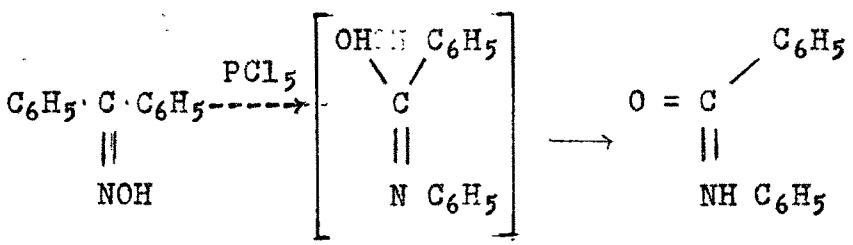
CHAPTER II

BECKMANN REARRANGEMENT OF SOME C-ACYLCOUMARINS

Beckmann rearrangement of some C-acylcoumarins

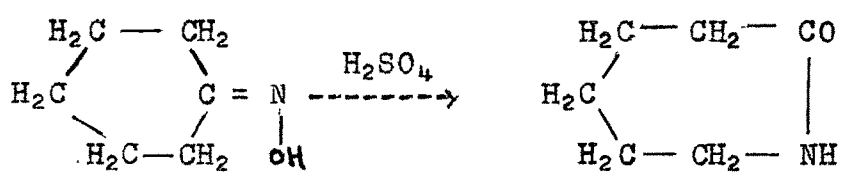
Ernst Beckmann in 1886 (1) first observed that when benzophenone oxime was treated with phosphorus pentachloride in etherial solution rearrangement to an amide took place. The product of the reaction after hydrolysis was benzanilide.



In its most general form the Beckmann rearrangement consists in the transformation of a ketoxime to an acid amide.

The rearrangement can be effected by a large number of reagents such as phosphorus pentachloride, phosphorus oxychloride, acetyl chloride, sulphuric acid and polyphosphoric acid.

Sulphuric acid is the most satisfactory reagent for the cyclic oximes of the type cyclohexanone oxime (2)



Phosphorus pentachloride remains the most generally applicable and most valuable reagent. The rearrangement is carried out in etherial solution and at a

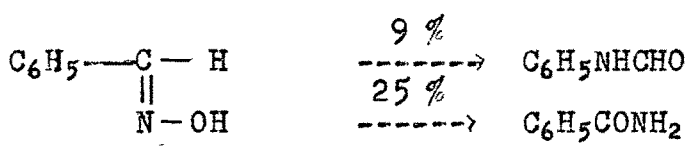
low temperatures.

The Beckmann rearrangement has been reviewed in detail by Popp and Mcewen (3).

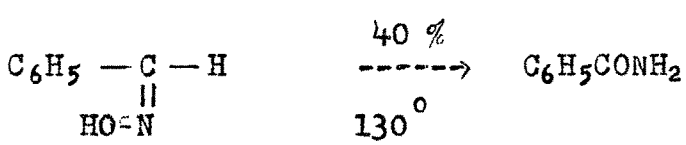
Lachmann (4) used hydrochloric acid satisfactorily. Polyphosphoric acid has been found in recent years to be an excellent reagent for this rearrangement (6).

Simple ketoximes undergo rearrangement with polyphosphoric acid in almost quantitative yields. The reactions are satisfactory when applied to the oximes of diaryl ketones, aryl alkyl ketones and cyclic ketones as observed by Horning and co-workers (5). Aldoximes also undergo the Beckmann rearrangement with polyphosphoric acid.

It is of interest that anti-benzaldoxime gave only benzamide when treated with polyphosphoric acid whereas syn-benzaldoxime gave a mixture of benzamide and formanilide (loc.cit.). These results are in agreement with the configurations obtained by other methods.



Syn-isomer

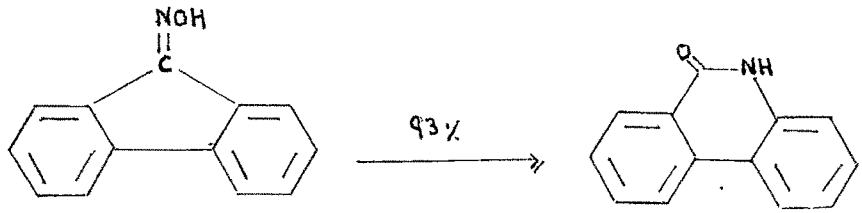


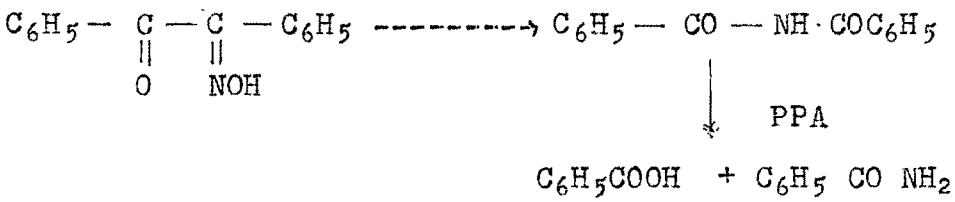
anti-isomer

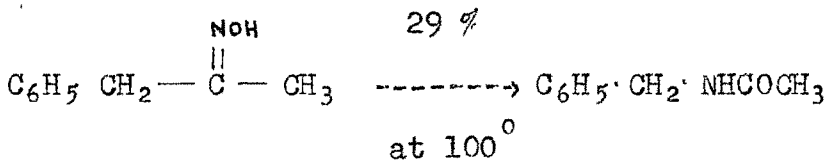
Horning, Stromberg and Lloyd (6) carried out transformation of ~~a-benzilmonoxime to benzoic acid~~,

α-benzil monoxime to benzoic acid

fluorenone oxime to phenanthridone and phenylacetone oxime to N-benzyl acetamide.





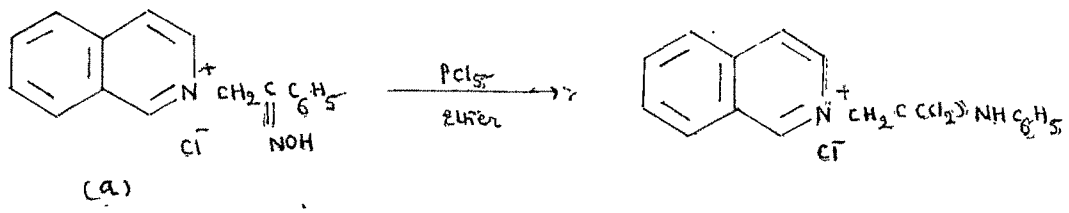


Ketoximes containing a variety of hetero atoms and ring members undergo the Beckmann rearrangement in the normal manner to yield amides or mixtures of isomeric amides. The usual catalysts and solvents employed in the rearrangement of other types of oximes may be used to rearrange heterocyclic ketoximes.

In certain cases, abnormal products may be formed by interaction of the oxime or product with the catalyst or because of elimination, cleavage, polymerization, or hydrolysis reactions of the oxime or amides in the reaction mixture.

