STUDIES ON SYNTHESIS AND TRANSFORMATIONS OF NITROGEN AND SULFUR-CONTAINING HETEROCYCLES

SYNOPSIS SUBMITTED

To

VIDYASAGAR UNIVERSITY

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

(IN CHEMISTRY)

BY

GOPAL CHANDRA PATRA

DEPARTMENT OF CHEMISTRY AND CHEMICAL TECHNOLOGY,

VIDYASAGAR UNIVERSITY, MIDNAPORE, WEST BENGAL

&

MIDNAPORE COLLEGE

MIDNAPORE – 721 101, IND

MARCH - 2013

SYNOPSIS

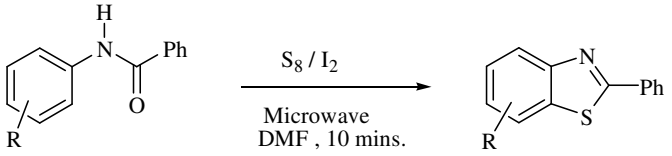
Thesis entitled **"Studies on Synthesis and Transformations of Nitrogen and Sulfur-Containing Heterocycles"** has been divided into three chapters.

CHAPTER I

SYNTHESIS OF 2-PHENYLBENZOTHIAZOLES

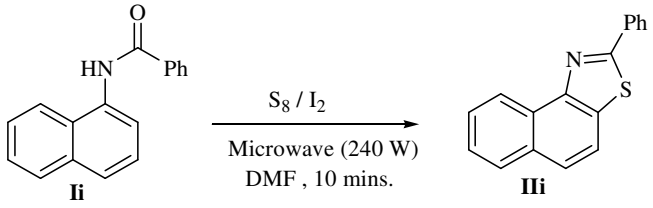
Chapter I of the dissertation describes microwave-assisted synthesis of an important class of heterocyclic compounds namely 2-phenylbenzothiazoles.

The synthesis of this class of compounds is a matter of continued interest to the chemists. Our synthesis starts with benzanilides that are easily prepared from the corresponding aniline by benzoylation with benzoyl chloride using standard procedure. These benzoyl derivatives are heated with sulfur in presence of 10 mol% iodine under microwave irradiation in domestic oven for a very short time when the desired compounds are formed. Solvent and power of oven are changed to find best condition for the reaction. Also some additives are tried to improve the yield. DMF is found to be better medium for the reaction. A few drops of formic acid as an additive result in an improvement of the yield probably by moderating the oxidising atmosphere of the reactions.



I a: R = H
b: R = 4-Me
c: R = 4-OMe
d: R = 3-Me
e: R = 3-Cl
f: R = 4-CO_2H
g: R = 3-OMe
h: R = 4-Br

II a: R = H
b: R = 6-Me
c: R = 6-OMe
d_1: R = 5-Me; **d_2**: R = 7-Me
e: R = 5-Cl
f: R = 6-CO_2H
g_1: R = 5-OMe; **g_2**: R = 7-OMe
h_1: R = H; **h_2**: R = 6-Br



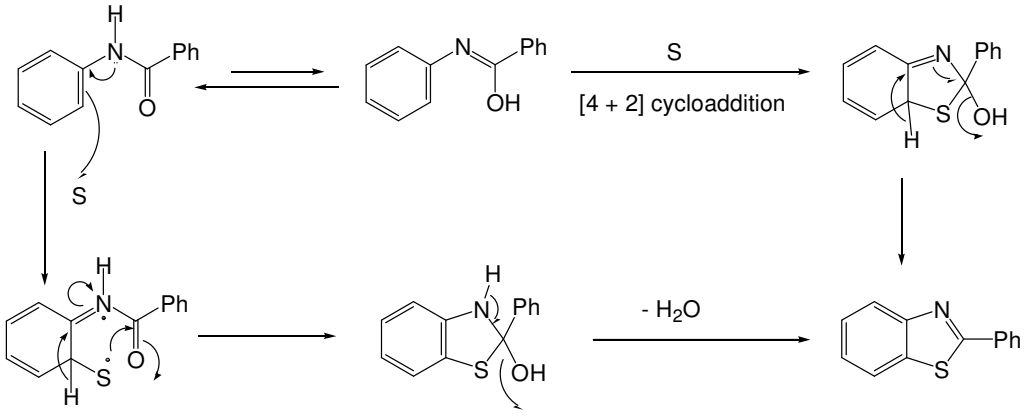
Ii **IIi**

Table 1: Yield 2-phenylbenzothiazoles on heating in the presence of I_2 / HCOOH

Serial No.	Substrate	MW Power	Time (min.)	Product	Yield (%)
1	**Ia**	240W	15	**IIa**	80
2	**Ib**	240W	15	**IIb**	58
3	**Ic**	240W	10	**IIc**	52
4	**Id**	160W	20	**IId_1**	32
				IId_2	25
5	**Ie**	320W	15	**IIe**	62
6	**If**	320W	10	**IIf**	54
7	**Ig**	240W	10	**IIg_1**	24
				IIg_2	18
8	**Ih**	240W	12	**IIh_1**	47
				IIh_2	11
9	**Ii**	240W	10	**IIi**	47

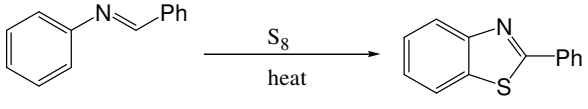
Benzoates of unsubstituted aniline **Ia** and 4-substituted anilines **Ib, Ic, If** gave single product each; but benzoates of 3-substituted anilines **Id, Ie, Ig** gave a mixture of two products, 5- and 7-substituted benzothiazoles. Benzoate **1f** of 4-aminobenzoic acid furnished expected 6-carboxy-2-phenylbenzothiazole *i.e.,* carboxy group survives the reaction condition. But benzoate **Ih** of 4-bromoaniline gave almost exclusively 2-phenylbenzothiazole **Ia (or Ih_1)** in contrary to the expected 6-bromocompound **IIh_2** *i.e*., Br is eliminated during the reaction. Benzoyl derivative of 1-naphthyl amine **Ii** also responded favorably to the reaction yielding the corresponding benzfused 2-phenylbezothiazole **IIi**.

All the products are characterized by spectral analyses. The results of these syntheses are given in **Table 1**. A rational mechanism (**Scheme 1**) for the thiation has been proposed:



Scheme 1

It can be mentioned in this connection that the preparation of 2-phenylbenzothiazole in 30 % yield was reported earlier starting from phenylimine of benzaldehyde (**Scheme2**).



