy-3-cyanocoumarin by condensing malononitrile with salicylaldehyde and 2-hydroxy-4-methoxybenzaldehyde respectively in presence of piperidine. Crawford and Rasburn (J. Chem. Soc., 1956, 2155) obtained 8-cyanocoumarin from 8-aminocoumarin by diazotization and treatment with potassium cuprocyanide.

In the present work various cyanocoumarins have been prepared from the corresponding iodocoumarins described in Chapter III by the Rosenmund-von Braun reaction. The iodo compounds were generally heated with anhydrous cuprous cyanide above their melting points to ~~give~~ get cyano derivatives in excellent yields. With pure cuprous cyanide yields were extremely poor but cuprous cyanide of some standing gave better results. For small lots upto 3 g. no dilutent was used. When working with lar~~t~~ger quantities sand was used as diluent. The hydrolysis of the above cyano compounds with alkali and sulphuric acid has been studied.

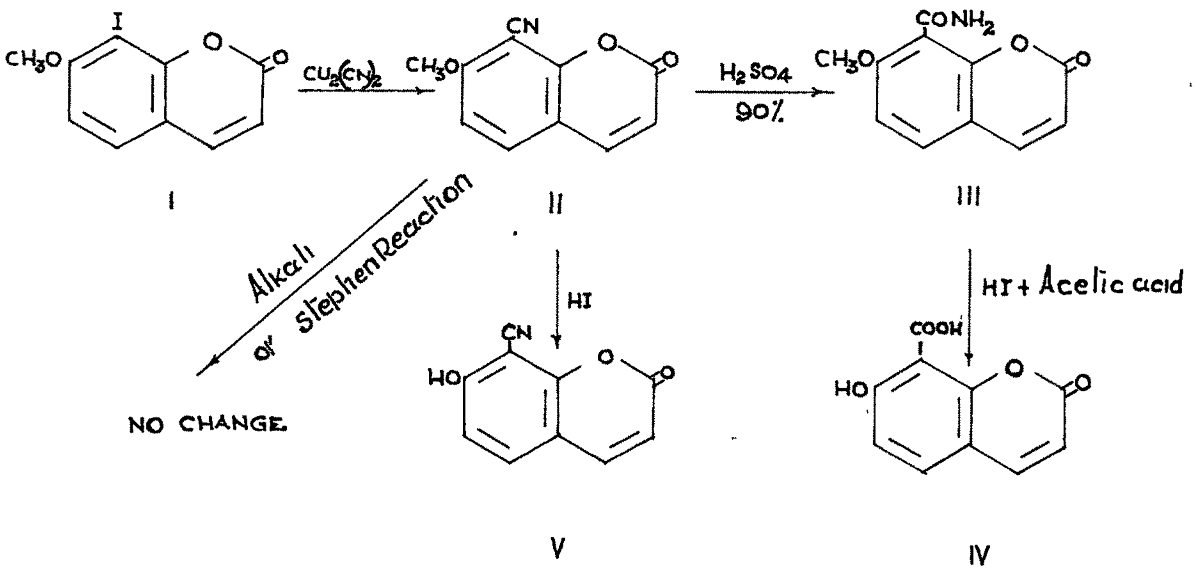
Rosenmund-von Braun reaction on 7-methoxy-8-iodocoumarin : 7-Methoxy-8-cyanocoumarin

7-Methoxy-8-iodocoumarin (I) when heated with anhydrous cuprous cyanide above its melting point gave the corresponding 8-cyanocoumarin derivative (II) in excellent yield. On heating with alcoholic as well as aqueous potassium hydroxide solution (10 % and 20 %) or with alcoholic concentrated hydrochloric acid 7-methoxy-8-cyanocoumarin remained unchanged. On heating with sulphuric acid (90 % by volume) it was only partially hydrolysed and yielded the corresponding 8-carbamoyl derivative (III), which on heating with hydriodic acid in acetic acid yielded 7-hydroxycoumarin-8-carboxylic acid (IV). Attempts to prepare the 8-formyl derivative from 7-methoxy-8-cyanocoumarin (II) by Stephen reaction did not succeed. The original cyanocoumarin was quantitatively recovered.