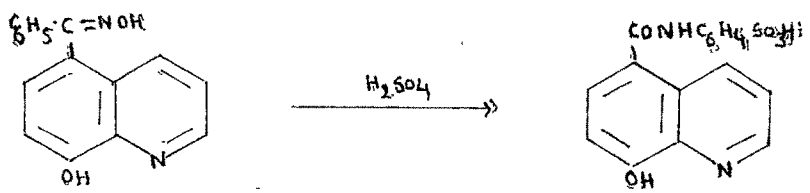
The oxime of N-phenacylisoquinolinium chloride (- α -), when rearranged with phosphorus pentachloride,

yields a chlorination product of the expected amide (6 a).



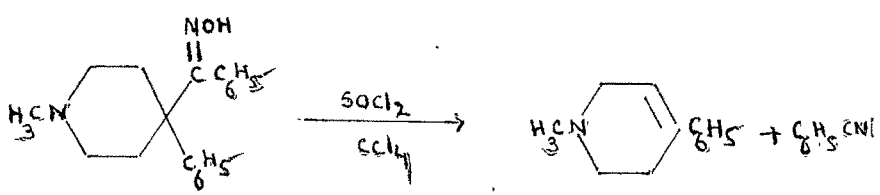
(a)

The oxime of 5-benzoyl-8-hydroxyquinoline (-b-) yields a ring-sulfonated anilide upon rearrangement with sulfuric acid (6 b).



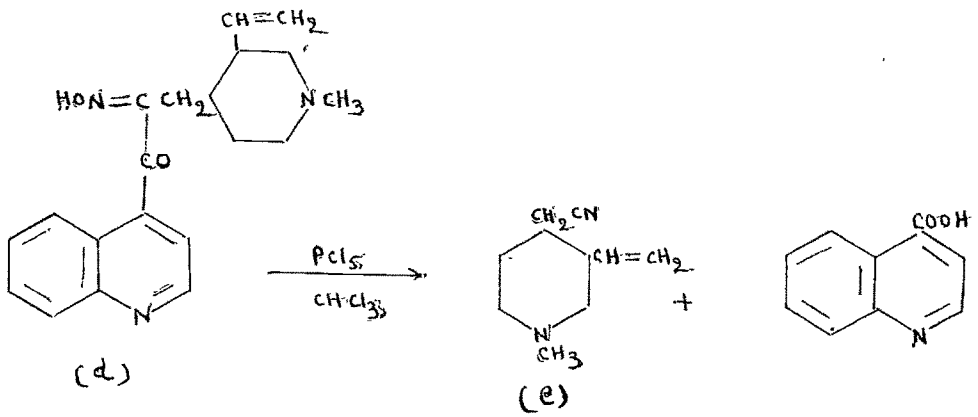
(b)

N-Methyl-4-phenyl-4-benzoylpiperidine oxime (-c-) undergoes an elimination reaction to yield an



(c)

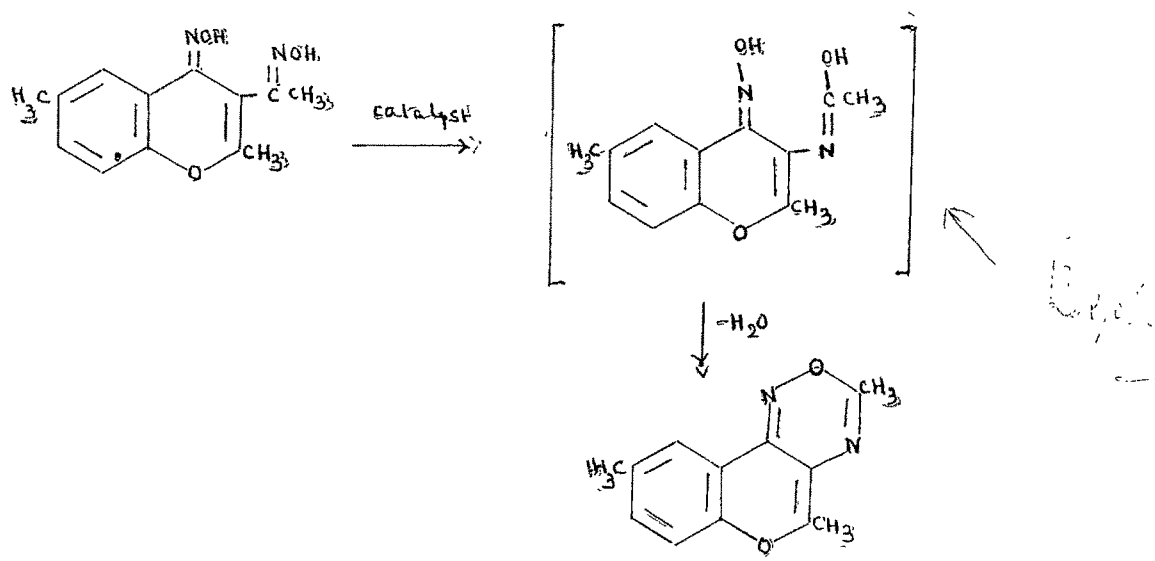
olefin and a nitrile (6 c). Another example of nitrile formation is shown by formulas (-d-) and (-e-) (6 d).



(d) (e)

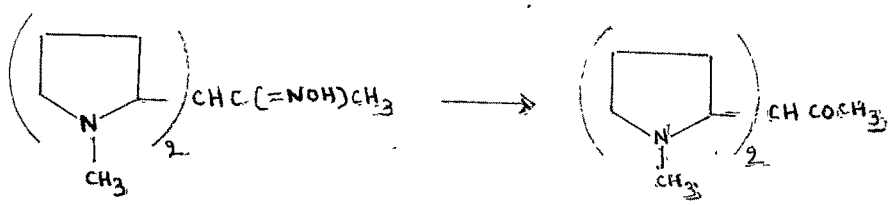
N-Methyl-4-piperidone oxime yields a polymer when treated with polyphosphoric acid (6 e).

The dioxime of 2-methyl-3-acetyl-6-methyl-benzopyran-4-one forms an oxadiazine (-f-) when treated with sulfuric acid, acetyl chloride, or phosphorus pentachloride (6 f).



(f)

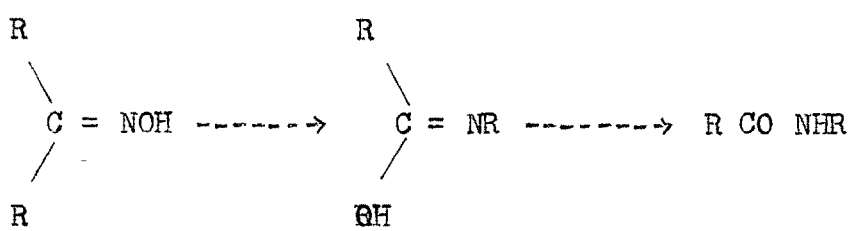
Cuskohygrine oxime (- 9 -) yields only cuskohygrine when treated with phosphorus pentachloride, hydrogen chloride, or sulfuric acid (6 g).



