Chemistry and application of 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde

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DOI: http://dx.doi.org/10.3998/ark.5550190.p009.020

Abstract
The publications on the title compound appearing mainly since 2007 to February 2014 are reviewed.

Keywords: 1-Benzopyran-4-one, 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde, nucleophilic addition, dipolar cycloaddition, cyclization

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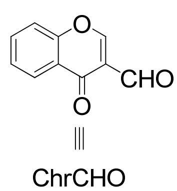
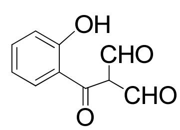
1. Introduction

The title aldehyde (trivial name: 3-formylchromone) **1**, an intramolecular enol ether of the β-ketoaldehyde **2**, possesses an endocyclic olefinic bond, an α,β-unsaturated carbonyl functionality, three electrophilic centres (C-2, aldehydic and ketonic carbons) and it can assume a pyrylium betaine structure in the presence of an appropriate reagent. These unique features make the chromone **1** amenable to various reactions as defunctionalisation, oxidation and reduction, radical and nucleophilic addition, and many types of annulations and cycloaddition reactions. The chemistry of 3-formylchromone has indeed evolved extensively since 1972. One aspect or the other of the compound **1** has been reviewed from time to time. As for example, Gasparova and Lacova[1] published in 2005 an overview (with 59 references) of the condensation of **1** with active methylene compounds and a few reactions of the resultant condensates.

Condensation of **1** with only some binucleophiles[2] covering the literature up to April 2011 and that with a number of carbon and nitrogen nucleophiles[3] covering the literature up to 2012 have been reviewed and these two reviews contain 132 and 173 references, respectively. Only three reviews, one authored by Sabitha[4] and the other two by the principal author[5,6] of the present article, dealing extensively with the general chemistry and application of 3-formylchromone have appeared, the last one covering the literature available through Sci-finder up to December 2006. The present article, primarily designed to complement the earlier one,[6] is a comprehensive survey of the chemistry of 3-formylchromone and utilization of the compounds easily available therefrom for the preparation of different chemical systems, and covers the literature published during January 2007 to February 2014. A few earlier works which either remained unmentioned in the earlier review[6] or are helpful for a better understanding of the present write-up are also briefly referred to. Patented works and the reactions of 2-substituted 4-oxo-4*H*-1-benzopyran-3-carbaldehyde not directly derived from the 2-unsubstituted analogue **1** are not included, and the biological properties of the reported compounds are least emphasized. The 4-oxo-4*H*-1-benzopyran-3-yl moiety is abbreviated as ‘Chr’ so that the title aldehyde **1** can be represented by ChrCHO. Alkyl, alkoxy and halogeno substituents in benzene ring of **1** remain unaffected in most of the reactions described here for the unsubstituted 3-formylchromone. The reactions of **1** are described in the following few sections and subsections based on the type of reactions and the nature of the reagents. One separate section is earmarked for annulation as well as cycloaddition reactions of **1** and its simple condensates, and another for one-pot multicomponent reactions involving **1** and two or more other reagents.



1



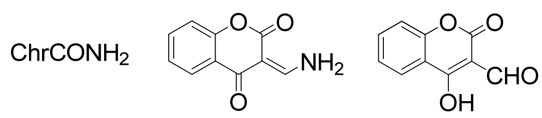
2

2. Decarbonylation

Microwave irradiation of ChrCHO in EtOAc containing $Pd(OAc)_2$ (~10mol%), K_2CO_3 (1.5 eq.) and molecular sieves (4Å) brings about its decarbonylation.[7] Decarbonylation of ChrCHO by using $Pd(OAc)_2$ does not need any exogenous ligand for palladium and any co-scavenger.[8]

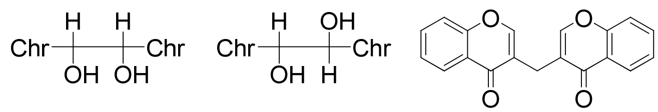
3. Oxidation, Reduction and Reductive Self Coupling

Treatment of a suspension of ChrCHO in CCl_4 with *N*-bromosuccinimide under UV-irradiation affords after quenching with ammonia at 0 °C the chromone-carboxamide **3**; a similar quenching at 40 °C yields the chroman-2,4-dione **4**. Treatment of **3** as well as **4** with NaOH followed by acidification produces 3-formyl-4-hydroxycoumarin **5**.[9]



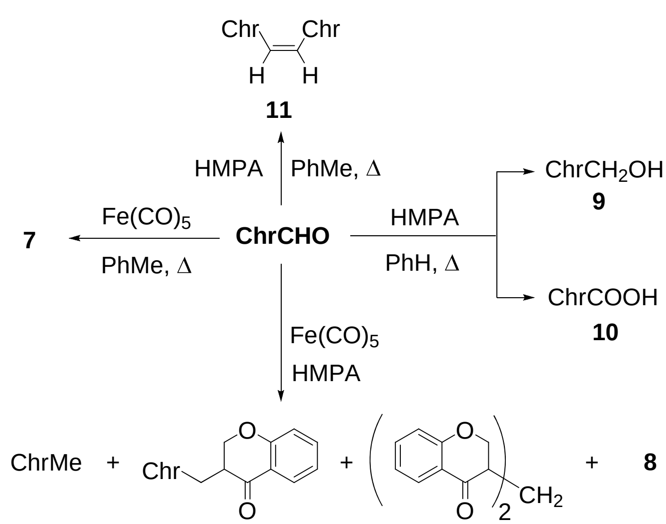
3 4 5

$ChrCH_2OH$, obtained by reduction of ChrCHO with 9-BBN has been converted to $ChrCH_2Br$, the phosphorus ylide of which has been reacted with several α,β-unsaturated and α,β,γ,δ-unsaturated aldehydes to get chromone based retenoids.[10] 3-Formylchromone on being treated with Zn-Hg in AcOH under reflux[11] gives two 1,2-diol products **6** and **7**; the major product identical with that obtained along with 3-hydroxymethylchromone and bis(chromon-3-yl)methane **8** by treating **1** with Zn-AcOH[12] is proved to the *meso*-1,2-diol **6**.



6 7 8

ChrCHO when heated with HMPA in benzene undergoes disproportionation to the alcohol **9** and acid **10**. The same reaction in refluxing toluene produces *cis*-1,2-di(chromon-3-yl)ethylene **11**. Pentacarbonyl iron in refluxing toluene brings about reductive dimerization of ChrCHO to the diol **7**. $Fe(CO)_5$-HMPA, converts **1** into 3-methylchromone **12** and the dihydrobischromone **13** at different ratios dependent on the solvent. The reaction in refluxing benzene gives **13** as the major product whereas **12** prevails in refluxing toluene; these two products may sometimes be admixed with trace amounts of **8** and bis(chroman-3-yl)methane **14**.[13] The formation of these products is schematically shown in Scheme 1.

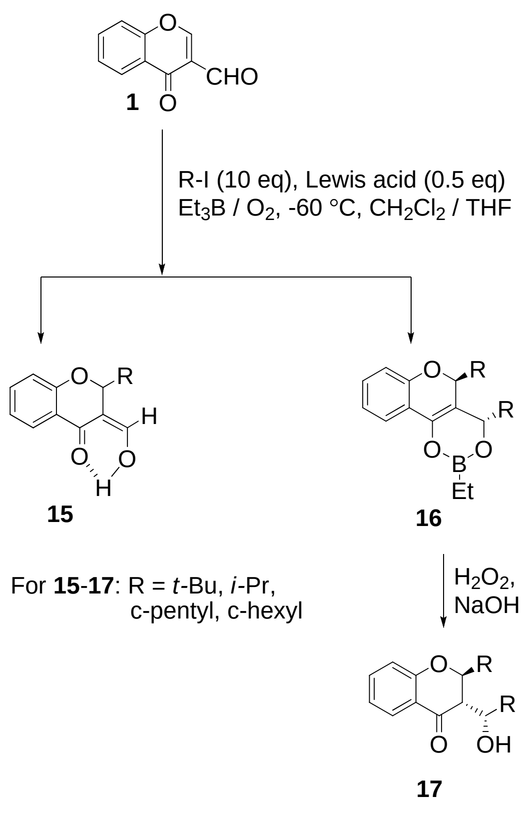


12 13 14

Scheme 1

4. Radical Addition

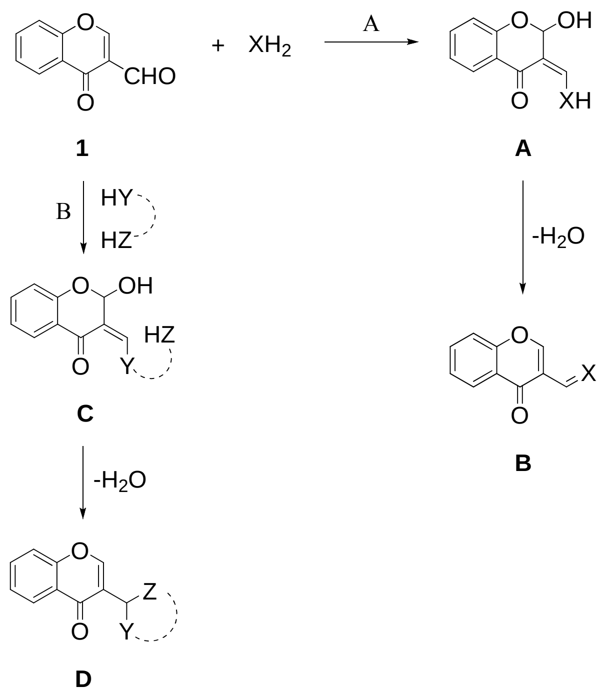
Diastereoselective tandem radical addition of an alkyl iodide to 3-formylchromone **1** (Scheme 2) has been reported by Zimmerman *et al*.[14] The product distribution is dependent on the reaction time and equivalent of the radical initiator. Using 1.0-2.0 equivalent of triethylborane and short reaction time (<5 min) excellent yield of **15** is obtained. With excess triethylborane and long reaction time the tandem adduct **16** is produced as a single diasteroisomer in excellent yield. Zinc triflate (0.5 eq) is the preferable Lewis acid catalyst for the reaction. The boron enolate **16** is remarkably stable and convertible to the alcohol **17** by treatment with alkaline hydrogen peroxide.



Scheme 2

5. Nucleophilic Addition

3-Formylchromone **1** is a good Michael acceptor towards most, if not all, nucleophiles. Thus, a nucleophile XH_2 such as an amine, hydrazine, monosubstituted hydrazine, hydroxylamine or an active methyl or methylene compound in conjugation with an appropriate base undergoes Michael addition to **1** with concomitant opening of the pyran ring and subsequent recyclization (i.e. domino Michael–retro-Michael–Intramolecular 1,2-addition) giving the hemiacetal **A** that leads to **B** by water elimination (Scheme 3-**A**). The same reaction sequence of a nucleophile YH or ZH representing ROH, RSH etc. with **1** gives the intermediate **C**. Michael addition of the second nucleophile ZH to the α,β-unsaturated carbonyl functionality of **C** with subsequent 1,4-elimination of water gives the final product **D** (Scheme 3-**B**); YH and ZH may be the same or different nucleophiles or two nucleophilic centres in a single reactant.

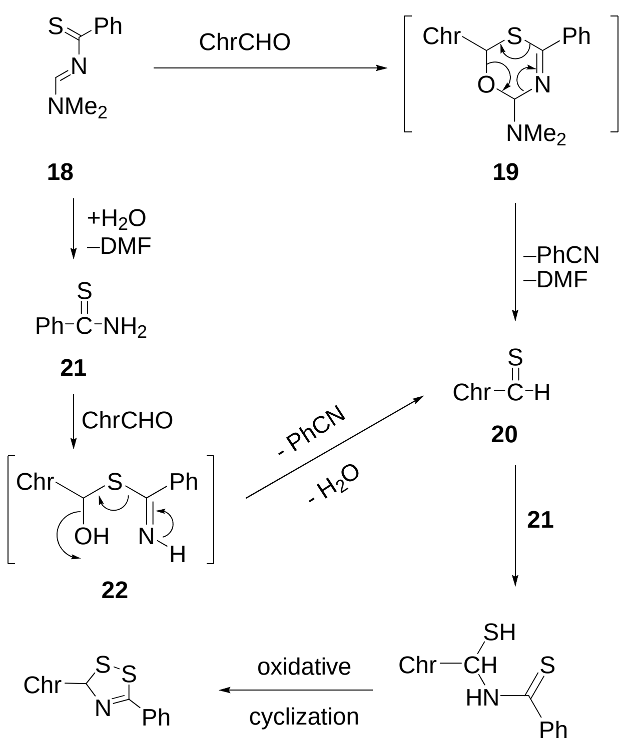


Scheme 3

5.1. Addition of oxygen and sulfur nucleophiles: protection and deprotection of carboxaldehyde group

Formation of acylal of ChrCHO with acetic anhydride involves reaction steps similar to those as written in Scheme 3-**B**. ChrCHO reacts readily with Ac_2O to give $ChrCH(OAc)_2$ in the absence of any Brönsted or Lewis acid catalyst in [bmim]BF_4 ionic liquid.[15] The said acylal formation is also catalyzed by 1,3-dibromo-5,5-dimethylhydantoin under neutral condition.[16] Titanium tetrafluoride,[17] boric acid[18] and alum[19] catalyze the above reaction under solvent-free condition at room temperature. Titanium tetrafluoride[17] also catalyzes deprotection of the gem-diacetate of ChrCHO in water. An efficient and solvent free synthesis of $ChrCH(OAc)_2$ and its deprotection to ChrCHO catalyzed by reusable Envirocat EPZ10R under microwave irradiation has been claimed by Shindalkar *et al*.[20] Conversion of ChrCHO into $ChrCH(SCH_2CH_2OH)_2$ with mercaptoethanol is catalyzed by silica supported sodium sulphate under solvent free condition.[21] Indium trifluoride catalyzed protection of the aldehyde group of ChrCHO with MeOH, $PhCH_2OH$, 2,2-dimethylpropane-1,3-diol, PhSH, $HSCH_2CH_2SH$, $HSCH_2CH_2CH_2SH$ in refluxing toluene is known.[22] Acetal as well as thioacetal of ChrCHO when refluxed in MeCN-H_2O (4:1) in the presence of InF_3 is converted to 3-formylchromone.[22]

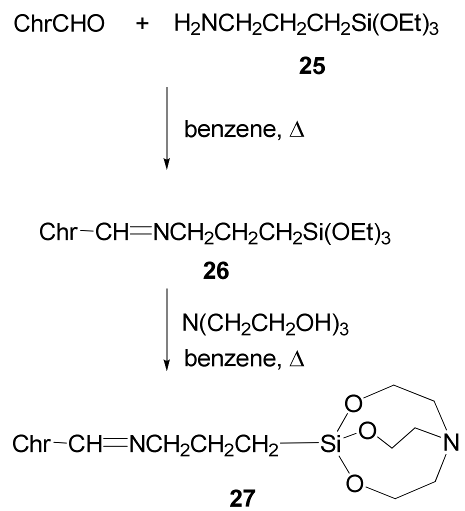
The formation of the 1,2,4-dithiazole **24** by heating **1** with 2-phenyl-4-dimethylamino-1-thia-3-azabutadiene **18** in a sealed tube has been rationalized in the following way (Scheme 4).[23] The first step involves thionation of **1** to **20** either through **19**, the [4+2] cycloadduct of **1** and thiazadiene **18**, or through the reaction of **1** with thiobenzamide **21**; the latter may be generated by the hydrolysis of **18** with a small amount of moisture and further hydrolysis can occur due to in situ generation of water. The second step most likely involves the reaction of 3-thioformylchromone **20** with another molecule of **21** followed by oxidative cyclisation. The dithiazole **24** is indeed formed when ChrCHO is heated with 1 or 2 equivalent of thiobenzamide under identical conditions. Later on several 6-substituted and 6,7-disubstituted 3-formylchromones have been reacted with 2.0 equivalent thiobenzamide in refluxing toluene and the resultant dithiazoles evaluated for their cytotoxic activity against a number of human cancer cell lines.[24,25]



Scheme 4

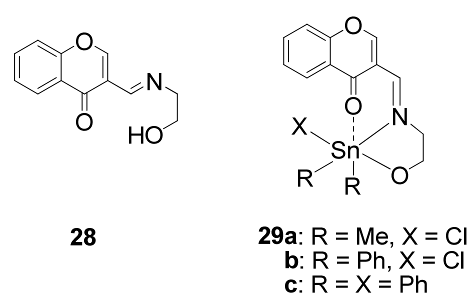
5.2. Addition of nitrogen nucleophiles

5.2.1. Addition of aliphatic amines. The Schiff base as well as its precursor having respectively general structures **B** and **A** (X = NR), obtainable from ChrCHO and an aliphatic or aromatic amine RNH_2 (Scheme 3-**A**) can function as a ligand for complexation with different metals. Many of these ligands as well as their metal complexes possess some biological activities. Cu(II), Ni(II) and Co(II) complexes with the chromone-based Schiff bases **26** (prepared from **1** and **25**) and **27** (Scheme 5) have been subjected to various spectral studies.[26]

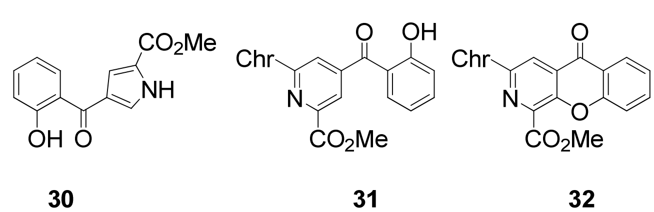


Scheme 5

Treatment of the Schiff base **28** with Me_2SnCl_2, Ph_2SnCl_2 and Ph_3SnCl gives respectively the organotin complexes **29a,b,c** which exhibit electrostatic mode of binding preferably via oxygen of sugar phosphate backbone of DNA helix.[27]

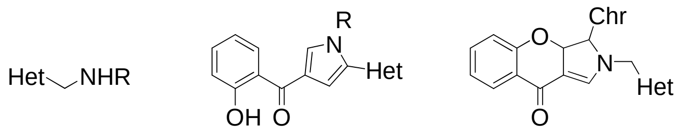


The formation of the pyrrole **30**, pyridine **31** and pyranopyridine **32** by treating ChrCHO with methyl glycinate hydrochloride in refluxing toluene containing K_2CO_3 has been rationalized.[28] The pyrrole **30** is, however, the sole product when the above reaction is carried out in TMSCl-DMF at 100 °C.[29]



TMSCl mediated reaction between **1** and hetarylmethylamine **33** strongly depends on their molar ratio. A 1:2 molar ratio of the aldehyde **1** and the amine **33** gives the pyrrole **35** in 68-91%

yields whereas a 2:1 molar ratio forms exclusively chromenopyrrole **37** in moderate yields. The reaction of **1** with a secondary hetarylmethylamine **34** leads to **36** independent of the molar ratio of the reactants.[29]

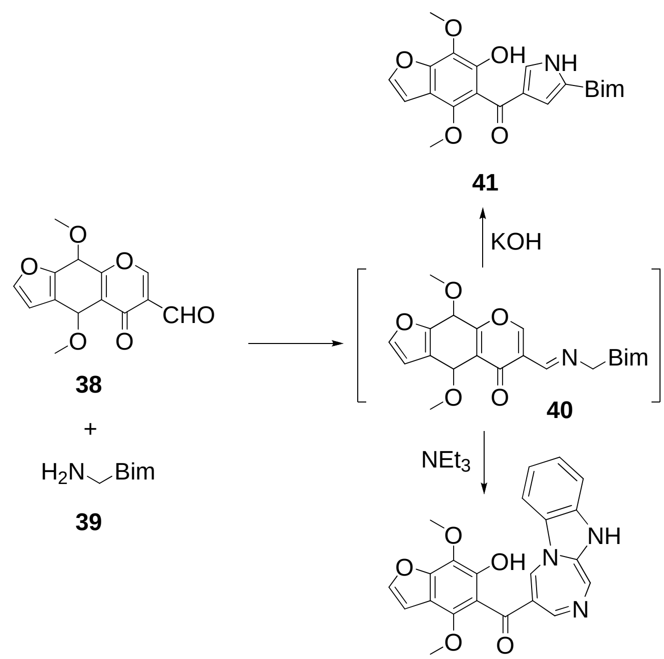


33: R = H **35**: R = H **37**

34: R = Alkyl **36**: R = Alkyl

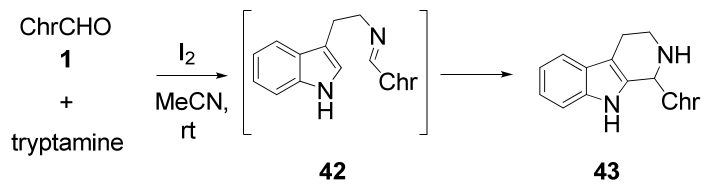
For **33**-**37** : **Het** = 2-, 4-pyridyl, 2-oxo-4-pyridyl, 2-(pyrid-1-yl)pyrid-4-yl, benzimidazol-2-yl, benzthiazol-2-yl, benzoxazol-2-yl