Scheme 2

Imines are difficult to store; in comparison benzoates are quite stable compounds and can be stored for a long time without any precautionary measure, and can be easily prepared, too. Moreover yields are better in our methods; probably the anilides are at a higher state of oxidation than imines and so responds better to this oxidative cyclisation.

CHAPTER II

BIGINELLI COMPOUNDS: SYNTHESIS OF NEW BIGINELLI COMPOUNDS, BROMINATION STUDIES AND DERIVATISATION INTO PYRIMIDO[4,5-*d*]PYRIDAZINES

Chapter II of the dissertation involves work mainly on Biginelli compounds (dihydropyrimidones: DHPMs)-their syntheses and characterization, studies on various methods of bromination, and derivatisation into products with new skeletons.

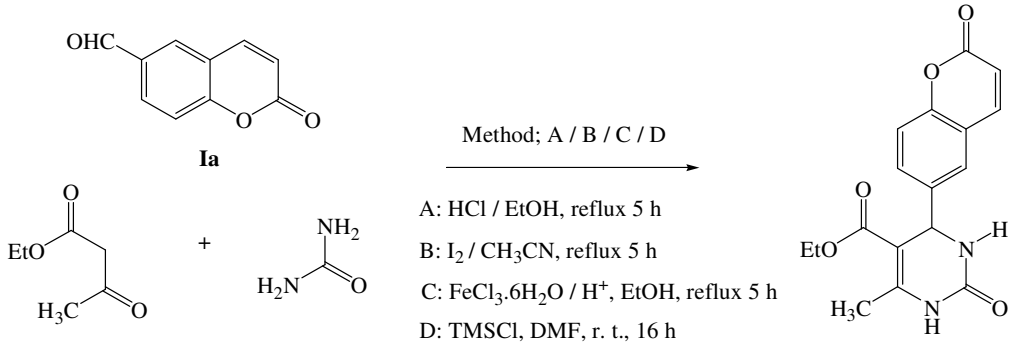
This chapter is subdivided into three sections: **Sections A, B** and **C**

Section A

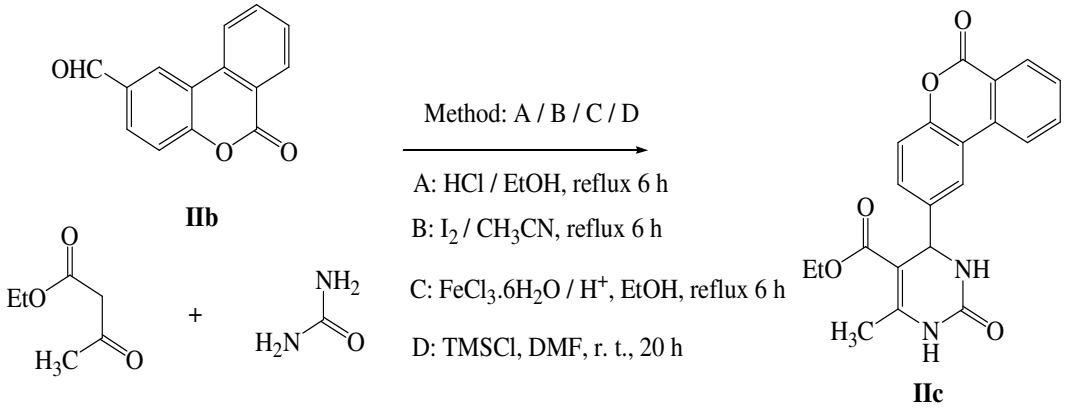
This section describes preparation of two new DHPMs from two coumarin carbaldehydes that have been prepared in our laboratory.

A lot of references are available in literature citing different conditions / catalysts that have been successfully used for the preparation of Biginelli compounds. We selected four different methods that are: (i) Method A - refluxing the reactants in ethanol in the

presence of HCl, (ii) Method B - heating the reactants in presence of iodine, (iii) Method C - refluxing the reactants in ethanol in the presence of $FeCl_3$ plus a trace of HCl, and (iv) Method B - stirring the reactants in DMF in the presence of chlorotrimethylsilane at room temperature. The syntheses are shown in **Schemes 3** and **4**, and a comparative account of the yield in different methods is cited in **Table 2**.



Scheme 3



Scheme 4

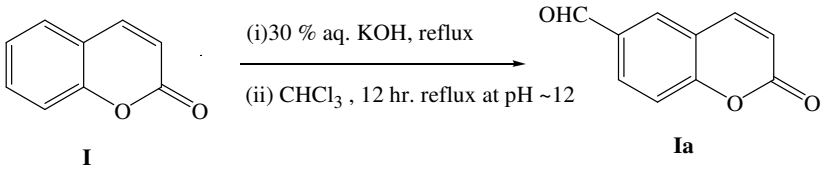
The last method *i.e.,* stirring at room temperature in Me_3SiCl (method D) is found to be best suited in these cases.

The structures of these new compounds have been well-established by IR, ^1H and ^{13}C NMR, and mass spectroscopic studies.

Table 2: A comparative account of the yield Ic and IIc in different methods

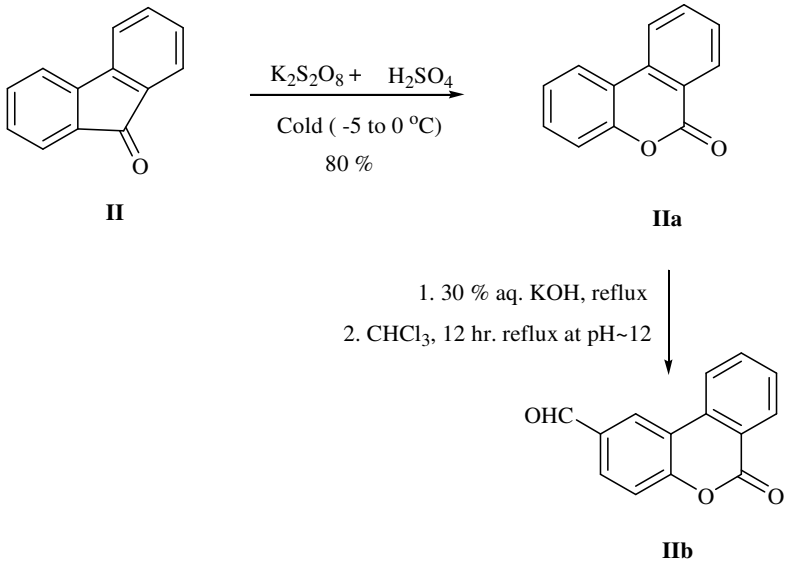
		% Yield			
Substrate	**Product**	**Method A**	**Method B**	**Method C**	**Method D**
Ia	**Ic**	50	40	60	80
IIb	**IIc**	55	45	70	85

The starting coumarin-carbaldehydes **Ia** and **IIb** have been prepared in an improved yield as shown in the following **Schemes 5** and **6** as given below:



I **Ia**

Scheme 5



II **IIa** **IIb**

Scheme 6

Section B

In this section studies on bromination of dihydropyrimidones and two other heterocycles are described.