(9)

Mechanism of the Beckmann rearrangement

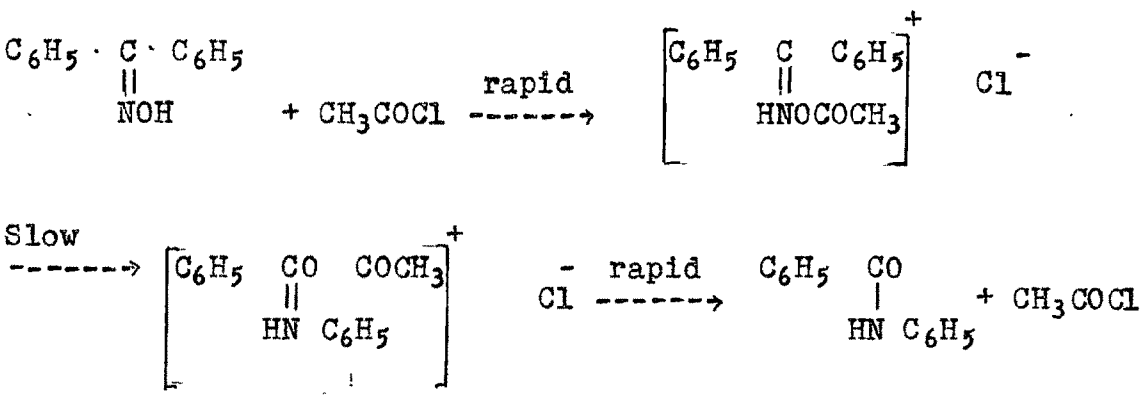
The rearrangement was represented by Beckmann as a direct interchange of the hydroxyl group of the oxime and one of the hydrocarbon groups followed by spontaneous migration of the hydrogen to give the true amide.



Because the rearrangement could be readily effected by a wide variety of reagents, Beckmann considered

it unlikely that any single intermediate compound or any single type of intermediate compound was involved and regarded the function of the reagent as simply that of a catalyst.

The most important of the earlier investigations of the mechanism of the rearrangement were those of Kuhara (7) who carried out an extensive investigation of the acid chlorides, and concluded that it is the esters (acyl derivatives) of the oximes and not the oximes themselves which undergo rearrangement. He found that certain esters such as benzene sulfonyl ester of benzophenone oxime rearranged spontaneously while others such as acetate required the presence of hydrochloric acid to bring about rearrangement. The conversion of benzophenone oxime under the influence of acetyl chloride was formulated by Kuhara as follows:



Chapmann (8) concluded that the Beckmann rearrangement of benzophenone oxime in presence of HCl proceeds by the following series of reactions.

(1) slow production of a small quantity of benzanilide

(2) The conversion of a trace of the benzanilide, into benzanilideiminochloride by hydrochloric acid.

$C_6H_5\ CO\ NH\ C_6H_5 + HCl \longrightarrow$

$C_6H_5\ C(Cl) = N\ C_6H_5 + H_2O$

(3) Condensation of the oxime and the iminochloride to form the oxime ether.

$(C_6H_5)_2\ C = NOH + C_6H_5\ C\ (Cl) = N\ C_6H_5 \longrightarrow$

$(C_6H_5)_2\ C = N\ OC\ (C_6H_5) = N\ C_6H_5 + HCl$

(4) The conversion of this oxime ether into the cation.

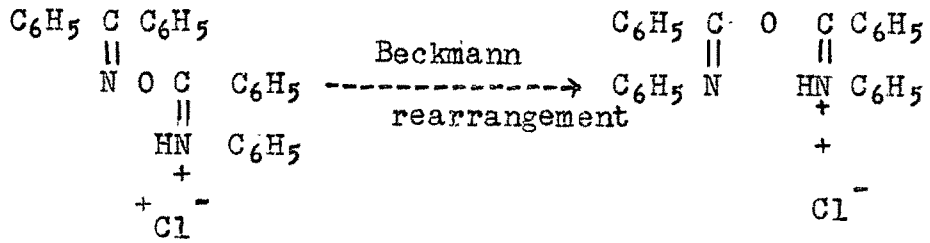
$(C_6H_5)_2\ C = N\ OC\ (C_6H_5) = N\ C_6H_5 + \overset{+}{H} \longrightarrow$

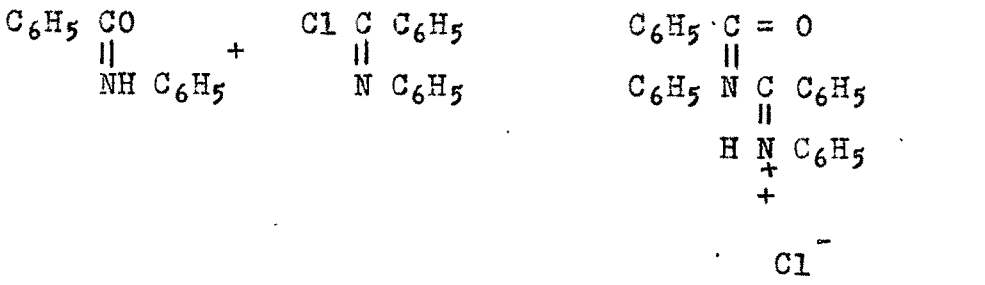
$(C_6H_5)_2\ C = N\ OC\ (C_6H_5) = \overset{+}{N}H\ C_6H_5$

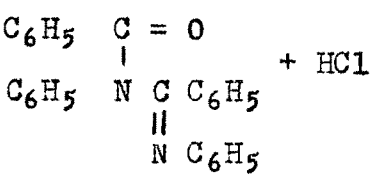
The positively charged nitrogen atom in this cation endows the radical - $OC\ C_6H_5 = NH\ C_6H_5$ with strong electron attracting properties and thereby enables to initiate the rearrangement to an imido ether type of compound which in presence of excess of hydrogenchloride may undergo two alternative reactions.

Process (a) would lead to the formation of benzanilide and benzanilideiminochloride, which may enter into further reaction with the oxime while the process (b) yields benzoyl-S-diphenylbenzenylamidine.

$$(C_6H_5)_2\ C = N\ OC\ C_6H_5 = N\ C_6H_5 + HCl \rightleftharpoons \underset{\text{(excess)}}{}$$



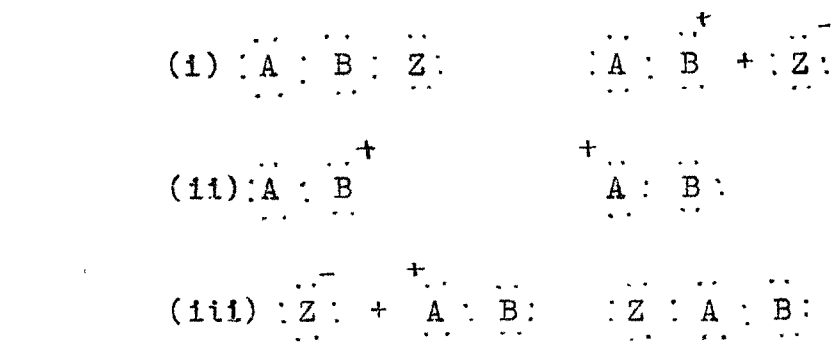




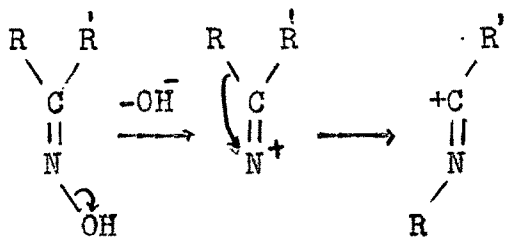
If the decomposition process (a) predominates over (b) then the above scheme accounts satisfactorily for the catalytic effect of imino chloride. While the alternative process furnishes reason for the presence of small quantity of s-diphenylbenzenylamidine in the benzanilide obtained when benzophenone oximehydrochloride undergoes rearrangement on heating.