On demethylation with hydriodic acid (II) yielded 7-hydroxy-8-cyanocoumarin (V)

Methyl 7-methoxy-8-cyanocoumarin-6-carboxylate

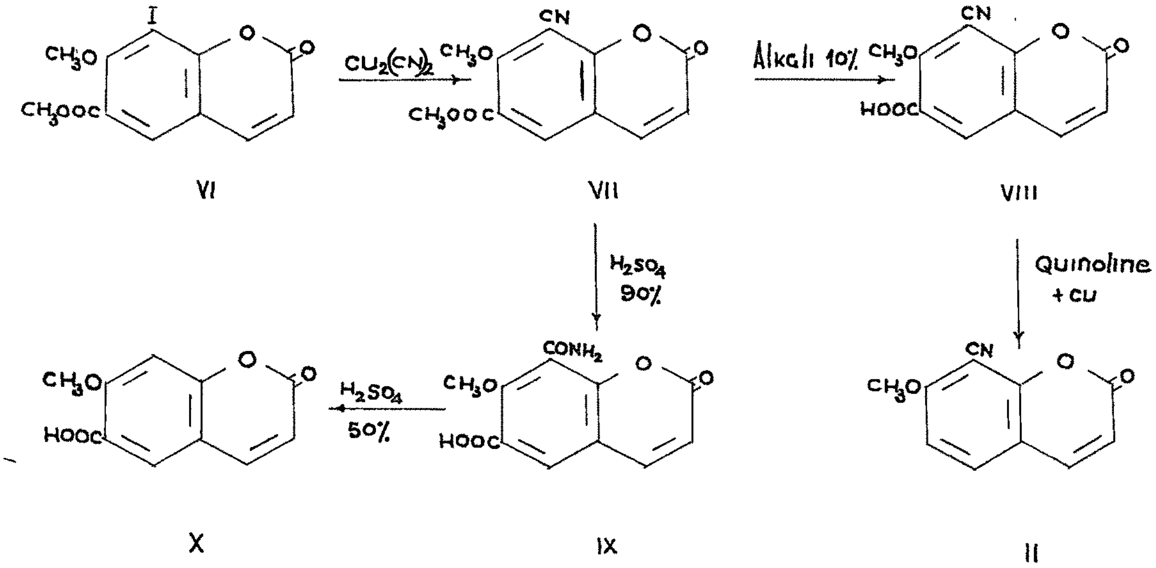
Methyl 7-methoxy-8-iodocoumarin-6-carboxylate (VI) when heated with anhydrous cuprous cyanide above its melting point gave the corresponding 8-cyanocoumarin derivative (VII). On heating with alcoholic or aqueous potassium hydroxide solution (10 %) the ester was only hydrolysed to the corresponding acid (VIII), the cyano group remaining intact.

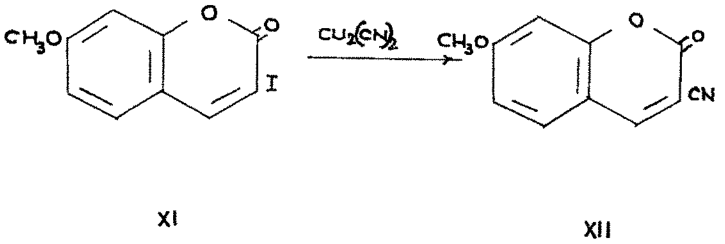


On decarboxylation the acid (VIII) gave 7-methoxy-8-cyanocoumarin (II) described earlier. On heating with sulphuric acid (90 % by volume) the cyanoester gave 7-methoxy-8-carbamoylcoumarin-6-carboxylic acid (IX) which on further hydrolysis with sulphuric acid (50 % by volume) gave a product which was found to be identical with the known 7-methoxycoumarin-6-carboxylic acid (X). Stephen reaction on (VII) did not succeed the original coumarin was recovered unchanged.

7-Methoxy-3-cyanocoumarin

7-Methoxy-3-iodocoumarin (XI) when heated with anhydrous cuprous cyanide above its melting point gave the corresponding 3-cyanocoumarin derivative (XII) previously prepared by W.Baker and C.S.Howes (J. Chem. Soc., 1953, 119) by the condensation of mono methyl ether of β-resorcyl aldehyde and malononitrile in presence of piperidine.