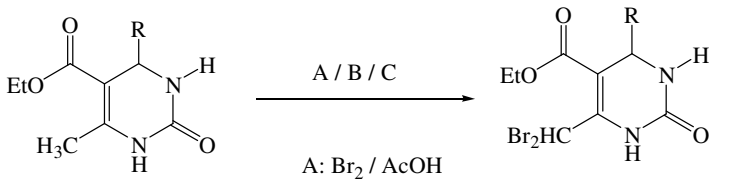
Dihydropyrimidones (Biginelli compounds) have several functionalities that offer scope of modification / derivatisation into new compounds keeping the basic DHPM pharmacophore unchanged.

The C_6-methyl can be a nucleophilic synthon in the presence of base. Several condensations however lead to degradation of the compounds. Bromination at this allylic site is very easy and several derivatives have been prepared through monobromodrivatives of these compounds. Only a limited number of examples are there where some derivatives have been prepared through dibromoderivatives at this site. In all these reports bromination is carried using molecular bromine in chloroform / acetic acid. We attempted to prepare C_6-$CHBr_2$ in order to convert the same into an aldehyde group. This is because aldehyde group will open the route to several interesting reactions like Morita-Baylis-Hillman, Petasis reaction, Hantzsch dihydropyridine synthesis, etc. including even Biginelli reaction once more. In fact this C_6-methyl group could not be converted into –CHO by SeO_2 oxidation. Again with the appearance of a large number of Biginelli compounds in literatures it is felt necessary to examine bromination reactions of all those compounds with various brominating agents. We decided to study brominations with four different brominating procedures using three brominating species. The methods include two reported procedures that employ molecular bromine as the brominating species:

(i) Br_2 in chloroform
(ii) Br_2 in acetic acid
(iii)*N*-bromosuccinimide (NBS) and
(iv)2,4,4,6-tetrabromocyclohexa-2,5-dien-1-one (TBCO)

Later in view of the preliminary results the studies were restricted to the last three methods.

The results are summarized below in **Table 3**.



(**III**): R = Ph or Ar

(**IV**): R = Ph or Ar

Table 3: A comparison of the yields of dibromides in different methods

Substrate	Product	Yield (%)		
		Br_2 / AcOH	**TBCO**	**NBS**
IIIa : R = Ph	**IVa:** R = Ph	60	80	10[b]
IIIb: R = 4-MeC_6H_4	**IVb:** R = 4-MeC_6H_4	80	85	52
IIIc: R = 4-$MeOC_6H_4$	**IVc:** R = 4-$MeOC_6H_4$	83	97	24[b]
IIId: R = 4-ClC_6H_4	**IVd:** R = 4-ClC_6H_4	78	92	57
IIIe: R = 4-BrC_6H_4	**IVe:** R = 4-BrC_6H_4	82	92	55
IIIf: R = 3-$NO_2C_6H_4$	**IVf:** R = 3-$NO_2C_6H_4$	58	90	55
IIIg: R = -Coumarin	**IVg:** R = -Coumarin	-[a]	87	-[a]
IIIh: R = -CH_3	**IVh:** R = -CH_3	57	84	62
IIIi: R = 4-HO-3-$MeOC_6H_3$	**IVi:** R = 4-HO-3-MeO C_6H_3	65	88	35[b]
IIIj: R = 4-$NO_2C_6H_4$	**IVj:** R = 4-$NO_2C_6H_4$	60	93	56

[a]The product was a mixture that could not be separated. [b]Aromatized products are given in **Table 2.2**

It has been found that molecular bromine did not give complete conversion even after long reaction time. It gave unsatisfactory yield of dibromides, and moreover the product obtained were mixture of mono- and dibromo-derivatives in addition to some unreacted starting compounds. TBCO gave much better result in following respects:

(i) Bromination can be controlled at the monobromination (C_6-CH_2Br) stage by using one equivalent of the reagent. Almost quantitative yield of the monobromides have been obtained.

(ii) Satisfactory yield of dibromides (C_6-$CHBr_2$) have been obtained in all the cases studied except in case of Biginelli compound **IIIg** from coumarin-6-carbaldehyde.

(iii) The method is green as compared to molecular bromine. TBCO is safe to handle and is nonhazardous, too.

In case of Biginelli compound **(IIIi)** from vanillin the ring bromination could not be avoided: the product was a mixture of C_6-$CHBr_2$ and C_6–CH_2Br derivatives both of which contain one Br at the ring at a position *ortho* to the –OH.

NBS did not give good results; moreover aromatized products (pyrimidones) are obtained in cases where the Biginelli compounds contain C_4-phenyl / aryl group with electron donating substituents like –OH (phenolic) or –OMe. A comparative account of the brominations of these substrates is given in **Table 4**.

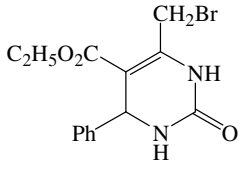
Almost all the products, especially the C_6-$CHBr_2$, are reported here for the first time. The structures are as usual characterized by spectral studies. The ^{1}H NMR spectra of the dibromide derivatives show a typical singlet at ~ δ 8.0 assignable to –C<u>H</u>Br_2. The mass spectra (HRMS) of (**IVg**) exhibits [M+1], [M+3] and [M+5] peaks in the intensity ratio of 1:2:1, and that of (**IVe**) shows four peaks in intensity ratio of 1:3:3:1 in consistent with the presence of two and three Br respectively.