A hot methanolic solution of furo[3,2-*g*]chromone-3-carbaldehyde **38** and benzimidazol-2-ylmethylamine **39** (Bim = benzimidazol-2-yl) gives the pyrrole **41** when treated with KOH but **42** with triethylamine, both arising through the Schiff base intermediate **40** (Scheme 6). Several transition metal complexes of these pyrroles possess antiviral activity.[30]



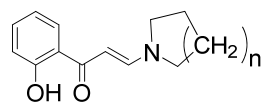
Scheme 6

Iodine-catalyzed Pictet-Spengler condensation between ChrCHO and tryptamine yielding 1,2,3,4-tetrahydro-β-carboline **43** evidently through the Schiff base intermediate **42** has been reported by Prajapati and Gohain (Scheme 7).[31]



Scheme 7

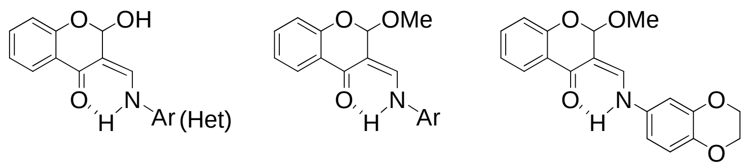
Synthesis of the propenone **44** from **1** and piperidine has been achieved by conventional method[32] as well as under ultrasound irradiation.[33] Ultrasonication of a mixture of **1** and pyrrolidine affords the propenone **45**.[34] Here piperidine or pyrrolidine undergoes aza-Michael addition to **1**; the resultant adduct by base catalyzed deformylative pyran ring opening gives the propenone **44** or **45**.[32]



44: n = 2
45: n = 1

5.2.2. Addition of aromatic amines. Ten aryl- and hetaryl- amines have been condensed with 3-formylchromone in refluxing water containing Zn[L(-)proline]$_2$ (10 mol%) as the catalyst to give the 2-hydroxychromanone **46**.[35] 2-Methoxychromanone derivatives **47-51** are obtained by reacting 3-formylchromone with the appropriate aniline in MeOH-PTS under reflux.[36-38] X-ray crystallography shows the presence of methoxy groups and intramolecular hydrogen bonding in all these compounds. The compound **49** is stable up to 90 °C and decomposes in three stages where as **51** is stable up to 100 °C and decomposes in five stages.[37] The compound **47** decomposes only when heated above 128 °C.[38] Some of the chromone based sulphonamides **52**, prepared from 3-formylchromones and the appropriate aminobenzenesulfonamide in refluxing EtOH containing catalytic amount of PTS are highly potent and selective inhibitors of alkaline phosphatase.[39,40] 2-Ethoxychromanone **52d** resulting from the reaction of 3-formylchromone and *o*-aminobenzenesulfonamide is always admixed with the benzothiadiazine derivative **53**. X-ray study reveals that one water molecule of crystallization is present in the crystal of the compound **52a** (R^1 = H).[39] The compounds **52a-c** (R^1 = H) possess excellent bovine carbonic acid anhydrase (BCA) inhibitory activities.[40] Kamal *et al.*[41] have reported reductive amination of ChrCHO with several aromatic amines ($ArNH_2$) to $ChrCH_2NHAr$ using sodium cyanoborohydride in methanol with a catalytic amount of acetic acid.

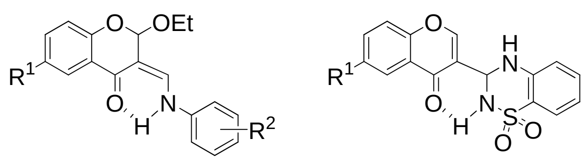
The Schiff bases prepared from **1** and several arylamines have been evaluated for their antibacterial activities.[42-44] The Schiff base **54** has been prepared from **1** and 4-aminoantipyrine by conventional method[45] as well as in an ionic liquid.[46] Many other hetarylamines such as 1,3-diaryl-5-aminopyrazole **55**,[47] 3-aminoquinazolone **56**,[48] thiazolylcoumarin **57**,[49] 4-amino-1,2,4-triazole **58**[50] and aminophenazone **59**[51] have been condensed with ChrCHO to give the corresponding Schiff bases. Pandey *et al.*[52] made a comparative study of conventional and microwave assisted synthesis of Schiff bases of ChrCHO.



46

47: Ar = phenyl
48: Ar = 3-carboxyphenyl
49: Ar = 5-carboxy-2-chlorophenyl
50: Ar = 3,4,5-trimethoxyphenyl

51

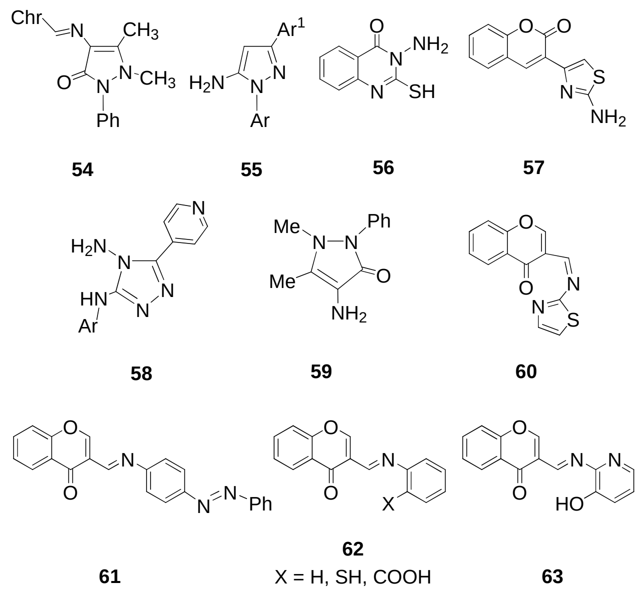


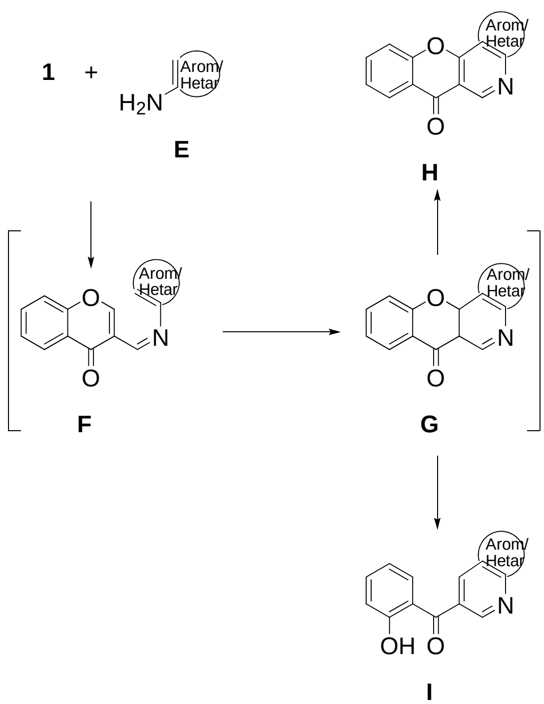
52a: R^2 = *p*-SO_2NH_2
52b: R^2 = *p*-SO_2NH-Hetaryl
52c: R^2 = *m*-SO_2NH_2
52d: R^2 = *o*-SO_2NH_2

53

For **52a-d** and **53:**
R^1 = H, Et, Br, F

3-Formylchromones as well as Schiff bases obtainable therefrom can function as ligands towards many metal ions. The complexes of Mn(II), Co(II), Ni(II) and Zn (II) with unsubstituted 4-oxo-4*H*-1-benzopyran-3-carboxaldehyde **1** are polycrystalline compounds with various formulae and different ratios of metal to ligand.[53] The Schiff base obtainable from **56** functions as a neutral bidentate ligand towards Co(II), Ni(II), Zn(II), Pd(II) and Cd(II), quinazolone carbonyl oxygen and azomethine nitrogen being involved in the corordination.[48] The Schiff base corresponding to hetaryl amine **57** coordinates as a neutral bidentate ligand with oxovanadium(IV), Co(II), Ni(II) or Pd(II) ions.[49] The Schiff bases derived from 3-formylchromones and aminophenazone **59** as well as their Ln(III) complexes can bind to DNA via an intercalation binding mode, the complexes having better DNA binding affinity than the free ligand alone.[51] The Schiff base **54** in its solid state as well as in solution has *E*-stereochemistry around its azomethine double bond and *S*-cisoid conformation for its α,β-unsaturated imine functionality. It functions as a fluorescent probe for Fe^{3+} in acetonitrile-water (1:9 by volume); while complexing with Fe(III) it assumes a conformation having *S*-transoid for CH=CH-CH=N and *Z*-stereochemistry around CH=N so that the metal can bind with azomethine nitrogen, chromone carbonyl oxygen and pyrazolinone oxygen.[54] Same is the case for the condensate from **1** and 2-aminothiazole; it assumes the conformation as shown in **60** so as to function as an NNO coordinating ligand for several metal ions. Its Cu(II) complex possesses tetrahedrally distorted square planar geometry whereas Co(II), Ni(II) and Zn(II) complexes show distorted tetrahedral geometry and VO(IV) complex shows square pyramidal geometry.[55] The azo-Schiff base **61** forms complexes with VO(IV), Co(II), Ni(II), Cu(II) and Zn(II); octahedral geometry is proposed for all those complexes from their electronic spectra and magnetic susceptibilities. The conductance data indicate non-electrolytic nature of the complexes except the VO(IV) one which is electrolytic in nature.[56] Cu(II) complexes of **62** and **63** having metal to ligand ratio as 1:2 have been subjected to rigorous spectral analysis.[57]

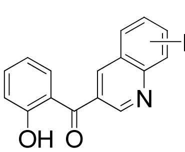




Scheme 8

An aryl- or hetaryl- amine of general structure **E** undergoes [3+3] annulation with α,β-unsaturated aldehyde functionality of **1** in TMSCl-DMF promoted reactions to give ultimately either the chromenopyridine **H** or 3-(2-hydroxybenzoyl)pyridine **I** or both (Scheme 8). Here the initially formed condensate having a structure akin to the Schiff bases **F** undergoes electrocyclization to **G**, the latter aromatizing to **H** by air oxidation and to **I** by pyran ring opening.

TMSCl mediated reaction of **1** with aniline or substituted aniline in DMF at 100 °C in a sealed tube produces either 3-(2-hydrobenzoyl)quinoline **64** or the chromenofused pyridine **65** depending on the structure of the starting aniline.[58,59] Substituents in aniline molecule that withdraw electron from the *ortho*-position or increase electron density on nitrogen favour the formation of **65**; on the contrary, electron rich anilines give only **64**. 4-Chloroaniline gives with **1** both **64** and **65**.[59] Similar reactions of 3-formylchromones with more than a dozen of aminoheterocycles promoted by either AcOH or PTS or TMSCl leading to only the heterofused pyridine **H** have been well documented in a Tetrahedron Report.[2] Iodine catalyzed condensation of ChrCHO with 1,3-disubstituted 5-aminopyrazole gives the pyrazolo[3,4-*b*]pyridine **66** (R, R^1 = alkyl, aryl).[60] Microwave irradiated condensation of **1** with 2-aminopyridine **67** (R^1, R^2 = H, Me, Br) in MeCN - PTS gives **68**; indium triflate catalyzed cyclization of the latter with *N*-aroylpropargylamine **69** (Ar = Ph, substituted phenyl, naphthyl etc.) under microwave irradiation furnishes the 2,10-dihydro-4a*H*-chromeno[3,2-*c*]pyridine **70** which has been evaluated for its preliminary in vitro and in vivo activity against MTB and MDR-TB.[61]



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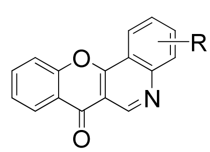

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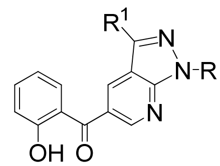

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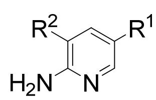

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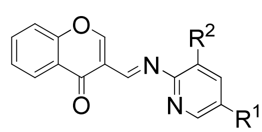

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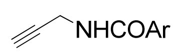

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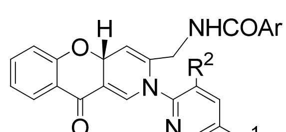
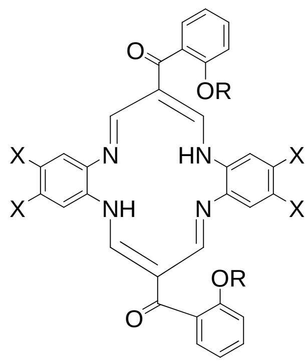
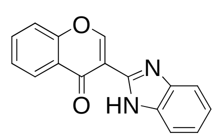


70

5.2.3. Addition of aryl- and hetaryl- amine having a second nucleophilic group attached to the ring. Dibenzotetraaza[14]annulene (DBTAA) **71**[6,62] has been recently synthesized by reacting **1** with *o*-phenylenediamine in an organised aqueous medium in the presence of a surfactant (viz. DBSA) as catalyst and iodine as co-catalyst.[63] Liquid crystalline DBTAA derivative as **72** bearing four 3,7-dimethyloctoxy peripheral tails[64] and its chiral variant **73** bearing four (*S*)- or (*R*)-enantiomeric 3,7-dimethyloctoxy groups have been prepared by condensing **1** with the appropriate 4,5-disubstituted 1,2-diaminobenzene in methanol.[65,66] DBTAA based lacunar type receptors **74-76** have been prepared by alkylation of both phenolic OH groups using the appropriate aliphatic dibromide or ditosylate.[67] Esterification of **71** with octane-1,8-dicarboxylic acid and benzene-1,4-diacetic (or di-n-propanoic acid) gives respectively **77** and **78**, 4-dimethylaminopyridine (DMAP) being used as an acylation catalyst and *N,N*-diisopropylcarbodiimide (DIC) as a dehydrating agent.[68]



71: R = X = H
72: R = H; X = $OCH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$
73: R = H; X = $OCH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$
74: R-R = $(CH_2)_5$; X = H
75: R-R = $(CH_2)_{10}$; X = H
76: R-R = $CH_2CH_2OCH_2CH_2O$-(*p*-C_6H_4)-OCH_2CH_2-OCH_2CH_2-
77: R-R = $OC(CH_2)_8CO$; X = H
78: R-R = OC-$(CH_2)_n$-(*p*-C_6H_4)-$(CH_2)_n$CO-; n = 1 or 2; X = H



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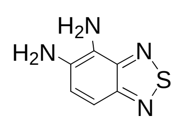

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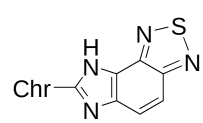

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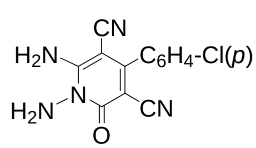

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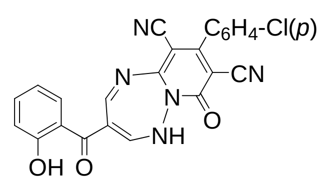

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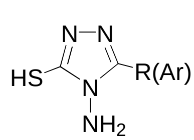

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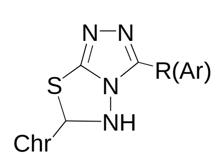
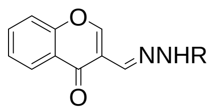


85

The annule **71** on digestion in acetic acid or oxidation with chloranil gives the chromonylbenzimidazole (bzch) **79**. A mononuclear rhenium(I) complex cuplex fac-

$[Re(CO)_3bzchCl]$ is formed by treating $[Re(CO)_5Cl]$ with bzch.[69] Grinding at ambient temperature a mixture of **1** and benzo[*c*][1,2,5]thiadiazole-4,5-diamine **80** with either xanthan sulphuric acid (XSA)[70] or cellulose sulphuric acid (CSA)[71] without any solvent affords the fused benzimidazole **81**. ChrCHO with 4-(4-chlorophenyl)-1,6-diamino-2-oxopyridine-3,5-dicarbonitrile **82** in hot pyridine gives the pyrido[1,2-*b*][1,2,4] triazepin **83**.[72] An Indian group[73] reports condensation of **1** with 3-alkyl(or aryl)-4-amino-5-mercapto-*s*-triazole **84** in the presence PTS to 4,5-dihydro-3-alkyl(or aryl)-s-triazolo[3,4-*b*][1,3,4]thiadiazole **85**.

