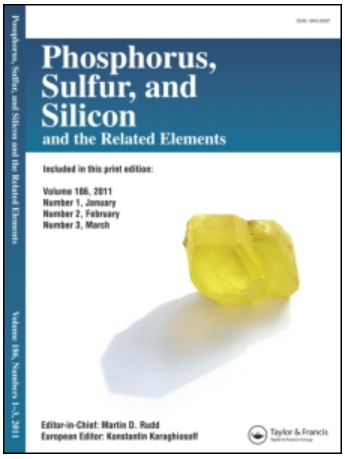


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

α-Oxoketene Dithioacetals as Intermediates for Aromatic Annelation

H. Junjappa[a]; H. Ila[a]
[a] Department of Chemistry, North-Eastern Hill University, Shillong, Meghalaya, INDIA

To cite this Article Junjappa, H. and Ila, H.(1994) 'α-Oxoketene Dithioacetals as Intermediates for Aromatic Annelation', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 35 — 54
To link to this Article: DOI: 10.1080/10426509408034200
URL: http://dx.doi.org/10.1080/10426509408034200

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95-96, pp. 35-54
Reprints available directly from the publisher
Photocopying permitted by license only

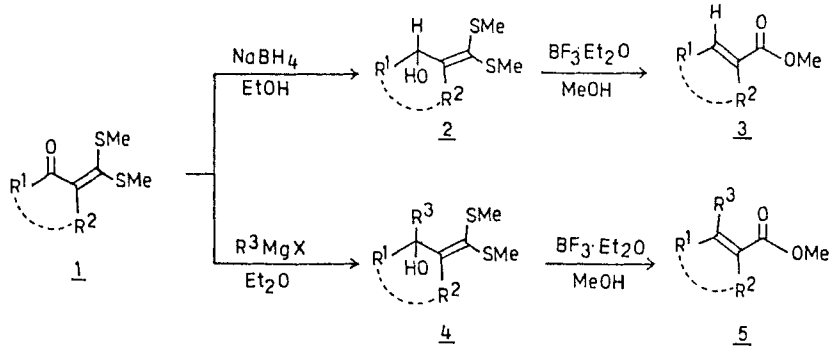
α-OXOKETENE DITHIOACETALS AS INTERMEDIATES FOR AROMATIC ANNELATION

H. JUNJAPPA AND H. ILA
Department of Chemistry, North-Eastern Hill University
Shillong - 793 003 (Meghalaya), INDIA

Abstract The α-oxoketene dithioacetals of general formula **1** (Scheme 2), undergo regioselective 1,2-addition with allyl anions to afford the corresponding carbinol acetals **6** in quantitative yields, which on treatment with $BF_3.Et_2O$ in refluxing benzene yield the corresponding aromatic systems. The method has been shown to be widely applicable as exemplified by a large number of allyl anions (Scheme 3) reacting with α-oxoketene dithioacetals with wide structural variation. However, when **1** carry the α-substituent the intermediate carbinol acetals **14** (Scheme 4) follow, different path to yield the corresponding indenes **15** in good yields. The cinnamoyl-ketene dithioacetals **16** react with allyl anions to afford the corresponding methylthiostilbenes **18** (Scheme 5), while the homologous dithioacetal **20** failed to yield the corresponding 1,4-biaryl-1,3-diene **22** (Scheme 6). This limitation was circumvented by reacting **23** with allyl anions to afford the corresponding stilbenes **24**, dienes **25** and triene **26** respectively. The method was successfully extended for naphthoannelation. Thus naphthalenes **28** (Scheme 7) were prepared by reacting benzylmagnesium chloride with **1**. In this case the reaction followed a sequential 1,4- and 1,2-addition mode and yielded the corresponding benzyl substituted naphthalenes. This problem was solved by reacting benzylmagnesium chloride with **8** to afford the corresponding naphthalenes **31** (Scheme 8) in excellent yields. Similarly the lithio derivatives derived from toluene followed 1,2-addition mode with **1** to afford the derived methylthionaphthalenes **39** (Scheme 9) in high yields. The other alkyl substituted naphthalenes **41**, **43** (Scheme 9), **45**, **47** (Scheme 10) were similarly prepared. Also **1** and ß-oxodithioacetals **8** reacted with 1-naphthylmethylmagnesium chloride to afford the corresponding phenanthrenes **49** and **51** respectively in good yields. The method was extended to benzanthracene **56** (Scheme 11) synthesis successfully. The 2-naphthylmethyl magnesium chloride reacted in a sequential 1,4- and 1,2-fashion to afford the corresponding naphthylmethyl hydrocarbons **58** while it reacted with ß-oxodithioacetals to give expected condensed aromatics **60**, **61** and **62** (Scheme 12) in high yields. The 1-naphthylmethylmagnesium chloride also reacted with ß-oxodithioacetals **23** to afford the corresponding styrylphenanthrenes **65**, dienes **66** and triene **67** respectively in high yields.

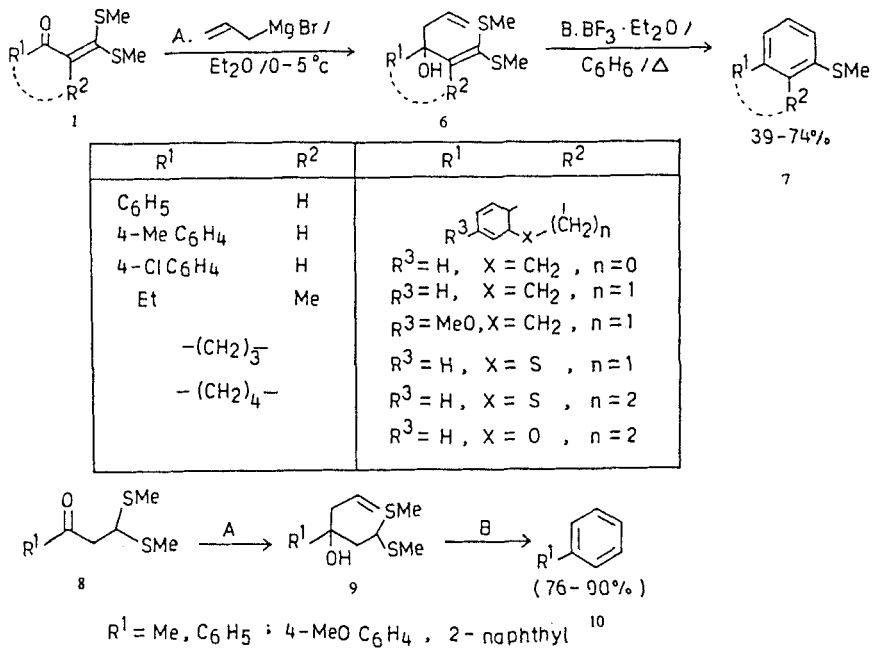
The intermediate **69** precursor in the synthesis of hexahelicine was also obtained by reacting **68** with 1-naphthylmethylmagnesium chloride (Scheme 13). The oxygenated benzylmagnesium halides reacted with **1** in 1,2-fashion (Scheme 14) with the exception of the formation of **79**. Five fold excess of Reformatsky reagent reacted with **1** to afford the corresponding salicylates **82** (Scheme 15) in high yields. Similarly **84** (Scheme 16) was formed. Propargylmagnesium chloride also reacted with **1** with the participation of solvent methanol to afford the corresponding thioresorcinol dimethylethers **86** (Scheme 17) in high yields. However, intermolecular solvent participation did not occur with open chain α-oxoketene dithioacetals (Scheme 18) and the possible mechanism for this transformation is proposed (Scheme 19). The anion derived from aminocrotonate **97** (Scheme 20) reacted with **1** to afford the corresponding aminosubstituted aromatics **100**. To prepare totally unsubstituted aromatics the allylanion was reacted with phenylthioacrolein **101** as exemplified by the synthesis of benzene **108a** (Scheme 23), naphthalenes **109, 110** and phenanthrene **111** (Scheme 24). In general our new method of aromatic annelation is a versatile, efficient and widely applicable for creating a large number of aromatics from easily accessible open chain precursors.