Table 4: Product composition from DHPMs with reactive aryl rings

Substrate	Reagent	Products (% yield)		
		C_6-CH_2Br	**C_6-$CHBr_2$**	**Aromatized**
IIIa : R = Ph	B r_2 / AcOH	**V**(20)[a]	**IVa** (60)	_
	TBCO	**V**(10)[a]	**IVa** (80)	_
	NBS	**V**(8)[a]	**IVa** (10)	**A** (72)[b]
IIIc: R = 4-$MeOC_6H_4$	Br_2 / AcOH	-[c]	**IVc** (83)	_
	TBCO	-[c]	**IVc** (97)	_
	NBS	-[c]	**IVc** (24)	**B** (21)[b]
IIIi: R = 4-HO-3-MeO C_6H_3	Br_2 / AcOH	-[c]	**IVi** (65)	_
	TBCO	-[c]	**IVi** (88)	_
	NBS	-[c]	**IVi** (35)	**C** (12)[b] & **D** (10)[d]

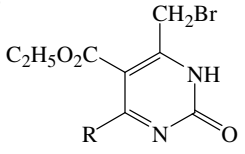
[c]The product was a complex mixture that could not be separated

a



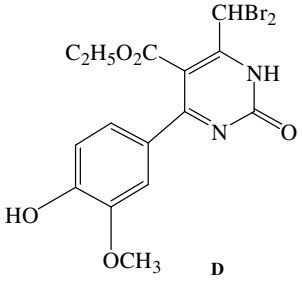
V

b



A : R = C_6H_5
B : R = 4-$CH_3OC_6H_4$
C : R = 4-HO-3-MeO-C_6H_3

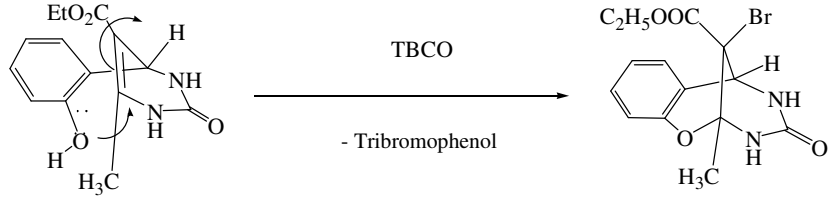
c



D

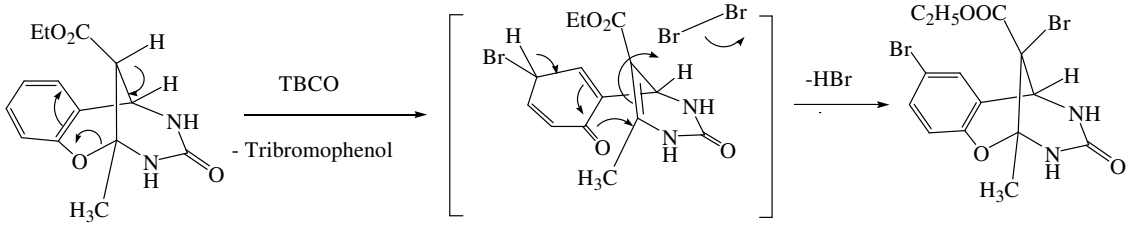
Section B (1)

In this section bromination of Biginelli products (normal / acyclic **IIIk** and abnormal / cyclic **IIIl**) of salicyldehyde has been described. This result is described separately as a typical behavior of neighbouring group participation of the *ortho*-phenolic hydroxyl in case of normal compound, leading to a bicyclic derivative **IVk** has been noticed. In all the earlier examples studied above the C=C bond remains unaffected. In those cases it is the allylic methyl that reacts in preference to C=C bond and benzylic position. But here the anchimeric assistance of *ortho*-phenolic hydroxyl facilitates reaction at C=C bond; the methyl group remains unaffected as a substituent at the bridgehead. In fact this is not unusual since salicyldehyde is reported to form an abnormal Biginelli product which is a bicyclic compound **IIIl**. Interestingly this abnormal Biginelli compound **IIIl** having no apparent reactive site also undergoes bromination yielding mainly a dibromo-compound **IVl** having one Br at the bridgehead and the other Br at the ring. These transformations are shown in **Schemes 7** and **8**.



IIIk **IVk**

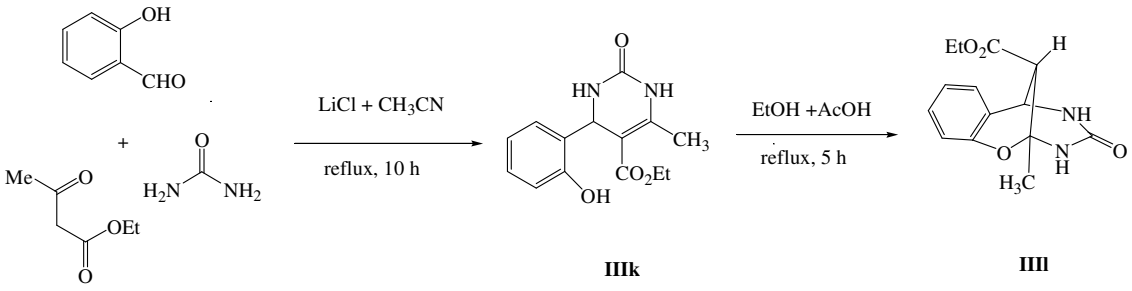
Scheme 7



IIIl **(Q)** **IVl**

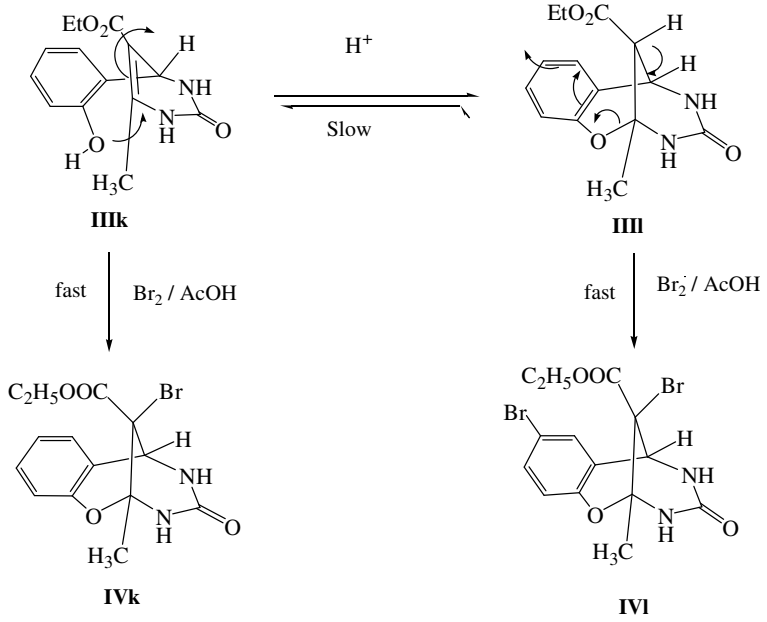
Scheme 8

Both the acyclic / normal **IIIk** and cyclic / abnormal Biginelli products **IIIl** of salicyldehyde have been prepared under two different conditions following literature reports (**Scheme 9**).