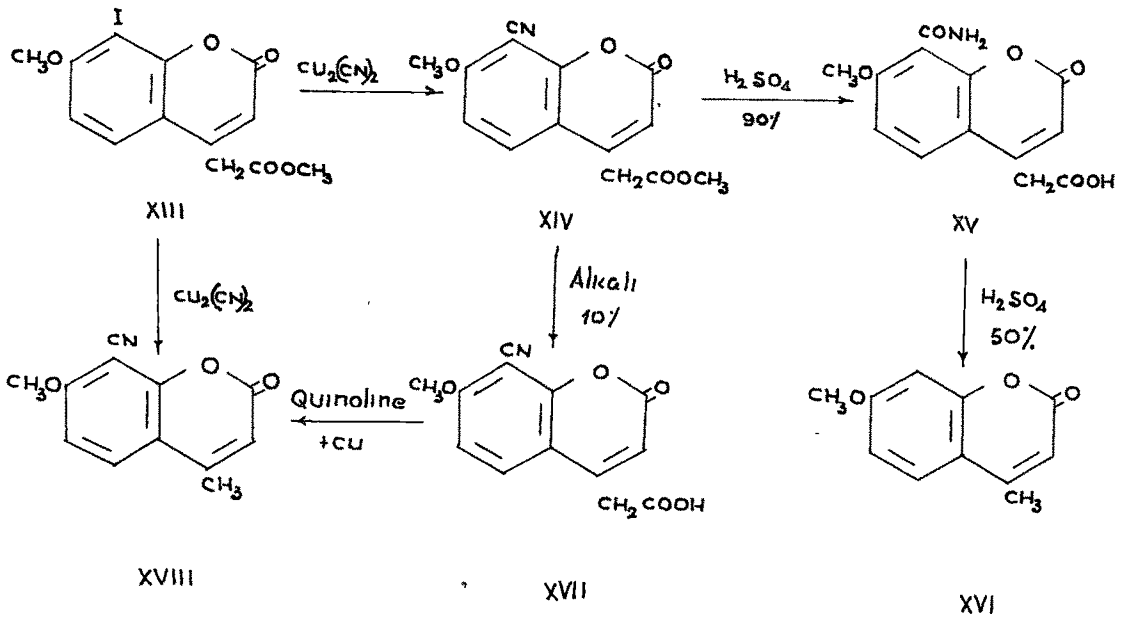




Methyl 7-methoxy-8-cyano-4-acetate

Methyl 7-methoxy-8-iodocoumarin-4-acetate (XIII) when heated with anhydrous cuprous cyanide above its melting point gave 8-cyanocoumarin derivative (XIV) in low yield. Along with a good quantity of 7-methoxy-8-cyano-4-methylcoumarin (XVIII) as seen by direct comparison with an authentic specimen prepared from 7-methoxy-8-iodo-4-methylcoumarin by the Rosenmund-von Braun reaction. The two cyano compounds were separated by extraction with benzene in which the cyanocoumarin (XIV) was more soluble than the cyanocoumarin (XVIII). Further purification was done by fractional crystallation from acetic acid.

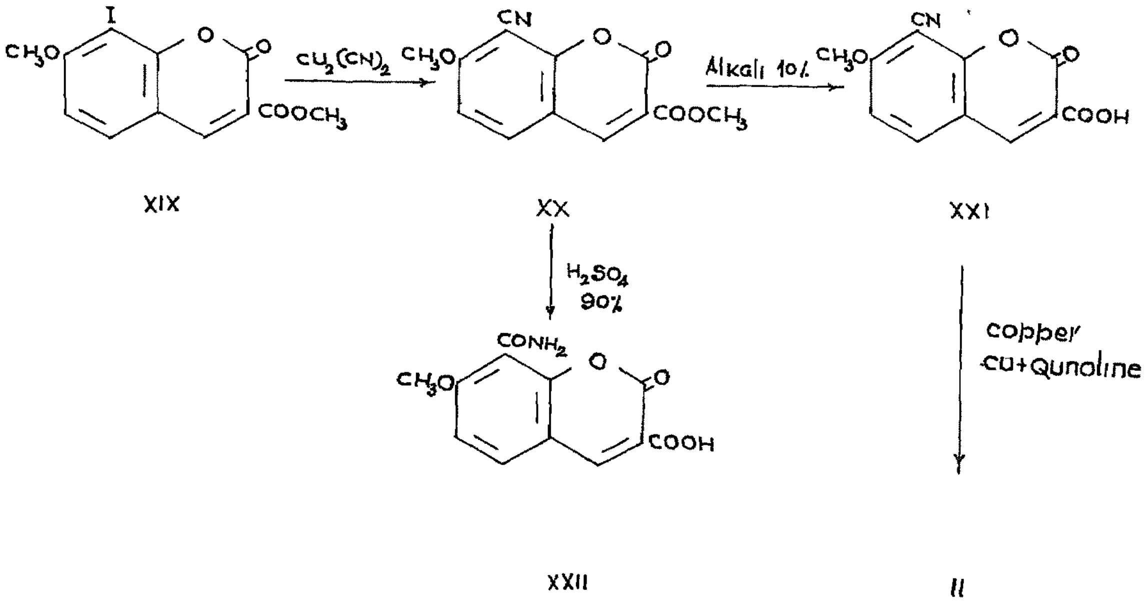
On heating with alcoholic as well as aqueous potassium hydroxide solution (10 %) the ester (XIV) gave the corresponding acid (XVII), the cyano group remaining intact. On decarboxylation the acid (XVII) gave 7-methoxy-8-cyano-4-methylcoumarin (XVIII) described above. On heating with sulphuric acid (90 % by volume) the cyano ester gave 7-methoxy-8-carbamoyl coumarin-4-acetic acid (XV) which on further hydrolysis with sulphuric acid (50 % by volume) gave the known 7-methoxy-4-methylcoumarin (XVI).



