SUMMARY

The present thesis deals with (i) the syntheses of 4-ketoquinazolines and (ii) the study of the Fries rearrangement of carboxyl substituted phenol esters and the syntheses of flavanoid derivatives starting with o-hydroxy acetophenones obtained. The thesis has been divided accordingly into Parts I and II respectively.

PART I
SYNTHESES OF 4-KETOQUINAZOLINES:

Simple* and 6-chloro-, 7-chloro- and 6,8-dichloro derivatives of 2-ethyl-, 2-benzyl-, 2-strylyl- and 2-(\(\beta\)-phenyl-ethyl) -3(H)- and 3-(Ar)-4-ketoquinazolines have been synthesised by two alternate methods:

(i) Condensation of the appropriate 3:1:4-benzoaxazone derivative with the necessary amine under proper conditions of the reaction and

(ii) condensation of properly substituted N-acyl anthranilic acid with an aromatic amine in presence of phosphorus trichloride.

The condensation of 3:1:4-benzoaxazone with ammonia and also with an appropriate aromatic amine has been studied systematically. The results obtained have thrown light on the effect of various

* Except in case of the 2-benzyl series.
groups, particularly the groups like 2-ethyl-, 2-benzyl, 2-styryl- and 2- (β-phenylethyl) on the reactivity of the so substituted 3:1:4-benzoxazole derivatives. It has also been found that the method (ii) mentioned above fails in case of the synthesis of 2-styryl-4-ketoquinazolines starting with the corresponding N-cinnamoyl anthranilic acid.

The 2-styryl-4-ketoquinazolines described here have also been synthesised by a third method consisting of the condensation of the properly substituted 2-methyl-4-ketoquinazoline with benzaldehyde. These 2-styryl-4-ketoquinazolines have been converted into the corresponding 2- (β-phenyl ethyl) -4-keto-quinazolines by reduction with sodium amalgam and ethanol; the latter have actually been synthesised by the two methods mentioned above.

The 3-aryl substituted-4-ketoquinazolines described in this part of the thesis contain a system =C(R')-N(Ar)-. They may therefore be regarded as potential hypnotics, as such a system containing a quaternary carbon especially when R' = methyl and a tertiary nitrogen situated -β- with respect to each other is an essential feature of a compound having that type of physiological activity (Eddy, J. Amer. Pharm. Soc., 1960, 39, 247).

**PART II**

**THE FRIES REARRANGEMENT AND SYNTHSES OF FLAVAN OIDS**

The Fries rearrangement of phenyl acetates and propionates derived from 5-chloro-, 5-bromo- and 5-methyl-2-hydroxy benzoic
acids (Type I) and 3(H), 3-chloro- and 3-bromo-4-hydroxy benzoic acids (Type II) have been studied systematically under different experimental conditions with a view to establish the best conditions of the reaction.

It has been found that the Fries rearrangement proceeded successfully affording an ortho migration in all the cases except in cases of phenyl propionates derived from 5-chloro- and 5-bromo-2-hydroxy benzoic acids. The ketones thus derived have been characterised by preparing their functional group derivatives. It has also been noted that the carboxyl group remains intact in the reactions. If the results of the Fries rearrangement of the phenol esters of the types I and II are compared, it will become evident that the yields of o-hydroxy ketones formed in the Series II are comparatively more than the yields of the ketones formed in the Series I.

The ketones obtained by this method have also been synthesised by the Friedel-Crafts acetylation or propionylation of the necessary phenols with acetyl or propionyl chlorides; but the yields are comparatively poor.

The o-hydroxy acetophenones obtained during this study have been used as the starting materials for the syntheses of flavanoid compounds. They have been condensed respectively with benzaldehyde and anisaldehyde and the chalcones thus formed have been (i) cyclo-isomerised by treating with ethanolic sulphuric acid to the corresponding flavanone, (ii) oxidised by selenium dioxide to the corresponding flavanol by the Algar-Flynn oxidation and
(iv) brominated with bromine in acetic acid to the corresponding \(\alpha:\beta\)-dibromo chalcones which could be debrominated to the original chalcone by potassium iodide in acetone.

In all these reactions leading to the syntheses of flavanoids the carboxyl group is not eliminated and has in no way hindered the reaction.