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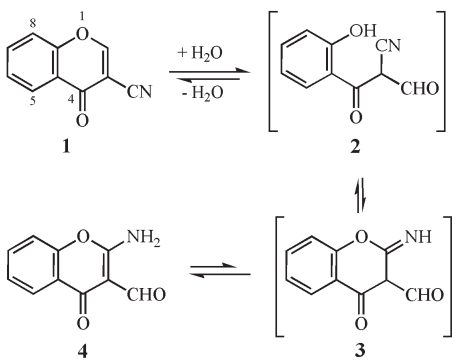
I Introduction.

Of all the cyano substituted 1-benzopyran-4-ones [1], the title nitrile (trivial name: 3-cyanochromone) **1** is unique because of diverse functionalities being imbedded in it. Being an α,β-unsaturated nitrile as well as α,β-unsaturated ketone, it possesses three electron deficient sites *viz*. C-2, cyano carbon and carbonyl carbon, the last one having obviously the least electrophilicity compared to the other two. So an initial addition of a nucleophile to **1** and any subsequent transformation, if possible, of the adduct will depend on the nature of the nucleophile as well as the reaction conditions. The presence of two electron-withdrawing groups at the same end of the pyran 2,3-olefinic bond is likely to make this olefin a sufficiently active dienophile in [4+2]cycloaddition with dienes, and dipolarophile in [3+2]cycloaddition with 1,3-dipoles. Furthermore, the chromone **1** can be regarded as an intramolecular enol ether of the aldehyde **2** that can give rise to 2-amino-3-formylchromone **4** *via* **3** (Scheme 1). So a nucleophilic 1,4-addition to the α,β-unsaturated nitrile (or ketone) functionality of **1** with concomitant opening of the pyran ring followed by recyclisation is equivalent to the nucleophilic 1,2-addition to the aldehyde function of **4**; in other words, the nitrile **1** is 'chemically equivalent' to the aminoaldehyde **4** under certain reaction conditions. Because of its above stated characteristics, the reactions of the title nitrile **1** alone are the subject matters of many publications. The present review gives a comprehensive account of its synthesis and reactions reported up to 2004. In this review the 4-oxo-4*H*-1-benzopyran-3-yl moiety is abbreviated as 'Chr' so that 1-benzopyran-4-one having 'X' substitution at its 3-position may be represented by Chr-X.

Scheme 1



1 **2** **4** **3**

II Synthesis.

3-Formylchromone **5** when refluxed with hydroxylamine hydrochloride in ethanol containing hydrochloric acid gives *via* the aldoxime **6** a mixture of the nitrile **1** (76%) and the isoxazole **8** (8%), the latter being converted to the former by heating in dimethyl sulphoxide [2,3]. Heating a mixture of **5**, hydroxylamine hydrochloride and sodium formate in formic acid under reflux produces **1** in 51% yield [4]. Sulphuric acid catalyzed conversion of the oxime ether **7** (R = Me) [5a] and zirconium tetrachloride mediated conversion of **7** (R = Ar) [5b] to the nitrile **1** are also known.

Chr-X

1: X = CN
5: X = CHO
6: X = CH=NOH
7: X = NOR

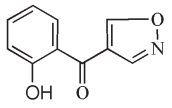


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Figure 1

III Initial Reaction at the Carbonyl Group.

The only known initial reaction at the carbonyl group of **1** is its thionation by Lawesson's reagent in refluxing toluene to 3-cyano-2-chromen-4-thione [6].

IV Reactions Involving Initial 1,2-Addition of a Nucleophile to the Cyano Group.

The nitrile **1** in conc. sulphuric acid yields the carboxamide **9**, which is hydrolysed with 6 *N* H_2SO_4-AcOH (1:1) to the acid **10** [7]. Klutchko *et al* [4] reported the formation of **10** in 55% yield by heating **1** with 55% sulphuric acid for 1 hr. The nitrile **1** when subjected to Ritter reaction (reaction with *t*-butanol in trifluoroacetic acid containing a small amount of conc. sulphuric acid at room temperature) affords *N*-*t*-butylcarboxamide **11** [7]. 1,2-Addition of *N*-pyridinium phenacylide, prepared from *N*-pyridinium phenacyl bromide **12**, to the nitrile function of **1** followed by cyclisation and isomerisation gives the 2-azirine **13** which due to extended π-conjugation is more stable than the corresponding 1-azirine [8]. The reaction of **1** with

sodium azide in the presence of aluminium chloride in tetrahydrofuran affords the tetrazole **14** [2,3].