Scheme 9

Brominations of each of these Biginelli copounds with all the three brominating agents were studied separately as it was done for other examples (**Section IIB**). TBCO appeared to react selectively furnishing a dibromo-compound from the abnormal / cyclic Biginelli product of salicyldehyde, and only a mono-bromoderivative from the normal / acyclic Biginelli compound of salicyldehyde. Molecular bromine in acetic acid furnished a mixture of mono- and dibromo-derivative from each of the two Biginelli compounds though in unequal amounts. This has been rationalized by the earlier observation that under acid condition the acyclic Biginelli product of salicyldehyde is converted into the cyclic product (**Scheme 10**). A summary of yield in different procedures for bromination of these compounds is tabulated (**Table 5**).



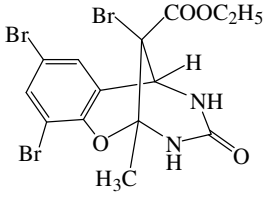
Scheme 10

Table 5: Yield of products from bromination of **(IIIk)** and **(IIIl)**

Reagent	**Substrate**	**% Yield of products**		
		(IVk)	**(IVl)**	**(IVm)**
TBCO	**(IIIk)**	82	10	0
(2 equiv. or more)[d]	**(IIIl)**	0	95	0
Br_2 / AcOH	**(IIIk)**	52	26	0
(3equiv.)[d]	**(IIIl)**	trace	64	0
NBS	**(IIIk)**	30	14	11
(3 equiv.)[e]	**(IIIl)**	0	35	20

[d]Time: 45 minutes; [e]Time: 48 hours.

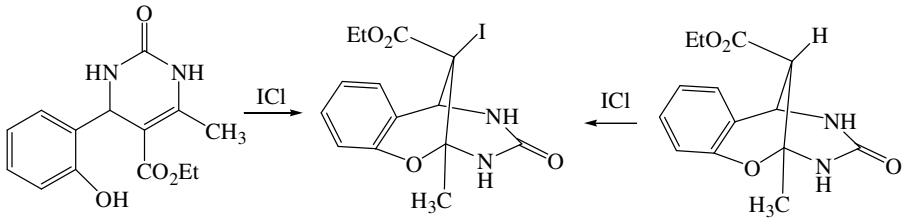
The reactions of these Biginelli compounds with NBS was found to be non-selective, and prolonged reaction time led to the formation of a tribromo-derivative (**IVm**) also.



IVm

Encouraged by these observations reactions of these Biginelli compounds with some other electrophilic reagents have been studied. Accordingly reaction with trimethyloxonium tetrafluoroborate, Me_3O^+ BF_4^-, has been attempted. But none of the two substrates responded.

Reaction of these Biginelli compounds with iodine in absence and in the presence of silver salt was tried. Starting materials remain unchanged. However, the reaction with Wijs' solution gave positive results. Both the cyclic and acyclic Biginelli compounds, **IIIk** and **IIIl** of salicyldehyde furnished only one mono-iodocompound **Va** having iodine at the bridgehead position. The observations can be explained by the reaction through the acyclic Biginelli compound; the cyclic Biginelli compound is gradually converted into the acyclic one under the acidic condition of Wijs' solution (**Scheme 11**).



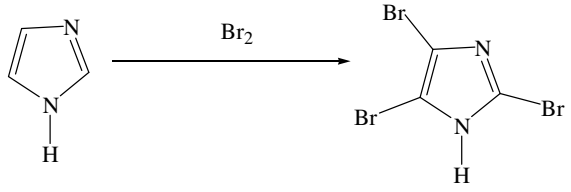
IIIk **Va** **IIIl**

Scheme 11

Section B (2)

As part of our bromination studies using TBCO we undertook bromination of a few more reactive (electron-rich) heterocycles. Bromination of two compounds, imidazole and 6-aminocoumarin, with TBCO was investigated, and the results are described in this section.

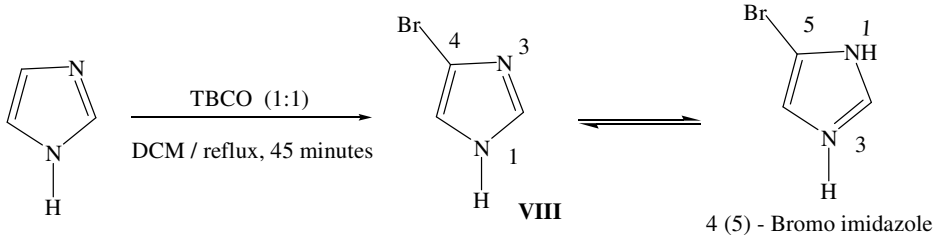
A search of literature reveals that imidazole **VI** upon bromination with molecular bromine gives a tribromo-derivative (**Scheme 12)**; the same was also observed by us.