As a part of our interest in α-oxoketene dithioacetals chemistry[1], we developed a new general highly stereo and regioselective method for homologation of ketones to α, ß- unsaturated esters using α-oxoketene dithioacetals as intermediates[2,3]. This methodology was based on regioselective reduction of the α-oxoketene dithioacetals **1** by sodium borohydride followed by their conversion to the corresponding α, ß-unsaturated esters **3** under $BF_3.Et_2O$ assisted methanolysis (Scheme 1). Similarly organometallic reagents reacted regioselectively in the 1,2- fashion to give the carbinol acetals in high yields which underwent similar



Scheme 1

solvolysis to give the corresponding ß-substituted α,ß-unsaturated esters (Scheme 1). Soon after this discovery we reasonned that the reaction of allylmagnesium bromide with **1** should give the expected carbinol acetals **6** which should undergo benzoannelation (Scheme 2) instead of observed solvolytic transformation[4]. The reaction from **6** to **7** was indeed discovered and not the corresponding α, ß-unsaturated eneesters. This new method of aromatic annelation has been extensively investigated to establish its general applicability through the use of a large number of allyl anions as precursors of 1,3- binucleophile and a wide variety of α-oxoketene dithioacetals as precursors of 1,3-electrophilic open chain fragments.



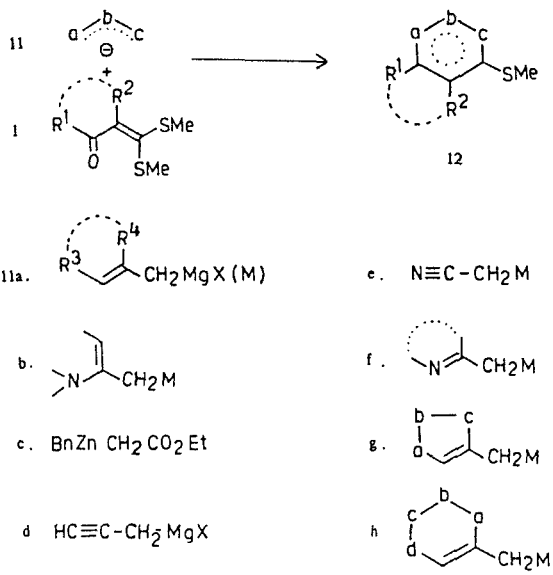
R^1	R^2	R^1	R^2
C_6H_5	H		
4-Me C_6H_4	H	R^3= H, X = CH_2 , n = 0	
4-Cl C_6H_4	H	R^3= H, X = CH_2 , n = 1	
Et	Me	R^3= MeO, X = CH_2 , n = 1	
$-(CH_2)_3-$		R^3 = H , X = S , n = 1	
$-(CH_2)_4-$		R^3 = H , X = S , n = 2	
		R^3 = H , X = O , n = 2	

Scheme 2

The number of 1,3-binucleophiles that could be employed in this reaction is very large and their basic structural types are given in scheme 3. From this list it is apparent that the method is not only applicable for the synthesis of condensed aromatics but the new strategy has been found to be highly successful for the construction of aromatic ring over the preconstructed heterocyclic molecules providing for the first time a new synthetic dimension to the entire

chemistry of benzoheterocyclic compounds and their condensed variants. However these results cannot be highlighted in this lecture due to limited time and will be confined to the application of our methodology only for the synthesis of benzenoids and thier condensed variants by using appropriate anion **11a-d** only.

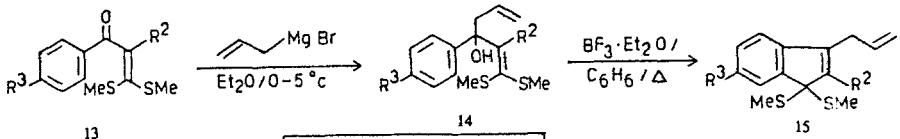
3-Carbon 1,3-Binucleophiles and α-Oxoketene Dithioacetals Approach for Aromatic Annelation



Scheme 3

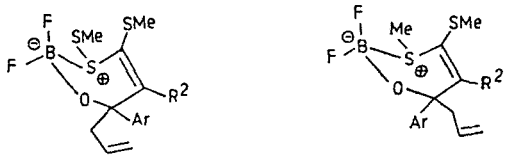
The reaction is a major discovery involving direct entry from highly functionalized open chain precursors to appropriately substituted aromatics in a simple two step sequence. The reaction was found to be general with a wide variety of α-oxoketene dithioacetals derived from both cyclic and acyclic ketones as well as equally large number of allyl anions making its synthetic scope unlimited. Six months after our first publication Dieter and co-workers[5] also published identical results by reacting methylallylmagnesium bromide with α-oxoketene dithioacetals to afford methyl substituted phenylthioethers.

The α-alkyl α-oxoketene dithioacetals of general formula **13** on addition of allylmagnesium bromide yielded the corresponding expected carbinol acetals **14** in high yields (Scheme 4). However when these acetals were treated with $BF_3.Et_2O$ in benzene the corresponding 3-allyl-1,1-bis(methylthio)-2-alkylindenes[6] **15** were



13 14 15

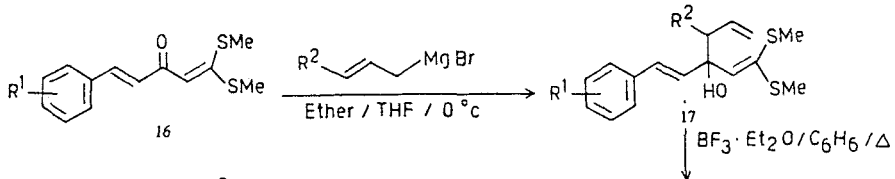
R^2	R^3	Yield
Me	H	80
Et	H	71
n-Pr	H	76
n-Pr	MeO	79



A R^2=H B R^2 = alkyl

Scheme 4

formed instead of the corresponding cycloaromatic products. The formation of either aromatics or indenes can be explained through cyclic transition states **A** and **B** respectively (Scheme 4). When R^2 = H or R^1R^2 = -(CH_2)-$_n$ the allyl group occupies the quasiaxial position and could interact with bis(methylthio)-methylene double bond to afford cycloaromatized product. However, when R^2 = alkyl or aryl, the phenyl group occupies the quasiaxial position **B** inorder to



16 17 18 19

(59-62%) (51-68%)