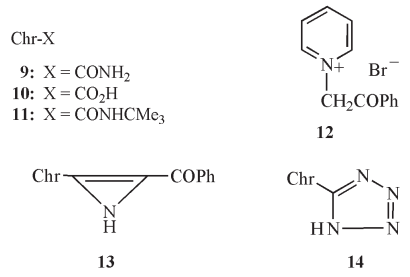


Figure 2

Hydrazine undergoes 1,2-addition to the nitrile function of **1** in ethanol under reflux, the resultant iminohydrazine intermediate **15** (non-isolable) cyclising to the fused pyrazole **19** [9]. The iminohydrazine **16** (isolable) obtained from **1** and phenylhydrazine under similar conditions undergoes, on further refluxing in ethanol, intramolecular 1,4-addition with concomitant opening of the pyran ring to yield the benzoylpyrazole **20** [9]. The 1,2-adduct **17**, similarly obtained from **1** and hydroxylamine, undergoes no further transformation [9]. Guanidine carbonate and **1** when heated together in ethanol under reflux produce the fused pyrimidone **22** *via* **18** and **21** [10].

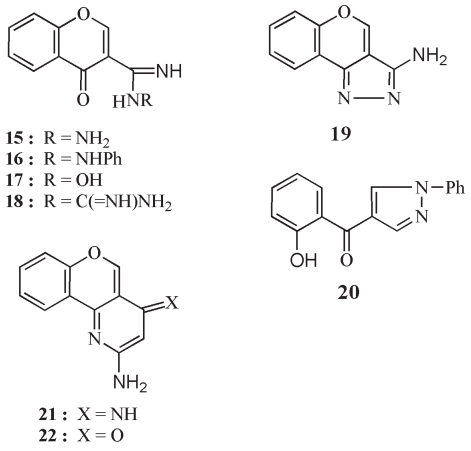
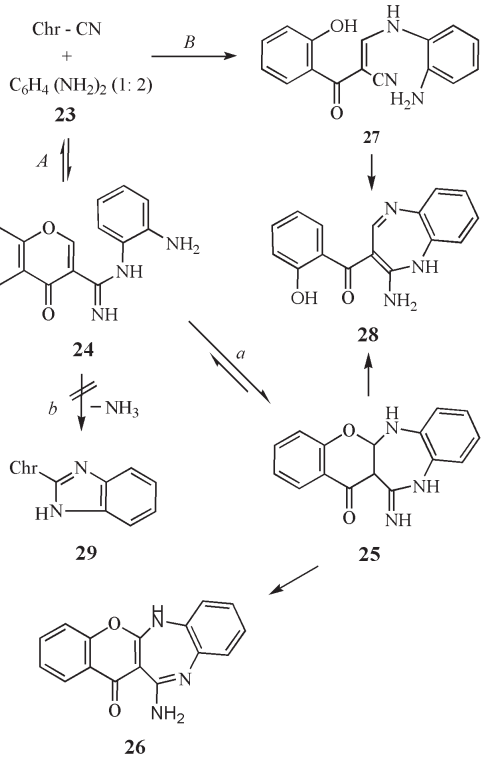


Figure 3

A minor change in the reaction conditions drastically changes the course of reaction between **1** and *o*-phenylenediamine (**23**). Thus, the amidine derivative **24**, initially obtained by refluxing an ethanolic solution of **1** and **23**, on further refluxing in acetic acid undergoes intramolecular 1,4-addition (→ **25**, non-isolable) and subsequent air oxidation to give the pyranodiazepin **26** [11] (Scheme 2 – path *Aa*). An Italian group [12] reported the formation of **27** and **28** from the reaction of **1** with **23** in refluxing ethanol. The enaminonitrile **27** arises by 1,4-addition of the amine **23** to **1** with concomitant opening of the pyran ring (Scheme 2 – path *B*). The diazepin **28** may arise by either cyclisation of **27** or base catalysed pyran ring opening of **25**. Though deaminative cyclisation of **24** to the benzimidazole **29** (Scheme 2 – path *Ab*) is not realised, the latter (**29**) is obtained by digesting **27** as well as **28** in glacial acetic acid [12].