Methyl 7-methoxy-8-cyanocoumarin-3-carboxylate

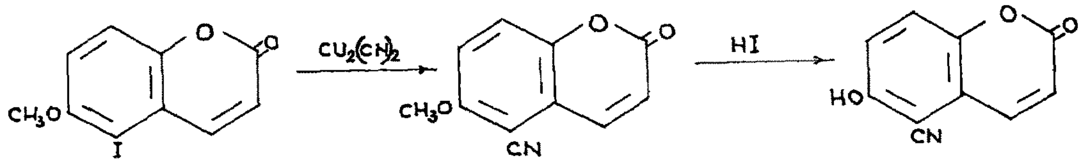
Methyl 7-methoxy-8-iodocoumarin-3-carboxylate (XIX) when heated with anhydrous cuprous cyanide above its melting point gave the corresponding 8-cyanocoumarin derivative (XX).

On heating with alcoholic or aqueous potassium hydroxide solution (10 %) the ester was only hydrolysed to the corresponding acid (XXI) the cyano group remaining intact. On decarboxylation the acid (XXI) gave 7-methoxy-8-cyano-coumarin (II) described earlier. On heating with sulphuric acid (90 %) the cyano ester gave 7-methoxy-8-carbamoyl-coumarin-3-carboxylic acid (XXII).



6-Methoxy-5-cyanocoumarin

6-Methoxy-5-iodocoumarin (XXIII) when heated with anhydrous cuprous cyanide above its melting point for half an hour gave the corresponding 5-cyanocoumarin derivative (XXIV) in good yield. No diluent was used in this reaction. On heating with alcoholic as well as aqueous potassium hydroxide solution (10 and 20 %) the cyanocoumarin remained unchanged. It also remained unchanged when heated with alcoholic hydrochloric acid for 8 hours. No product could be isolated in hydrolysis with sulphuric acid (50 and 90 % by volume). Stephen reaction on (XXIV) failed, the original cyanocoumarin was recovered unchanged. 6-Methoxy-5-cyanocoumarin was demethylated to the corresponding 6-hydroxy derivative (XXV) by heating with acetic anhydride and hydriodic acid.



XXIII * XXIV * XXV *

Methyl 7-methoxy-3-iodocoumarin-6-carboxylate on Rosenmund-von Braun reaction with anhydrous cuprous cyanide under varying condition did not give any cyano derivative. At lower temperatures the original iodocoumarin was obtained. At higher temperature the charring took place.

EXPERIMENTAL

Rosenmund-von Braun reaction on 7-methoxy-8-iodocoumarin : 7-Methoxy-8-cyanocoumarin

An intimate mixture of 7-methoxy-8-iodocoumarin (3.02 g. ; 0.01 mole) and anhydrous cuprous cyanide (1.78 g. ; 0.02 mole) was heated in an oil bath at 190° for fifteen minutes. The reaction mixture melted first and resolidified again. The solid mass was powdered and extracted several times with hot acetone. The needles which separated from the acetone extract were recrystallised from acetic acid in fine pink needles, m.p. 265°. Yield 1.2 g. The cyano derivative was sparingly soluble in common organic solvents. Its alcoholic solution showed blue fluorescence. It was not affected by boiling 10% aqueous or alcoholic potassium hydroxide solution.

Analysis :

4.700 mg. of the substance gave 11.348 mg. of carbon dioxide and 1.678 mg. of water.

6.62 mg. of the same substance gave 0.396 ml. of nitrogen at 32° and 762 mm.

Found : C = 65.89 % ; H = 3.99 % ; N = 6.71 %.