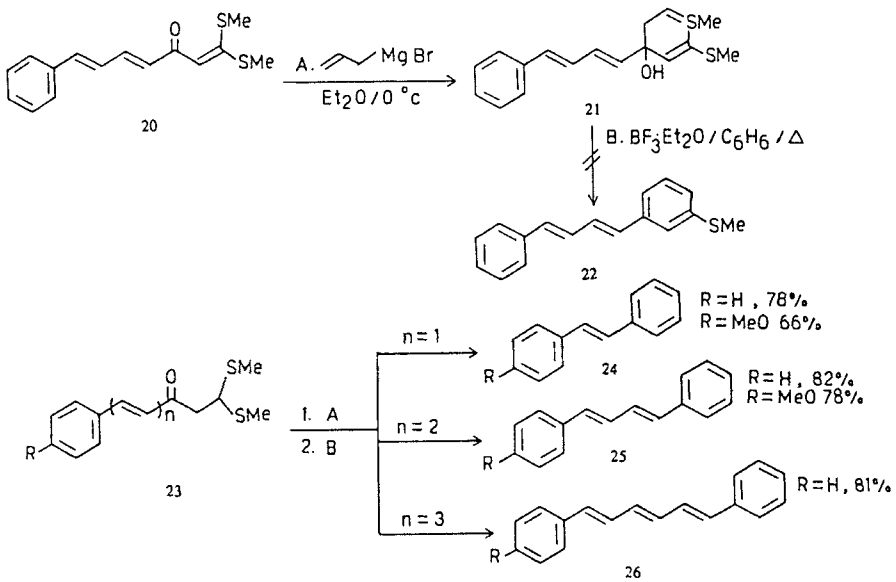
R^1	R^2
H	H
4-Me	H
4-Cl	H
H	Me

R^1	R^2	R^1	R^2
H	H	2,6-Cl_2	H
4-Me	H	3,4-Cl_2	H
4-Cl	H	H	Me
3-MeO	H	4-Me	Me
2-Cl	H	4-Cl	Me

Scheme 5

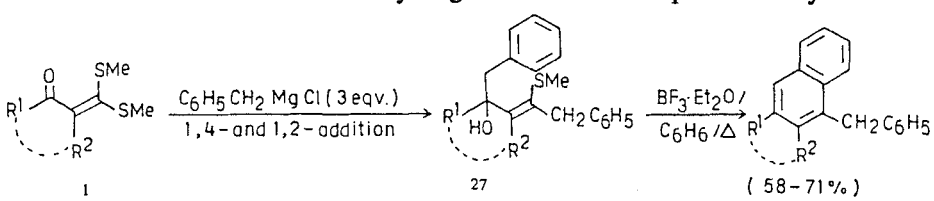
minimize the steric interaction between 1,2- substituents so that the aromatic π cloud can attack the developing cation stablized by the bismethylthio functionality to afford 3-allylindenes **15**.

The reaction was extended to α-cinnamoylketene dithioacetals of general formula **16** (Scheme 5). The resultant intermediate carbinol acetals **17** underwent smooth $BF_3.Et_2O$ assisted cyclization to afford the 3-methylthiostilbenes **18** in 51-68% overall yields[7]. Thus the reaction constitutes a novel entry to substituted stilbenes through the construction of one of the aromatic rings from acyclic precursors. However, when it was extended to homologous 5-aryl-2,4-pentadienoylketene dithioacetals **20** to afford 1,4-biarylbutadienes **22**, only intractable tar was formed in these reactions (Scheme 6). This limitation was successfully circumvented by reacting ß-oxoenyldithioacetals **23** with allyl anions to afford not only the corresponding stilbenes **24** in improved yields, but also the corresponding dienes **25**, and triene **26** in good yields[8] (Scheme 6). The corresponding ß-oxodithioacetals **23** were prepared in excellent yields from the corresponding aroyl, cinnamoyl, polyenoylketene dithioacetals by chemoselectively reducing the mercapto double bond either with $NaBH_4$/AcOH or with Zn/AcOH medium developed in our own laboratory[9].



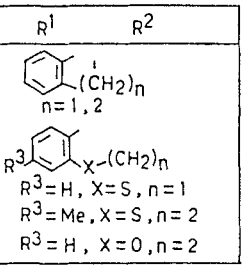
Scheme 6

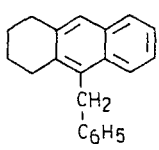
Subsequently this method of aromatic annelation was extended to naphtho-annelation by our group[10]. The strategy to achieve this transformation was conceived by reacting benzylmagnesium chloride with α-oxoketene dithioacetals **1** to afford the intermediate carbinol acetals **27** which on treatment with $BF_3.Et_2O$ should yield the corresponding naphthalene derivatives **28** through benzene ring participation (Scheme 7). However when the cyclic oxoketene dithioacetal derived from cyclohexanone **1** (R^1R^2 = -$(CH_2)_4$ was reacted with benzylmagnesium chloride (1.2 equiv.) the product isolated (31%) after treatment with $BF_3.Et_2O$ was characterised as 10-benzyl- 1,2,3,4-tetrahydroanthracene **29** while 35% of the starting material was recovered unreacted. Apparently 2 equivalents of benzylmagnesium chloride were added sequentially in 1,4-and 1,2-manner resulting in low yield of tetrahydroanthracene **29** which was raised to 81% when 3 equivalent of benzylmagnesium chloride were used and no starting material was recovered. Many substituted naphthalenes and other condensed aromatics were prepared in good yields. The 1,4-followed by 1,2-addition sequence could not be eliminated since the benzylmagnesium chloride preferentially added in



