SUMMARY OF THE ORIGINAL WORK

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The present work deals with the synthesis of 9-(p-anisyl)-6a,7,8,9-tetrahydro-6-oxo-6H-benzo [d] naphtho [1,2-b] pyran-7,8-dicarboxylic acid and 6-acetyl-7-hydroxy-4-methylcoumarin as δ-lactones and synthesis 2,8-dimethyl-4,6-dioxo-4,6-dihydro [6,7-b] pyranochromene as γ-lactone to study the relative reactivity of δ-lactone in coumarin derivatives and γ-lactone in chromone derivatives towards different nucleophilic and electrophilic reagents.

The thesis is classified into two parts:

Part-I:

Synthesis and reactions of 9-(p-anisyl) 6a,7,8,9-tetrahydro-6-oxo-6H-benzo [d] naphtho [1,2-b] pyran-7,8-dicarboxylic acid.

9-(p-Anisyl) 6a,7,8,9-tetrahydro-6-oxo-6H-benzo [d] naphtho [1,2-b] pyran-7,8-dicarboxylic acid (III) has been prepared by cycloaddition of 4-(p-methoxystyryl)-2H-naphtho [1,2-b] pyran-2-one (II) with maleic anhydride. Naphthocoumarin derivative reacts with primary amines namely; aniline, hydrazine hydrate, phenylhydrazine, benzoylhydrazine and isobutyrolhydrazine to yield the corresponding 4-(p-anisyl)-6-(1-hydroxynaphth-1-yl) 2,3-dicarboxycyclohex-5-ene-1N-(substituted) carbamides (IVa-f). Naphthocoumarin derivative(IVd) reacts with dimethyl sulphate and/or ethyl bromoacetate in dry acetone or dry pyridine and anhydrous potassium carbonate as catalyst to give the corresponding methoxy compound (V).

Condensation of IVb with benzaldehyde in presence of acetic anhydride and anhydrous sodium acetate give the corresponding azalactone derivative (VI). Azalactone react with p-anisidine to afford the corresponding 1,3-imidazolin-5-one derivative (VII). On the other hand, naphthocoumarin derivative reacts with

p-toluidine and/or benzylamine under fusion to give 9-(p-anisyl)-6-aryl-6a,7,8,9-tetrahydro-6-oxo-6H-benzo[d]naphtho[1,2-b]pyridine-7,8-dicaroxylicacid(VIIIa,b). The naphthocoumarin derivative reacts with $POCl_3/PCl_5$ to give 9-(p-anisyl)-6-chloro-6a,7,8,9-tetrahydrobenzo [d] naphtho [1,2-b] pyran-7,8-dicarboxylic anhydride(IX), which reacts with phenylhydrazine and give compound (X). Naphthocoumarin derivative reacts with nucleophiles e.g Grignard reagents to give 4-(p-anisyl)-alkyl or aryl-2,3-dicarboxy-6-(1-hydroxynaphth-2-yl) cyclohex-5-en-1-yl-ketones (XIa-c). Compound (XIa) reacts with hydrazine derivatives to give 6-(substituted amino) tetrahydrobenzo [d] pyridine derivatives (XIIa,b). Reaction of naphthocoumarin with different aromatic hydrocarbons in the presence of anhydrous aluminium chloride gives 9-[(p-anisyl)-7-aroyl-6a,7,8,9-tetrahydro-6-oxo-6H-benzo [d] naphtho [1,2-b] pyran-8-carboxylic acid (XIIIa-c). Condensation of (XIIIa) with hydrazine and/or phenylhydrazine gives the corresponding phthalazinone derivatives (XIVa,b).

Perkin condensation of 2,4-diacetyl resorcinol (XV) with acetic anhydride and fused sodium acetate affords 6-acetyl-7-hydroxy-4-methylcoumarin (XVI). Nitration of (XVI) with a mixture of conc. HNO_3/conc. AcOH gives 6-acetyl-7-hydroxy-4-methyl-3-nitrocoumarin (XVII), reduction of (XVII) with zinc powder in acidic medium affords 6-acetyl-7-hydroxy-4-methyl-3-aminocoumarin (XVIII). Diazotization of (XVIII) gives (XIX). Coupling of (XIX) with phenols and/or active methylene compounds gives 3-azocoumarin derivatives (XXa-d).

Alkylation of (XVI) by ethyl bromoacetate in the presence of dry acetone and anhydrous potassium carbonate as catalyst gives 6-acetyl-7-carbethoxymethoxy -4-methylcoumarin (XXI). Condensation of (XXI) with anthranilic acid affords 2-(6-acetyl-4-methyl-2-oxo-2(H)-1-benzopyran-7-yloxymethyl)-4(H)-3,1-benzoxazin-4-one (XXII).

Bromination of 6-acetyl-7-hydroxy-4-methylcoumarin (XVI) in carbon

tetrachloride at room temperature gives 3,4,8-tribromo-6-bromoacetyl-7-hydroxy-4-methyl-3,4-dihydrocoumarin (XXIII), while in boiling acetic acid affords 3,8-dibromo-6-bromoacetyl-7-hydroxy-4-methylcoumarin (XXIV).

Claisen condensation reaction of 6-acetyl-7-hydroxy-4-methylcoumarin with ethyl acetate in presence of sodium metal gives 4-acetonyl-6-acetonylcarbonyl-7-hydroxycoumarin (XXV). The latter compound reacts with different aromatic aldehydes in presence of piperidine to give 8-styryl-2,6-dioxo-2,6-dihydro [6,7-b] pyran-4-arylidine acetonylcoumarin (XXVIa-c). Coumarin derivative (XVI) reacts with nucleophiles e.g Grignard reagents to give 6-acetyl-4-alkyl (or aryl)-7-hydroxy-4-methyl-3,4-dihydrocoumarin (XXVIIa-c).

Part-II:

Synthesis and reactions of 2,8-dimethyl-4,6-dioxo-4,6-dihydro [6,7-b] pyranochromene.

2,8-Dimethyl-4,6-dioxo-4,6-dihydro [6,7-b] pyranochromene (III) has been prepared via cyclization of 2,4-bis-(1,3-dioxo-butanyl) resorcinol (II) with a mixture of acetic anhydride and concentrated hydrochloric acid. Aminolysis of pyranochromene derivative (III) with primary amines gives 2,4-bis-diamide resorcinol derivatives (IVa-c).

On the other hand, hydrazinolysis of pyranochromene (III) with hydrazines affords 2,4-bis-pyrazolyl resorcinol derivatives (Va,b).

Condensation of pyranochromene (III) with anisaldehyde in presence of piperidine affords 2,8-bis-styryl derivative (VI) which underwent Diels-Alder reaction to give Diels-Alder adduct (VII).

Aminolysis of Diels-Alder adduct (VII) with different amines gives 2,12-bis-pyrrolodione derivatives (VIIIa-c). Also, hydrazinolysis of Diels-Alder adduct (VII)

with hydrazine hydrate and/or phenylhydrazine affords bis-phthalazindione derivatives (IXa,b).

Diels-Alder adduct (VII) reacts with Grignard reagent to give the corresponding xanthone derivatives (X). Alkylation of Diels-Alder adduct (VII) under Friedel-Crafts conditions gives the corresponding bis toluyl xanthone derivative (XI).

The structure of the new compounds prepared was confirmed chemically and spectroscopically.

INTRODUCTION