SUMMARY

PART I: CHALKONES DERIVED FROM 2-HYDROXY-5-CHLORO-, 2-HYDROXY-
-3-CHLORO-, 4-HYDROXY-3-CHLORO- AND 2-HYDROXY-4-CHLORO-
ACETOPHENONES:

In the present work ortho-hydroxy acetophenones containing
chlorine in different positions (viz., 2-hydroxy-5-chloro-, 2-hydroxy-
3-chloro-, 4-hydroxy-3-chloro- and 2-hydroxy-4-chloro acetophenones) have been condensed with various aldehydes to
synthesize chalkones and various hetero-cyclic compounds like
flavones, flavanones and flavonols by using appropriate reaction.
These hydroxy acetophenones on condensation with several aldehydes
(benzaldehyde, salicylaldehyde, m-hydroxy benzaldehyde, p-hydroxy
benzaldehyde, anisaldehyde, vanillin, veratraldehyde, piperonal,
o-chloro benzaldehyde, p-chloro-benzaldehyde, m-chloro anisaldehyde,
m-nitro-benzaldehyde, p-nitro-benzaldehyde) in presence of alkali
gave the corresponding chalkones in good yields.

Section I: Chalkones derived from 2-hydroxy-5-chloro-
acetophenone. — 2-Hydroxy-5-chloro acetophenone was condensed
with various aldehydes mentioned above in presence of alkali
(40·0 %) and the chalkones were obtained in each case.

The following other reactions of these chalkones have been studied:—

(1) The chalkones on treatment with bromine in acetic acid
gave the corresponding dibromides which regenerated the original chalkones on treatment with acetone and potassium iodide; but the bromo-chalkones containing free hydroxy group in the styryl nucleus on similar treatment did not regenerate the original chalkones. The product obtained by treating 2:2'-dihydroxy-5'-chloro-chalkone with bromine in acetic acid appeared to be a flavylium bromide. The ortho-hydroxy chalkone dibromides when treated with alcoholic potassium hydroxide gave the corresponding benzyliidene coumaranones.

(2) Ortho-hydroxy chalkones on treatment with alcoholic hydrochloric acid or sulphuric acid gave the corresponding flavanones, which on oxidation with selenium dioxide in amyl alcohol gave the corresponding flavones. The same flavones were also obtained directly from the chalkones by similar oxidation with selenium dioxide (K. Venkataraman, et al., J. Chem. Soc., 1935, 866). Further the flavanones when treated with N-bromo-succinimide in carbon-tetrachloride gave 3-bromo-flavanones which when treated with alcoholic alkali either gave flavones or benzyliidene coumaranones.

(3) The chalkones on Algar-Flynn oxidation with alkaline hydrogen peroxide gave flavonols.

(4) The chalkones when treated with ethyl acetoacetate gave the cyclo-hexanone derivatives. The chalkones when treated with phenyl hydrazine in acetic acid gave the pyrazolines. In some cases the chalkone and flavanone were condensed together.
(5) 6-Chloro-3':4'-methylenedioxy flavanone was treated with sodium in a dry solvent and the sodio-derivative obtained was subsequently treated with ethyl iodide, when 3-ethyl-6-chloro-3':4'-methylenedioxy flavanone was obtained, the constitution of which was established by hydrolysis.

**Section II : Chalkones derived from 2-hydroxy-3-chloro-acetophenone.** — 2-Hydroxy-3-chloro acetophenone has been condensed with various aldehydes mentioned before in presence of alkali and the chalkones were obtained in each case.

Some of the reactions mentioned above were studied.

**Section III : Chalkones derived from 4-hydroxy-3-chloro-acetophenone.** — 4-Hydroxy-3-chloro acetophenone was condensed with various aldehydes mentioned before in presence of alkali and the chalkones were obtained in each case. Deoxybenzoins of some of the chalkones were prepared. The action of bromine on the chalkones was studied. Some of the chalkones were also condensed with ethyl-acetoacetate.

**Section IV : Chalkones derived from 2-hydroxy-4-chloro-acetophenone.** — 2-Hydroxy-4-chloro acetophenone was condensed with various aldehydes mentioned before in presence of alkali and chalkones were obtained in each case.

The action of bromine on these chalkones was studied.
PART II: SYNTHESIS OF 5-CHLORO-BENZYLIDENE COUMARANONES:

The work described in this part was undertaken with a view to confirm the constitution of the benzylidene coumaranones described in Part I.

Minton and Stephen (J. Chem. Soc., 1922, 121, 1598) have prepared 5-chloro-benzylidene coumaranone by condensing 5-chloro-coumaranone with benzaldehyde. In the present work 5-chloro-coumaranone has been condensed with various aldehydes (salicylaldehyde, veratraldehyde, piperonal, vanillin) and the corresponding benzylidene coumaranones were obtained in each case.

The benzylidene coumaranone when treated with bromine in acetic acid gave the dibromide which when treated with alcoholic alkali gave the corresponding flavonol.

PART III: SYNTHESIS OF FLAVYLUM CHLORIDES FROM VARIOUS CHLORO-HYDROXY ACETOPHENONES:

During the synthesis of chalkones described in Part I, it was observed that when o-hydroxy aldehydes are condensed with ketones, satisfactory yields are generally not obtained. The condensation was, therefore, attempted in presence of phosphorus oxychloride and dry hydrogen chloride gas when the corresponding flavylum chlorides were obtained. The picrates of all these flavylum chlorides and perchlorates of some of them have been prepared. Hydrolysis of some of the flavylum chlorides has also been studied and the corresponding acetophenones and acids have been obtained.