1 27 (58-71%) 28

R^1	R^2
C_6H_5	H
4-Me C_6H_4 ,	H
4-MeO C_6H_4 ,	H
n-naphthyl ,	H

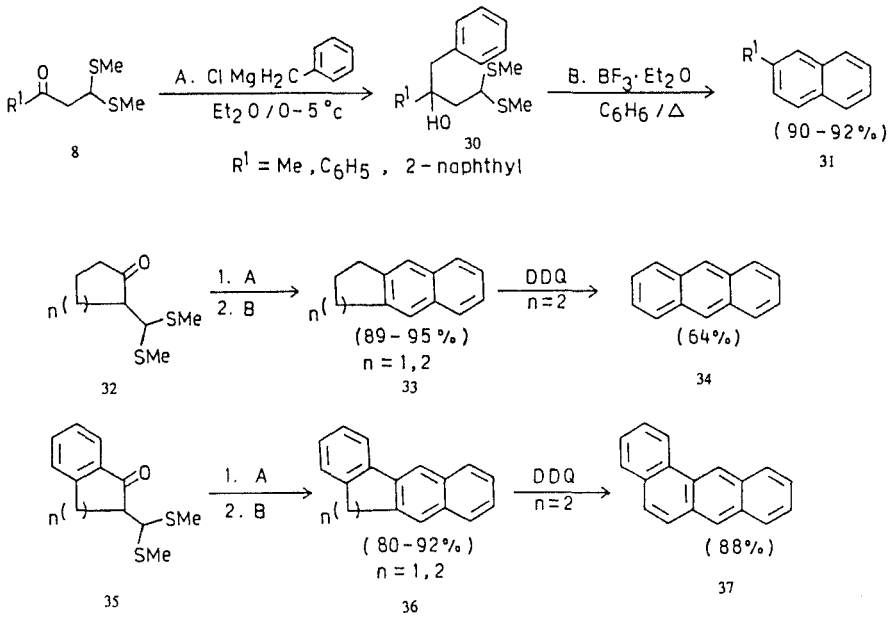




29

Scheme 7

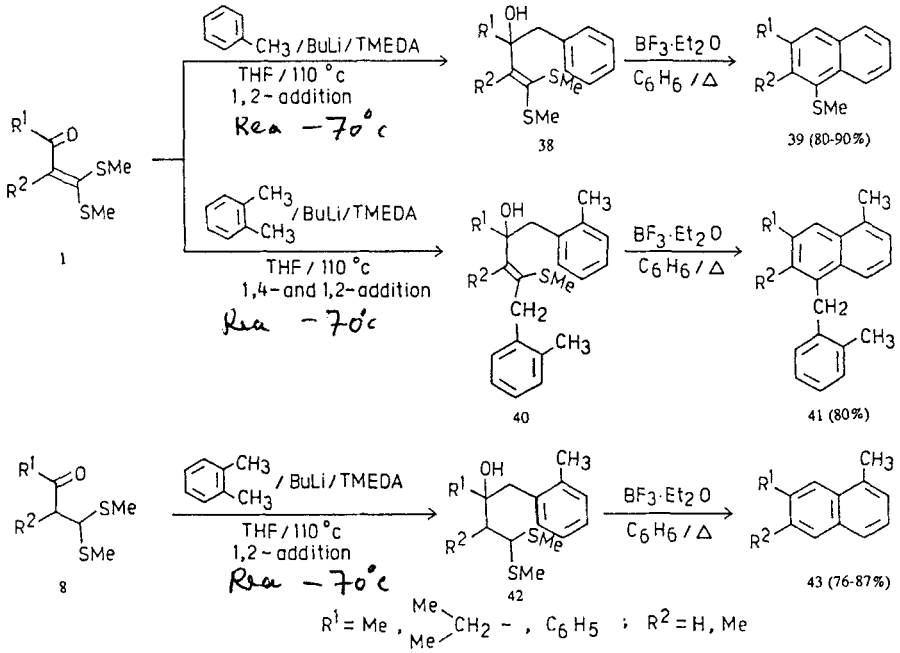
the 1,4- fashion followed by competetive 1,2-addition resulting in the benzyl group carried to the product naphthalenes and other condensed aromatics. To eliminate this limitation the benzylmagnesium chloride was reacted with ß-oxodithioacetals **8** when the corresponding substituted naphthalenes **31** were



Scheme 8

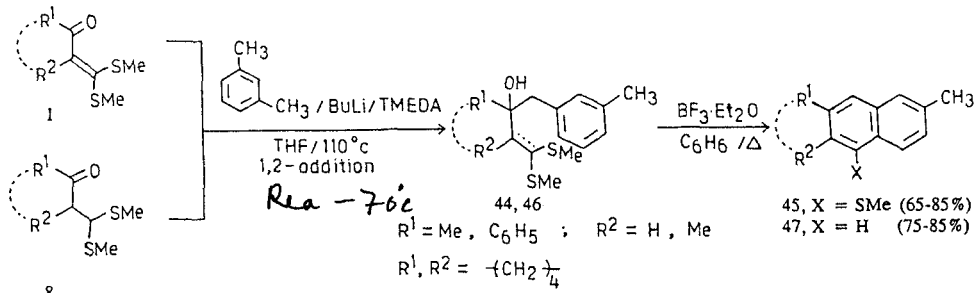
formed in high yields[11] (Scheme 8). Similarly the cyclic ß-oxodithioacetals **32** and their condensed variants **35** reacted with benzylmagnesium chloride and $BF_3.Et_2O$ to afford the corresponding linearly fused naphthalenes **34** in 89-95% overall yields. The tetrahydroanthracene **33** (n = 2) on treatment with DDQ yielded the corresponding anthracene in 64% yield. Similarly the dihydrobenzanthracene **36** (n = 2) on treatement with DDQ yielded the corresponding benzoanthracene **37** in 88% yield (Scheme 8). Thus the limitation of our earlier observation of 1,4-followed 1,2-addition sequence could be successfully eliminated.

Also the reaction of lithiomethylbenzene with α-oxoketene dithioacetals was found to follow interestingly only 1,2- addition mode to afford the corresponding carbinol acetals **38** in high yields followed by its successful $BF_3.Et_2O$ assisted cyclization to afford the corresponding naphthalenes **39** in 80-90% overall yields[12] (Scheme 9). Here again the lithiomethyl derivative derived from *ortho*-xylene yielded the product based on 1,4-followed by 1,2-addition sequence resulting in the corresponding naphthalene **41**. To overcome this limitation the anion derived from *ortho*-xylene was reacted with ß-oxodithioacetals



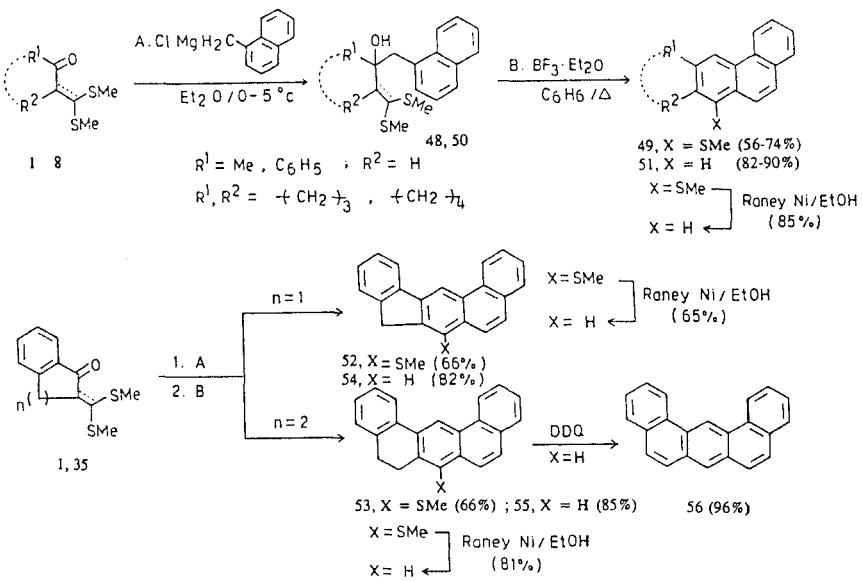
Scheme 9

8 when the corresponding regioselectively substituted naphthalenes **43** could be isolated in high yields (Scheme 9). The naphthalene **43** with R^1 = isopropyl group is a precursor of hydrocarbon obtained after dehydrogenation of the terpene Eudelene. Thus the method is very efficient for the synthesis of regioselectively substitued naphthalenes in high yields. Similarly the lithio derviative derived from *meta*-xylene reacted with both α-oxoketene dithioacetals **1** and their corresponding ß-oxodithioacetals **8** exclusively in the 1,2- fashion to afford the corresponding regioselectively substituted naphthalenes **45** and **47** respectively in excellent yields (Scheme 10).