VI **VII**

Scheme 12

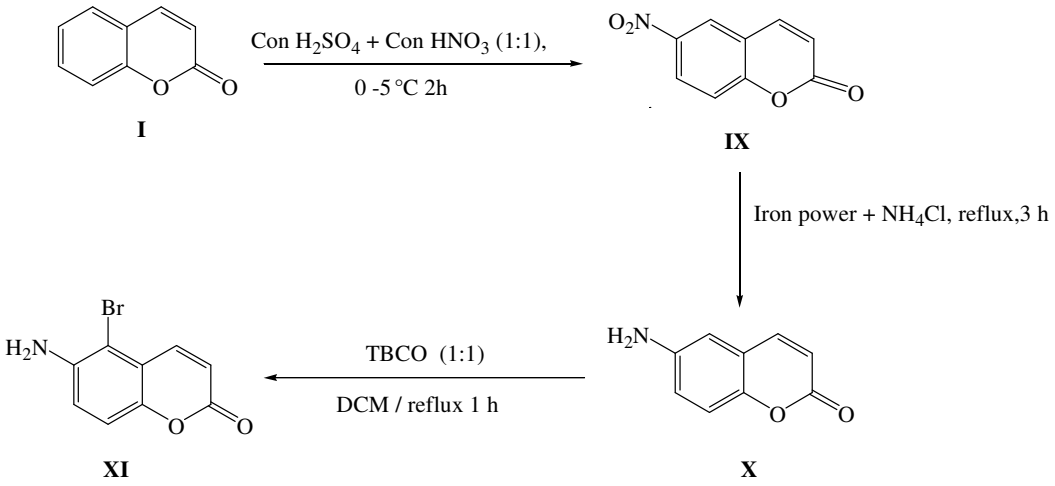
Monobromination has not been reported. TBCO (1 equivalent) has been found to be an effective and selective reagent to produce 4(5)-bromoimidazole from imidazole in excellent yield:



VI **VIII** 4 (5) - Bromo imidazole

Scheme 13

Our group has been studying reactions of coumarins for some time. 6-aminocoumarin **X** was prepared employing known methods, and then it was subjected to bromination with TBCO (1 equivalent). Regioselective and controlled reaction occurred to give 5-bromo-6-aminocoumarin **XI** as the only product (**Scheme 14**). Reaction of molecular bromine has not been investigated since it is known that bromine attacks C=C bond of the lactone ring in coumarin.



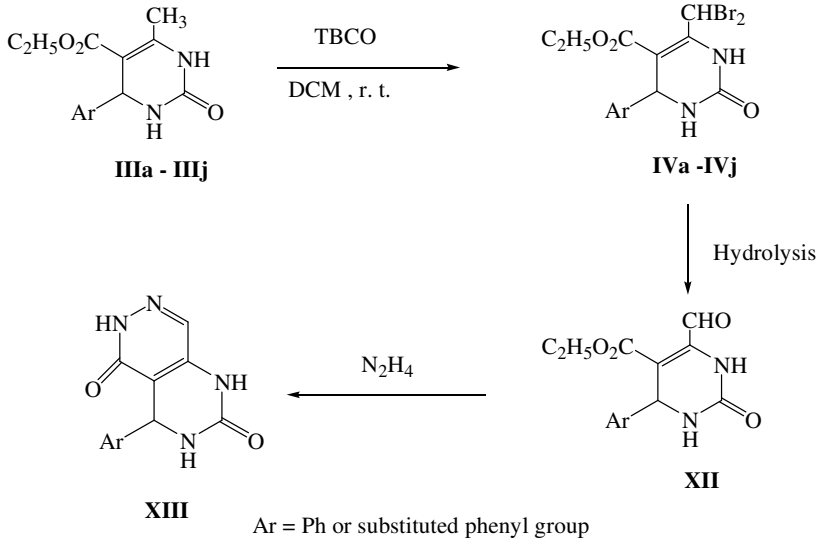
Scheme 14

So TBCO is once again proved to useful reagent for selective and controlled bromination of reactive heterocycles.

Section C

There are several scopes of structural modifications of the Biginelli compounds keeping the basic DHPM pharmacophore unchanged. Elaboration of some groups and functionalities are carried in an attempt to find new derivatives that would be tested for their biological activities.

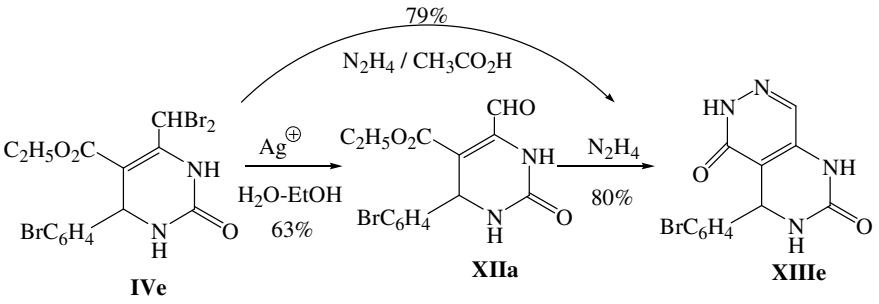
As scheme for the preparation of some pyrimido-pyridazines **XIII** especially using the C_6-$CHBr_2$ derivatives of Bignelli compounds **III** has been chalked out. The latter compounds were prepared in an excellent yield by the TBCO assisted bromination Biginelli compounds (**Section B**). In the beginning we tried to hydrolyse the $–CHBr_2$ into aldehyde **IV** using alkaline conditions. The procedure did not succeed. We then used silver ion catalysed process, and achieved the goal. Subsequent treatment of this aldehyde **IV**with hydrazine hydrate furnished the targeted product **XIII**.



Scheme 15

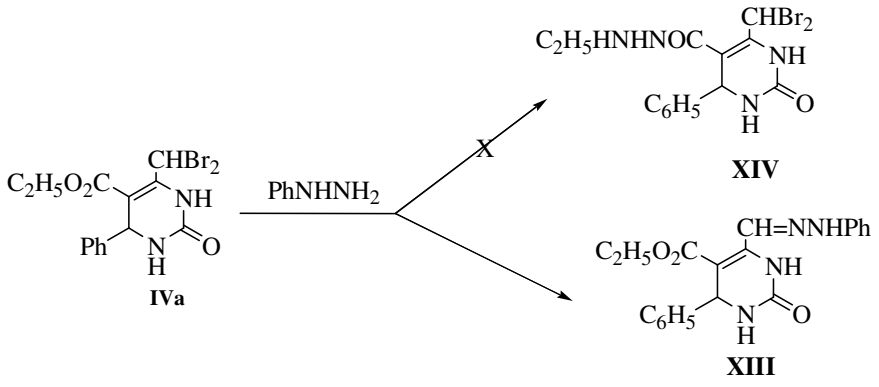
But the method is expensive as more than one equivalent of silver salt was needed to complete the hydrolysis. And only a moderate yield (63 %) was obtained. A short-cut procedure was therefore adopted in which dibromide **III** was directly treated with

hydrazine hydrate. The result was not only satisfactory but also better (79 % yield) than the two-step procedure (over-all yield 50. 4 %). The protocol was then firmly established procedure by carrying out the reaction with five dibromoderivatives **IIIa - IIIj**, and in the process established a novel synthetic route to these fused ring heterocycles **XIII** (**Scheme 16**).