$C_{11}H_7O_3N$ requires : C = 65.67 % ; H = 3.50 % ; N = 6.96 %.

7-Hydroxy-8-cyanocoumarin

7-Methoxy-8-cyanocoumarin (0.5 g.) was heated with acetic anhydride (10 ml.) and hydriodic acid (10 ml. ; d. 1.7) in an oil bath at 130-140° for 3 hours. The reaction mixture was then cooled and poured in ice cold sodium bisulphite solution. The separated product was purified through sodium hydroxide solution. It crystallised from acetic acid in needles, m.p. 305° (decomp.). It did not give any colour with alcoholic ferric chloride. Its alcoholic solution showed blue fluorescence.

Analysis :

4.942 mg. of the substance gave 11.628 mg. of carbon dioxide and 1.152 mg. of water.

10.12 mg. of the same substance gave 0.708 ml. of nitrogen at 30° and 754 mm.

Found : C = 64.21 % ; H = 2.61 % ; N = 7.81 %.

$C_{10}H_5O_3N$ requires : C = 64.18 % ; H = 2.67 % ; N = 7.50 %.

7-Methoxy-8-~~amide~~Carbamoylcoumarin

7-Methoxy-8-cyanocoumarin (0.5 g.) was heated with sulphuric acid (9 ml.) and water (1 ml.) on a steam bath for 2 hours. The reaction mixture was then cooled and poured in ice water. The separated shining product crystallised from alcohol in thin plates, m.p. 288°.

Analysis :

4.210 mg. of the substance gave 9.360 mg. of carbon dioxide and 1.480 mg. of water.

9.740 mg. of the same substance gave 0.598 ml. of nitrogen at 33° and 754 mm.

Found : C = 60.67 % ; H = 3.93 % ; N = 6.79 %.

$C_{11}H_9O_4N$ requires : C = 60.29 % ; H = 4.11 % ; N = 6.40 %.

7-Hydroxycoumarin-8-carboxylic acid

The above ~~8-amido~~coumarin (0.3 g.) was heated with hydriodic acid (5 ml.) in acetic acid (5 ml.) for 2 hours at 120-130° in an oil bath. The solution was then added to a saturated solution of sodium bisulphite. The product obtained was purified through sodium hydrogen carbonate. It crystallised from water in needles, m.p. 220°. It gave a violet colouration with alcoholic ferric chloride.

Analysis :

4.372 mg. of the substance gave 9.326 mg. of carbon dioxide and 1.226 mg. of water

Found : C = 58.21 % ; H = 3.14 %.

$C_{10}H_6O_5$ requires : C = 58.25 % ; H = 2.93 %.

Attempted Stephen reaction on 7-methoxy-8-cyanocoumarin

Anhydrous hydrochloric acid gas was passed through a suspension of anhydrous stannous chloride (2.3 g.) in dry ether (100 ml.) for 2 hours when two layers appeared. 7-Methoxy-8-cyanocoumarin (0.4 g.) was then added with good stirring but the substance did not go in solution it only remained in suspension. The mixture was stirred for 3 hours and kept over-night. Next day ether was removed and the x solid was boiled with water. The solid which separated on cooling was found to be the original cyanocoumarin. Dry stannous chloride was prepared by taking stannous chloride dihydrate and treating it with acetic anhydride according to Stephen (J. Chem. Soc., 1930, 2786).

Rosenmund-von Braun reaction on methyl 7-methoxy-8-iodocoumarin-6-carboxylate : Methyl 7-methoxy-8-cyanocoumarin-6-carboxylate

An intimate mixture of methyl 7-methoxy-8-iodocoumarin-6-carboxylate (3.6 g. ; 0.01 mole) and anhydrous cuprous cyanide (1.78 g. ; 0.02 mole) was heated in an oil bath at 220° for 15 minutes. The solid reaction mixture was extracted several times with hot acetone. The product obtained after removal of acetone crystallised from acetic acid in needles, m.p. 192°. Yield 1.4 g. It was moderately soluble in acetone, acetic acid, alcohol and benzene. Its alcoholic solution showed blue fluorescence.

Analysis :

4.518 mg. of the substance gave 9.974 mg. of carbon dioxide and 1.482 mg. of water.

6.30 mg. of the same substance gave 0.307 ml. of nitrogen at 31° and 761 mm.

Found : C = 60.25 % ; H = 3.67 % ; N = 5.47 %.

$C_{13}H_9O_5N$ requires : C = 60.23 % ; H = 3.47 % ; N = 5.40 %.