Scheme 10

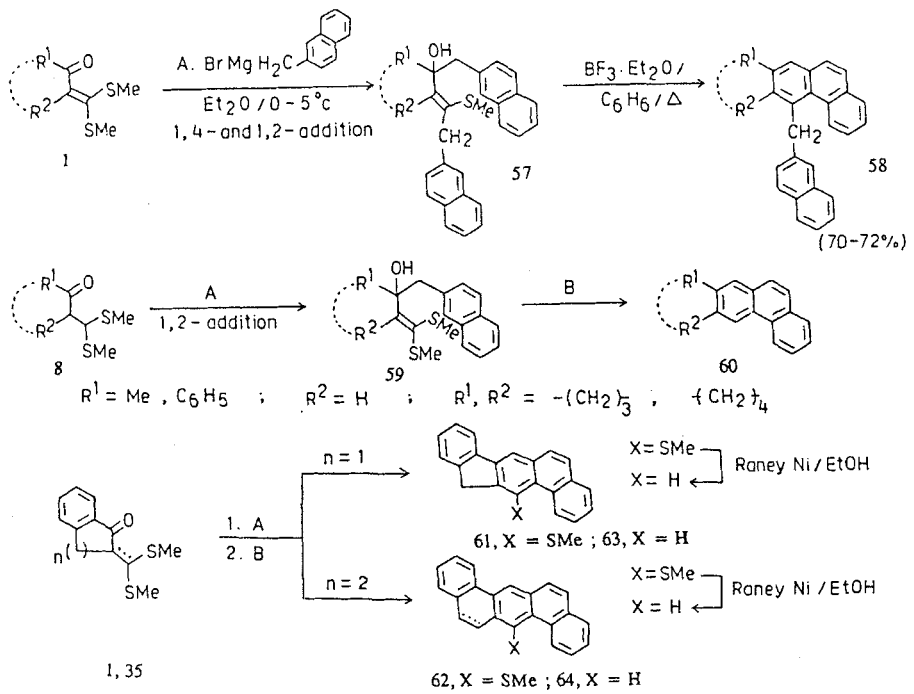
The method was further extended to the reaction of 1 and 2 naphthylmethyl magnesium halides with both **1** and **8** to assess the possible *peri* interaction of 1-naphthylmethylmagnesium chloride which is known to exhibit the possible *peri* interaction and consequently the expected liberal delocalization will be restricted over the ring and allow the preferred charge controlled 1,2-addition[11]. On the otherhand the corrsponding 2-naphthylmethylmagnesium halide might simply follow 1,4-followed 1,2-addition in the absence of steric inhibition for the charge delocalization. Our experiments indeed corroborate these expectations that the 1-naphthylmethylmagnesium chloride underwent charge controlled 1,2-addition while the 2-naphthylmethylmagnesium bromide underwent orbital controlled 1,4-addition followed by 1,2-addition with a few exceptions in each case. Thus the α-oxoketene dithioacetals **1** and ß-oxodithioacetals **8** (Scheme 11) reacted with



Scheme 11

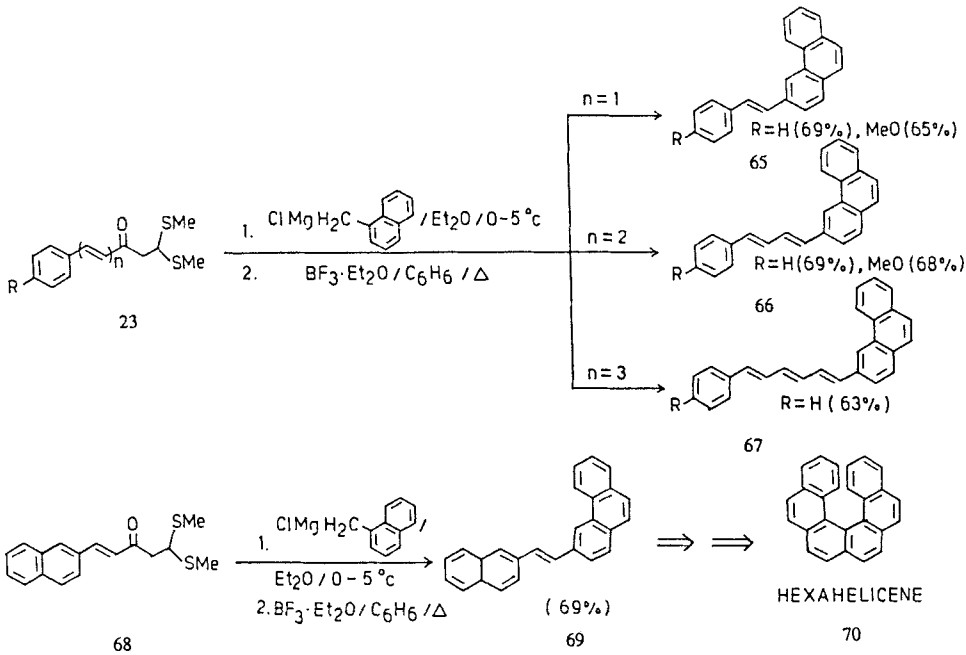
1-naphthylmethylmagnesium chloride to give exclusively the corresponding 1,2-adducts **48** and **50** which on $BF_3.Et_2O$ treatement in refluxing benzene yielded the corresponding phenanthrenes **49** and **51** respectively in good yields. The other α-oxoketene dithioacetals and the corresponding ß-oxodithioacetals derived from

indanone and tetralone similarly yielded the corresponding condensed aromatics **52-55** in 66-85% overall yields. The dihydrobenzanthracene **55** was subsequently desulphurized and dehydrogenated to yield the corresponding dibenzanthracene **56** in 96% yield. On the other hand the 2-naphthylmethylmagnesium bromide reacted with **1** in the expected 1,4- followed by 1,2- addition pattern which on cyclization yielded the corresponding methylnaphthyl substituted phenanthrenes **58** in 70-72% overall yields (Scheme 12). When the 2-naphthylmethylmagnesium bromide was reacted with ß-oxodithioacetals **8** the corresponding phenanthrenes **60** were formed through the 1,2-addition pattern. However the 2-naphthylmethyl-magnesium bromide followed the 1,2- addition pattern when it was reacted with α-oxoketene dithioacetals and corresponding ß-oxodithioacetals derived from indanone and tetralone to yield the corresponding condensed aromatics **61 - 64** in good yields (Scheme 12).



Scheme 12

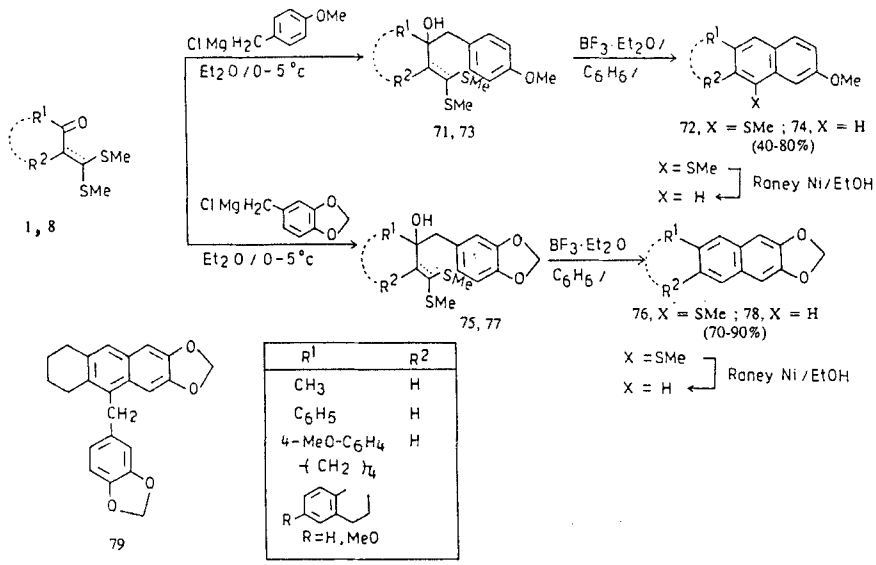
The 1-naphythylmethylmagnesium chloride was also reacted with ß-oxo-cinnamoyl, dienoyl and trienoyl dithioacetals to yield the corresponding styryl **65**,



Scheme 13

dienyl **66** and trienyl **67** phenanthrenes in 63-69% overall yields (Scheme 13). 1-(2-Naphthyl)-2- phenanthrylethylene **69** which is a useful photochemical precursors for the synthesis of hexahelicene **70** was obtained in 69% yield by reacting 1-naphthyl-methylmagnesium chloride with the corresponding ß-oxodithioacetal **68** (Scheme 13). Thus a new efficient method for the synthesis of 1,2-diarylethylenes, 1,4-diarylbutadienes and 1,6-diaryl-1,3-hexatrienes has been formulated. The overall strategy of creating an aromatic ring through open chain precursors to yield the otherwise difficultly accessible polyenylaromatics has been efficiently realized.