5.2.4. Addition of hydrazine. The hydrazone **86** and acylhydrazone **87** can function as ligands to coordinate with metal ions; these hydrazones and their metal complexes may have some biological activities. As for example, the hydrazone **86** (R = Ph) is a neutral bidentate ligand coordinating through its azomethine nitrogen and carbonyl oxygen with tripositive Fe, dipositive Fe, Ni, Cu and Pd ions.[73] DNA binding properties of the ligand **87** (R = Ph) and its complexes with several metals have been studied.[74,75] Many members of **87** (R = mono- or disubstituted phenyl) have been evaluated against cyanobacteria fructose-1,6-biphosphatase and sedoheptulose-1,7-biphosphatase.[76,77] Chromone-3-carboxaldehyde isonicotinylhydrazone **87** (R = 4-pyridyl) and lanthanide ions form mononuclear 10-cordinate complexes with 1:2 metal to ligand stoichiometry.[78] Acylhydrazone **88** (R^1 = R^2 = H; R^1-R^2 = bond) has been prepared by reacting the appropriate 6-oxopyridazine-3-carboxylic acid hydrazide with ChrCHO.[79] The thiosemicarbazone **89** forms complexes with Cu(II), Zn(II), Ni(II) nitrates having 1:1 metal to ligand stoichiometry; these complexes bind to calf thymus DNA via an intercalation binding mode.[80,81] Cytotoxicity activity and DNA binding of the semicarbazone **89** itself have also been studied.[82] $PhNHNHCOCONHNH_2$, obtainable by treating diethyl oxalate sequentially with phenylhydrazine and hydrazine has been condensed with ChrCHO to form the acylhydrazone **90**. An octahedral geometry for its Co(II), Cu(II) and $U(VI)O_2$ and a tetrahedral structure for its Ni(II), Cd(II), Zn(II) and Hg(II) complexes have been proposed. The ligand **90** and its metal complexes have been screened against some gram (+)ve and gram (-)ve bacteria.[83] The hydrazone **86** (R = 3-chlorophenyl,[84] 2,4-dichlorophenyl,[85] fluorophenyl,[86] 2-pyridylphenyl[87]) have been converted to the corresponding 4-salicyloyl-1-arylpyrazole **91**. The pyrazole **91** (Ar = Ph) on treatment with *O*,*O*-diethylphosphochloridothiate gives the biologically active organophosphorus compound **92**.[88] The ketoxime of **91** on treatment with phosphorus oxychloride undergoes Beckmann rearrangement and cyclization to the benzoxazole **93**.[84-87] The hydrazone **94** in the presence of iodobenzene diacetate $[PhI(OAc)_2]$ on solvent free microwave irradiation undergoes oxidative cyclization to 1,2,4-triazolo[4,3-*a*]-1,8-naphthyridine **95**.[89] Azomethine functionality in acylhydrazone **87** (R = aryl or hetaryl) behaves similarly as that in a Schiff base towards mercaptoacetic acid and chloroacetyl chloride to give the corresponding thiazolidine and β-lactam, respectively.[90,91] The phosphorohydrazone **96** exhibits high in vitro antileukemic activity.[92]



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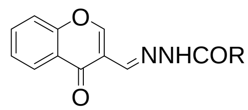

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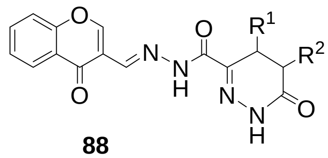

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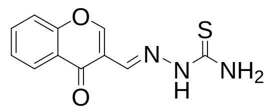

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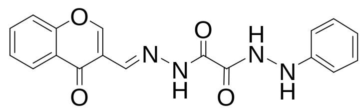

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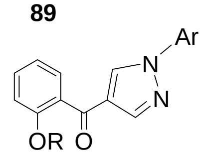
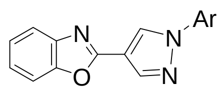


91: R = H
92: R = P(=S)(OEt)$_2$



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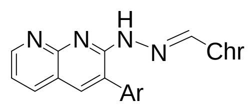

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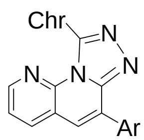

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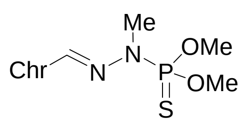

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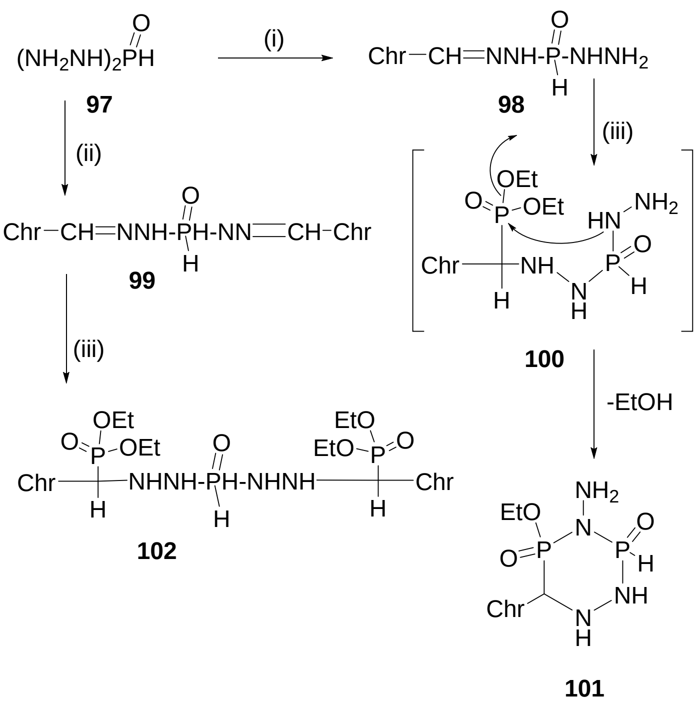
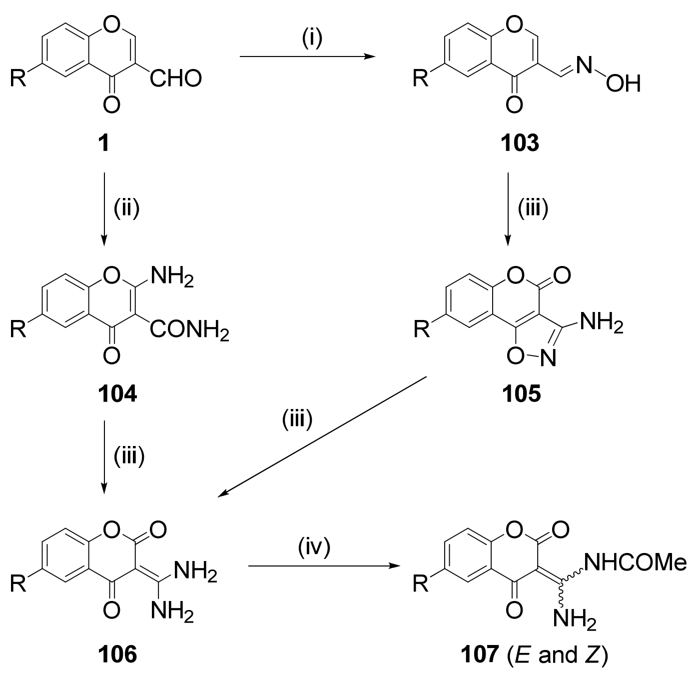


Scheme 9. Reagents and conditions: (i) 1 eq. ChrCHO, EtOH, Δ; (ii) 2 eq. ChrCHO, EtOH, Δ; (iii) HP(=O)(OEt)$_2$, EtOH, Δ.

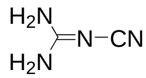
An ethanolic solution of phosphonic dihydrazide **97** gives the hydrazones **98** and **99** with 1 and 2 equivalents of ChrCHO, respectively. Diethylphosphite converts **98** to the 1,2,3,4,5-triazadiphosphinane **101** most likely *via* the intermediate **100** formed by addition of diethyl phsphite to the azomethine double bond of **98** followed by cyclization whereas it simply adds to **99** giving **102** (Scheme 9).[93]

5.2.5. Reaction with hydroxylamine. Intricacy of the reaction between **1** and hydroxylamine has been discussed earlier.[5] A later detailed study of the reaction by Sosnovskikh *et al*.[94] gives interesting results (Scheme 10). The initially formed aldoxime **103** when treated with alkaline hydroxylamine gives the chromane-2,4-dione **106** *via* the isolable isoxazolocoumarin intermediate **105**. Here the O-N bond in **105** is reduced by hydroxylamine to form **106**. The amide **104** obtainable from **1** is also transformed into **106** under similar conditions. Reflux of **106** in acetic anhydride gives an *E*-, *Z*-isomeric mixture of the monoacetate **107**. The chromanedione **106** (R = H, Me) is formed in 46-51% yield upon reflux of an ethanolic solution of **1** (R = H, Me) (1 eq) with aq $NH_2OH.HCl$ (8 eq) in the presence of NaOH (14 eq) for 3 h, no intermediate as **104** and **105** (R = H, Me) being isolated. The reaction of **1** (R = Cl) with hydroxylamine under the same conditions furnishes a mixture of **106** and **105** in 7:3 proportion.[94] Zirconium oxychloride ($ZrOCl_2.8H_2O$) in aqueous acetone (1:1) can regenerate 3-formylchromone from its aldoxime **103**.[95]



Scheme 10. Reagents in hot conditions: (i) $NH_2OH.HCl$, EtOH; (ii) $NH_2OH.HCl$, pyridine-water; (iii) $NH_2OH.HCl$, NaOH, EtOH, H_2O; (iv) Ac_2O.

5.2.6. Reaction with guanidine. Reaction of **1** with cyanoguanidine **108** or metformine **109** gives biologically important pyrimidine **110** or **111**.[88]



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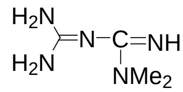

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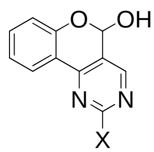
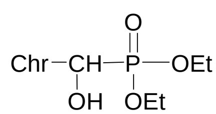


110: X = NHCN
111: X = NHC(=NH)NMe_2

5.3. Addition of phosphorus nucleophiles

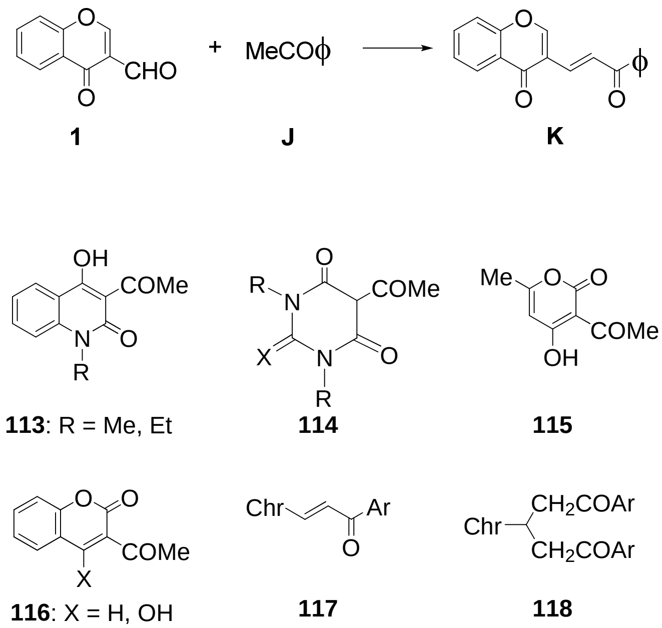
Ammonium metavanadate (NH_4VO_3) catalyzes addition of triethyl phosphite to ChrCHO at room temperature under solvent free conditions yielding the α-hydroxyphosphonate derivative **112**.[96] Potassium dihydrogen phosphate[97] and sulfamic acid[98] are also effective catalysts for the solvent free ultrasound irradiated synthesis of **112** from the above said two reactants.



112

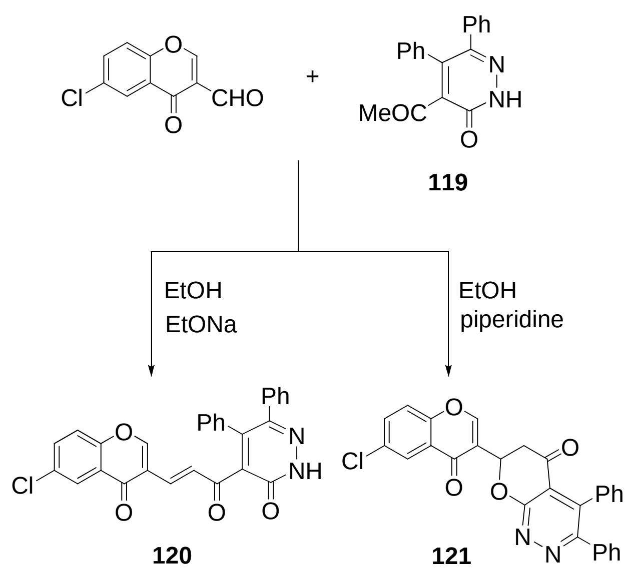
5.4. Addition of carbon nucleophiles

5.4.1. Addition of active methyl and acyclic methylene compounds. The aryl(or hetaryl) methyl ketone **J** condenses with 3-formylchromone **1** under various conditions to give the chalcone **K** (Scheme 11). Several 2- or 4- substituted acetophenones have been condensed with ChrCHO in ethanol containing either pyridine[99] or sodium hydroxide[100] or under solvent free condition.[101] The hetaryl methyl ketones **113-116** have been used for preparation of chalcones in refluxing ethanol containing pyridine or water containing Zn(L-proline)$_2$.[102,103] Synthesis of chalcones by Claisen-Schmidt condensation of ChrCHO with ketones using ecofriendly non-toxic bismuth(III) chloride catalyst under solvent free conditions is also reported.[104] Many of the chalcones and the products obtained therefrom by treatment with NH_2NHR (R = H, Ph) have been screened against many gram (+)ve and (-)ve bacteria and fungi.[101,103d] Gold(III) mediated condensation of **1** with aryl methyl ketone to produce the 1,5-diketone **118** admixed with a little amount of the chalcone **117** deserves special mention. Here the initially formed condensate **117** functions as a Michael acceptor towards a second molecule of aryl methyl ketone to give the adduct **118**. The best result is obtained when the reaction is conducted in MeCN at ambient temperature using $AuCl_3$ (5 mol%), $AgSbF_6$ (15 mol%) and aryl methyl ketone (2.2 eq).[105]



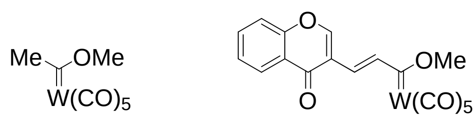
Scheme 11

Interaction of 6-chloro-3-formylchromone with the pyridazinone **119** (1:1) in NaOEt-EtOH gives the corresponding chalcone **120** whereas the above reaction when carried out in EtOH containing piperidine gives the pyrano[2,3-*c*]pyridazone **121** *via* an intramolecular 1,4-addition in the compound **120** (Scheme 12).[106]



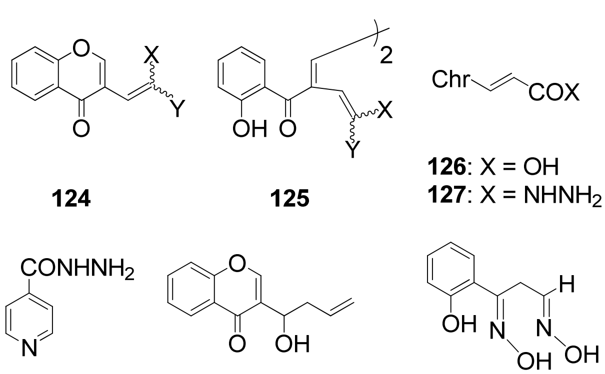
Scheme 12

The methyl group directly linked to a very few aromatic or heterocyclic rings is sufficiently active to undergo condensation with ChrCHO giving ChrCH=CH-Φ (Φ = Ar, Het). This aspect mainly studied before 2000 has been the subject matter of seven publications well comprehended in a recent review.[3] ChrCHO has been reacted with methoxy(methyl)pentacarbonyltungsten carbene complex **122** in the presence of TMSCl and triethylamine; the carbanion generated from the carbene complex **122** condenses with the pyrylium salt generated from **1** and TMSCl to give the benzopyran Fischer carbene complex **123**.[107]



122 **123**

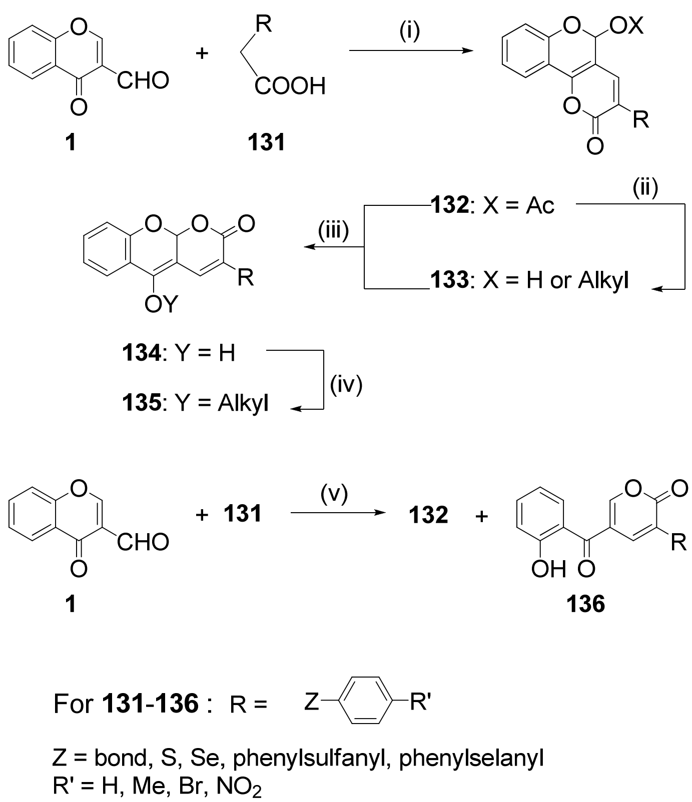
Several new catalysts have been used for the Knoevenagel condensation of **1** with active methylene compounds. As for example, ChrCHO has been condensed with XCH_2CN (X = CN, COOH, COOEt, $CONH_2$) under polyethylene glycol-400 (PEG-400) catalysis and microwave irradiation.[108] Alum [$KAl(SO_4)_2.12H_2O$] mediated solvent free microwave induced clean process for preparation of α,β-unsaturated carboxylates is known, only 10 mol% of alum being sufficient for optimum yields.[109] Knoevenagel condensation of **1** with ethyl cyanoacetate, Meldrum's acid etc. using biosupported cellulose sulphuric acid (CSA) in the solid state under solvent free condition is reported.[110] The condensate **124** resulting from **1** and XCH_2Y (X = Y = COMe; X = Y = CO_2Et; X = CN, Y = CO_2Et; X = COPh, Y = CO_2Et) undergoes chemoselectively reductive dimerisation to **125** with Sm in THF containing aq NH_4Cl whereas Zn under similar conditions brings about chemoselective reduction of exocyclic olefinic bond.[111] *E*-(chromon-3-yl)acrylic acid **126** obtained by conventional pyridine catalyzed Knoevenagel condensation of **1** with malonic acid[112,113] has been subjected to molecular hybridization with isoniazide **128** using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI) and 1-hydroxybenztriazole (HOBt) under ultrasonication to afford the hydrazide **127**.[114] A mixture of allyl bromide and zinc dust in THF containing saturated NH_4Cl converts ChrCHO to the homoallylic alcohol **129**; the latter when heated with formalin in AcOH containing a few drops of H_2SO_4 is reconverted to 3-formylchromone **1**. Hydroxylamine converts **129** to the dioxime **130** (diastereoisomeric mixtures).[115]



124 **125** **126**: X = OH **127**: X = $NHNH_2$

128 **129** **130**

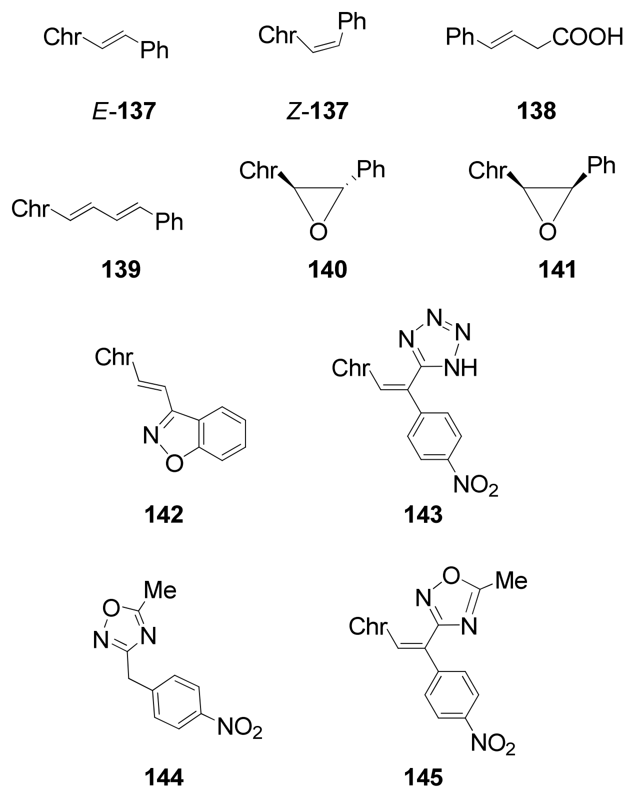
3-Formylchromone **1** when reacted with the substituted acetic acid **131** under Perkin reaction condition gives the pyranopyran **132** that on treatment with XOH (X = H or alkyl) in the presence of PTS affords **133** (Scheme 13). The compounds **132** and **133** when heated in aqueous acid at elevated temperature rearrange to **134** that can be alkylated to **135** by an alkanol in the presence of PTS.[116] Another publication reveals the formation of small amounts of 5-(2-hydroxybenzoyl)pyran-2-one **136** along with the major product **132** in the above mentioned condensation of **1** with **131** under MWI.[117] Recently several *p*-substituted phenylacetic acids have been condensed with 3-formylchromones in Ac_2O-AcONa under reflux to give pyranochromone **132**.[3] Coumarin-3- or 4-acetic acid similarly condenses with **1** giving **132** (R = coumarin-3- or 4-yl).[118]



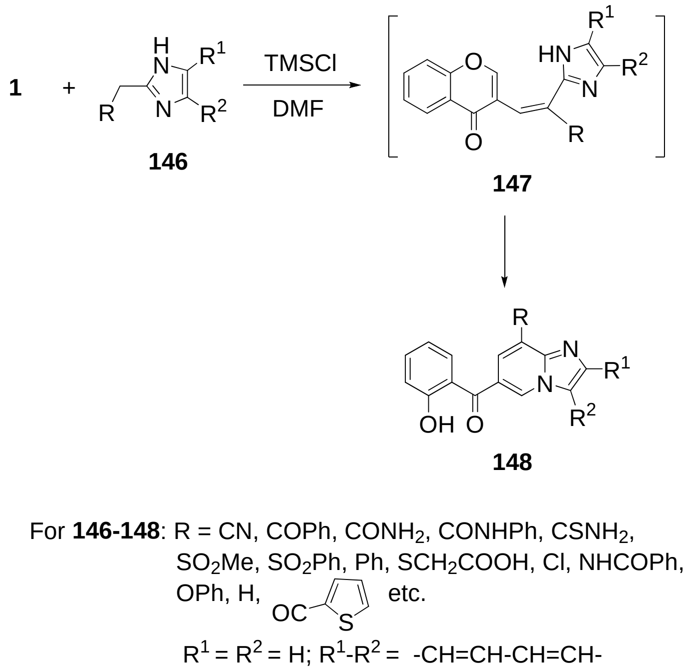
Scheme 13. Reagents and conditions: (i) Ac_2O, AcOK, Δ; (ii) XOH (X = H, Alkyl), PTS; (iii) H_2O, H^+, Δ; (iv) YOH (Y = alkyl), PTS; (v) Ac_2O, AcOK, MWI.