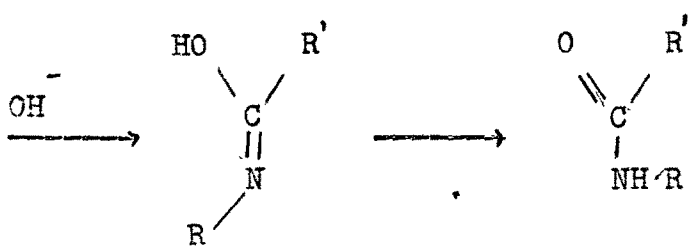
This mechanism of the rearrangement of benzophenone oxime in presence of hydrogen chloride was tested and confirmed by experiments.

The mechanism of the Beckmann rearrangement is however still not certain ; one mechanism favoured by many is that based on the Whitmore mechanism, which may be formulated in the following general terms



If B has a greater electron-affinity than A, the electrons rearrange as in (ii), the shift in the electron pair including the atom or group which it holds. Then recombination with Z occurs to form the rearranged product ZAB (reaction iii). Thus, on this basis, the Beckmann rearrangement may be formulated as follows :





The radical that leaves the carbon atom is the one on the opposite side to the hydroxyl group, i.e. there is an anti-exchange of groups, and this leads to the inversion of the configuration of the nitrogen atom. It is interesting to note in connection with the above mechanism that it is in keeping with Beckmann's idea that the rearrangement occurred by a direct interchange of groups, the reagent acting as a catalyst.

Configuration of isomeric ketoximes

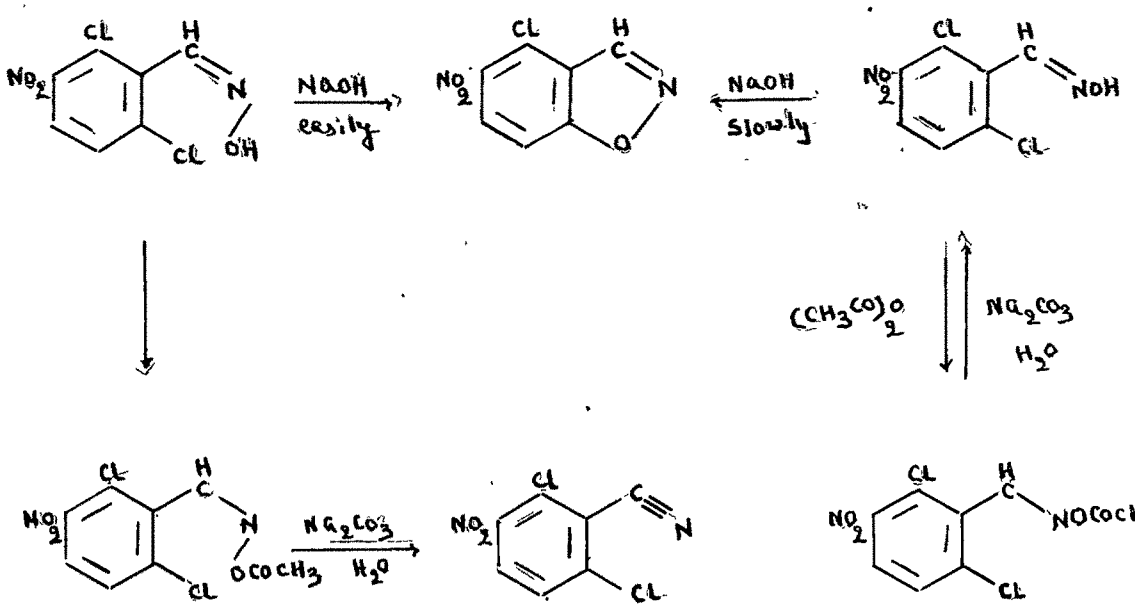
With the discovery that unsymmetrical ketones furnished in many cases two isomeric oximes, several theories were advanced to account for this isomerism. Of these theories the one which has received general acceptance is that of Hantzsch and Werner (9)

Hantzsch and Werner in 1890 proposed a stereochemical explanation for the isomerism. They assumed that the three nitrogen valences are non-planer and that a carbon nitrogen double bond can give geometrical isomers in the same way as a carbon-carbon double bond. Hantzsch proposed the terms syn and anti for the two forms.

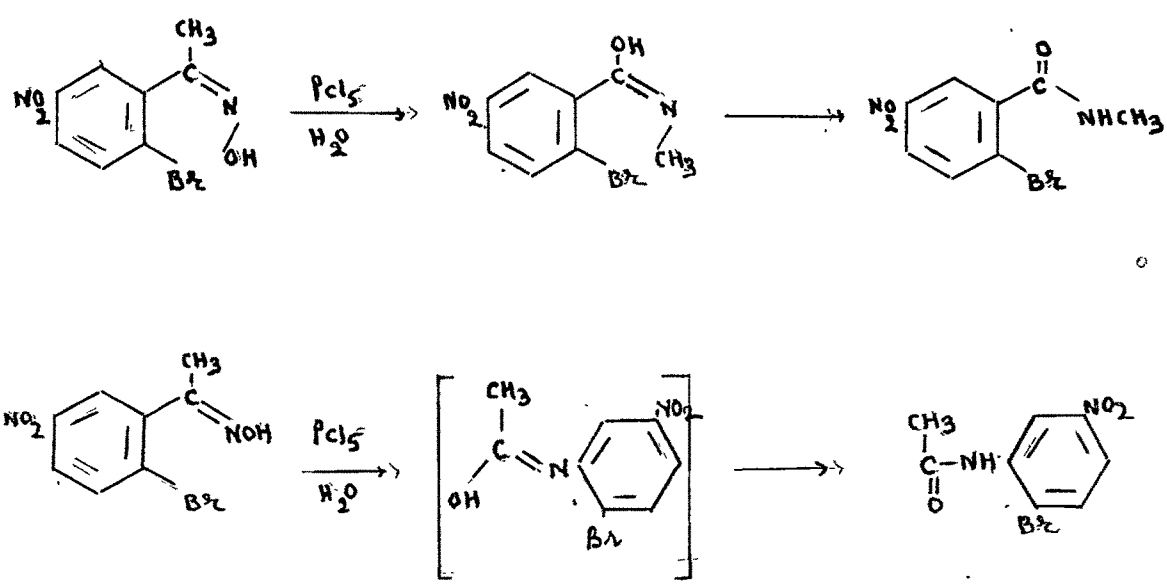
The currently accepted configurations of the isomeric forms were assigned by Meisenheimer (10). If a reactive halogen atom is ortho to aldoximinogroup one form of the aldoxime undergoes ring formation easily in presence of alkali where as the other form gives the same product much more slowly.

It seems likely therefore that the form undergoing ready cyclisation is the anti-aldoxime and that the

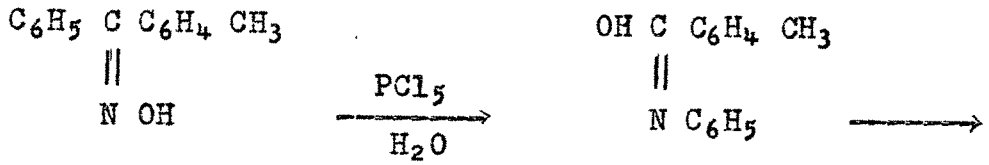
syn-aldoxime first must rearrange to the anti-form before cyclisation takes place. Furthermore, the form that undergoes easy ring closure gives an acetate which reacts with alkali to form a nitrile where as the acetate of the other form regenerates the original oxime.