Scheme 2



V Reactions Involving Only the Pyran 2,3-π Bond.

Epoxidation of the pyran 2,3-double bond by treatment with 40% peracetic acid in chloroform containing sodium bicarbonate at room temperature is feasible [13]. Chr-CN dissolved in acetic acid reacts with aqueous sodium hypochlorite, the product **30** being formed by anti addition of an acetoxyl anion and a chloronium cation to the 2,3-olefinic bond; **30** on hydrolysis with aqueous acetic acid in the presence of sodium acetate produces a rearranged compound **31** [14]. Treatment of **1** with lithium dimethylcuprate in tetrahydrofuran at –10 ºC gives a stereoisomeric mixture of the chromanone **32** [15]. Condensation of the 3-cyanobenzopyrilium triflate **33**, prepared from **1** and trimethylsilyl triflate in dichloromethane at 0 ºC, with 1,3-bis-silyl enol ether **34** (R^1 = H, Me, Et, OMe; R^2 = Me, Et, iPr) in dichloromethane at 20 ºC followed by treatment with 10% hydrochloric acid gives a stereoisomeric mixture of the chromanone **35** [16].

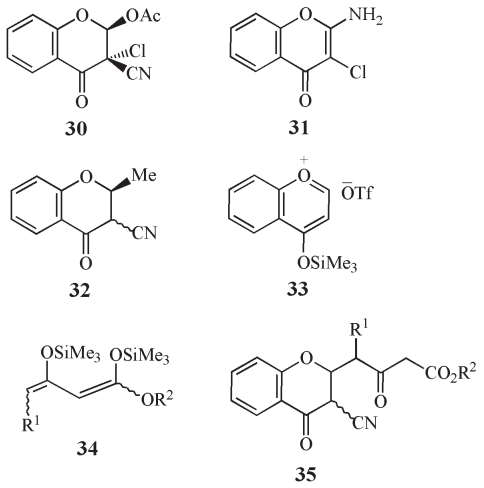


Figure 4

The chromone **1** on being refluxed separately with 2-bromoethanol and chloroacetone in acetone containing potassium carbonate gives respectively the furo[2,3-*b*][1]benzopyran **36** [17] and cyclopropapyran **37** [18], the annulation proceeding *via* conjugate addition of haloethanol or halocarbanion generated from chloroacetone to the chromone followed by intramolecular alkylation.

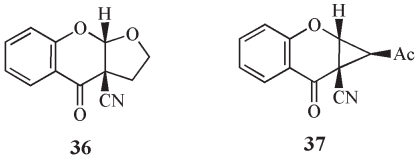
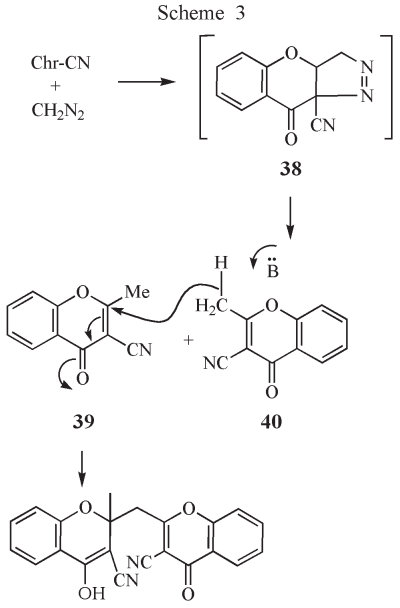


Figure 5

2,3-Olefinic bond of **1** also participatates in proper cycloaddition reactions. Diazomethane undergoes [3+2]cycloaddition with the said olefinic bond giving the 1-pyrazoline intermediate **38** that by a concerted electrocyclic elimination of nitrogen and migration of hydrogen yields 3-cyano-2-methylchromone **39**; base catalysed Michael addition of **39** to the α,β-unsaturated keto function of a second molecule of **39** gives **40** [19a], diazomethane or the pyrazoline **38** functioning as the base (Scheme 3). Diazomethane, diazoethane, 2-diazopropane and *t*-butyldiazomethane bring about alkylation at 2-position of 3-cyano-6-methylchromone [19b].