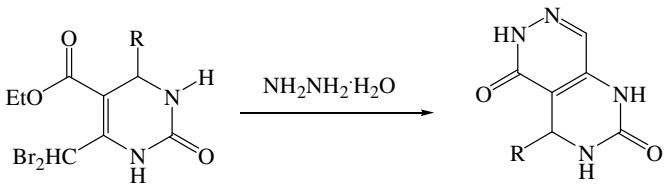
Scheme 16

The mechanistic path followed by the reaction was also investigated. It is to be examined whether hydrazine first reacts (i) with $-CO_2Et$ group to form hydrazide derivative as intermediate which then cyclises or (ii) with $-CHBr_2$ first to give an intermediate (hydrazone of the aldehyde) and thereafter cyclisation takes place. For this purpose the reaction of a dibromide **IVa** with phenyl hydrazine was carried out. The product isolated was the phenylhydrazone **XIII** of the corresponding aldehyde and not *N*-phenylhydrazide **XIV** (**Scheme 17**). Mechanistic path is then ascertained as (ii).



Scheme 17

Table 6 enlists the yield of these syntheses.



R = Ph or Ar

R = Ph or Ar

Table 6: Reaction conditions, m.p. and yield of pyrimidopyridazines (**XIIIa -XIIIe**)

Substrate	**Reflux time (hrs)**	**M.P. (^oC)**	**Product**	**Yield (%)**
IVa: R = Ph	8	335	**XIIIa**: R = Ph	74
IVb: R = 4-MeC_6H_4	9	552	**XIIIb**: R = 4-MeC_6H_4	82
IVc: R = 4-$MeOC_6H_4$	10	336	**XIIIc**: R = 4-$MeOC_6H_4$	57
IVd: R = 4-ClC_6H_4	7	343-44	**XIIId**: R = 4-ClC_6H_4	75
IVe: R = 4-BrC_6H_4	7	361	**XIIIe**: R = 4-BrC_6H_4	79

All the five pyrimidopyridazines **XIIIa - XIIIe** have been characterised by spectroscopic analyses. The ^1H and ^{13}C NMR data of the common structural moiety are shown in the **Figure 1**:

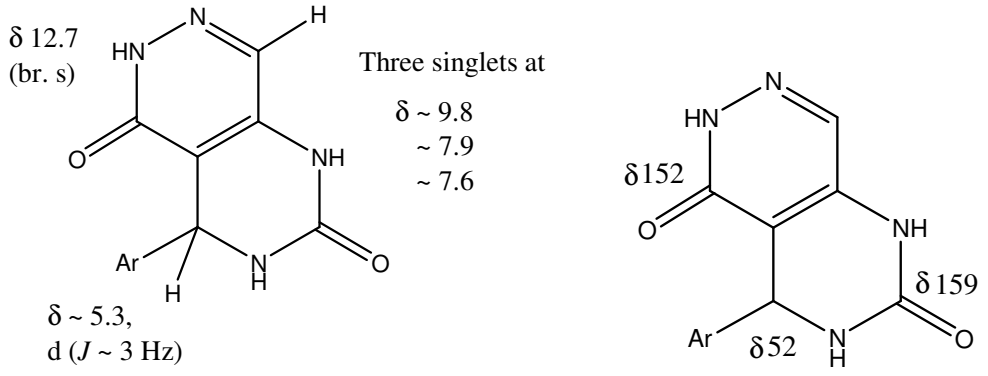


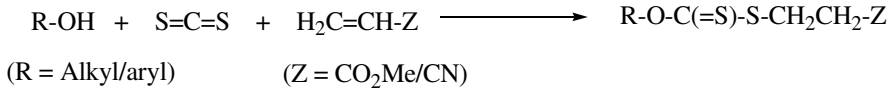
Figure 1

CHAPTER III

MULTICOMPONENT SYNTHESIS OF FUNCTIONALISED *O,S*-DIALKYLDITHIOCARBONATES

In this part three component syntheses of *O,S*-dialkyldithiocarbaontes in which the *S*-alkyl part contains an ester / nitrile functional group have been described.

Multicomponent synthesis has numerous advantages over linear type synthesis, and hence enormous work on the development of these reactions (MCR) is going on. Quite a number of publications have appeared recently on the MCR in which CS_2 is an important component. Some of these literatures describe the synthesis of dithiocarbonates from a three-component reaction of secondary amine, CS_2 and a Michael acceptor like α,β-unsaturated ketone / ester / nitrile etc. A scheme for the synthesis of dithiocarbonates has been proposed by a similar reaction replacing the amine by an alcohol / phenol (**Scheme 18**) with a goal to prepare *O,S*-dialkyldithiocarbaontes:



Scheme 18

However uncatalysed reactions failed to yield any product. The reactions occurred in the presence of triethyl amine as a basic catalyst; but only in case of alcohols, not phenols. A certain amount of side products were also formed (TLC monitoring). The tertiary amine was varied to find the best catalyst that will give the desired product avoiding side reactions in reasonable time. Four different amines namely (i) triethyl amine (ii) 1,4-

diazabicyclo-[2.2.2]octane (DABCO) (iii) 4-dimethylaminopyridine (DMAP) and (iv) N-ethylmorpholine were utilized in separate experiments. Four different combination of reactants namely (A) phenethyl alcohol and methacrylate, (B) phenethyl alcohol and acrylonitrile, (C) menthol and methacrylate and (iv) menthol and acrylonitrile were tried in the presence of 10 mol% of each of the above four bases in CS_2. The time required for completion of reactions, and isolated yield of the products is summarized in **Table 7**.