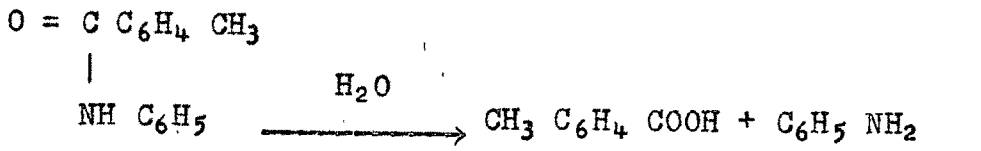
The syn- and anti-ketoximes yield different products on Beckmann rearrangement for example bromo-nitro acetophenone.

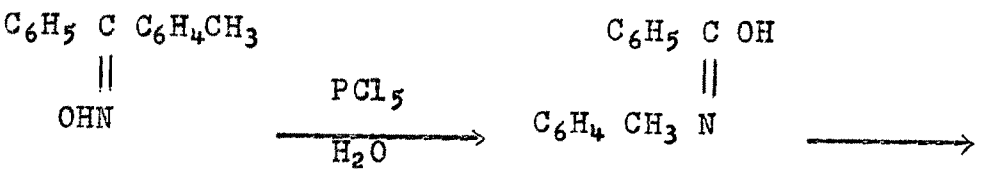


Thus the groups that exchange places in the rearrangement are those that are anti to each other.

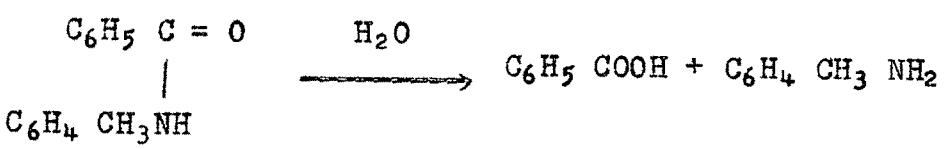


anti-phenyl-tolyl ketoxime



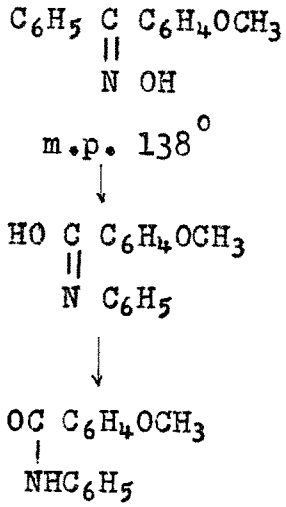


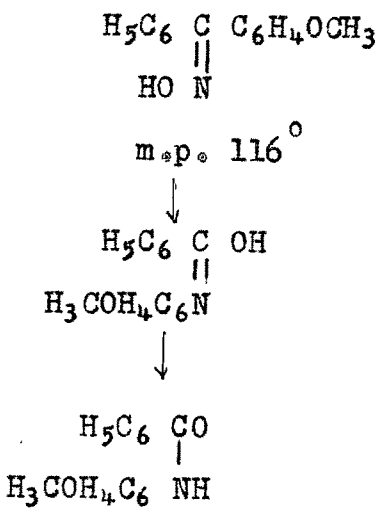
syn-phenyl tolyl ketoxime



As a further example of stereoisomeric ketoximes the two p-methoxybenzophenone oximes may be mentioned, one of which melts at 138° and the other at 116°. The Beckmann rearrangement of the first gives rise to the anilide of anisic acid, whilst that of the isomeride melting at 116°

gives the methoxyanilide of benzoic acid.



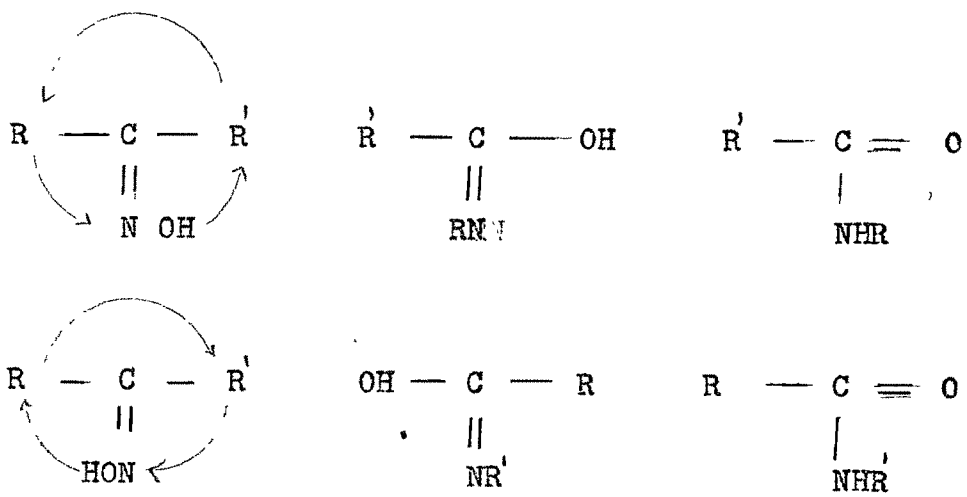


Anilide of anisic acid

Methoxyanilide of benzoic acid.

Aliphatic aldehydes and ketones do not give isomeric oximes[5], probably because one form is much more stable than the tother.

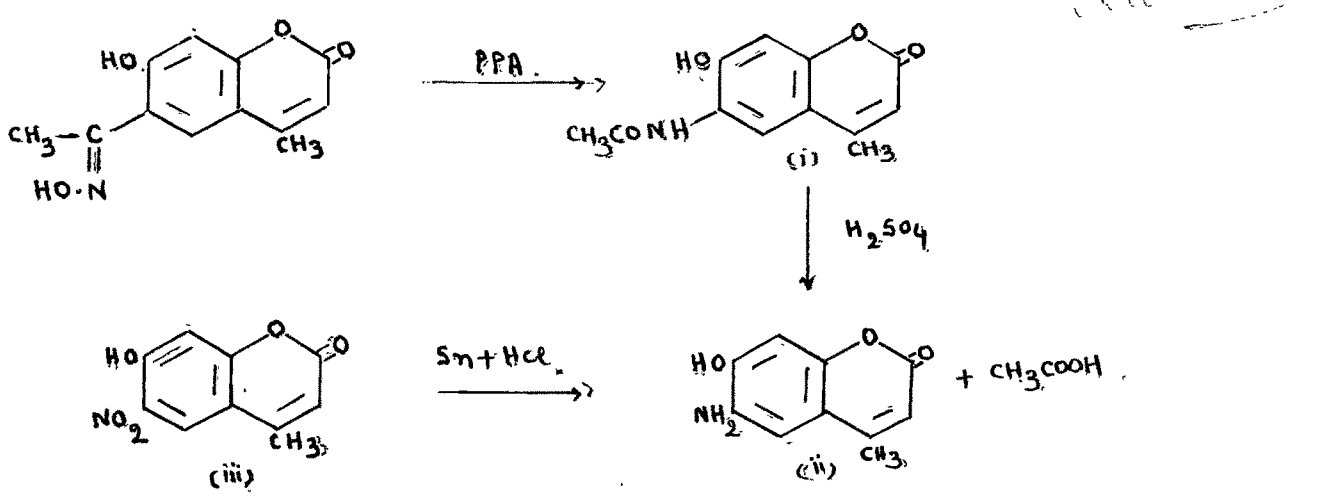
Meisenheimer pointed out that the oxime hydroxyl group moves up to occupy the space on the carbon atom, previously filled by the syn-R-group whereas the anti-R-group moves to the nitrogen atom. The following scheme was used to visualizing the transformations.