The reaction of **1** with phenylacetic acid when conducted in the presence of *t*-BuOK under MWI, however, takes a different course; here initial condensation followed by decarboxylation produces only the *E*-isomeric form of 3-styrylchromone (***E*-137**).[119] *Z*-3-Styrylchromone (***Z*-137**) can be conveniently prepared by reacting ChrCHO with benzylic ylid.[119] Patonay *et al.*[120] prepared the ***E*-137** by exposing a mixture of **1** and phenylmalonic acid on solvent free NaOAc support to MWI. The compounds ***E*-137** and **139** are obtained by treating **1** in dry pyridine-

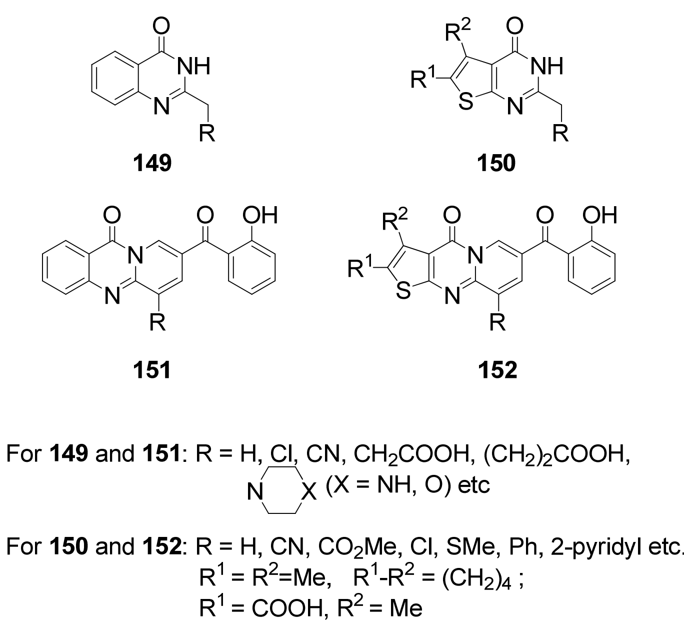
^{t}BuOK with phenylacetic acid and *E*-styrylacetic acid **138**, respectively.[121] A dichloromethane solution of dimethyldioxirane (DMD) brings about epoxidation of 3-styrylchromone with complete regio- and diastereo-selectivity, *E*-isomer giving the epoxide **140** and *Z*-isomer the epoxide **141**; On the contrary, treatment with H_2O_2 under alkaline condition affords the corresponding 2,3-epoxy-3-styrylchromone.[120] ChrCHO with benzisoxazole-3-acetic acid under MWI gives *E*-dihetaryl substituted ethene **142**. In its reaction with urea, thiourea and guanidine, the α,β-unsaturated carbonyl functionality of **142** is involved, the hetarylvinyl moiety remaining unaffected.[122] (*p*-Nitrophenyl)(tetrazol-5-yl)methane with **1** in dry pyridine gives the *Z*-isomer of trihetarylethene **143**; similar condensation of **144** with **1** gives **145** having *Z*-stereochemistry around its exocyclic olefinic bond. Both the chromone based compounds **143** and **145** have been assayed against gram (+)ve and (-)ve bacteria.[123]



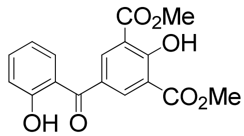
Heating 3-formylchromone **1** with a variety of imidazole (**146**, R^1=R^2=H) and benzimidazole **146** (R^1-R^2 = -CH=CH-CH=CH-) in DMF in the presence of TMSCl as a promoter and scavenger gives the midazole[1,2-*a*]pyridine **148**. The reaction goes *via* an intermediate having a structure akin to **147** that by a domino aza-Michael – retro-Michael gives **148** (Scheme 14).[124] The pyrido[1,2-*a*]benzimidazole **148** (R = CN; R^1-R^2 = -CH=CH-CH=CH-) is also obtained by reacting **1** with benzimidazole-2-acetonitrile under Perkin condition.[3] TMSCl mediated cyclization of **1** with pyrimidinones **149** and **150** yields the pyridopyrimidinones **151** and **152**, respectively.[125]



Scheme 14



A few acyclic compounds having two active methylene groups have been condensed with **1**. As for example, dimethyl acetonedicarboxylate functions as a 1,3-C,C-binucleophile in condensing with **1** in THF under DBU catalysis to give the benzophenone **153**.[126] Wittig reaction of the ylid **154** with **1** in THF containing NaH gives **155**.[127] The compound **156**, obtained by condensing **1** with triethyl 3-methylphosphocrotonate under Wittig-Horner-Emmons reaction conditions, is sequentially subjected to reduction with LAH, oxidation with MnO_2, Wittig reaction with (methoxycarbonylmethyl)triphosphonium bromide and hydrolysis by LiOH to give the benzophenone based retinoid **157**.[128] Acetoacetanilide functions as a 1,3-C,N-binucleophile towards **1** in CH_2Cl_2 containing $FeCl_3.6H_2O$, Cs_2CO_3 and $MgSO_4$ so as to form the pyridine **158**.[129]



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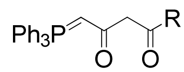

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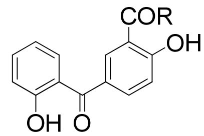
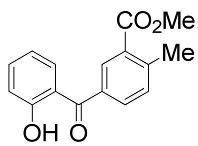


155

For **154** and **155**: R = OMe, OEt, OPr^i, NH_2, $N(CH_2)_4$, $N(CH_2)_5$



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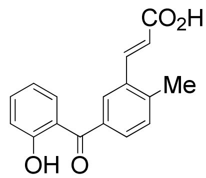

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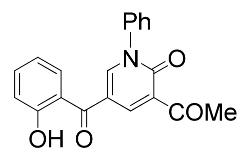
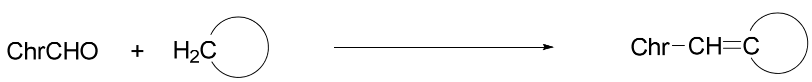


158

5.4.2. Addition of cyclic active methylene compounds. A methylene group incorporated in some cyclic, mostly heterocyclic, systems **L** is sufficiently active so as to condense with 3-formylchromone **1** giving the product **M** (Scheme 15). A number of such cyclic active methylene compounds that have been condensed with **1** and the condensation conditions with the appropriate references are given in Table 1.



1 **L** **M**

Scheme 15

Table 1. Condensation of **1** with the compound **L**

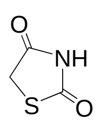
Active methylene compound **L**	Reaction conditions[ref.]
 **159**	(a) gl. AcOH, AcONa, Δ[130] (b) Zn nanobelts, Solvent free, Δ[131a] (c) 1,13,3-tetramethyl-guanidine lactate [TMG][Lac] ionic Liquid, solvent free, ultrasonication[132] (d) PEG-400, MWI[108]

Table 1. Continued

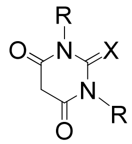
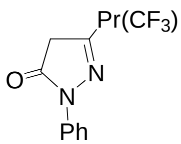
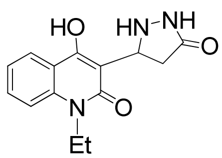
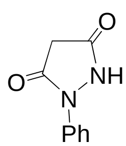
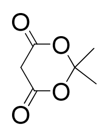
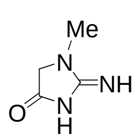
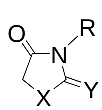
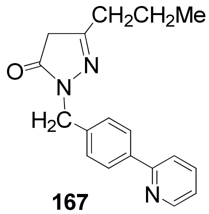
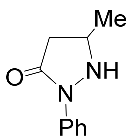
Active methylene compound **L**	Reaction conditions[ref].
 **160** R = H, Me; X = O, S	(a) $NaHCO_3$/MWI[133a] (b) Solid state, Δ[133b]
 **161**	AcOH, Δ or MWI or ultrasonication[134]
 **162**	AcOH, AcONa[135]
 **163**	AcOH, AcONa, Δ[136]
 **164**	(a) PEG-400/ MWI[108] (b) solid state, Δ[137] (c) solid state, MWI[138] (d) cellulose sulphuric acid (CSA), solvent free[110] (e) 1-Benzyl-3-methylimidazolium chloride [bnmim]Cl ionic liquid, room temp.[139]
 **165**	PEG-400/MWI[108]
 **166** X = S, NH; Y = O, S; R = H, Ar	AcOH, Δ[140-142]

Table 1. Continued

Active methylene compound **L**	Reaction conditions[ref].
 **167**	AcOH, Δ or ultrasonication[143]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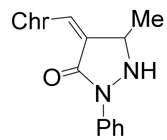
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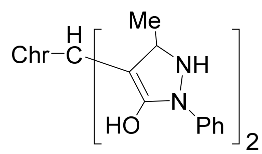
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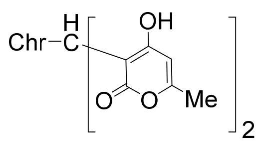
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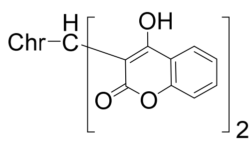
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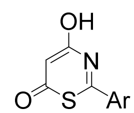
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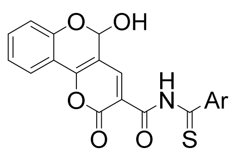
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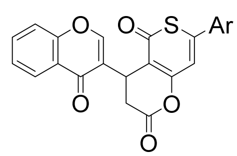
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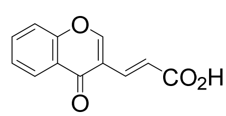
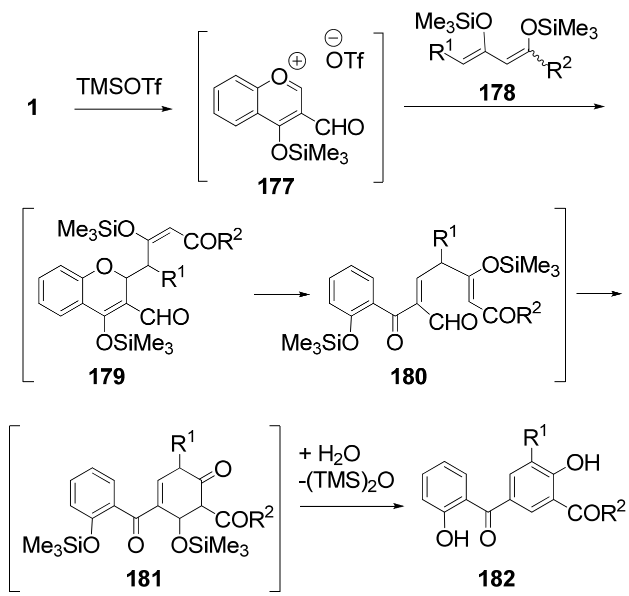

176

The compound **166** (X = O, S; Y = O; R = CH_2Ar),[144] naphtho[2,1-*b*]furan-3-(or 2)-ones[145] and 7-methoxychromanone[146] have been condensed with **1** by one or other method mentioned in Table 1. 8-Allyl-3-formylchromone like its 8-unsubstituted analogue **1** has been condensed with hippuric acid in AcOH-AcONa, with barbituric acid and dimedone in dry pyridine to give the expected condensates.[112] Condensation of 1-phenyl-3-methylpyrazolidin-5-one **168** with ChrCHO either in aqueous medium containing B_2O_3-ZrO_2 solid catalyst[147] or with PEG-400 under MWI[108] or under MWI without any catalyst[133b] gives the normal condensate **169**. A mixture of **1** and **168** in 1:2 molar ratio on MWI gives **170** that arises by a Michael addition of **168** to **169**.[148] Xanthan sulphuric acid (XSA) has also been used as a solid catalyst for the formation of **170** from **1** and **168**.[149] Similar condensation of **1** with triacetic acid lactone (4-hydroxy-6-methylpyran-2-one) and 4-hydroxycoumarin (2 eq) under conventional or solvent free conditions gives the trihetarylmethanes **171** and **172**, respectively.[148] The compound **172** is also formed from **1** and 3-bromo-4-hydroxycoumarin (1:2 molar ratio) in MeOH-pyridine under reflux.[150] Shutov *et al*.[151] have rectified their earlier report[152] on the reaction of **1** with 2-aryl-4-hydroxy-1,3-thiazin-6(6*H*)-one **173** (Ar=Ph, p-$MeOC_6H_4$). The said reaction at 50-58 °C in THF containing pyridine as catalyst is now claimed to give a mixture of the pyrano fused heterocycles **174** and **175** admixed with a little amount of the byproduct **176**. The condensates of **1** and different active methylene compounds as well as the products easily obtainable therefrom by reaction with some N-N, N-O, N-C-N binucleophiles have been evaluated for their biological activities.

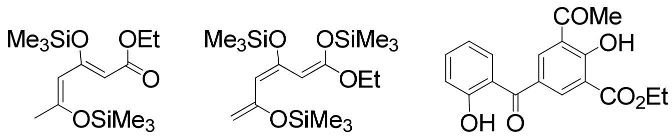
5.4.3. Addition of enol ethers. The formation of benzophenones by reacting 3-formylchromone **1** with 1,3-*bis*-silyl enolates of general formula **178** as the synthetic equivalent of 1,3-dicarbonyl compounds in the presence of trimethylsilyl triflate (TMSOTf) has been exploited by Langer and co-workers;[153,154] the earlier works in this aspect has been accounted by Langer himself.[155] Here the terminal carbon of the butadiene moiety of **178** undergoes Michael addition to the benzopyrylium triflate **177**, generated from **1** and TMSOTf; the adduct **179** undergoes sequentially retro-Michael (→**180**), intramolecular aldol reaction (→**181**) and hydrolytic elimination of siloxane to give the product **182** (Scheme 16).



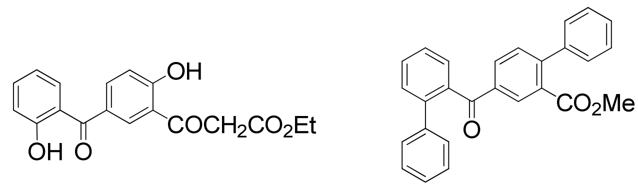
For **178-182**: R^1 = H, Me, Et, *n*-Bu, Bn, CH_2-CH=CH_2, $(CH_2)_3Cl$ etc.
R^2 = Me, Et, Ph, OEt, OMe

Scheme 16

The *bis*-silyl enolates **178** (R^1 = SC_6H_4-R^3, R^3 = H, Me, Cl, OMe; R^2 = OEt)[156] and **178** (R^1 = Cl; R^2 = OMe, OEt)[157] have been similarly utilized for the formation of the corresponding benzophenones **182**. Deprotonation of ethyl 3,5-*bis*(trimethylsiloxy)-2,4-hexadienoate **183** with LDA and subsequent addition of TMSCl gives 1,3,5-tris(silyloxy)-1,3,5-triene **184**. TMSCl catalyzed reaction of ChrCHO with **183** gives the benzophenone **185** and that with **184** gives **186**, the latter product being a regioisomer of the former one.[158] **182** (R^1 = H; R^2 = OMe) derived from **1** and **178** (R^1 = H; R^2 = OMe) has been reacted with phenylboronic acid in the presence of $Pd(PPh_3)_4$, K_3PO_4 in 1,4-dioxane to get the 2,4'-diphenylbenzophenone **187**.[159]

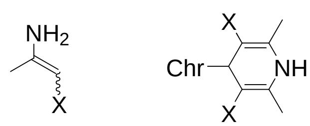


183 **184** **185**

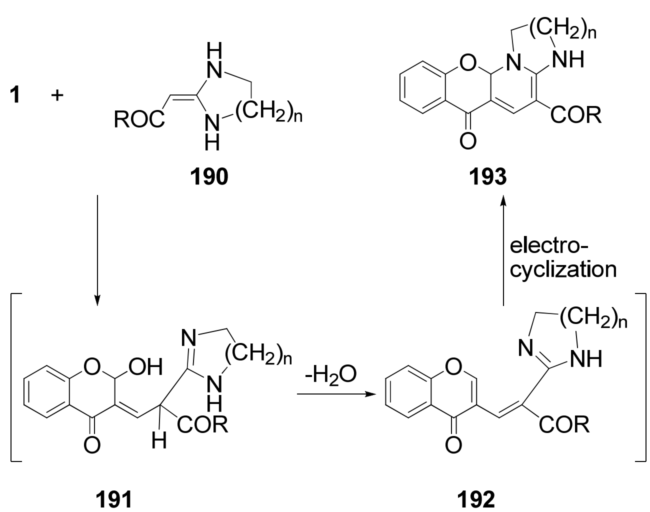


186 **187**

5.4.4. Reaction with enamines. β-Aminocrotonic ester or β-aminocrotononitrile **188** (X = CO_2Et, CO_2Me, CN) with **1** in acetic acid[160] or in the presence of TMSCl[161] forms only the Hantzsch type dihydropyridines **189**. The keten-aminal **190** functions as an enamine to undergo Michael addition to **1** with pyran ring opening and ring closure (→**191**), water elimination (→**192**) and electrocyclization to the tetracyclic heterocycle **193** as the final product (Scheme 17).[162]



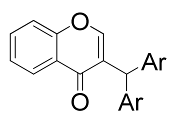
188 **189**



For **190-193** : n = 1,2,3
R = C_6H_5, 4-Cl, -F, -Me, $-C_6H_4$, 2-furyl

Scheme 17

5.4.5. Electrophilic substitution reaction of aromatic and heterocyclic compounds with 3-formylchromone. 3-[(Bisarylmethyl)chromone **194** (Ar = 4-*N*,*N*-dialkylaminophenyl) and **194** (Ar = 2,4-dimethoxybenzene) are prepared by treating **1** with *N,N*-dialkylaminobenzene in aq. H_2SO_4 and 1,3-dimethoxybenzene in CH_2Cl_2 containing $BF_3.Et_2O$, respectively. The chromone **194** on oxidation with *p*-chloranil followed by treatment with NaOMe gives the acetal **195**. The pyrazoles derived from **195** and NH_2NH_2 as well as NH_2NHMe have also been subjected to oxidation by *p*-chloranil.[163] Condensation of **1** with *β*-naphthol in the presence of CSA under solvent free condition affords the chromenyl-14*H*-dibenzo[*a*, *j*]xanthene **196**.[164]



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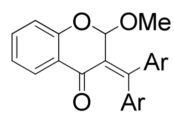

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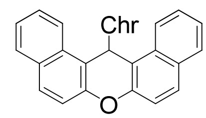

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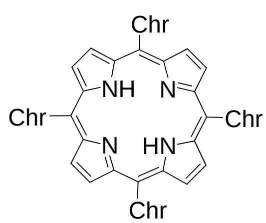

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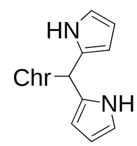

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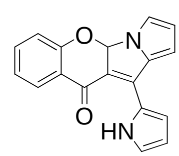

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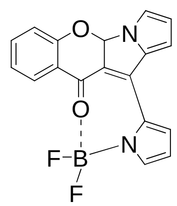