Hsung *et al* [20-23] have extensively studied the Diels-Alder reaction of the unsaturated nitrile **1** with several dienes. A solution of **1** in toluene when heated separately with the TBS- and TMS-protected Danishefsky's dienes **41** and **42** in a sealed tube at 200-300 ºC for 72-96 hr gives the cycloadducts **44** and **45** in the *endo*:*exo* ratio of 1.3:1 [20] and 1:2 [21], respectively. The chromone **1** and the diene **43** under the same conditions gives **46** with an

Scheme 3



endo:*exo* ratio of 92:8 [20]. The stereochemistry of [4+2]cycloaddition of **1** with electron rich dienes is influenced by the reaction concentrations of the γ-pyrone dienophile **1** [22]. Cycloaddition of **1** with non-oxygenated dienes like 2,3-dimethylbutadiene and cyclohexadiene is to be promoted by the use of titanium tetrachloride, the Lewis acid assisted reaction requiring less time (~ 10 hr) and the *endo*-adduct overwhelmingly predominating over the *exo*-adduct [20].

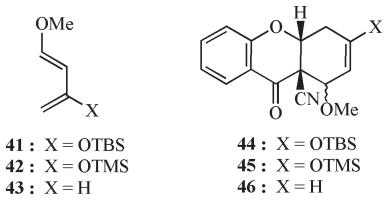


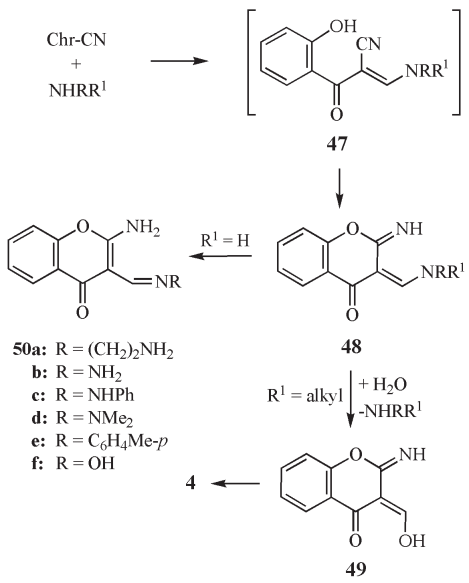
Figure 6

VI Conjugate Addition of Oxygen and Nitrogen Nucleophiles Followed by Pyran Ring Opening and Recyclisation: Formation of 2-Amino-3-formylchromone or Its Derivatives.

The formation of the aldehyde **4** by heating **1** with an aqueous solution (2%) of sodium hydroxide at 70 ºC [24] involves a reaction mechanism akin to the one shown in Scheme 1. The title sequence of reaction of an amine $HNRR^1$ with **1** is depicted in Scheme 4. The nitrile **1** when heated in the presence of morpholine in DMF-H_2O at 60 ºC [25,26] gives **4** through the intermediates **47-49** (RR^1 = $CH_2CH_2OCH_2CH_2$). The formation of **4** by refluxing **1** with ethylenediamine in aqueous ethanol [11] involves

hydrolysis of the aldimine **50a**. Stirring a solution of **1** in dichloromethane with alumina at ambient temperature also produces **4** [18].

Scheme 4



Unlike the initial 1,2-addition of hydrazines to the nitrile function of **1** in refluxing ethanol (Section IV), refluxing benzene induces 1,4-addition of hydrazine and phenylhydrazine producing ultimately the hydrazones **50b** and **50c**, respectively [10]. 1,1-Dimethylhydrazine and *p*-toluidine with **1** under similar conditions yield respectively the hydrazone **50d** and Schiff's base **50e** [27]. The formation of the imidazole **51** together with **4** from **1** and ethylenediamine in refluxing aqueous ethanol also involves initial 1,4-addition of the nucleophile to the α,β-unsaturated nitrile function of **1** [11]. A Polish group [28,29] reported the formation of the oxime **50f** and pyrazolinone **52** by adding **1** at 20 ºC to an aqueous solution of hydroxylamine hydrochloride and sodium hydroxide. The oxime **50f**, like its analogues **50a-e**, arises by cyclisation of the intermediate **54** (Scheme 5 – path *a*) and **52** is formed by conversion of the nitrile **54** to the