7-Methoxy-8-cyanocoumarin-6-carboxylic acid

The above 8-cyanocoumarin ester (0.5 g.) was refluxed with alcoholic potassium hydroxide solution (10 % ; 20 ml.) on a steam bath for 2 hours. The product obtained on acidification was purified through sodium bicarbonate solution. It crystallised from glacial acetic acid in needles, m.p.232°. Its alcoholic solution showed blue fluorescence.

Analysis :

4.012 mg. of the substance gave 8.668 mg. of carbon dioxide and 0.948 mg. of water.

11.876 mg. of the same substance gave 0.643 ml. of nitrogen at 39° and 753 mm.

Found : C = 58.96 % ; H = 2.64 % ; N = 5.87 %.

$C_{12}H_7O_5N$ requires : C = 58.78 % ; H = 2.88 % ; N = 5.71 %.

The above acid (0.3 g.) in quinoline (8 ml.) was heated in an oil bath at 230° with a speck of copper powder for half an hour. The mixture was then filtered and poured in dilute hydrochloric acid. The separated product crystallised from acetic acid in needles, m.p. 265°. Mixed m.p. with 7-methoxy-8-cyanocoumarin described earlier was not depressed.

7-Methoxy-8-~~amido~~carbamoyl coumarin-6-carboxylic acid

Methyl-7-methoxy-8-cyanocoumarin-6-carboxylate (0.5 g.) was heated with sulphuric acid (9 ml.) and water (1 ml.) on a steam bath for 3 hours. The product obtained was purified through sodium bicarbonate solution. It crystallised from hot water in needles, m.p. 268-270°(efferv.).

Analysis :

4.332 mg. of the substance gave 8.698 mg. of carbon dioxide and 1.278 mg. of water.

9.740 mg. of the same substance gave 0.501 ml. of nitrogen at 33° and 754 mm.

Found : C = 54.80 % ; H = 3.30 % ; N = 5.69 %.

$C_{12}H_9O_6N$ requires : C = 54.76 % ; H = 3.45 % ; N = 5.32 %.

Rosenmund-von Braun reaction on 7-methoxy-3-iodocoumarin : 7-Methoxy-3-cyanocoumarin

An intimate mixture of 7-methoxy-3-iodocoumarin (3.02 g. ; 0.01 mole) and anhydrous cuprous cyanide (1.78 g. ; 0.02 mole) was heated in an oil bath at 190° for 15 minutes. The solid obtained was powdered and extracted with acetone. The product obtained on removal of acetone crystallised from benzene, m.p. 225-226°. Yield 0.8 g. Baker and Howes (J. Chem. Soc., 1953, 119) gave m.p. 221-222°. It was soluble in acetic acid, alcohol, acetone and benzene. Its alcoholic solution showed blue fluorescence.

Analysis :

4.630 mg. of the substance gave 11.142 mg. of carbon dioxide and 1.328 mg. of water.

10.140 mg. of the same substance gave 0.643 ml. of nitrogen at 32° and 754 mm.

Found : C = 65.67 % ; H = 3.21 % ; N = 7.04 %.

$C_{11}H_7O_3N$ requires : C = 65.67 % ; H = 3.50 % ; N = 6.96 %.

Attempted Rosenmund-von Braun reaction on methyl-7-methoxy-3-iodocoumarin-6-carboxylate

An intimate mixture of methyl-7-methoxy-3-iodocoumarin-6-carboxylate (3.6 g. ; 0.01 mole) and anhydrous cuprous cyanide (1.78 g. ; 0.02 mole) was heated in an oil bath at 250-255° for 15 minutes. The solid mass obtained was powdered and extracted with acetone. The product obtained on removal of acetone could not be purified. Variation in heating time or the reaction temperature also did not give any pure product.

Rosenmund-von Braun reaction on methyl 7-methoxy-8-iodocoumarin-4-acetate : Methyl 7-methoxy-8-cyanocoumarin-4-acetate and 7-methoxy-8-cyano-4-methylcoumarin

An intimate mixture of methyl 7-methoxy-8-iodocoumarin-4-acetate (3.74 g. ; 0.01 mole) and anhydrous cuprous cyanide (1.78 g. ; 0.02 mole) was heated in an oil bath and the temperature allowed to rise from 190 to 210° during 15 minutes. The solid reaction mixture was powdered and extracted several times with benzene. The residue obtained after removal of benzene was crystallised successively from benzene and acetic acid in needles, m.p. 192-193°. Yield 0.5 g. Its alcoholic solution showed blue fluorescence.