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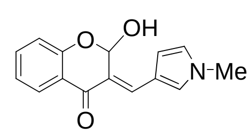
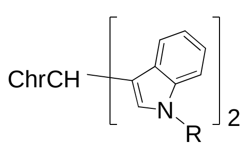
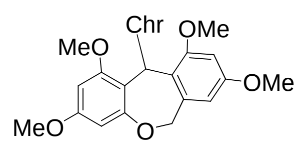


201



202: R = H, Me

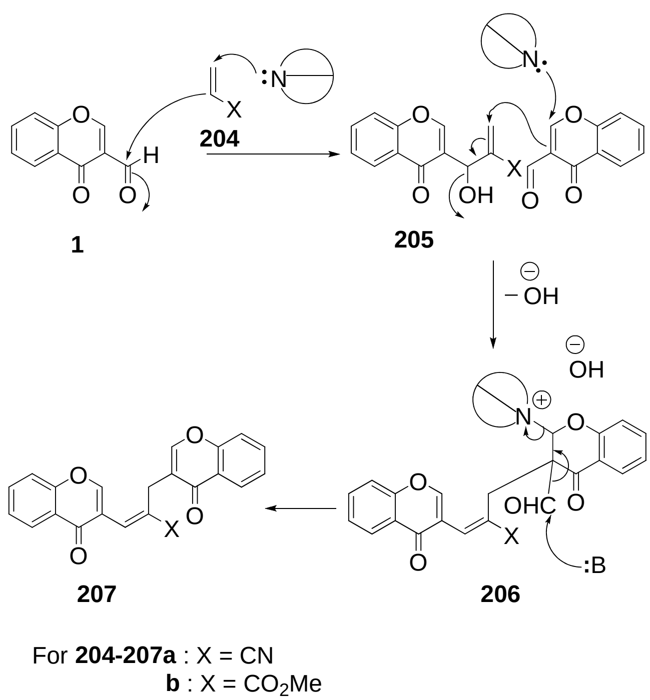


203

Pyrrole and indole have been subjected to react with ChrCHO under different conditions. The reaction of **1** with pyrrole in DMF-PTS forms the meso-tetrakis(chromon-3-yl)porphyrin **197**[165] whereas that in TFA gives the trisubstituted methane **198**.[166] The porphyrin **197** exhibits antioxidative activity against DNA damage induced by bleomycin-iron complex.[165] The trihetarylmethane **198** on DDQ oxidation gives the chromanone **199** that can form a luminescent N,O-chelated chroman BF_2 complex **200** with BF_3-etherate in triethylamine.[166] Sosnovskikh *et al*.[167a] reported the formation of **201** having *E*-stereochemistry around its exocyclic olefinic bond from the uncatalyzed reaction of **1** with 1-methylpyrrole under solvent free conditions; in a later publication[167b] **1** is reported to form with indole as well as 1-methylindole the trihetarylmethane **202** under the same condition. A solid complex, conveniently prepared from sodium triphenylphosphine-m-sulfonate and carbon tetrachloride[168] as well as XSA under solvent free conditions at room temperature[169] has been used for the Friedel-Craft alkylation of indole with ChrCHO to produce **202** (R = H). (3,5-Dimethoxyphenyl)(3,5-dimethoxybenzyl)ether undergoes $BF_3.Et_2O$ (10 mol%) catalyzed alkylation with ChrCHO in CH_2Cl_2 at room temperature to give 6,11-dihydrodibenzo[*b*,*e*]oxepine **203**.[170]

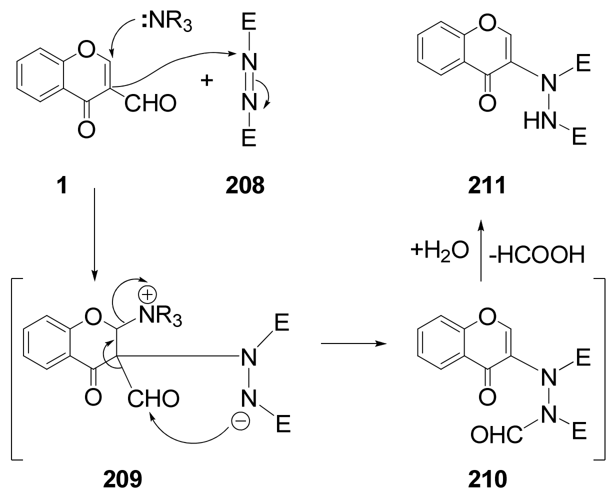
5.5. Baylis-Hillman reaction

Baylis-Hillman reaction of the electron deficient olefin **204** (X = CN, CO_2Me) with **1** using as catalyst 3-hydroxyquinnuclidine (3HQ) or DBU in chloroform or DABCO in 1-methylpyrrolidine gives the adduct **205**. DABCO catalyzed reaction in chloroform between **1** and acrylonitrile **204a** gives **205a** admixed with a small amount of **207a** whereas that between **1** and methyl acrylate **204b** gives exclusively the dimer **207b** (Scheme 18).[171] The olefin **204** in the presence of the tertiary nitrogeneous base catalyst undergoes Baylis-Hillman reaction with the aldehyde function of **1** to give the alcohol **205**. A second Baylis-Hillman reaction involving Michael addition of the carbanion at C-3 of **1** to the exocyclic α,β-unsaturated nitrile or ester functionality of **205** followed by elimination of HO¯ (→**206**) and base catalyzed deformylation gives the trisubstituted propene **207**.



Scheme 18

Synthesis of 3-hydrazinochromone **211** from **1** and azidodicarboxylate **208** (E = CO_2Et or CO_2Me) in the presence of DABCO (here written as NR_3) involves an aza-Baylis-Hillman type reaction (→**209**→**210**) followed by deformylation (Scheme 19).[172] ChrCHO and **208** in the presence of PPh_3 take a different reaction course (vide section 6.5).

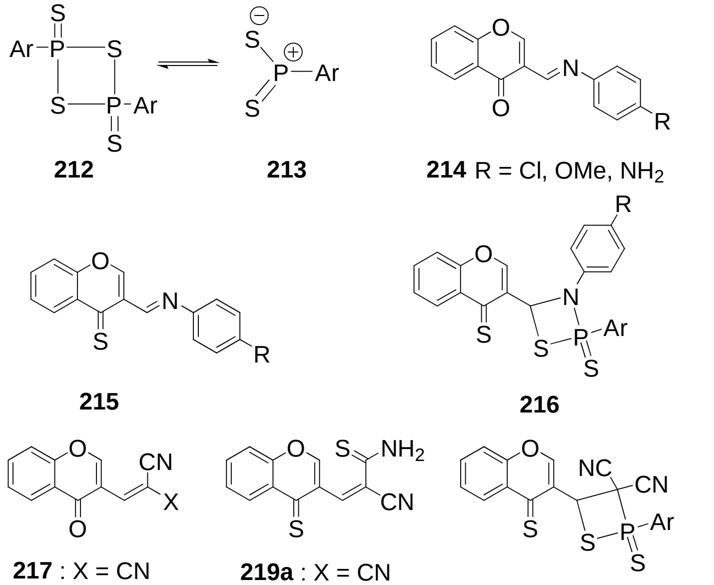


Scheme 19

6. Cycloaddition

6.1. [2+2]Cycloaddition

2,4-*Bis*-(4-methoxyphenyl)-1,3,2,4-thiaphosphetane-2,4-disulfide (Lawesson's reagent, LR) **212** capable of thiating a carbonyl group stays at elevated temperature in equilibrium with the monomeric 1,2-dipolar species **213**. It can convert the Schiff base **214** into the chromonethione **215** and 1,3,2-thiazaphosphetidine derivative **216**, the latter arising through [2+2]cycloaddition of **213** with the azomethine double bond of **215**. LR under similar conditions converts **217** into **219a** and **220**; it also converts **218** to **219b** that involves its NH_2 and ester groups to further undergo cyclization with a second molecule of **213**.[173]



212 213 214 R = Cl, OMe, NH_2

215 216

217 : X = CN
218 : X = CO_2Et

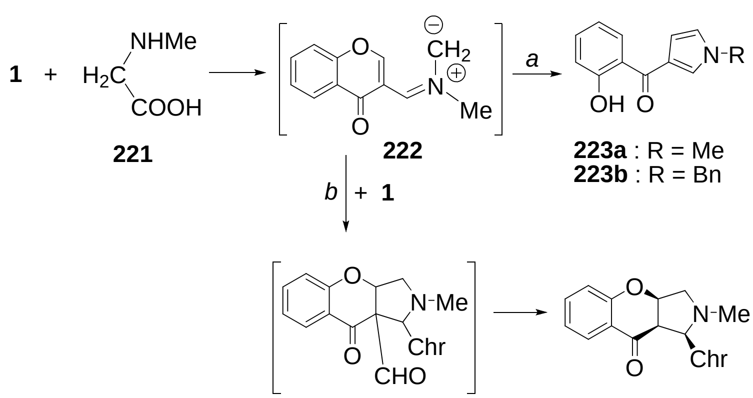
219a : X = CN
219b : X = CO_2Et

220

For **212**, **213**, **216** and **220** : Ar = C_6H_4-OMe(*p*)

6.2. [3+2]Cycloaddition

Reaction of ChrCHO with *N*-methylglycine (sarcosine) **221** is dependent on the reaction conditions. The reaction in refluxing toluene containing PTS forms 1-methyl-3-salicyloylpyrrole **223a**.[174] Here the dipolar compound **222** undergoes 1,5-electrocyclization with concomitant opening of the pyran ring (Scheme 20 – path a). The above reaction in refluxing toluene in the absence of any acid catalyst gives the pyrrolo[3,4-*b*]chroman **225** in addition to **223a**. The compound **225** arises by 1,3-dipolar addition of the ylid **222** to the pyran 2,3-olefinic bond of **1** followed by deformylation (Scheme 20 – path b).[175a] ChrCHO and **221** together in DMF under reflux, however, produces the pyran ring opened form of **225**.[175b] ChrCHO with *N*-benzylglycine hydrochloride in refluxing 1,4-dioxane containing K_2CO_3, however, gives only the pyrrole **223b**.

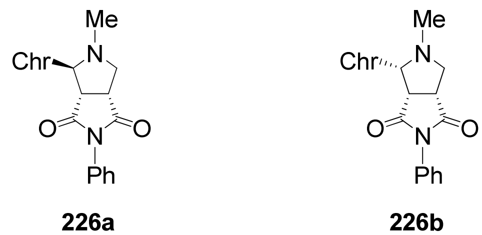


221 222 223a : R = Me
223b : R = Bn

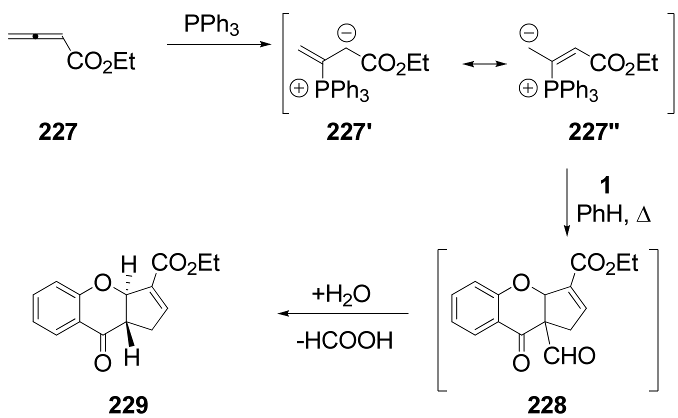
224 225

Scheme 20

When the azomethine ylid **222** is generated in the presence of *N*-phenylmaleimide, the cycloadducts **226a** and **226b** are obtained in 60% yield as a mixture of *cis*/*trans* diasteroisomers, the pyrrole **223a** also being formed in 27% yield. The ylid **222** fails to add to dipolarophiles as dimethyl fumarate, DMAD, 1,4-naphthoquinone, only pyrrole **223a** being formed in nearly 80% yield.[175a]



The 1,3-dipole **227'** generated in situ from the allene ester **227** and PPh_3 adds to ChrCHO, the resultant adduct **228** undergoing deformylation to the cyclopentenobenzopyranone **229** (Scheme 21).[176]

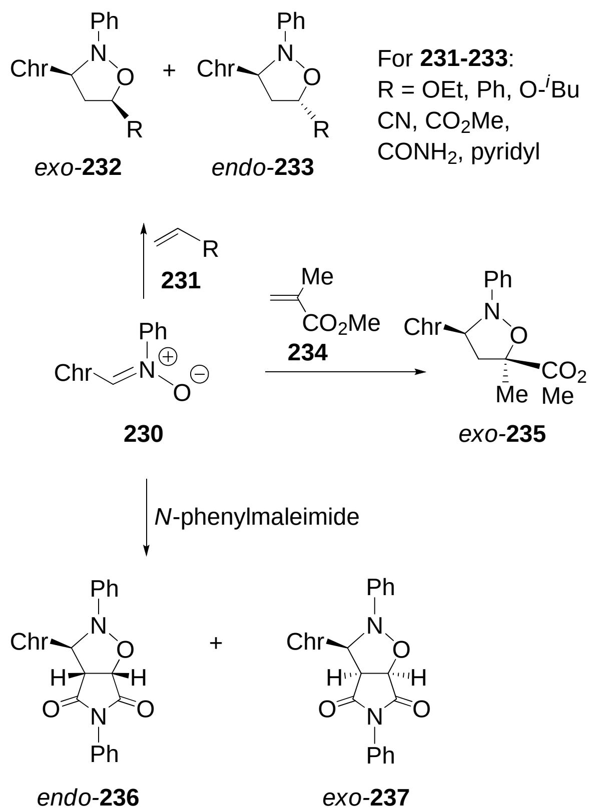


Scheme 21

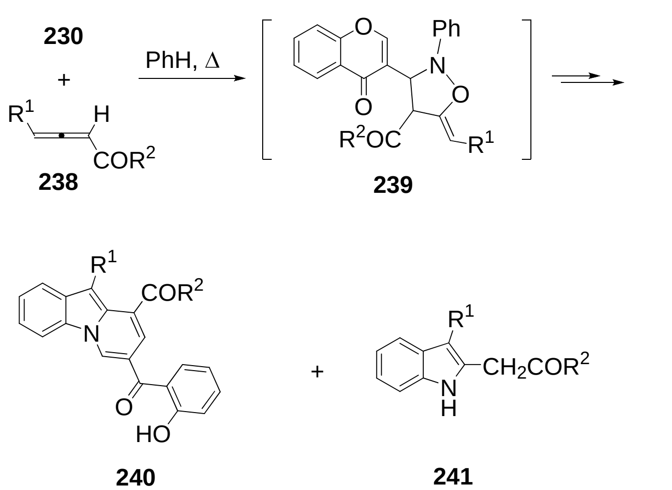
Regio- and steroeselective 1,3-dipolar cycloadditions of *C*-(chromon-3-yl)-*N*-phenylnitrone **230** with several dipolarophiles in dry DCM at room temperature have been carried out. With **230** the dipolarophile **231** (R = OEt, Ph, *i*-BuO, CN, CO_2Me, $CONH_2$, pyridyl) gives a mixture of exo- and endo- adducts **232** and **233**, methyl α-methylacrylate **234** only the exo-adduct **235**, and *N*-phenylmaleimide a mixture of endo-**236** and exo-**237** adducts (Scheme 22).[177] Many of these chromenylisoxazolidines possess excellent antiproliferative activity against some selected human cancer cells.

The allenic ester **238a** with the nitrone **230** in benzene under reflux gives the benzindolizine **240a** and a trace amount of the indole **241a** whereas the ketone **238b** and the nitrone **230** under the same conditions give indolizine **240b**, no indole as **241b** is detected; in both cases the products are admixed with varying amounts of the nitrone rearrangement product namely 3-

formyl-2-phenylaminochromone and both the products **240** and **241** arise through the initially formed [3+2] cycloadduct **239** of the nitrone **230** and the allene **238** (Scheme 23).[178]



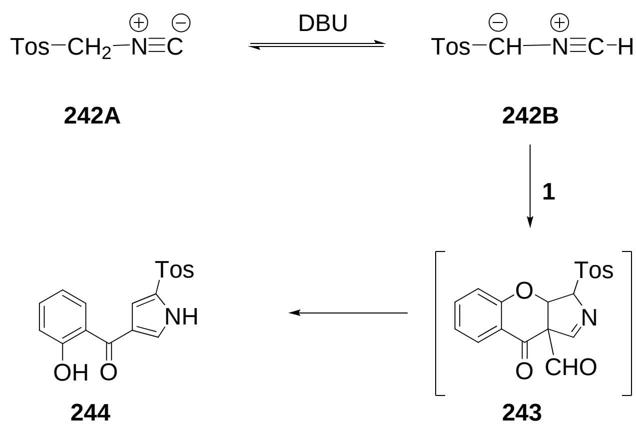
Scheme 22



For **238-241**:**a** = R_1 = H, Me; R_2 = OEt
b = R_1 = H, Ph; R_2 = Me, CH_2Ph,$CH_2C_6H_4OMe$(*p*)

Scheme 23

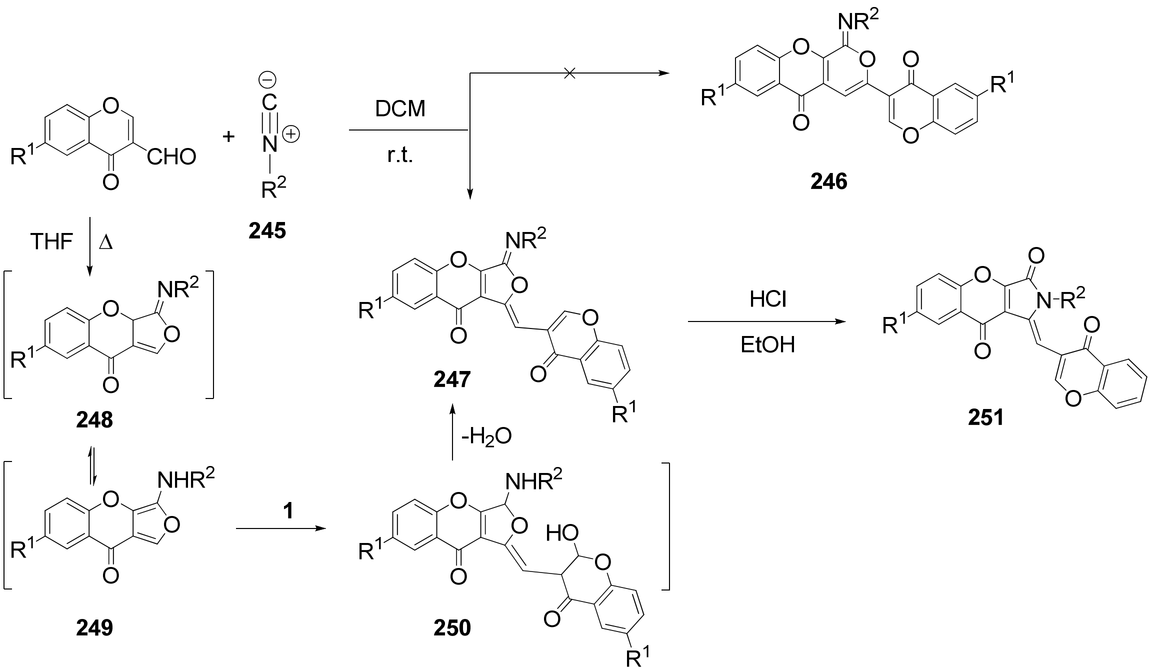
In the presence of the base DBU, tosylmethylisocyanide (TosMIC) **242A** remains in equilibrium with the 1,3-dipole **242B**; the latter is likely to undergo 1,3-dipolar cycloaddition to the olefinic bond of **1** and the resultant adduct **243** by base catalyzed deformylative pyran ring opening and a subsequent 1,5-H shift to form 2-tosyl-4-(2-hydroxybenzoyl)pyrrole **244** (Scheme 24). DBU catalyzed reaction of **1** with TosMIC in THF at room temperature indeed gives the pyrrole **244** in ~60% yield. The pyrrole **244** is also obtained but in lower yield (~25%) when the above reaction is performed with K_2CO_3 in MeOH under reflux; use of a strong base like NaOH forms only a small amount of *E*-Chr-CH=N-CO-Tos along with a polymeric material.[179]