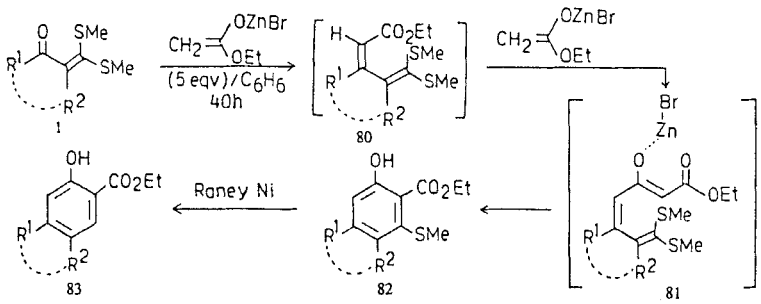
It was also considered of interest to extend this aromatic annelation methodology for the synthsis of oxygenated naphthalenes many of which are presursors of natural products. The electron donating substituent on the benzene ring may render the corresponding benzylmagnesium chloride hard enough to follow charge controlled 1,2- addition to **1** and **8** unlike the naked benzyl-magnesium chloride as exemplified in the preceding paragraphs. Thus 4-methoxy-benzyl magnesium chloride reacted with **1** and **8** only in 1,2-fashion to yield the



Scheme 14

corresponding carbinol acetals **71** and **73** which on treatment with BF3.Et2O yielded regioselectively substituted methoxynaphthalenes **72** and **74** respectively in excellent yields[13] (Scheme 14). Similarly 3,4-methylenedioxymagnesium chloride yielded the corresponding naphthalenes **76** and **78** having the methylenedioxy functionality in the linear fashion. Only cyclohexanone mercaptal followed 1,4- and 1,2- addition sequence to yield the corresponding tetrahydroanthracene **79**.

An interesting cycloaromatization leading to substituted and annelated ethyl 2-hydroxy-6-(methylthio)benzoates[14] **82** was accomplished through the reaction sequence described in the Scheme 15. The five fold excess of Reformatsky reagent was reacted with **1** to afford the corresponding zinctrienoate **81** which underwent electrocyclic ring closure followed by elimination of methyl mercaptan to yield the corresponding salicylates **82** in 55-84% overall yields. Some of them were subjected to Raney Nickel desulphurization to afford the corresponding sulphur free regioslectively substituted or annelated salicylates **83** in high yields. The method is therefore of considerable synthetic importance for the synthesis of salicylates and their annelated analogs. The reaction of



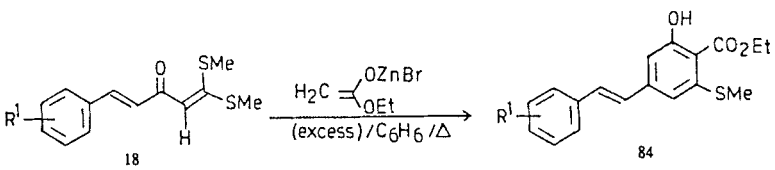
R^1	R^2	% yield
Me	H	84
4-ClC_6H_4	H	88
	-$(CH_2)_4$-	76
	-$(CH_2)_5$-	79
R=H ; n=1		63
R=OMe ; n=2		81

R^1	R^2	% yield
Me	H	60
4-ClC_6H_4	H	63
C_6H_5	H	60
2-Thienyl	H	63
2-Furyl	H	58
Me	Me	32
-$(CH_2)_3$-		52

R^1	R^2	% yield
	-$(CH_2)_4$-	57
	-$(CH_2)_5$-	60
R^3=H ; n=1		55
R^3=MeO ; n=2		58

Scheme 15

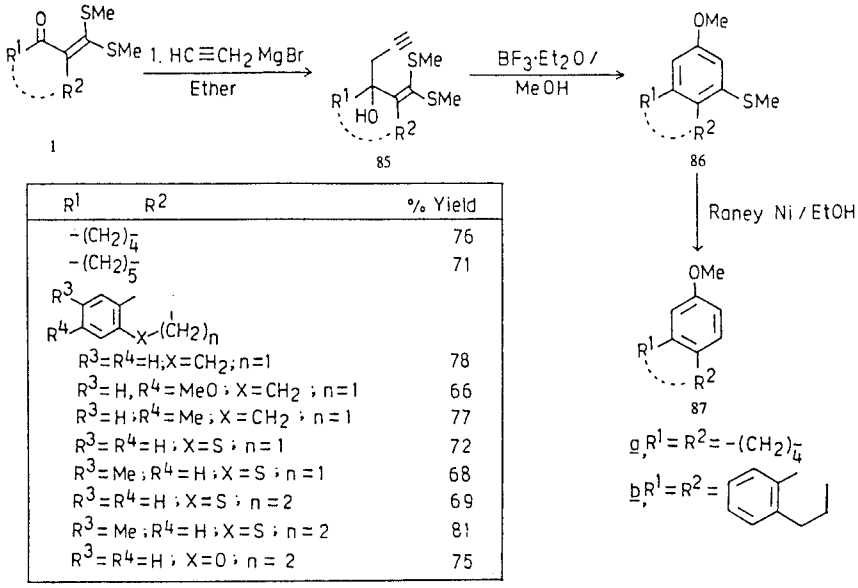
Reformatsky reagent with cinnamoylketene dithioacetals was equally successful to yield the corresponding stilbenes **84** in excellent yields[15] (Scheme 16).



R^1=H ; 4-Me ; 4-MeO ; 4-Cl ; 2,6-Cl_2 ; 3,4-$(MeO)_2$ 3,4,5-$(MeO)_3$; 4-NO_2 ; 60-74 %

Scheme 16

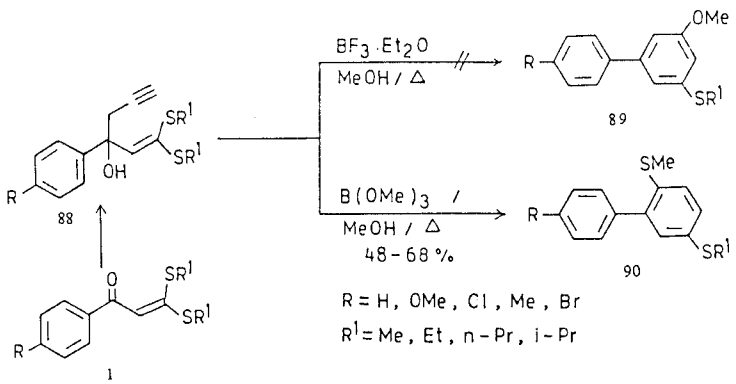
We have successfully demonstrated the aromatic ring participation when benzylmagnesium chloride was reacted with α-oxoketene dithioacetals. In continuation of this work, it was considered of interest that the carbinol acetals derived from propargylmagnesium bromide and α-oxoketene dithioacetals should cyclize by participation of an external nucleophile to yield the corresponding functionalized aromatic compounds. The cyclic α-oxoketene dithioacetals **1** underwent 1,2-addition smoothly with propargylmagnesium bromide to give the