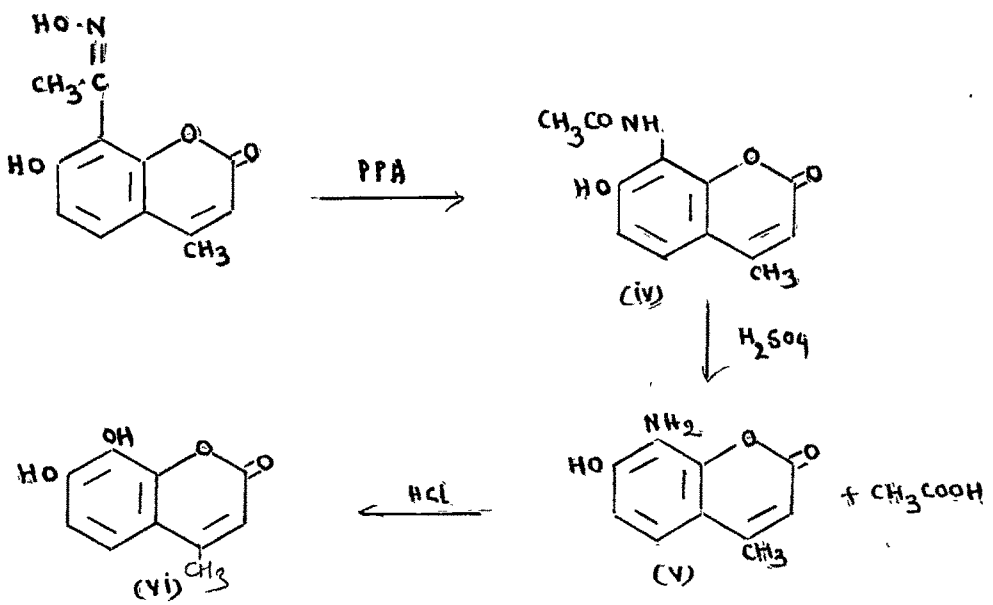
The present work deals with the Beckmann rearrangement of the oximes of some C-acylcoumarins. Linch (11) carried out the Beckmann rearrangement of the oxime of 3-acetylcoumarin and obtained 3-aminocoumarin. This appears to be the only instance in the literature of the Beckmann rearrangement of the oxime of a C-acylcoumarin.

In the present work the Beckmann rearrangement of the oxime of (a) 7-hydroxy-6-acetyl-4-methylcoumarin (b) 7-hydroxy-8-acetyl-4-methylcoumarin (c) 5-hydroxy-6-acetyl-4-methylcoumarin and (d) 8-hydroxy-7-acetylcoumarin have been carried out. The oximes were subjected to rearrangement by heating on a steam bath with polyphosphoric acid.

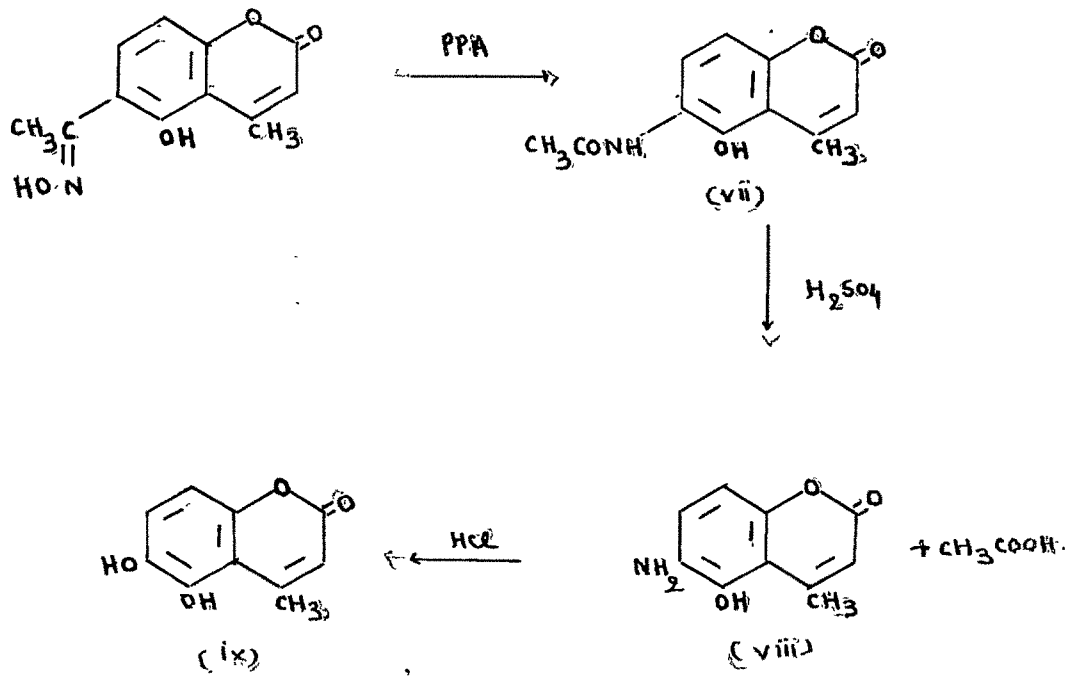
(a) Rearrangement of the oxime of 7-hydroxy-6-acetyl-4-methylcoumarin :- The oxime of 7-hydroxy-6-acetyl-4-methylcoumarin on treatment with polyphosphoric acid gave an acetamido derivative (i) which on hydrolysis gave 7-hydroxy-6-amino-4-methylcoumarin (ii). Its structure was proved by the synthesis of an authentic speciman of the amine by the reduction of the known 7-hydroxy-6-nitro-4-methylcoumarin (12) (iii).



(b) Rearrangement of the oxime of 7-hydroxy-8-acetyl-4-methylcoumarin :- The oxime of 7-hydroxy-8-acetyl-4-methylcoumarin on Beckmann transformation with polyphosphoric acid gave an acetamido derivative (iv) which on hydrolysis gave 7-hydroxy-8-amino-4-methylcoumarin (v). The structure of the aminocoumarin was proved by converting it into the known 7,8-dihydroxy-4-methylcoumarin (13) (vi) by heating with hydrochloric acid in a sealed tube at 150°.