Table 7: Comparative reaction time and yield using different bases

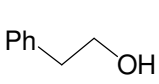
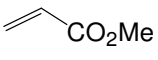
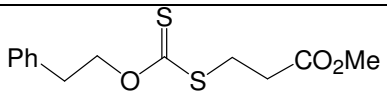
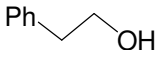
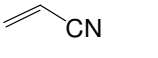
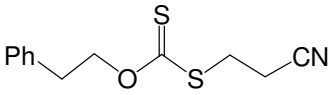
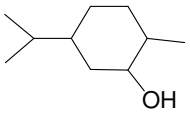
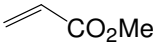
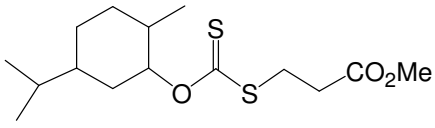
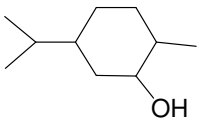
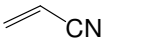
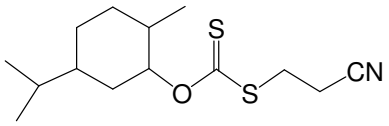
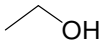
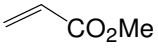
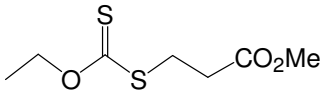
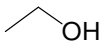
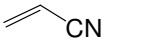
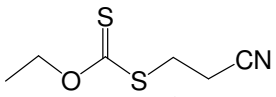
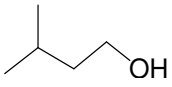
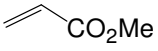
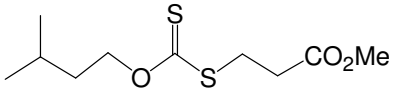
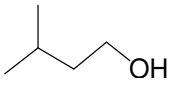
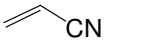
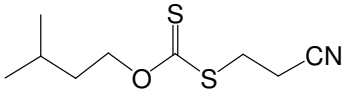
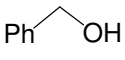
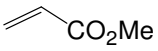
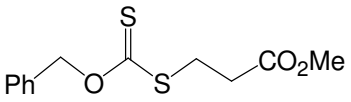
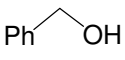
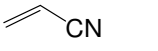
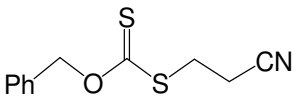
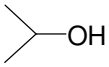
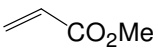
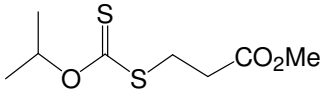
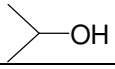
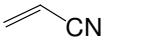
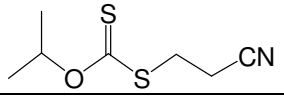
Entry	**Reactants**	**Time[a] (hrs.) required and yield when base[b] used**			
		Et_3N	DMAP	DABCO	*N*-Ethyl-morpholine
1	($PhCH_2CH_2OH$ + CS_2 + H_2C=$CHCO_2Me$)	5 (72%)	6 (85%)	8 (92%)	10 (92%)
2	($PhCH_2CH_2OH$ + CS_2 + H_2C=CHCN)	5 (70%)	6 (81%)	8 (87%)	12 (88%)
3	(Menthol + CS_2 + H_2C=$CHCO_2Me$)	48(52%)	60 (63%)	72 (65%)	--[c]
4	(Menthol + CS_2 + H_2C=CHCN)	48(46%)	60 (62%)	72 (62%)	--[c]

[a]until no further conversion was noted (TLC). [b]10 mol% of base is used in each case. [c]much low conversion was noted.

DABCO appears to be the best choice in affording a clean product in reasonable time. Thereafter reactions of four more alcohols – alkyl and aralkyl, primary and secondary - in carbon disufide have been carried out successfully with those two vinyl compounds in the presence of DABCO. The yield and time of the reactions are presented in **Table 8**. The reaction using a tertiary alcohol, 2-methylpropan-2-ol (*tert*-butyl alcohol), with CS_2 and methacrylate / acrylonitrile did not give the expected dithiocarbonate.

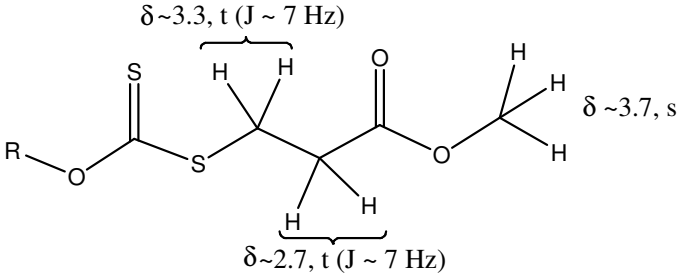
A green methodology for a solvent-free efficient multicomponent synthesis of functionalized *O,S*-dialkyldithiocarbonates has thus been achieved.

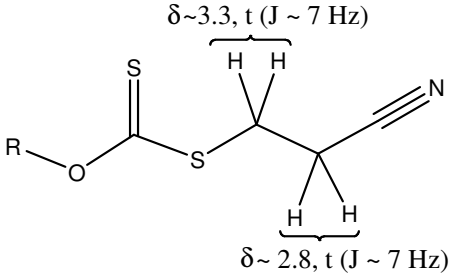
Table 8: Reaction conditions and yield of dithiocarbonates using 10 mol% DABCO

Entry	**Alcohol**	**Vinyl compd.**	**Time (hrs.)**	**Product**	**Yield (%)**
1			8		92
2			10		87
3			72		65
4			72		62
5			8		82
6			9		77
7			8		84
8			8		78
9			12		67
10			15		66
11			10		70
12			12		68

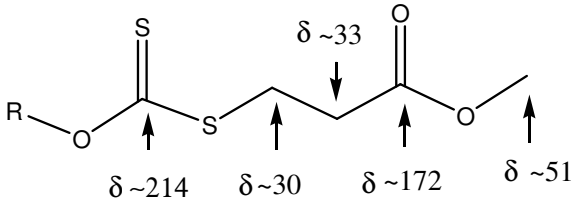
The structures of all the products have been established by spectral studies of the compounds. The products can be represented by the following two general structures; the common spectral range of the common parts is shown below:

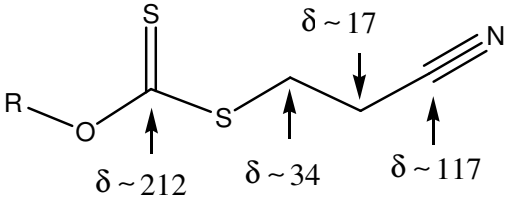
^{1}H NMR:





^{13}C NMR:





IR: In addition to bands ~1740 cm^{-1} (ester C=O) and ~2250 cm^{-1} (C≡N) in the two category of compounds there is a band ~1050 – 1100 cm^{-1} in both possibly due to C=S.