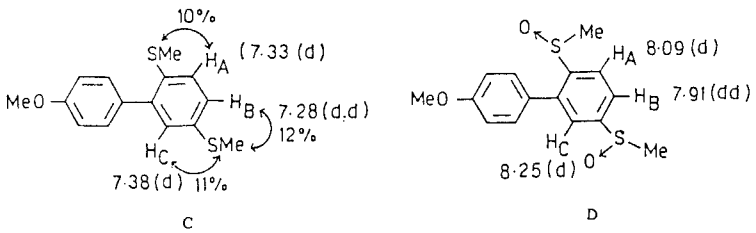


R^1	R^2	% Yield
$-(CH_2)_4-$		76
$-(CH_2)_5-$		71
$R^3=R^4=H; X=CH_2; n=1$		78
$R^3=H, R^4=MeO; X=CH_2; n=1$		66
$R^3=H; R^4=Me; X=CH_2; n=1$		77
$R^3=R^4=H; X=S; n=1$		72
$R^3=Me; R^4=H; X=S; n=1$		68
$R^3=R^4=H; X=S; n=2$		69
$R^3=Me; R^4=H; X=S; n=2$		81
$R^3=R^4=H; X=O; n=2$		75

Scheme 17

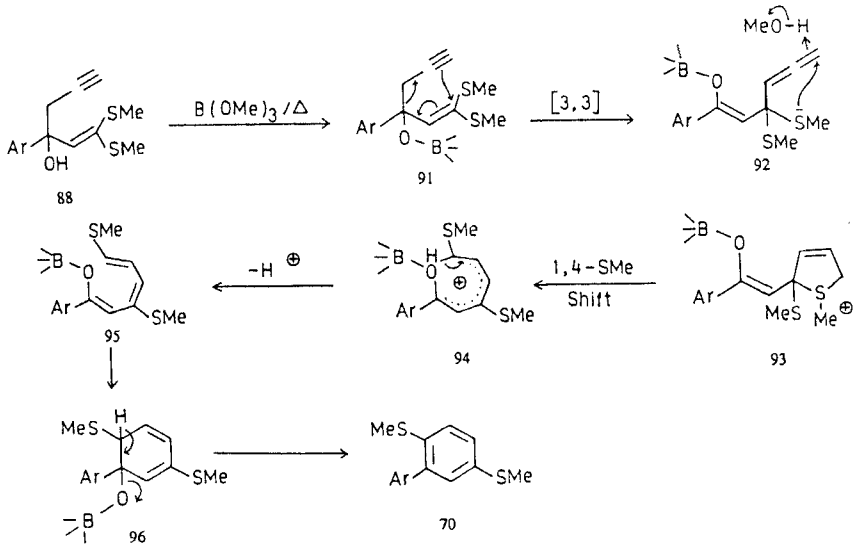
corresponding carbinol acetals **85** in excellent yields[16] (Scheme 17). These acetals when treated with methanolic $BF_3.Et_2O$, the corresponding thioresorcinol dimethyl-





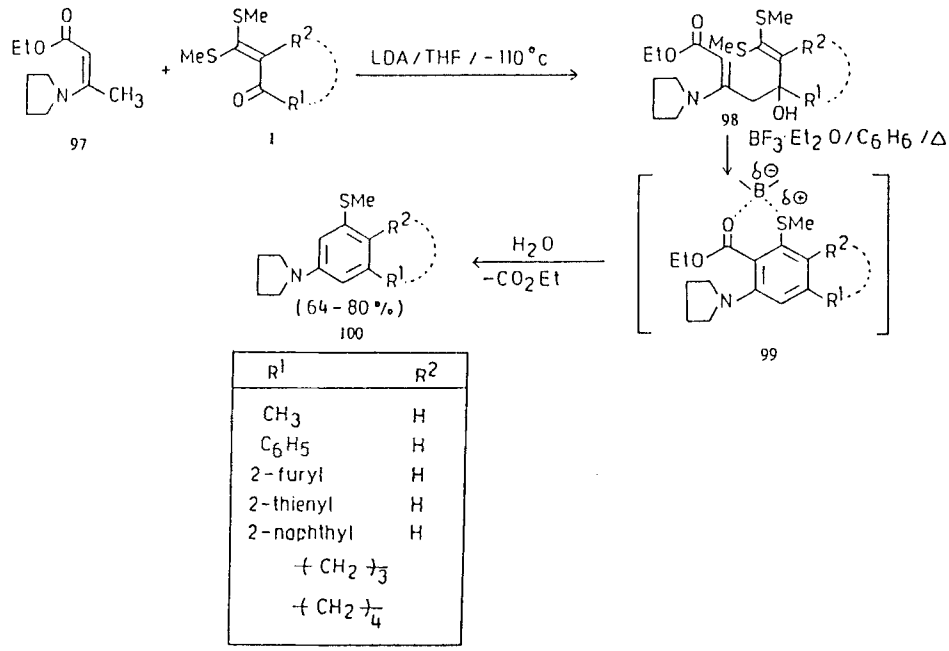
Scheme 18

ethers **86** were obtained in 66-81% overall yields. The selected compounds were also desulphurized in the presence of Raney Nickel/ethanol medium to yield the corresponding sulphur free methoxy compounds **87** in high yields. When the carbinol acetals **88** were treated with $BF_3.Et_2O$ in methanol the methoxy group participation with the triple bond was not observed to yield the corresponding diaryls **89**. However, when the carbinol acetals **88** were treated with trimethyl borate in methanol the corresponding biaryls **90** were formed involving intramolecular transfer of SMe group (Scheme 18). The structure **90** was confirmed from NOE studies of both sulphide **C** and sulphoxide **D**. The mechanism for the formation of **90** is depicted in scheme 19. In the presence of trimethyl borate the carbinol acetals **88** seems to undergo [3,3] sigmatropic shift to give the corresponding allenic intermediate **92** which undergoes 1,4- SMe shift through cyclic transition state **93** to afford **94** —> **95** on a loss of proton followed by electrocyclic ring closure.



Scheme 19

Recently we have also examined anions derived from aminocrotonate **97** involving heteroatom assisted deprotonation with LDA at -110°C. The reaction underwent smooth 1,2-addition followed by expulsion of carboethoxy group to afford the corresponding amino substituted aromatics **100** in 64-80% overall

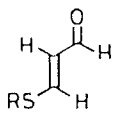


97 1 98 99 100

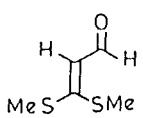
R^1	R^2
CH_3	H
C_6H_5	H
2-furyl	H
2-thienyl	H
2-naphthyl	H
$-(CH_2)_3-$	
$-(CH_2)_4-$	

Scheme 20

yields[17] (Scheme 20). The method is applicable to the synthesis of these aminoaromatics with variety of N,N-disubstituted aminocrotonates.