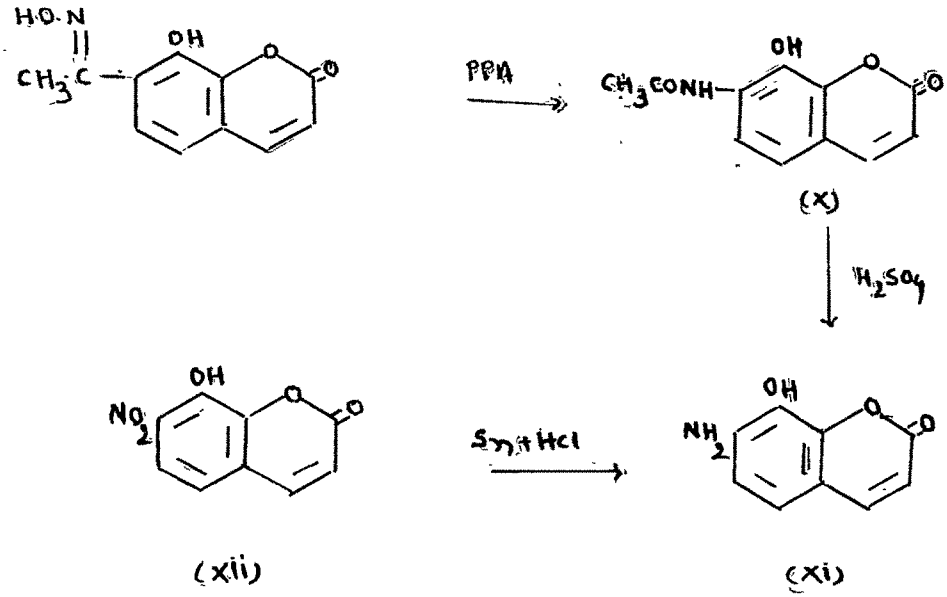
(c) Rearrangement of the oxime of 5-hydroxy-6-acetyl-4-methylcoumarin :- The oxime of 5-hydroxy-6-acetyl-4-methylcoumarin on Beckmann rearrangement gave an acetamido derivative (vii) which on hydrolysis gave 5-hydroxy-6-amino-4-methylcoumarin (viii). This structure has been assigned as the aminocoumarin afforded the known 5,6-dihydroxy-4-methylcoumarin (14) (ix), on heating with dilute hydrochloric acid in a sealed tube at 150°.



(vii) (viii) (ix)

(d) Rearrangement of the oxime of 8-hydroxy-7-acetylcoumarin :- The above oxime on polyphosphoric acid catalysed Beckmann rearrangement gave an acetamido derivative (x). Hydrolysis of the acetamido derivative furnished 8-hydroxy-7-aminocoumarin (xi) identical with an authentic specimen prepared by the reduction of 8-hydroxy-7-nitrocoumarin (15)(xii).

The isolation of the aminocoumarin in each case leads to the conclusion that the oximes have a syn-methyl structure. The Beckmann rearrangement furnishes another route to the aminocoumarins such as 5-hydroxy-6-aminocoumarin which are otherwise obtainable through the reduction of nitro derivatives.



Attempts to carry out the Beckmann rearrangement of the oximes of 7-hydroxy-8-formylcoumarin and 7-hydroxy-8-formyl-4-methylcoumarin with either polyphosphoric acid or with phosphorus pentachloride did not succeed,and no pure product could be isolated from the reaction mixtures.

EXPERIMENTAL

Oxime of 7-hydroxy-6-acetyl-4-methylcoumarin

7-Hydroxy-6-acetyl-4-methylcoumarin (6 g.) in alcohol was added to the mixture of hydroxylamine hydrochloride (5 g.) and potassium hydroxide (3 g.). The reaction mixture was refluxed for one hour and then kept over night at room temperature. The product which separated was crystallised from alcohol and then from benzene in buff coloured needles, m.p. 259-60°.

Analysis : Found : C=61.4 % ; H=4.5 % ; N=6.2 %.
$C_{12}H_{11}O_4N$ requires : C=61.8 % ; H=4.7 % ; N=6.0 %.

7-Hydroxy-6-acetamido-4-methylcoumarin

The above oxime (2 g.) was added to the polyphosphoric acid (10 g. P_2O_5 and 6 ml. of ortho-phosphoric acid). The reaction mixture was heated in an oil bath at 125-30° for 3 hours, protected from moisture, ice water was then added and the mixture kept over night. The product which separated was throughly washed with water and crystallised from alcohol-benzene mixture, m.p. 295-6°.

Analysis : Found : C=61.6 % ; H=4.9 % ; N=6.1 %.
$C_{12}H_{11}O_4N$ requires : C=61.8 % ; H=4.7 % ; N=6.0 %.

7-Hydroxy-6-amino-4-methylcoumarin

The above acetamido derivative (2 g.) was hydrolysed by refluxing with sulphuric acid (4 ml. Conc.

sulphuric acid + 2 ml. acetic acid + 2 ml. water) for 2 hrs. This was cooled and neutralised with dilute ammonia till just alkaline. It was then repeatedly extracted with ether. The residue obtained after removal of ether crystallised from benzene-alcohol in brown plates, m.p. 273-4°.

Analysis : Found : C=63.0 % ; H=4.8 % ; N=7.2 %.
$C_{10}H_9O_3N$ requires : C=62.8 % ; H=4.7 % ; N=7.0 %.

The same coumarin was obtained when 7-hydroxy-6-nitro-4-methylcoumarin (2.5 g.) was treated with stannous chloride (5 g.), tin (5 g.), alcohol (5 cc.) and hydrochloric acid (25 cc.) and the reaction mixture was allowed to stand over night, then shaken for 6 hrs. and the yellow solid so obtained was mixed with twice its weight of sodium carbonate and sodium acetate and continuously extracted with benzene. The residue obtained on removal of benzene crystallised twice from benzene, yellow needles, m.p. 273-4°. Mixed m.p. with the above amino-coumarin was not depressed.

Oxime of 7-hydroxy-8-acetyl-4-methylcoumarin

7-Hydroxy-8-acetyl-4-methylcoumarin (6 g.) in alcohol was added to a mixture of hydroxylamine hydrochloride (5 g.) and potassium hydroxide (3 g.), heated for 1 hr. It was cooled and kept over night at room temperature. The product obtained crystallised from benzene-methanol in needles, m.p. 232-3°.

Analysis : Found : C=61.2 % ; H=4.9 % ; N=6.4 %.
$C_{12}H_{11}O_4N$ requires : C=61.8 % ; H=4.7 % ; N=6.0 %.

7-Hydroxy-8-acetamido-4-methylcoumarin

The above oxime (2 g.) was added to the polyphosphoric acid prepared as before and heated on a steam bath protected from moisture for 6 hrs. This was cooled to room temperature and worked as before. The product obtained crystallised from methanol-benzene, m.p. 273-5°.
Analysis : Found : C=62.1 % ; H=4.6 % ; N=6.2 %.
$C_{12}H_{11}O_4N$ requires : C=61.8 % ; H=4.7 % ; N=6.0 %.

7-Hydroxy-8-amino-4-methylcoumarin

7-Hydroxy-8-acetamido-4-methylcoumarin (2 g.) was hydrolysed by sulphuric acid as before. The product obtained was crystallised from benzene, m.p. 275-6°.
Analysis : Found : C=62.7 % ; H=4.7 % ; N=7.1 %.
$C_{10}H_9O_3N$ requires : C=62.8 % ; H=4.7 % ; N=7.0 %.

The above aminocoumarin (0.2 g.) was heated in a sealed tube in nitrogen atmosphere with hydrochloric acid (4 ml.) and water (24 ml.) at 150-60° for 3 hrs. The product obtained was crystallised from alcohol, m.p. 237-9°. Mixed m.p. with an authentic sample of 7,8-dihydroxy-4-methylcoumarin, prepared by the condensation of pyrogallol with ethyl acetoacetate, was not depressed.