After extraction with benzene the residue was extracted several times with acetone. The product obtained on removal of acetone crystallised from acetic acid in needles, m.p. 285-287°. It was sparingly soluble in acetic acid, benzene, acetone. Mixed m.p. with 7-methoxy-8-cyano-4-methylcoumarin prepared from 7-methoxy-8-iodo-4-methylcoumarin by the Rosenmund-von Braun reaction according to Lele (unpublished work) was not depressed.

Analysis :

4.618 mg. of the substance gave 10.468 mg. of carbon dioxide and 1.742 mg. of water.

11.58 mg. of the same substance gave 0.554 ml. of nitrogen at 35° and 754 mm.

Found : C = 61.85 % ; H = 4.22 % ; N = 5.26 %.

$C_{14}H_{11}O_5N$ requires : C = 61.53 % ; H = 4.02 % ; N = 5.13 %.

7-Methoxy-8-cyanocoumarin-4-acetic acid

The above 8-cyanoester (0.5 g.) was refluxed with alcoholic potassium hydroxide solution (10 % ; 20 ml.) on a steam bath for 2 hours. The product obtained on acidification was purified through sodium bicarbonate solution. It crystallised from acetic acid in needles, m.p. 268-270°. Its alcoholic solution showed blue fluorescence.

Analysis :

4.186 mg. of the substance gave 9.254 mg. of carbon dioxide and 1.312 mg. of water.

8.016 mg. of the same substance gave 0.416 ml. of nitrogen at 39° and 753 mm.

Found : C = 60.33 % ; H = 3.50 % ; N = 5.62 %.

$C_{13}H_9O_5N$ requires : C = 60.23 % ; H = 3.47 % ; N = 5.40 %.

The above cyano acid (0.2 g.) in quinoline (5 ml.) was heated in an oil bath at 220-225° with a speck of copper powder for half an hour. The product obtained on working up the reaction mixture as usual crystallised from acetic acid in needles, m.p. 285-287°. Mixed m.p. with 7-methoxy-8-cyano-4-methylcoumarin was not depressed.

7-Methoxy-8-carbamoylcoumarin-4-acetic acid

Methyl 7-methoxy-8-cyanocoumarin-4-acetate (0.5 g.) was heated with sulphuric acid (9 ml.) and water (1 ml.) on a steam bath for 2 hours. The product obtained on pouring the reaction mixture in ice cold water was purified through sodium bicarbonate solution. It crystallised from hot water in silky needles, m.p. 230-232° (efferv.). Its alcoholic solution showed blue fluorescence.

Analysis :

4.628 mg. of the substance gave 9.548 mg. of carbon dioxide and 1.662 mg. of water.

9.100 mg. of the same substance gave 0.452 ml. of nitrogen at 34° and 754 mm.

Found : C = 56.30 % ; H = 3.83 % ; N = 5.48 %.

$C_{13}H_{11}O_6N$ requires : C = 56.30 % ; H = 3.97 % ; N = 5.05 %.

This cyanocoumarin on further hydrolysis with (50 %) sulphuric acid in an oil bath at 110° for 2 hours or with (10 %) alcoholic potash on a water bath for 2 hours gave the known 7-methoxy-4-methylcoumarin.

Rosenmund-von Braun reaction on methyl-7-methoxy-8-iodocoumarin-3-carboxylate : Methyl 7-methoxy-8-cyanocoumarin 3-carboxylate

Methyl 7-methoxy-8-iodocoumarin-3-carboxylate (1.8 g. ; 0.005 mole) and anhydrous cuprous cyanide (0.9 g. ; 0.01 mole) was heated at 220° for half an hour. The solid mass obtained was powdered and extracted several times with acetone. The product obtained on removal of acetone crystallised first from alcohol and then from acetic acid in needles, m.p. 238-240°.

Analysis :

4.218 mg. of the substance gave 9.274 mg. of carbon dioxide and 1.398 mg. of water.

9.63 mg. of the same substance gave 0.494 ml. of nitrogen at 42° and 752 mm.

Found : C = 60.00 % ; H = 3.71 % ; N = 5.49 %.

$C_{13}H_9O_5N$ requires : C = 60.23 % ; H = 3.47 % ; N = 5.40 %.