Scheme 24

6.3. [4+1]Cycloaddition

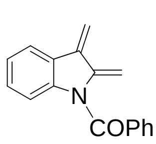
An Indian group[180] reported the formation of the pyranochromene **246** (R^1 = H, Me, Cl; R^2 = *c*-hexyl) from the reaction of 3-formylchromone with cyclohexyl isocyanide **245** (R^2 = *c*-hexyl) in DCM at room temperature whereas Teimouri[181] assigned the furochromene structure **247** (R^1 = H, Me, Cl; R^2 = *n*-Bu, *t*-Bu, *c*-hexyl, $PhCH_2CH_2CH_2$, Me_3C-CH_2-CMe_2-, $PhCH_2CH_2$) to the product arising from ChrCHO and several alkyl isocyanides under identical reaction conditions, no unequivocal arguments being given in favour of these proposed structures. Later the Indian group[182] subjected the product previously assigned by **246** [R^1 = H; R^2 = *c*-hexyl] to X-ray analysis and rectified its structure as **247** (R^1 = H, R^2 = *c*-hexyl), the stereochemistry around both C=C and C=N bonds being Z. Neo *et al.*[183] apparently unaware of this corrected report[182] reinvestigated the reaction of 3-formylchromones (2 eq.) and several alkyl isocyanides (1 eq.) in THF under reflux and the resultant products were assigned the structure **247** (R^1 = H, Me, Cl, Br; R^2 = *t*-Bu, C_5H_{11}, $PhCH_2$ etc) based on X-ray diffraction analysis and two dimensional NMR methods. Aryl isocyanides are found to be unreactive towards ChrCHO.[183] The mechanism for the formation of **247** from 3-formylchromone and an alkyl isocyanide is shown in scheme 25. The isocyanide **245** undergoes [4+1]cycloaddition with 3-formylchromone to give the adduct **248**; its tautomer **249** functions as a dienamine to undergo Michael addition to the α,β-unsaturated carbonyl functionality of a second molecule of **1** with concomitant opening of the pyran ring, recyclization (→**250**) and water elimination to give furo[3,4-*b*]chromene **247**. The imine **247** in ethanol – conc HCl under conventional heating or MWI rearranges to the pyrrolochromone **251**.[183]



Scheme 25

6.4. [4+2]Cycloaddition or annulation

6.4.1. ChrCHO as a 2π component. ChrCHO can function as a dienophile. Its [4+2]cycloaddition with the appropriate four carbon components followed by *in situ* deformylation leading to either xanthone or benzophenone derivatives or both has been compiled in a recent review article.[184] The publications in this aspect appearing only since 2007 are briefly discussed here. [4+2]Cycloaddition of indole-o-quinodimethane **252**, generated by treating 1-benzoyl-2,3-*bis*(bromomethyl)indole with sodium iodide in DMF or PhMe containing 18-crown-6 under reflux, with **1** is neither regiospecific nor stereoselective in giving after in situ deformylation a stereoisomeric mixture of the dihydroxanthones **253** and **254**.[185] D-A reaction of **1** with pyrazole-*o*-quinodimethane **255** is regiospecific giving only the stereoisomeric mixture of the deformylated cycloadduct **256**. On air oxidation, **253** and **254** are aromatized to the corresponding chromenocarbazoles and **256** to chromeno[3,2-*f*]indazole.[185]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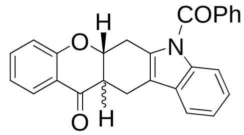
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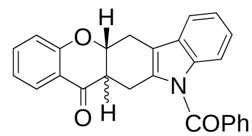
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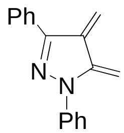
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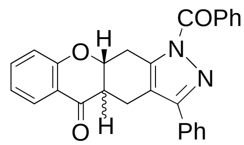
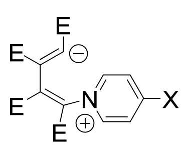

256

Organocatalyzed reaction of 3-formylchromones with acetylenedicarboxylate depends on the nature of the substituents in the chromone substrates and that of the catalyst. The zwitterion **257** (E = CO_2Me or CO_2Et, X = Me or NMe_2) arising from acetylenedicarboxylate and the catalyst 4-picoline or 4-dimethylaminopyridine (DMAP) gets annulated with the 2,3-olefinic bond of 3-formylchromone having an electron-withdrawing bromo or nitro group at its 6-position and the resultant annulated intermediate ultimately gives the xanthone **258** (R = Br or NO_2) by an organocatalyzed elimination process. In contrast, the organocatalyzed reaction of 3-formylchromone **1** and its 6-chloro- and 6-methyl-analogues with acetylenedicarboxylate leads to benzophenones **259** if catalyzed by DMAP or to pyrano[4,3-*b*]chromones **260** if catalyzed by 4-picoline. In the formation of **260**, 3-formylchromone functions as a heterodiene to undergo [4+2]annulation with acetylenedicarboxylate in the presence of 4-picoline.[186,187]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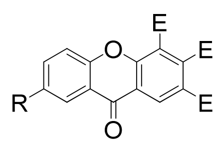
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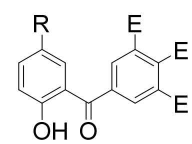
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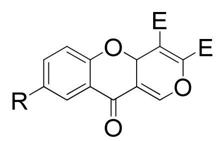
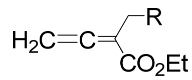
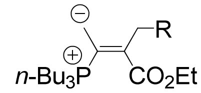

260

For **259-260** : R = H, Cl, Me

A cascade reaction sequence of [4+2] annulation of the zwitterion **262**, generated by addition of tri-*n*-butylphosphine to the allene **261**, with 3-formylchromone followed by deformylation affords in excellent yield and with good diastereoselectivity (~8:1) the tetrahydroxanthone **263** that can be dehydrogenated by DDQ under microwave heating in 1,2-dichlorobenzene to the xanthone **264**.[188]



261 : R = H, Ph, CO_2Et



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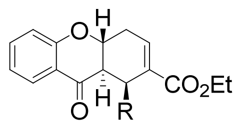

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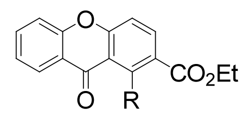
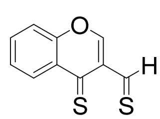


264

6.4.2. ChrCHO as 4π component. ChrCHO when reacted with Lawesson's reagent in boiling toluene gives a mixture of the thione **265** (20%) and [1,3,2]-oxathiaphosphino[4,5-*b*]chromene-5-thione **266** (60%), the former resulting from thiation of ChrCHO by LR and the latter by a [4+2]cycloaddition of **1** with the monomeric 1,2-dipolar species **213** of LR followed by thiation.[173]



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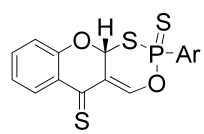
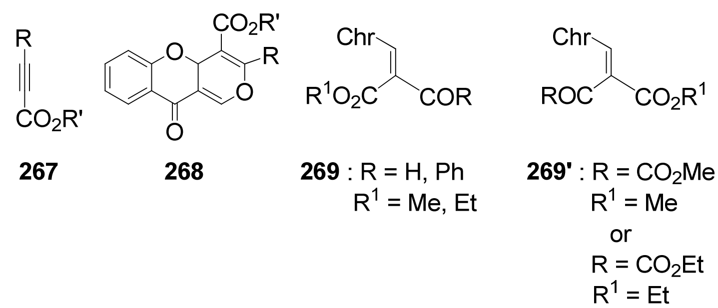
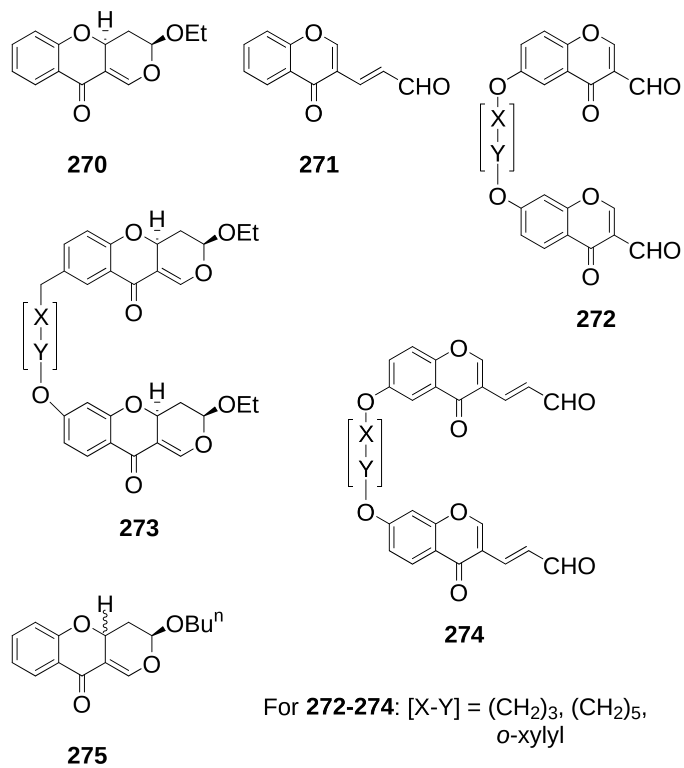


266 : Ar = $C_6H_4OMe(p)$

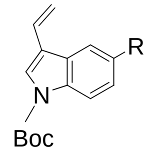
[4+2]-Ring annulation reaction of **1** with electron poor acetylene as **267** (R = H, Ph, CO_2Me,; R^1 = Me, Et, *t*-Bu) in the presence of triphenyl(or tributyl)phosphine in toluene at 80 °C giving pyrano[4,3-*b*]chromone **268** has been reported by Waldman *et al*.[189a] This organocatalyzed hetero-Diels-Alder type reaction proceeds well in PhH and PhMe but not in more polar solvents like DCM or THF, and tributylphosphine drives the reaction faster. This reaction also successfully performed by using DABCO[189a] as well as 4-picoline[186] generates a tricyclic benzopyran with one stereocentre. So an enantioselective version of this reaction has been attempted by using several chiral catalysts.[189b] Five chiral phosphines and naturally occurring alkaloids like cinchonine, cinchonidine, *O*-methylhydroquinidine fail to catalyze the reaction whereas *S*-isomer of the fused pyran **268** (R = CO_2Me, R^1 = Me) is formed in nearly 54% *ee* when **1** is annulated with DMAD in the presence of β-isoquinidine.[189b] Under mild acidic conditions (10% TFA in CH_2Cl_2, rt) the pyranochromone **268** rearranges to ***Z*-269** or ***E*-269'**.[190]



IEDDA reaction of **1** with ethyl vinyl ether leading to the endo-adduct **270** and its conversion by treatment with aqueous acid to *E*-β-(chromon-3-yl)acrolein **271** have been reported long back.[191] Similar cycloaddition of 6,6'-tethered *bis*(3-formylchromone) **272** with ethyl vinyl ether gives **273** that on treatment with NaOMe in MeOH followed by acidification affords the *bis*-acrolein derivative **274**.[192] IEDDA reaction between **1** and *n*-butyl vinyl ether performed under inductive heating with superparamagnetic nanoparticles coated with silica (MAGSILICA) inside the flow reactor gives a mixture of endo-and exo- adducts **275**.[193]



Asymmetric IEDDA reaction of **1** with 3-vinylindole **276** (R = H, Cl, Br, F, OMe) as dienophile catalyzed by various chiral tertiary amine thiourea gives a mixture of endo and exo-adducts **277** (~3.4:1) with enantiomeric excess approaching to 97%. The endo-adduct **277** has been isomerized by Wilkinson's catalyst [Rh(PPh_3)$_3$Cl] (5 mol%) and Et_3SiH (7 mol%) in toluene under reflux to the pyranochromone **278**.[194]



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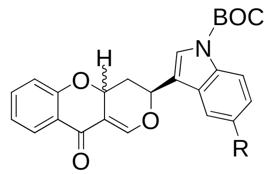

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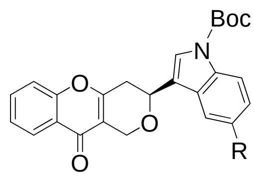
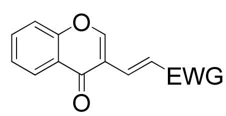


278

6.4.3. [4+2]Cycloaddition of 3-(2-substituted vinyl)chromone. IEDDA reaction of the vinylchromone **279** (EWG = COMe, COPh, CO_2Et, $CONEt_2$, SO_2Ph, CN, Ar) with electron rich ethene **280** (R = R^1 = OMe; R = H, R^1 = NMe_2) is followed by elimination to produce the xanthone **281**.[195] 5-Hydroxychromone **282** with ethyl vinyl ether produces the xanthone **283** along with two other minor products.[196] It is relevant to mention here that the reaction between **279** (EWG = CO_2Et) and several acyclic or cyclic enamine **284** (X = H, Y = Ph; X = Ph, Y = H; XY = $CH_2(CH_2)_{1\text{-}4}CH_2$ involves a domino IEDDA, elimination of dialkylamine and pyran ring opening to give benzophenone **285**, no xanthone being formed at all.[197]



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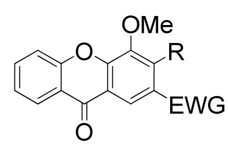

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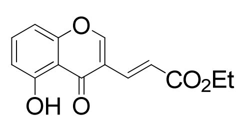

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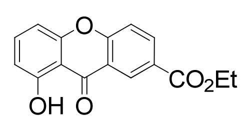
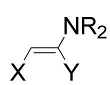
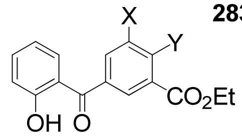


283

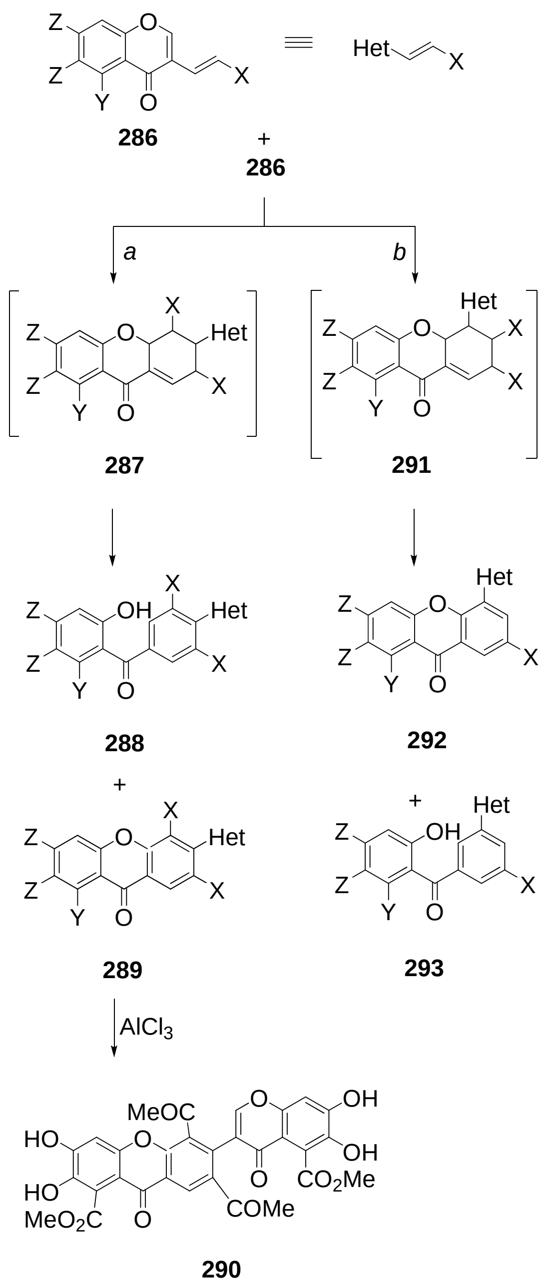


284



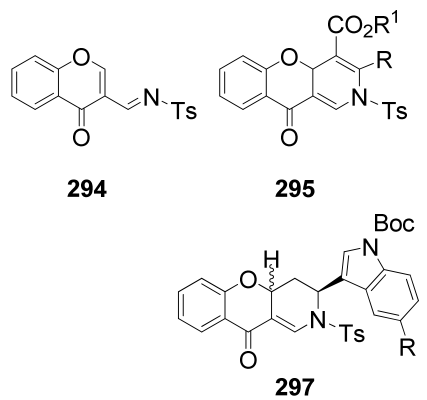
285

Intermolecular [4+2]cycloaddition involving the diene system present in 3-(2-acetylvinyl)chromone) **286** (X = COMe, Y = CO_2Me, Z = OMe) with the acetyl olefinic functionality (dienophile) of its second molecule has been utilized for the synthesis of naturally occurring vinaxanthone. When a solution of **286** in PhMe with 4.0 equivalent of 2,6-di-*t*-butyl-4-methoxyphenol(DTBMP) is heated in a sealed tube at 200 °C for 24 h with air, the cycloadduct **287** (non-isolable) gives xanthone **289** (40%) by aromatization and benzophenone **288** by pyran ring opening (Scheme 26-path a). This intermolecular cycloaddition is not regiospecific, the regioisomer **291** producing the deacylated products **292** and **293** respectively in 17% and 5% yields (Scheme 26-path b). The additive DTBMP is assumed to be oxidized to quinone that brings about aromatization of **287** to **289** and of **291** to **292**. Demethylation of dimethoxyxanthone **289** by $AlCl_3$ in PhMe at 110 °C gives vinaxanthone **290**.[198]

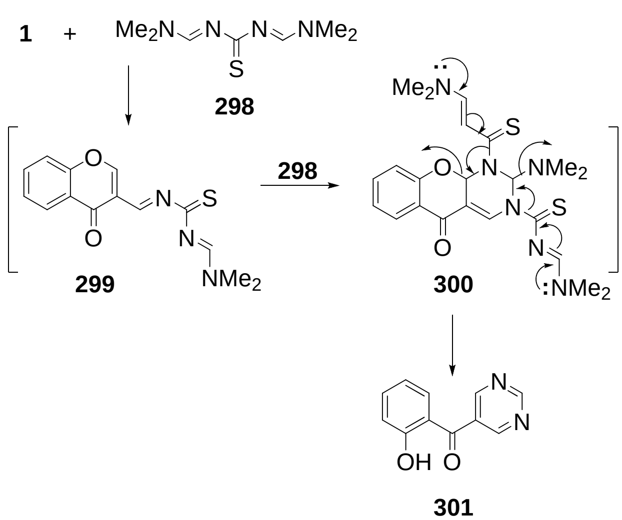


Scheme 26

6.4.4. [4+2]Cycloaddition of 3-iminomethylchromone. 3-Iminomethylchromones function as azadienes to undero [4+2]cycloaddition with several dienophiles. Cycloaddition of the tosylimine **294** with DMAD under PPh_3 or PBu_3 catalysis in boiling toluene gives the chromenopyridine **295** and salicyloylpyridine **296** (R = CO_2Me; R^1 = Me) in 50% and 40% yields whereas PPh_3 catalyzed reaction of **294** with methyl propiolate gives **296** (R = H, R^1 = Me) in 60% yield, the dihydropyridine **295** being obtained in trace amounts.[189b] Chiral tertiary amine thiourea catalyzed IEDDA reaction of **294** with 3-vinylindole **276** (R as before) gives a mixture of exo- and endo- adducts **297**.[194]