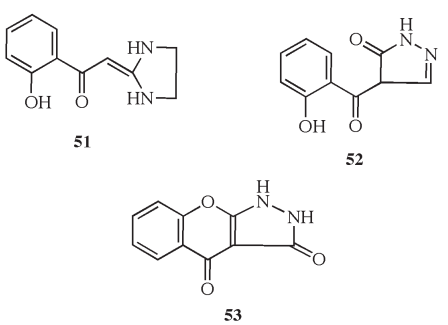
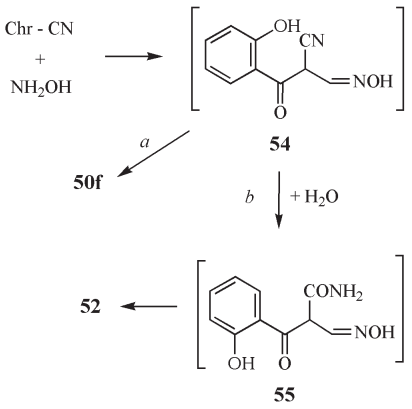


Figure 7

Scheme 5

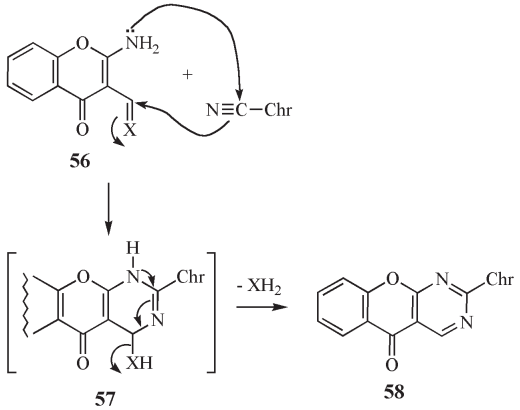


amide **55** and its subsequent cyclisation (Scheme 5 – path *b*). The formation of the fused pyrazole **53** through the intermediacy of the oxime **50f** and of 2-amino-3-cyanochromone by treating 3-formylchromone with $NH_2OH.HCl$ and NaOH in aqueous ethanol [28,29] warrants further scrutiny.

VII Self-condensation of 3-Cyanochromone through 2-Amino-3-formylchromone or Its Derivatives.

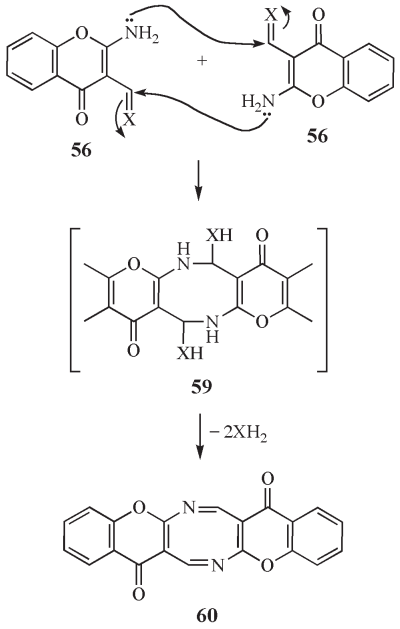
The first report on self-condensation of Chr-CN to [1]benzopyrano[2,3-*d*]pyrimidine **58** by refluxing the substrate with ammonium acetate or 2-amino-3-formylchromone in acetic acid comes from the present laboratory [11]. Here the benzopyran-3-carboxaldehyde **56** (X = O) or the corresponding aldimine **56** (X = NH), generated from **1** and NH_3, reacts with the nitrile functionality of **1** to give the intermediate **57** that eliminates XH_2 to form **58** (Scheme 6). The reported formation of **58** by refluxing the Schiff's base **50e** in DMF [27] or the aldehyde **4** in toluene containing *p*-toluene sulphonic acid [30] entails that each of the above named 2-aminochromone substrates is reconverted under the reaction conditions to Chr-CN that reacts with **50e** or **4** to give **58** *via* **57** (X = NC_6H_4Me-*p* or O).