7-Methoxy-8-cyanocoumarin-3-carboxylic acid

The above cyanocoumarin ester (0.2 g.) was refluxed with alcoholic potassium hydroxide solution (10 ml. ;10 %) on a steam bath for 2 hours. The product obtained on working up the reaction mixture as usual crystallised from dilute alcohol in needles, m.p. 260-262°. Its alcoholic solution showed blue fluorescence.

Analysis :

4.428 mg. of the substance gave 8.910 mg. of carbon dioxide and 1.426 mg. of water.

8.222mg. of the same substance gave 0.397ml. of nitrogen at 30° and 750 mm.

Found : C = 54.91 % ; H = 3.60 % ; N = 5.37 %.

$C_{12}H_7O_5$ H_2O requires : C = 54.75 % ; H = 3.42 % ; N = 5.32 %.

7-Methoxy-8-cyanocoumarin

The above cyano acid (0.1 g.) was refluxed with quinoline (5 ml.) and copper powder for half an hour. The product obtained on working up the reaction mixture crystallised from acetic acid in needles, m.p. 265°. Mixed m.p. with 7-methoxy-8-cyanocoumarin described earlier was not depressed.

7-Methoxy-8-carbamoylcoumarin-3-carboxylic acid

The above cyanocoumarin ester (0.2 g.) was heated with sulphuric acid (10 ml. ; 90 % by volume) on a steam bath for 2 hours. The reaction mixture was poured over crushed ice and the product obtained was purified through sodium bicarbonate solution. It crystallised from acetic acid in needles, m.p. 258-260°.

Analysis :

4.306 mg. of the substance gave 8.604 mg. of carbon dioxide and 1.436 mg. of water.

9.082 mg. of the same substance gave 0.417 ml. of nitrogen at 32° and 752 mm.

Found : C = 54.52 % ; H = 3.73 % ; N = 5.08 %.

$C_{12}H_9O_6N$ requires : C = 54.75 % ; H = 3.42 % ; N = 5.32 %.

Rosenmund-von Braun reaction on 6-methoxy-5-iodocoumarin : 6-Methoxy-5-cyanocoumarin

An intimate mixture of 6-methoxy-5-iodocoumarin (3.02 g. ; 0.01 mole) and anhydrous cuprous cyanide (1.78 g. ; 0.02 mole) was heated in an oil bath at 190-210° for half an hour. The solid mass was powdered and extracted several times with acetone. The product obtained on removal of acetone crystallised from acetic acid in needles, m.p. 191-192°. Yield 1 g. It remained unchanged on boiling with aqueous or alcoholic potassium hydroxide solution (10 % ; 20 ml.). Its alcoholic solution showed blue fluorescence.

Analysis :

4.022 mg. of the substance gave 9.642 mg. of carbon dioxide and 1.348 mg. of water.

10.410 mg. of the same substance gave 0.702 ml. of nitrogen at 34° and 752 mm.

Found : C = 65.42 % ; H = 3.75 % ; N = 7.25 %.

$C_{11}H_7O_3N$ requires : C = 65.67 % ; H = 3.50 % ; N = 6.96 %.

6-Hydroxy-5-cyanocoumarin

The above 5-cyanocoumarin (0.5 g.) was heated with acetic anhydride (10 ml.) and hydriodic acid (10 ml. ; d. 1.7) in an oil bath at 130-140° for 2 hours. The product obtained on pouring the reaction mixture in cold sodium bi-sulphite solution was purified through dilute sodium hydroxide solution. It crystallised from dilute alcohol in needles, m.p. 275°. It did not give any colour reaction with alcoholic ferric chloride. Its alcoholic solution showed blue fluorescence.

<u>Analysis</u> :

4.624 mg. of the substance gave 10.940 mg. of carbon dioxide and 1.158 mg. of water.

11.29 mg. of the same substance gave 0.71 ml. of nitrogen at 34° and 754 mm.

Found : C = 64.57 % ; H = 2.80 % ; N = 6.94 %.

$C_{10}H_9O_3N$ requires : C = 64.18 % ; H = 2.67 % ; N = 7.50 %.

Attempted Stephen reaction on 6-methoxy-5-cyano-coumarin

Anhydrous hydrochloric acid gas was passed through a suspension of anhydrous stannous chloride (2.3 g.) in dry ether (100 ml.) for 2 hours when two layers separated. 6-Methoxy-5-cyanocoumarin (0.4 g.) was then added with good stirring. Chloroform (5 ml.) was added to keep 6-methoxy-5-cyanocoumarin in solution and the mixture was stirred for 3 hours. It was kept over night. Next day on working up as usual only 6-methoxy-5-cyanocoumarin was recovered unchanged.