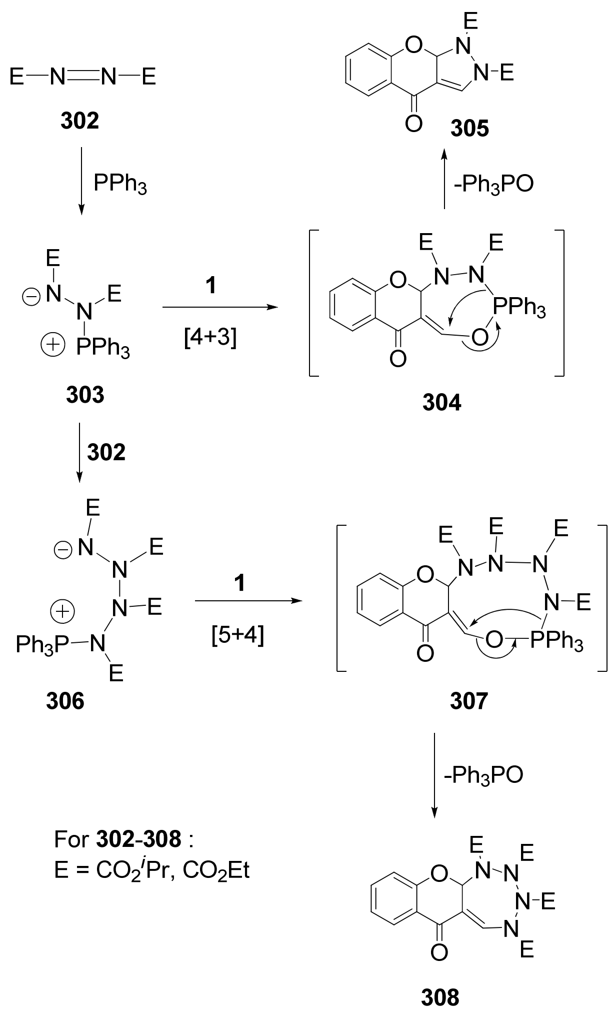
A mixture of ChrCHO and 1,3-*bis*(dimethylaminomethylene)thiourea **298** (1:2) in toluene under reflux gives 5-(2-hydroxybenzoyl)pyrimidine **301** in 78% yield.[199] A plausible mechanism for the formation of **301** is shown in Scheme 27. The initially formed azadiene **299** undergoes IEDDA reaction with the azaenamine functionality of a second molecule of **298**, the resultant intermediate **300** by an elimination – pyran ring opening sequence gives the pyrimidine **301**. Several 6- or 7-monosubstituted 3-formylchromones have been subjected to react with **298** and the resultant pyridines have been evaluated for their antibacterial property.[199]



Scheme 27

6.5. [4+3]-, [5+3]- and [5+4]-Annulation

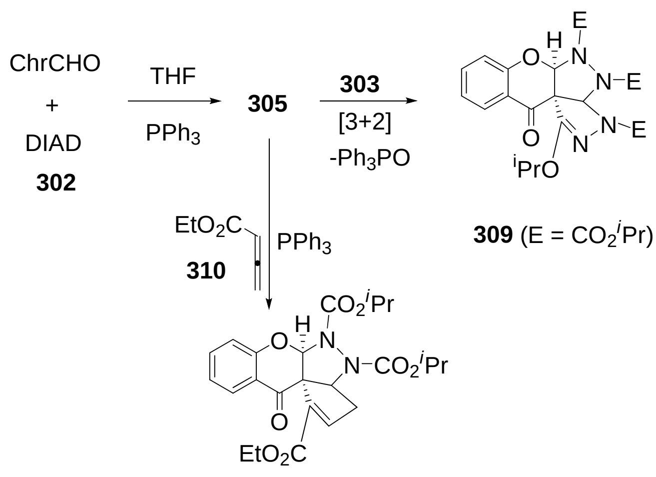
The zwitterionic intermediates generated from dialkyl azidocarboxylates and triphenylphosphine undergo Mitsunobu reaction with 3-formylchromone in toluene under reflux to afford a mixture of chromeno[2,3-*c*]pyrazoline **305** and chromeno[2,3-*e*]tetrazepine **308**.[200] Here the Huisgen zwitterion **303** generated from azidocarboxylate **302** and PPh_3 undergoes [4+3]annulation with ChrCHO and the resultant intermediate **304** elides triphenylphosphine oxide to give fused the pyrazoline **305** (Scheme 28), this elimination of $OPPh_3$ being the driving force of the reaction. The zwitterion **303** adds on to a second molecule of the azo-ester **302** yielding the zwitterion **306** which by a domino [5+4]annulation with 1 (→**307**) and elimination of $OPPh_3$ gives the seven membered ring compound **308** (Scheme 28).



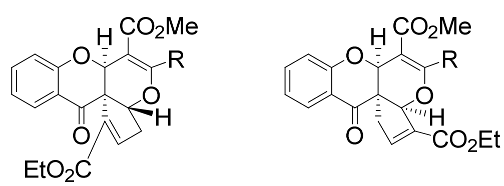
Scheme 28

Baskar and coworkers[201] have reported that an equimolar mixture of **1** and diisopropyl azidodicarboxylate (DIAD) **302** ($E = CO_2{}^iPr$) in THF on treatment with PPh_3 gives **305** (26%)

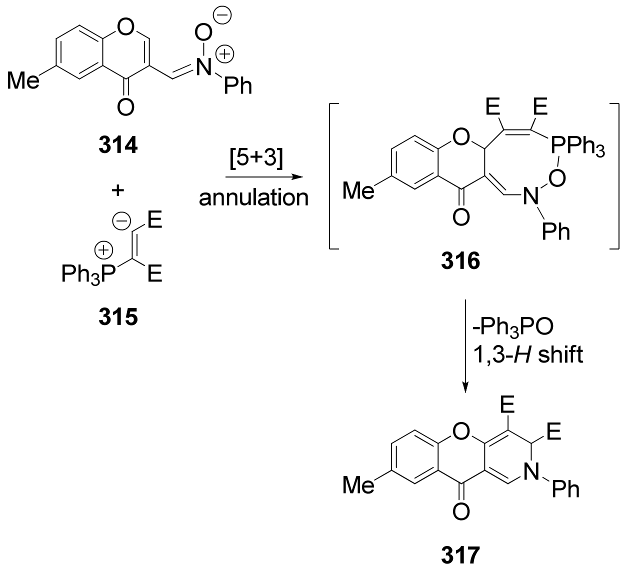
and the tetracyclic compound **309** (27%). Increased amount of DIAD and phosphine in the above reaction gives a higher yield of **309**. Evidently this is an example of stereoselective cascade double annulations, the initially formed pyranopyran **305** undergoing [3+2] cycloaddition with the Huisgen zwitterions **303** followed by elimination of triphenylphosphine oxide. Similar cascade double annulation of **1** first with **303** (E = $CO_2{}^iPr$) and then with allenic ester **310** gives the tetracyclic pyranone **311** (Scheme 29). In contrast to the PPh_3 catalyzed regiospecific [3+2] cycloaddition of **310** with **305**, that with **268** (R = H or CO_2Me, R^1 = Me), the [4+2] adduct of **1** and R-C≡C-CO_2Me (R = H, CO_2Me), gives the two regioisomers **312** and **313**.[201]



Scheme 29



N-Phenylnitrone **314** reacts with DMAD in the presence of PPh_3 (1.2 eq.) to give the pyrido[4,3-*b*]chromone **317**. Here the nitrone **314** and the zwitterion **315** (E = CO_2Me) derived from DMAD and PPh_3 add initially in a [5+3]annulation mode (either in a concerted or stepwise manner) to give the intermediate **316** that by a sequential phosphine oxide elimination and a 1,3-H shift gives the fused pyridine **317** (Scheme 30).[202]



Scheme 30

7. 3-Formylchromone as a Component in One Pot Multicomponent Synthesis

This section deals in the reaction of 3-formylchromone with at least two other different reactants, if not more, put together at a time in one reaction vessel. As ChrCHO contains three electropositive centres, most of the other reacting partners should function as nucleophiles either in the absence or in the presence of a suitable catalyst. The final product arises through a sequence of reactions between the reactants and the reaction intermediates. This reaction is further divided into a few subsections based on the number and nature of the components involved in the multi-component (M-C) reactions.

7.1. Three component condensation between ChrCHO, a nitrogen nucleophile and a third reactant

For the sake of brevity, a few examples of the title type of condensation involving an amine as the nitrogen nucleophile are tabulated in Table 2.

Table 2. Products from 3-C condensation of ChrCHO, an amine and a third reactant along with reaction conditions and references

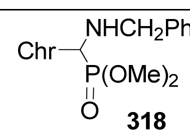
Entry No	Third Reactant	Amine component	Reaction conditions	Product	Ref.
1	$P(OMe)_3$	$PhCH_2NH_2$	Yittria-Zirconia Lewis acid catalyst, aq. MeCN, 60 °C	 318	203

Table 2. Continued

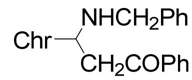
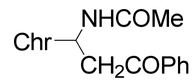
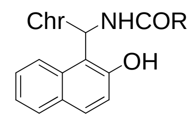
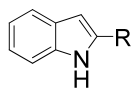
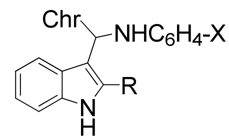
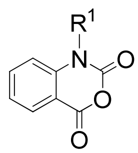
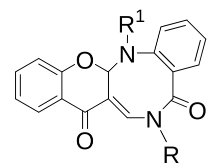
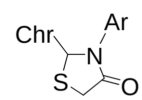
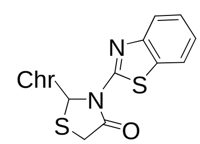
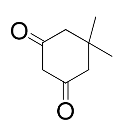
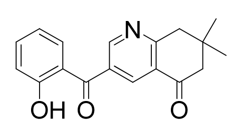
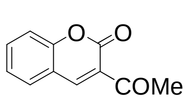
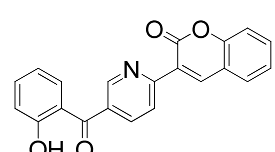
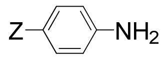
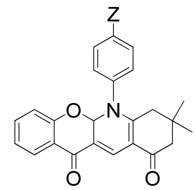
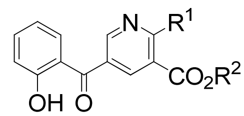
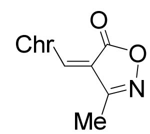
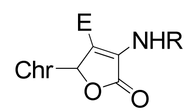
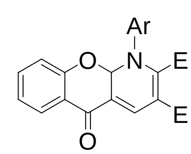
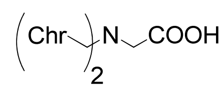
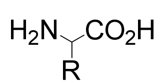
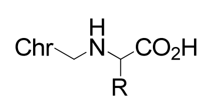
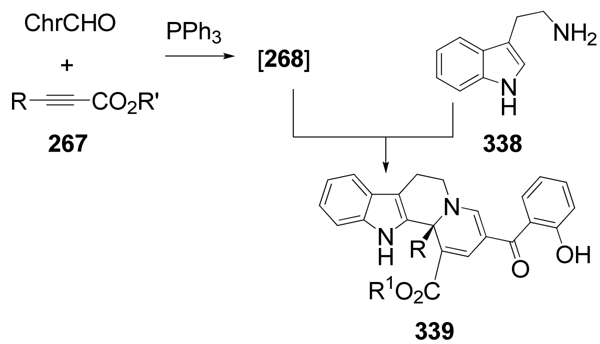
Entry No	Third Reactant	Amine component	Reaction conditions	Product	Ref.
2	PhCOMe	$PhCH_2NH_2$	-do-	 **319**	204
3	PhC≡CH	$MeCONH_2$	MeCN–AcOH–TFA, $AlCl_3$, reflux	 **320**[a]	205a
4	β-Naphthol	$RCONH_2$ (R = Me or OEt)	Ethylammonium nitrate (EAN), neat, r.t.	 **321**	206
5	 R = H, Me	X-$C_6H_4NH_2$ (X = H, Me, Cl, Br, NO_2)	$In(OTf)_3$, MeCN, Δ or MWI	 **322**[b]	207
6	 R^1 = H, Me	RNH_2 (R = H, Me, Ph, $PhCH_2$ etc.)	PhMe, Δ	 **323**	208
7	$HSCH_2COOH$	ArNH2	MWI	 **324**	209
8	$HSCH_2COOH$	2-Aminobenz-thiazole	$ZnCl_2$, PhH, Δ	 **325**	210
9	 (Dimedone)	NH_4OAc	EtOH, Δ	 **326**	211
10		NH_4OAc	EtOH, Δ	 **327**	212

Table 2. Continued

Entry No	Third Reactant	Amine component	Reaction conditions	Product	Ref.
11	Dimedone	 Z = H, Me, OMe	TBAB, H_2O, 70-80 °C	 **328**	213
12	$R^1COCH_2CO_2R^2$ (R^1 = Me, Ph; R^2 = Me, Et)	NH_4OAc	Wells-Dawson heteropolyacid $H_6P_2W_{18}O_{62}.24H_2O$ (WD) catalyst, solvent free, 80 °C	 **329**[c]	214
13	$MeCOCH_2CO_2Et$	$NH_2OH.HCl$	Sodium salt of saccharin, water, Δ	 **333**	215
14	E-C≡C-E (E = CO_2Me, CO_2Et)	RNH_2 (R = alkyl or aryl)	PhMe, $POCl_3$, 80 °C	 **334**	216
15	-do-	$ArNH_2$	EtOH, Δ	 **335**	208
16	CH_2O	H_2NCH_2COOH	MeOH, Δ	 **336**	217
17	CH_2O	 R = Me, CH_2CHMe_2, CH_2CH_2SMe	MeOH, Δ	 **337**	217

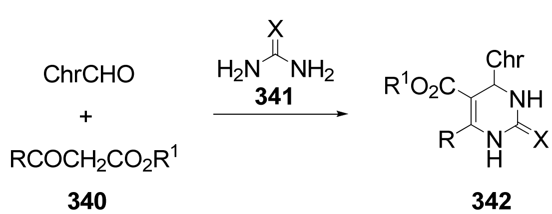
[a] It is also obtained by $SiCl_4$-$ZnCl_2$ catalyzed 3-C condensation of ChrCHO, PhCOMe and MeCN in CH_2Cl_2 at r.t.;[205b] [b]the product **322** is admixed with a little amount of 3-bis(indol-3-yl)methylchromone; [c]the product **329** is contaminated with the corresponding Hantzsch 1,4-dihydro-4-(chromon-3-yl)pyridine derivative.

One pot reaction of 3-formylchromone, alkyne **267** (R = H, CO_2Me; R[1] = Me, Et) and 3-(2-aminoethyl)indole **338** in the presence of PPh_3 gives the tetrahydroindolo[2,3-*a*]quinolizine (centrocountin) **339**. Here the alkyne **267** gives with **1** in the presence of PPh_3 the pyranochromone **268**.[189] Aza-Michael addition of indole **338** through its primary amino group to **268** is succeeded by a domino sequence of reactions to give ultimately the indoloquinolizine **339** (Scheme 31).[218,219] This 3-C condensation is also catalyzed by $ZnCl_2$ (1.2 equiv) in DMSO. Some chiral 1,1'-binaphthyl-2,2'-dihydrogenophosphates have been used to form **339** (R = CO_2Me, R_1 = Me) in 48-63% *ee*.[219]



Scheme 31

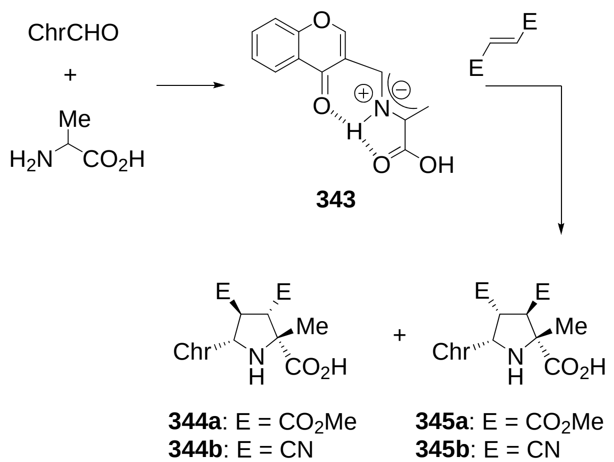
ChrCHO when subjected to Biginelli reaction with a β-ketoester **340** and guanidine or urea or thiourea **341** behaves as a simple aldehyde to give the 1,4-dihydropyrimidine derivative **342** (Scheme 32). Thus ChrCHO, ethyl acetoacetate and guanidine together in DMF-$NaHCO_3$ at 70 °C gives **342** (R = Me, R[1] = Et; X = NH).[220] PTS in ethanol,[221] trifluoroethanol[222] and xanthan sulphuric acid[223] as well as $TaBr_5$[224] under solvent free condition can catalyze the formation of **342** (X = O, S) from ChrCHO, different β-ketoesters **340** (R = Me, R[1] = Me, Et) and **341** (X = O, S).



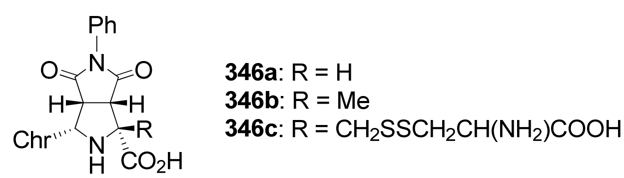
Scheme 32

When a methanolic solution of ChrCHO, DL-alanine, dimethyl fumarate and a few drops of acetic acid is refluxed for 1 h, proline **344a** (60%) without any trace of the other diastereoisomer **345a** is isolated. Here ChrCHO and alanine forms the *syn*-dipole **343** stabilized by double hydrogen bond formation that captures the dipolarophile dimethyl fumarate (Scheme 33).[225]

When dimethyl fumarate is replaced by fumaronitrile, both the diastereoisomers **344b** and **345b** (4.5:1) are obtained. 3-C condensation involving ChrCHO, *N*-phenylmaleimide and an α-aminoacid also leads to a proline derivative; use of glycine, alanine and L-cysteine as the aminoacid in the above 3-C reaction yields **346a,b** and **c**, respectively.[225]

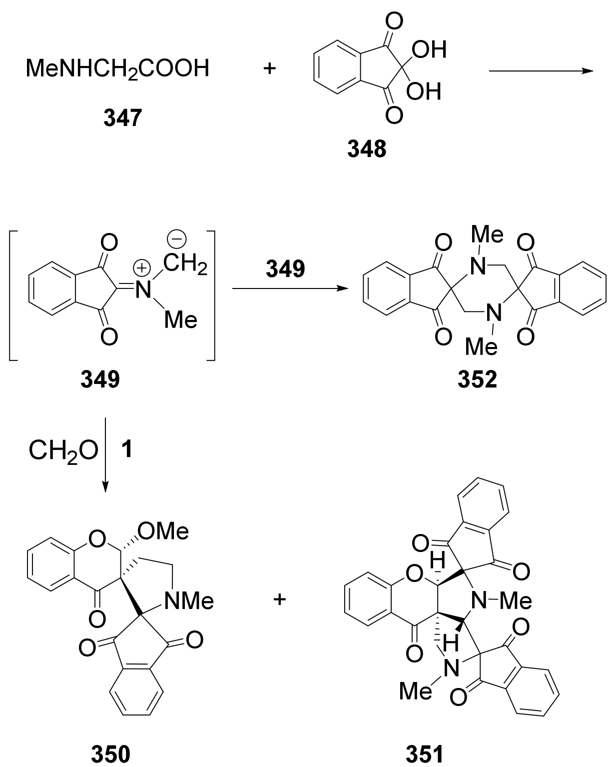


Scheme 33

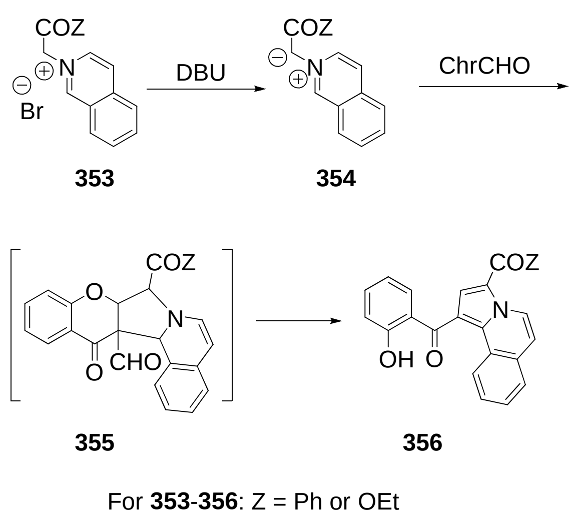


A mixture of ChrCHO, sarcosine **347** and ninhydrin **348** in methanol under reflux produces the dispiropyrrolidines **350** and **351** sometimes admixed with dispiropiperazine **352**.[226] Ninhydrin being far more reactive than ChrCHO forms with sarcosine the azomethine ylid **349** that adds to ChrCHO to give **351**; the compound **350** arises through the reaction of **349** with in situ generated formaldehyde followed by interaction with **1**. Addition of formalin in the reaction mixture produces **350** exclusively.[226] The piperazine **352** arises by dimerization of the ylid **349** (Scheme 34).