Oxime of 5-hydroxy-6-acetyl-4-methylcoumarin

5-Hydroxy-6-acetyl-4-methylcoumarin (6 g.) was dissolved in alcohol and added to a mixture of hydroxylamine

hydrochloride (5 g.) and potassium hydroxide (3 g.). The reaction mixture was stirred vigorously at room temperature for 1 hr. and then kept over night. The product which separated was crystallised twice from alcohol and then from benzene in light green needles, m.p. 255-6°.

Analysis : Found : C=61.9 % ; H=4.6 % ; N=5.6 %.

$C_{12}H_{11}O_4N$ requires : C=61.8 % ; H=4.7 % ; N=6.0 %.

5-Hydroxy-6-acetamido-4-methylcoumarin

The above oxime (2 g.) was added to polyphosphoric acid (10 g. P_2O_5 and 6 ml. of orthophosphoric acid) with cooling. The reaction mixture was then heated on a steam bath for 3 hrs., protected from moisture, ice water was then added and the mixture kept over night. The product which separated was throughly washed with water and crystallised from alcohol in tufts, m.p. 238-40°.

Analysis : Found : C=61.7 % ; H=5.2 % ; N=5.7 %.

$C_{12}H_{11}O_4N$ requires : C=61.8 % ; H=4.7 % ; N=6.0 %.

5-Hydroxy-6-amino-4-methylcoumarin

5-Hydroxy-6-acetamido-4-methylcoumarin (2 g.) was hydrolysed as before. The residue obtained was crystallised from benzene in light brown needles, m.p. 262-3°.

Analysis : Found : C=62.9 % ; H=4.5 % ; N=7.0 %.

$C_{10}H_9O_3N$ requires : C=62.8 % ; H=4.7 % ; N=7.0 %.

The above aminocoumarin was heated in a sealed tube in nitrogen atmosphere with hydrochloric acid (4 ml.) and water (24 ml.) at 150-60° for 3 hrs. The product obtained was crystallised from alcohol in brown needles, m.p. 248-9°.

Mixed m.p. with an authentic sample of 5,6-dihydroxy-4-methylcoumarin was not depressed.

Oxime of 8-hydroxy-7-acetylcoumarin

8-Hydroxy-7-acetylcoumarin (6 g.) was dissolved in alcohol and added to the mixture of hydroxylamine hydrochloride (5 g.) and potassium hydroxide solution (3 g.) and stirred vigorously at room temperature for two hours and kept over night. It was diluted with water and the separated product was crystallised from benzene-alcohol, m.p. 243-4°.

Analysis : Found : C=60.0 % ; H=4.2 % ; N=6.3 %.

$C_{11}H_9O_4N$ requires : C=60.2 % ; H=4.1 % ; N=6.3 %.

8-Hydroxy-7-acetamidocoumarin

The above oxime (2 g.) was added to polyphosphoric acid solution. This was kept at room temperature over night and worked as usual. The product which separated on dilution was crystallised from benzene alcohol mixture, m.p. 217-8°.

Analysis : Found : C=60.0 % ; H=4.2 % ; N=6.2 %.

$C_{11}H_9O_4N$ requires : C=60.2 % ; H=4.1 % ; N=6.3 %.

8-Hydroxy-7-aminocoumarin

8-Hydroxy-7-acetamidocoumarin (2 g.) was hydrolysed with sulphuric acid as usual and the product obtained was crystallised from benzene, m.p. 199-200°.

Analysis : Found : C=60.9 % ; H=4.0 % ; N=7.5 %.

$C_9H_7O_3N$ requires : C=61.0 % ; H=3.9 % ; N=7.9 %.

The same coumarin was obtained when 8-hydroxy-7-nitrocoumarin (2.5 g.) was treated with stannous chloride (5 g.), tin (5 g.), alcohol (5 cc.) and hydrochloric acid (25 cc.) and the reaction mixture was allowed to stand over night, then shaken for 6 hrs. and the yellow solid so obtained was mixed with twice its weight of sodium carbonate and sodium acetate and continuously extracted with benzene. The residue obtained on removal of benzene when crystallised twice from benzene gave yellowish brown needles, m.p. 199-200°. Mixed m.p. with the above amino coumarin was not depressed.

Attempted rearrangement of the oximes of some formylcoumarins

Oxime of 7-hydroxy-8-formylcoumarin

The oxime was prepared from 7-hydroxy-8-formylcoumarin as usual. It was crystallised from alcohol, m.p. 243-4°.

Analysis : Found : C=58.9 % ; H=3.4 % ; N=6.5 %.

$C_{10}H_7O_5N$ requires : C=58.5 % ; H=3.4 % ; N=6.8 %.

The above oxime was treated with polyphosphoric acid as in the previous rearrangements but no product could be isolated. Rearrangement was also tried with phosphorous pentachloride in ether solution. No positive result was obtained.

Oxime of 7-hydroxy-8-formyl-4-methylcoumarin

7-Hydroxy-8-formyl-4-methylcoumarin similarly gave an oxime which crystallised from alcohol, m.p. 250-2°.

Analysis : Found : C=60.5 % ; H=4.6 % ; N=5.9 %.

$C_{11}H_9O_5N$ requires: C=60.2 % ; H=4.1 % ; N=6.3 %.

The above oxime was subjected to the action of polyphosphoric acid as before but no product could be isolated from the reaction mixture. Phosphorus pentachloride in ether also gave negative results.

REFERENCES

1. Beckmann., Ber., 19, 988 (1886).
2. Wallach., Ann., 309, 3 (1899).
3. Popp and Mcewen., Chem.Rev., 58, 370 (1958).
4. Lachmann., J.Am.Chem.Soc., 46, 1477 (1924).
5. Horning and co-workers., 74, 2680 (1952).
6. Horning, Stromberg and Lloyd., J.Am.Chem.Soc., 74, 5153 (1952).

6(a) Imlder., Arch.Pharm., 240, 691 (1902).

6(b) Matsumura and Sone., J.Am.Chem.Soc., 52, 4433 (1930); 53, 1493 (1931).

6 (c) Lyle and Lyle., J.Org.Chem., 18, 1058 (1953).

6 (d) Rabe and Ritter., Ann., 350, 180 (1906).

6 (e) Barkenbus, Diehl, and Vogel., J.Org.Chem., 20, 871 (1955).

6 (f) Wittig and Bangert., Ber., 58, 2627 (1925).

6 (g) Hess and Fink., Ber., 53, 781 (1920).

7. Kuhara., Mem.coll.Sci. Kyoto. Imp.Uni., ~~(1926)~~ 1, 24-34 (1914); C.A. 9, 1612 (1915).

8. Chapmann., J.Chem.Soc., 806 (1933).

9. Hantzsch and Werner., Ber., 23, 11 (1890).

10. Meisenheimer and co-workers., Ann., 468, 202 (1929).

11. Linch., J.Chem.Soc., 101, 1758 (1912).

12. Shah and Mehta., J.I.C.S., 31, 784 (1954).

13. Pechmann and Duisberg., Ber., 16, 2119 (1883).

14. Dalvi, Desai and Sethna., J.Ind.Chem.Soc., 28, 366 (1951).

15. Dey and Kutti., Proc.Nat.Inst.Sci. India., 6, 641 (1940).