Scheme 6



Chr-CN when warmed with ethylenediamine in ethanol affords the bis[1]benzopyrano[2,3-*b*:2',3'-*f*][1,5]diazocine **60** hydrolysable to **4** [10]. The hydrazone **50d** in DMF under reflux also produces **60** [27]. The formation of **60** is rationalised by 1,2-addition of the amino group of one molecule of **56** (X = $NNMe_2$ or $NCH_2CH_2NH_2$), derived from **1** and 1,1-dimethylhydrazine or ethylenediamine (Section V), to the hydrazono or imino functionality of a second molecule of **56**; the intermediate **59** thus formed eliminates two molecules of XH_2 giving **60** (Scheme 7). Heating under reflux a solution of 6-ethyl-3-cyanochromone and piperidine in ethanol affords in 80% yield the diazocine **60** having ethyl substitution at its 2-, and 10-position [31]. Here the iminoenamine initially formed from the chromone substrate and piperidine is akin to **48** [$RR^1 = (CH_2)_5$] and a [4+4]cycloaddition reaction involving two such molecules followed by elimination of two molecules of piperidine leads to the said diazocine.

Scheme 7



Three other self-condensation products (**61-63**) of **1** have been reported from a German Laboratory [30,32]. The formation of **61** and **62** by heating **4** in isopropanol containing conc. HCl has been explained in the following way. The aminoaldehyde **4** through its tautomeric form **3** undergoes acid catalysed deformylation to 2-iminochromanone **64** [33] that on aldol condensation with **4** forms **67** (X = NH) (isolable); cyclisation of **67** (X = NH) involving its amino and imino groups forms **61** whereas that involving amino and pyrone carbonyl groups followed by hydrolysis of the imino group forms **62** (Scheme 8). The lactone **62** is also obtained in 30% yield by reacting **1** with 4-hydroxycoumarin **65**, chemically equivalent to **64**, in refluxing ethanol containing DBN *via* the intermediate **67** (X = O). Schurreit [32] has reported without giving any mechanism the formation of **63** in 18% yield by refluxing a mixture of **1** and coumarin **65** in ethanol-piperidine; **63** when refluxed with 30% hydrogen peroxide in trifluoroacetic acid is converted into the lactone **62**. The present authors contend that **63** is formed by condensation of three molecules of 3-cyanochromone, the coumarin **65** having no role in the formation of **63**. Piperidine brings about transformation of **1** to **4** and **64**. Base catalysed 1,4-addition of **64** to the α,β-unsaturated nitrile **1** with concomitant opening of the

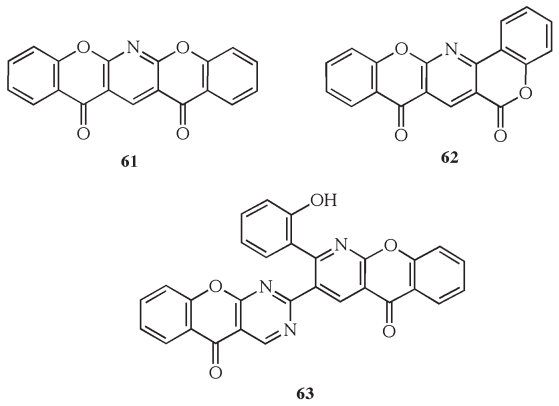
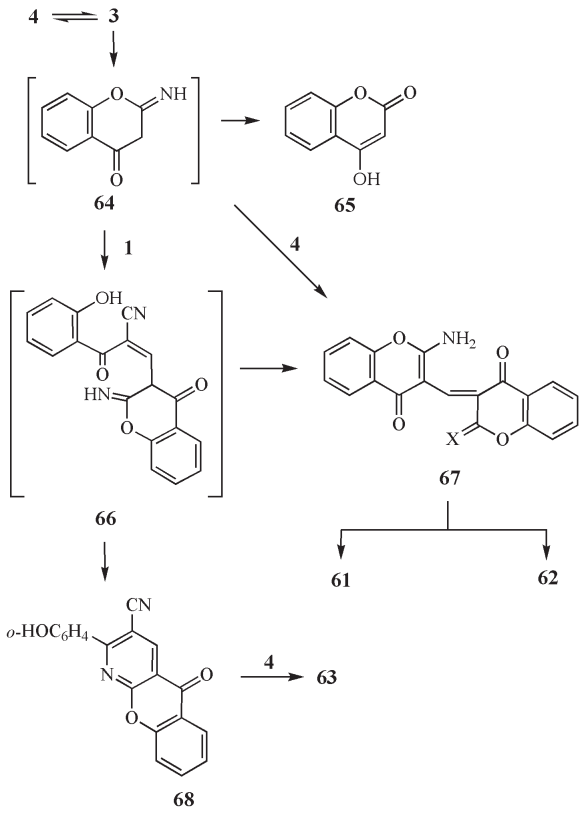