Formation of the pyrrolo[2,1-*a*]isoquinoline by stirring a mixture of **1**, isoquinoline and phenacyl bromide (or ethyl bromoacetate) in water containing a surfactant as CTAB and a base as DBU has been reported by Naskar and co-workers.[227] Here the isoquinolinium bromide **353**, derived from isoquinoline and $BrCH_2COZ$ (Z = Ph or OEt), gives in the presence of DBU the dipole **354** that undergoes [3+2]cycloaddition with the pyran-2,3-double bond of **1**; the resultant adduct **355** (non-isolable) undergoes base catalyzed deformylation followed by pyran ring opening and air oxidation to give the fused isoquinolidine **356** (Scheme 35).

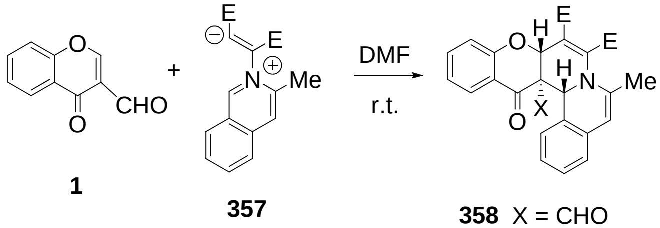


Scheme 34



Scheme 35

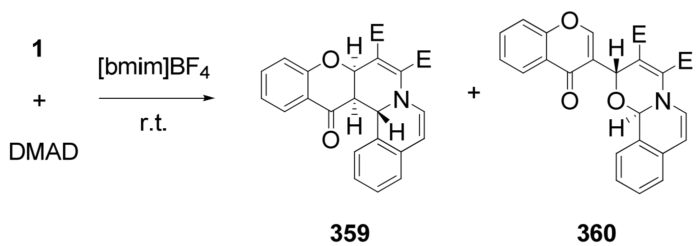
The 1,4-dipole **357** derived from 3-methylisoquinoline and acetylene dicarboxylate undergoes [4+2]cycloaddition with the pyran 2,3-olefinic bond of **1** to give the chromenopyridoisoquinoline **358** (Scheme 36).[228]



For **357** and **358** : E = CO_2Me or CO_2Et

Scheme 36

[4+2]-Dipolar cycloaddition of the zwitterion generated from isoquinoline and DMAD in ionic liquid [bmim]BF_4 at room temperature with pyran 2,3-olefinic bond of **1** followed by deformylation gives **359** and that with its aldehyde carbonyl group gives **360** (Scheme 37), the two products being formed in 8:2 proportion in 72% total yield.[229]



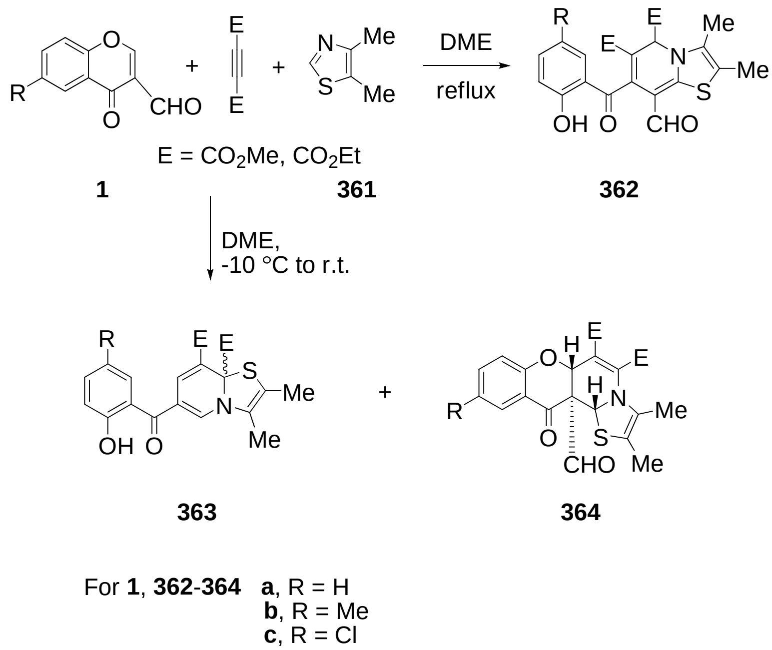
For **359** and **360** : E = CO_2Me

Scheme 37

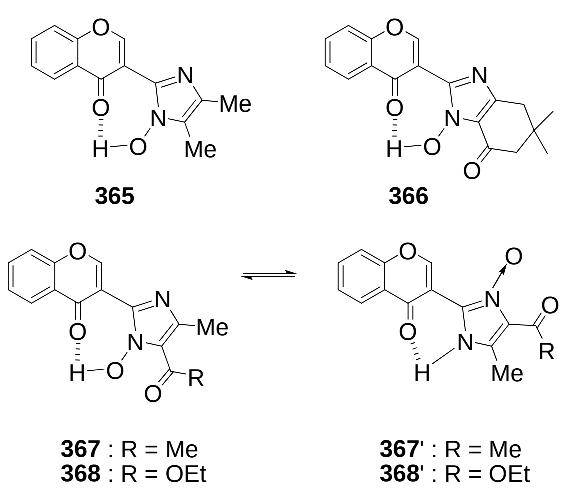
The 1,4-zwitterion derived from 4,5-dimethylthiazole and acetylenedicarboxylate has been shown to react at low temperature readily with 3-formylchromone **1** giving the thiazolo[3,2-*a*]pyridines **363** and **364**. The said reaction with **1a** as the substrate in DMF at -10 °C to r.t. gives **363a** and **364a** in 45 and 4% yield, respectively whereas **1b** and **1c** having electron donating substituents at *p*-position of the pyran oxygen, the yields of **363b,c** and **364b,c** being around 7 and 35%. However, at higher temperature the thiazolopyridine **362** is formed as a mixture of two rotamers presumably after a 1,2-aryl migration from **364** (Scheme 38).[230]

An example of 3-C reaction involving 3-formylchromone and two nitrogen nucleophiles is also known. 2-(3-Chromenyl)-1-hydroxyimidazoles **365-368** have been prepared by one pot three component condensation of unsubstituted 3-formylchromone, $AcONH_4$ and the appropriate α-hydroxyiminoketone in hot glacial acetic acid and their protropic tautomerism studied.[231] C2-H of the chromone moiety of all these 1-hydroxyimidazoles in CD_3CN +CF_3SO_3H as well as in TFA appears as a narrow singlet (at $\delta \sim 9.50$) precluding the tautomeric exchange process. 4,5-

Dimethylimidazole **365** exists in solution exclusively as the *N*-hydroxytautomer regardless of the nature of the solvent. In a hydrogen bond acceptor DMSO-d_6, 5-carbonylimidazoles **366-368** exist in the *N*-oxide form. In a weak hydrogen donor $CDCl_3$, **366** also exists as the *N*-oxide tautomer whereas **367-368** exist in a tautomeric equilibrium, the *N*-oxide forms **367'** and **368'** prevailing over the *N*-hydroxy ones **367** and **368**.

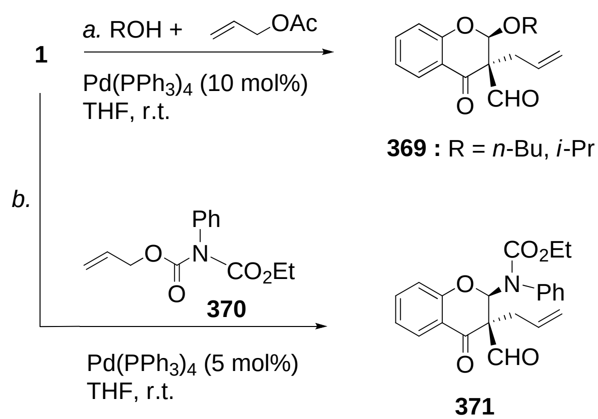


Scheme 38



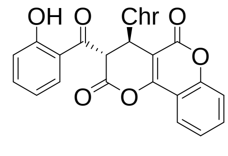
7.2. Three component reactions of 3-formylchromone with reagents other than a nitrogen nucleophile

Palladium catalyzed three component coupling reaction between 3-formylchromone, alcohol and allyl acetate leads to the highly substituted chromanone **369** (Scheme 39 – path a).[232] This reaction most probably proceeds via the formation of the benzopyrylium cation, generated from the Pd-catalyzed reaction between chromone **1** and allyl acetate. The subsequent trapping of the benzopyrylium cation by alcohol gives the corresponding product **369** in excellent yield. This alkoxy-allylation reaction is highly diastereo-selective and only one diasteroisomer is obtained. The chromanone **371** very much analogous to **369** is obtained by Pd-catalyzed decarboxylative aza-Michael addition – allylation reaction between **1** and allyl carbamate **370** (Scheme 39 – path b).[233] The plausible formation of **371** by Pd-catalyzed three component coupling among **1**, allyl acetate and ethyl *N*-phenylcarbamate has not been attempted.

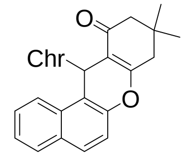


Scheme 39

Diastereoselective synthesis of the pyrano-fused coumarin **372** via DBU catalyzed 3-C reaction of ChrCHO, 4-hydroxycoumarin and 3-bromo-4-hydroxycoumarin has been achieved.[234] The compound **372** arises by a sequence of intramolecular lactonization-delactonisation of the initially formed *bis*(coumarin-3-yl)(chromon-3-yl)methane **172**.[149,151] An equimolar mixture of **1**, dimedone and *β*-naphthol in hot AcOH gives the naphthopyran **373**; use of Meldrum's acid in place of dimedone in the above reaction produces the naphthopyrone **374** admixed with the pentacyclic compound **375**. Proper mechanisms for the formation of **373-375** have been proposed.[235] The heterodiene **376** (R^1 = H, R^2 = Ph; R^1 = R^2 = Me), preformed from 3-boronoacrolein pinacolate and hydrazine $H_2NNR^1R^2$ (R^1 = H, R^2 = Ph; R^1 = R^2 = Me) is heated together with *N*-methylmaleimide and 3-formylchromone in toluene at 85 °C; the initially formed bicyclic allylic boronate intermediate **377** reacts with ChrCHO to give the highly substituted piperidine derivative **378** after hydrolytic workup.[236] Passerini reaction involving ChrCHO, tosylmethylisocyanide and benzoic acid gives chromenyl-amido ester **379** that can be transformed into chromenylacetamide **380** by treatment with NaOEt-EtOH.[237]



372



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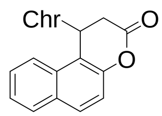

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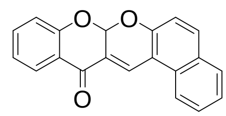

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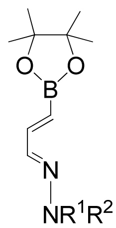

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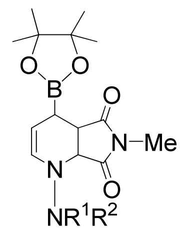

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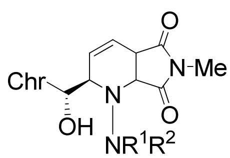

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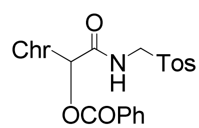

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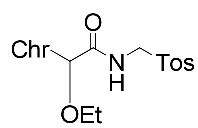
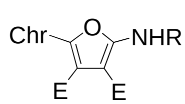


380

An equimolar mixture of ChrCHO, alkylisocyanide RNC (R = *t*-Bu, *c*-hexyl) and methyl (or ethyl) acetylenedicarboxylate in PEG-400 at room temperature is reported to give the chromenylfuran **381**[238] but that in benzene at 40 °C a mixture of **381** and the cyclopentanochromone **382**.[239] The reaction of ChrCHO with the zwitterionic intermediate generated *in situ* from RNC and acetylenecarboxylate (1:2) in benzene at 40 °C affords an isomeric mixture of the cyclohepta[*b*]chromene carboxylates **383** and **384**.[239]



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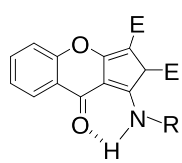

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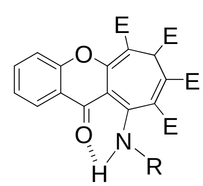

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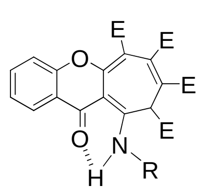
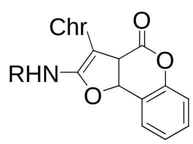


384

For **381**-**384** : E = CO_2Me or CO_2Et

The formation of the furocoumarin **385** and biscoumarin **386** by treating ChrCHO with 4-hydroxycoumarin and cyclohexylisocyanide in ethanol-pyridine under reflux has been rationalized.[240] The compound **386** is also obtained by reacting *bis*(coumarin-3-yl)(chromon-3-yl) methane **172**[149,151] with cyclohexylamine under similar condition.[240] An equimolar mixture of ChrCHO, cyclohexylisocyanide and ninhydrin in a boiling mixture of DCM and MeOH (7:1 by volume) affords the furochromone **387a** that on hydrolysis by HCl-MeOH leads to the fused furanone **387b**, no dehydration taking place.[182] The one pot three component reaction of ChrCHO, 1,3-disubstituted barbituric acid and R^2NC (R^2 = alkyl) in DMF at room temperature furnishes the furo[2,3-*d*]pyrimidine **388**. The product **388** presumably arises via [4+1]cyclization of R^2NC with the initially formed condensate of **1** and barbituric acid followed by a 1,3-H shift.[241]



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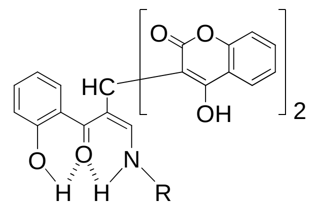

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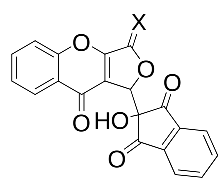
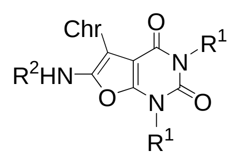


387a X = NR
387b X = O

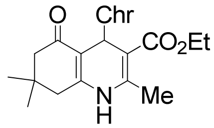


388 R^1, R^2 = Alkyl

For **385**-**387** : R = c-hexyl

7.3. 3-Formylchromone as a component in the four component reactions

Application of the Hantzsch procedure for synthesis of 1,4-dihydropyridine in one-pot reaction of ChrCHO, dimedone, ethyl acetoacetate and ammonium acetate gives the cyclohexanopyridine derivative **389**.[242,243] An Ugi four component reaction of 3-formylchromone $ArNH_2$, RNC (R = *t*-Bu, *c*-hexyl, 2,6-dimethylphenyl) and cyanoacetic acid at room temperature gives the diamide **390**.[244] Similar 4-C reaction involving 3-formylchromone, 2-haloaniline **391** (X = Cl, Br, I), RNC (R = *t*-Bu, *c*-hexyl) and R^1COOH (R^1 = Me, Et) provides the Ugi product **392** convertible into 1-benzopyrano[3,2-*c*]quinolin-12-one **393** by a ligand free Pd-catalyzed intramolecular C-H arylation protocol [$PdCl_2$ or $Pd(OAc)_2$, KOAc, DMF, Δ) at the C-2 position of the chromone moiety.[245] Synthesis of chromone containing tripeptide **394** *via* a pseudo-five-component reaction between ChrCHO, Meldrum's acid, alkylisocyanide RNC and $ArNH_2$ (2-equivalent) in CH_2Cl_2 at room temperature has been achieved.[246]



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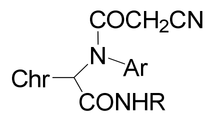

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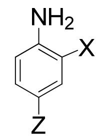

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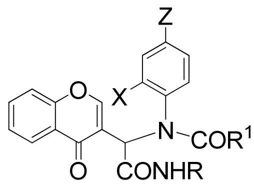

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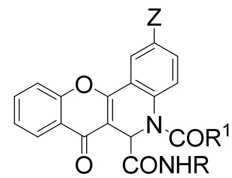
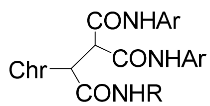
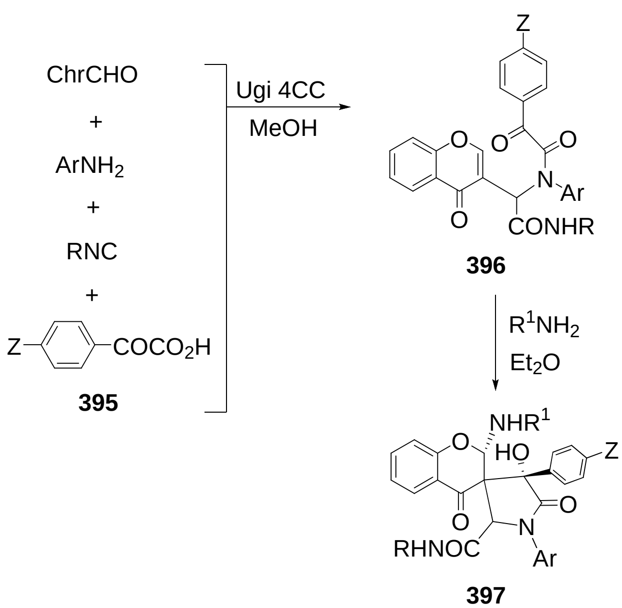


393 : R = *t*-Bu, c-hexyl
R^1 = Me, Et; Z = H, Me



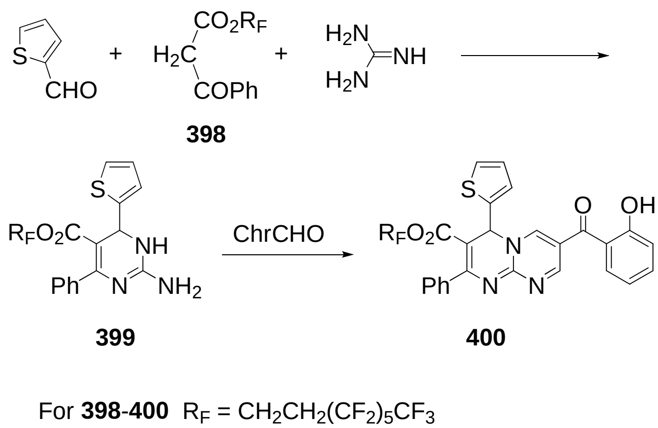
394

Marcaccini *et al*.[247] have reported a diastereoselective, one-pot, two step synthesis of the spiropyrrolidinochromanone **397**. Their method consists of an Ugi 4-C condensation of 3-formylchromone, $ArNH_2$ (Ar = Ph, substituted phenyl), RNC (R = *t*-Bu, *c*-hexyl, 2,6-diphenylphenyl) and glyoxylic acid **395** (Z = H, OMe) followed by an aza-Michael addition of a second amine R^1NH_2 (R^1 = $CH_2C_6H_4$-X; X = H, Cl etc.) to the resultant Ugi product **396** and subsequent cyclization (Scheme 40).[247]



Scheme 40

One pot three component reaction of thiophene-2-carbaldehyde, the β-ketoester **398** and guanidine followed by addition of 3-formylchromone as the fourth component in the pot gives the pyrimidopyrimidine **400** evidently through the intermediacy of the 3,4-dihydropyrimidine **399** (Scheme 41).[248]



Scheme 41

8. Conclusions

Interest in the chemistry of 3-formylchromone and its use as a synthon for several novel heterocyclic systems has been amply vindicated by a spate of publications. The present article, complementary to an earlier one[6] is a comprehensive survey of a huge number of publications that have appeared mainly since 2007 to February 2014 and it provides a quick view of the research work already done in the title topic.

Acknowledgements

Helpful discussion with Dr. C. Bandyopadhyay, Department of Chemistry, R. K. Mission Vivekananda Centenary College, Rahara, Kolkata 700118 India, who is presently having significant contribution in the title subject is gratefully acknowledged. A.C. acknowledges IACS for a research fellowship.

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