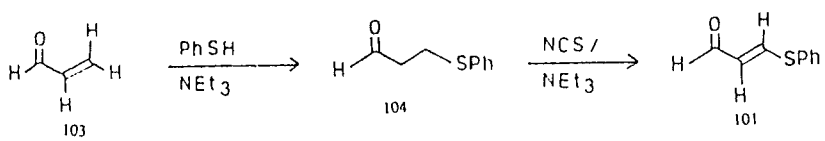


101a , R=Me
b , R=Ph



102

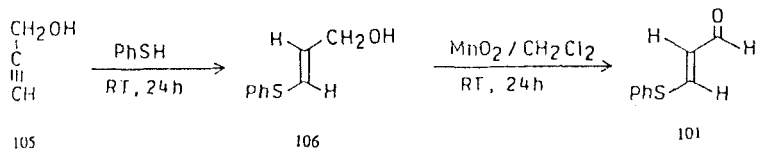
In all the above transformations the product benzenes and their condensed analogs invariably carry substituents. However, it is possible to design the three carbon 1,3-dielectrophilic fragment that could provide aromatic annelation which could result in unsubstituted aromatic ring. There are many possiblities



103 104 101

Scheme 21

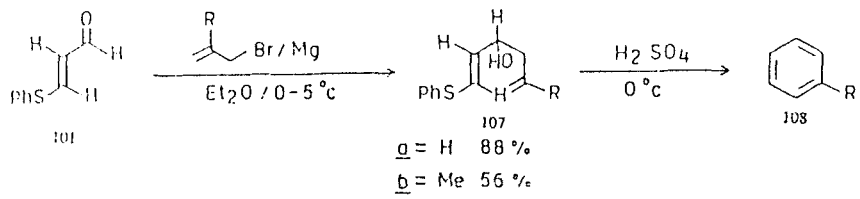
theoretically to create these 1,3-electrophilic carbon fragments. The ß-(aryl/methyl)acrolein **101** and allylmagnesium bromide should yield either benzene directly or thioanisole when **102**[18] is used in the above described reaction. The synthesis of **101b** is reported in the literature[19] as depicted in Scheme 21, which has been prepared in our laboratory with improved yield[20] as depicted in Scheme 22.



105 106 101

Scheme 22

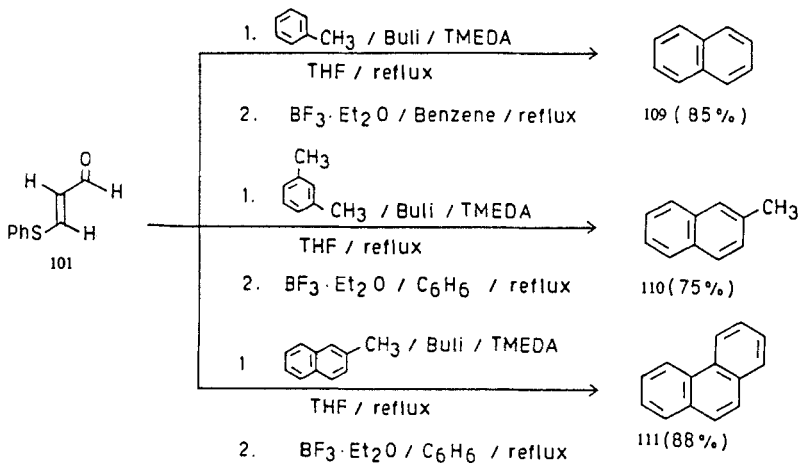
When **101b** was reacted with allylmagnesium bromide the corresponding carbinol acetal **107a** (Scheme 23) was obtained in quantitaive yield, which on treatment H_2SO_4 at O°C yielded unsubstituted benzene **108a** (R=H) in 88% yield[20]. Similarly the corresponding toluene **108b** (R=Me) was obtained in 56% yield by reacting methylallylmagnesium bromide with **101b**.



a = H 88 %
b = Me 56 %

Scheme 23

When lithiomethylbenzene was reacted with **101b** the corresponding unsubstituted naphthalene **109** was obtained in 85% yield under the described reaction conditions. Similarly ß-methylnaphthalene **110** (75%) and phenanthrene **111** (88%) were obtained by reacting anions derived from *meta*-xylene and ß-methylnaphthalene respectively (Scheme 24). Thus to our knowledge this is the first report on the direct annelation of benzene ring to the alkylaromatics in overall high yields. The method is likely to be of great synthetic potential to annelate benzene ring to any aromatic hydrocarbon carrying methyl group. It is further being explored to realize its full synthetic potential.



Scheme 24

It is apparent, from the examples illustrated above that the new aromatic annelation methodology developed through α-oxoketene dithioacetals and the related sulphur containing intermediates has already yielded highly promising results of immense synthetic utility. Further, synthetic potential of this methodology to create the vast majority of aromatic hydrocarbons from open chain precursors described in this lecture hold promising feature. Similarly it's application to heteroaromatic annelation is equaly versatile for the synthesis a large variety of heteroaromatic systems which are not covered in this lecture.

ACKNOWLEDGEMENTS

We thank all the graduate students who have been responsible for the success of the entire work whose names have appeared in the appropriate references. Financial assistance from Department of Science and Technology, New Delhi, Govt. of India, CSIR, New Delhi, Govt. of India and University Grant Commission (UGC), New Delhi through COSIST programme and Organon Research Centre, Calcutta is gratefuly acknowledged.

REFERENCES

1. Review : H. Junjappa, H. Ila and C.V. Asokan, Tetrahedron, 46, 5423 (1990).
2. B. Myrboh, H. Ila and H. Junjappa, J. Org. Chem., 48, 5327 (1983).
3. B. Myrboh, C.V. Asokan, H. Ila and H. Junjappa, Synthesis, 50 (1984).
4. G. Singh, H. Ila and H. Junjappa, Tetrahedron Lett., 25, 5095 (1984).
5. R.K. Dieter and L.Y. Jenkitkasemwong, Tetrahedron Lett., 26, 39 (1985).
6. G. Singh, H. Ila and H. Junjappa, unpublished results.
7. C.V. Asokan, H, Ila and H. Junjappa, Synthesis, 284 (1982).
8. Ch. Srnivasa Rao, O. M. Singh, H. Ila and H. Junjappa, Synthesis, 1075 (1992).
9. Ch. Srinivasa Rao, R. T. Chakrasali, H. Ila and H. Junjappa, Tetrahedron, 46, 2195 (1990).
10. M. P. Balu, G. Singh, H. Ila and H. Junjappa, Tetrahedron Lett., 27, 117 (1986).
11. Ch. Srinivasa Rao, M.P. Balu, H. Ila and H. Junjappa, Tetrahedron, 47, 3499 (1991).
12. K. Mallaiah, H. Ila and H. Junjappa, unpublished results.
13. B.K. Mehta, Ch. Srinivasa Rao, H. Ila and H. Junjappa, unpublished results.
14. A. Datta, H. Ila and H. Junjappa, Tetrahedron Lett., 29, 497 (1988).
15. A. Datta, H. Ila and H. Junjappa, J. Org. Chem., 55, 5589 (1990).
16. A. K. Gupta, H. Ila and H. Junjappa, Tetrahedron Lett., 28, 1459 (1987).
17. J. Satyanarayana, K. Raghava Reddy, H. Ila and H. Junjappa, Tetrahedron Lett., 33, 6173 (1992).
18. R.K. Dieter, J.R. Fishpaugh, J. Org. Chem., 53, 2031 (1988).
19. P. Bakuzis, M.L.F. Bakuzis, J. Org. Chem., 46, 236 (1981).
20. K. Mallaiah, Ch. Srinivasa Rao, H. Ila and H. Junjappa, Unpublished results.