Figure 8

Scheme 8



pyran ring gives **66** that cyclises to **67** (X = NH) as well as **68**. The condensation of 2-amino-3-formylchromone **4** with the cyano group of **68** by a mechanism as shown in Scheme 6 leads to **63**, the formation of **61** and **62** in this reaction *via* **67** is also possible. So far five different products (**58**, **60-63**) arising through self-condensation of 3-cyanochromone have been reported. A slight change in these condensation reaction conditions overwhelmingly changes the reaction courses leading to one or the other of these five products.

VIII Conjugate Addition of Carbon Nucleophiles and Subsequent Transformations of the Adducts.

An active methylene compound like acetylacetone reacts with **1** in the presence of piperidine giving the 2,3-disubstituted 1-benzopyrano[2,3-*b*]pyridin-10(10*H*)-one (trivial name:4-azaxanthone) **70** (R = Me, X = Ac) *via* an ANRORC mechanism [9,34]. 4-Azaxanthones **70** (R = Me, OH, NH_2, OAc, H; X = Ac, CO_2Me, CO_2Et, NHCOPh, CN), prepared up to 1985 from either **1** or **4** [9,24-26,34,35], have already been compiled in a review article [36]. The nitrile **1** gives under base catalysis **70** (R = CH_2CO_2Me, X = CO_2Me) with dimethyl β-ketoglutarate, **70** (R = $CH_2CH_2CO_2Et$, X = CO_2Et) with diethyl β-ketoadipate, and the oxazolone **71** *via* **70** [R = C(=NOH)CO_2Me, *Z*-form, X = CO_2Me] with *Z*-isomer of dimethyl β-keto-α-oximinoglutarate [37]. Stirring a mixture of **1**, chloroacetone and alumina in dichloromethane gives **70** (R = Me, X = Cl) together with **4** [18]. Chromanone (or 6-chlorochromanone) when heated with **1** in ethanol-piperidine gives **72** (R = H or Cl) [38]. The enamine **73** (R = H, Me), prepared from the appropriate 2-methylchromone and dimethylformamide dimethylacetal, reacts with **1** in refluxing DMF giving the azaxanthone **70**

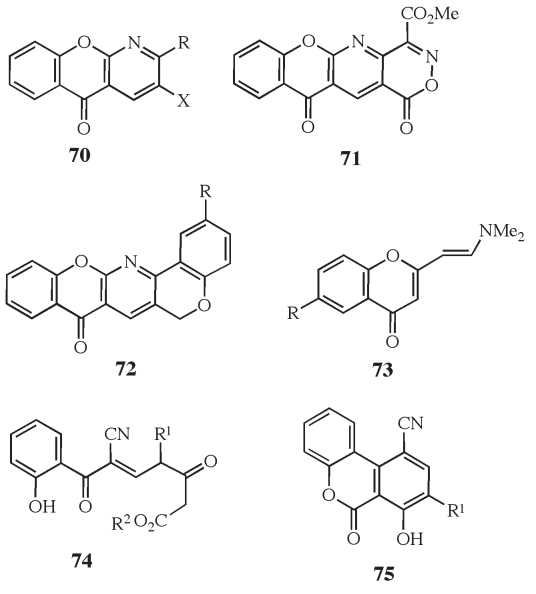
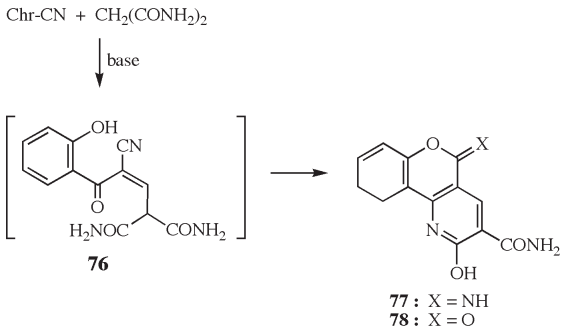


Figure 9

(R = H, X = 6-unsubstituted or 6-methyl-4-oxo-4*H*-1-benzopyran-2-yl) [39]. The pyran ring opened intermediate **74** (R^1 = H, Me, Et, OMe; R^2 = Me, Et, iPr), obtained by treating an ethanolic solution of **35** (Section V) with triethylamine at 20 ºC undergoes depending on the nature of its R^1 group two different modes of cyclisation; **74** with R^1 = H gives **70** (R = $CH_2CO_2R^2$, X = H) whereas **74** (R^1 = Me, Et, OMe) predominantly leads to the benzocoumarin **75** [16].

In contrast to the formation of azaxanthones from **1** and several active methylene compounds, 1-benzopyrano[4,3-*b*]pyridine **78** is formed by heating **1** and malonamide together in MeOH-MeONa [31]. Here the intermediate **76** arising through a sequence of Michael addition and pyran ring opening cyclises to **77** that on hydrolysis yields the coumarin **78** (Scheme 9).

Scheme 9



The phosphorus ylid, generated from triphenylmethylphosphonium bromide and *n*-butyllithium, gives with **1** in hexane-tetrahydrofuran the compound **79** in *E*-isomeric form [40]. The addition of the cuprate **80** (R = TMS, Ph) to **1** in ether at –10 ºC furnishes **81** of (*E*) geometry whereas **80** (R = CH_2CH_2Me) and **1** under the same reaction conditions give the pyrano-azaxanthone **87** [41].

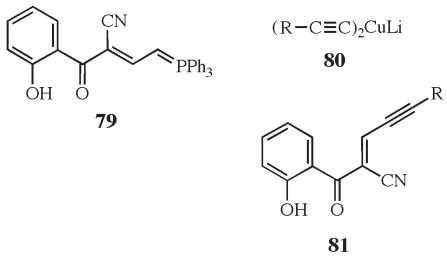
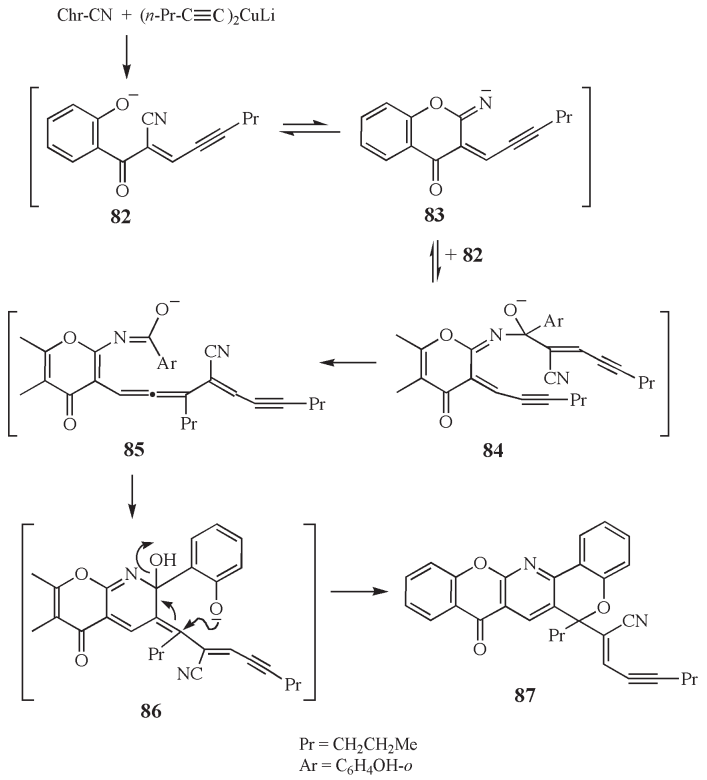


Figure 10

The intermediate imine **83**, generated from **1** and **80** (R = *n*-Pr) *via* an ANRORC mechanism, undergoes 1,2-addition to the keto function of **82** giving **84**; the latter (**84**) ultimately leads to **87** by a sequence of a [1,7] sigmatropic

Scheme 10



shift of the alkenyl function (→ **85**), 6π electrocyclisation (→ **86**) and ring closure reactions (Scheme 10) [41].

Acknowledgements.

Thanks are due to Dr. A. Dasgupta, Department of Biochemistry, University of Calcutta for help with literature search through Sci-Finder.

REFERENCES AND NOTES

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