CHAPTER - I

INTRODUCTION

Photochemical and Thermal Transformations of Organic Sulphur Compounds

There has been considerable interest in the photochemistry of organic sulphur compounds in recent years and several systems have been examined by different groups of workers. It was therefore, felt appropriate to review some aspects of both the photochemical and thermal transformations of a few representative organic sulphur compounds.

1. Photochemical Transformations of Organic Sulphur Compounds

1.1 Mercaptans

These compounds occur in petroleum and they are produced by the photochemical reaction of hydrogen sulphide with alkenes.[1] (Scheme 1).

The photochemical transformations of mercaptans have been reported in the literature.[2-8] For example, photolysis of methanethiol gave dimethyldisulphide, methane and hydrogen.[3,4] The formation of these products has been explained by the homolysis of S-H bond to give hydrogen atom and mercaptyl radicals which can further combine as shown in Scheme 2.

SCHEME - 1

$$H_2S \xrightarrow{h\nu} HS\cdot + H\cdot$$

$$HS\cdot + CH_2{=}CHR \longrightarrow HSCH_2{-}\dot{C}HR$$

$$HSCH_2{-}\dot{C}HR + H_2S \longrightarrow HSCH_2CH_2R + HS\cdot$$

SCHEME - 2

$$CH_3-S-H \xrightarrow{h\nu} CH_3-S\cdot + H\cdot$$

$$2\,CH_3-S\cdot \longrightarrow CH_3-S-S-CH_3^{*}$$

$$H_3-S-S-CH_3^{*} + CH_3-SH \longrightarrow CH_3-S-S-CH_3 + CH_3-SH^{*}$$

$$CH_3-SH^{*} \longrightarrow CH_3\cdot + HS\cdot$$

$$CH_3\cdot + CH_3-SH \longrightarrow CH_4 + CH_3-S\cdot$$

$$HS\cdot + CH_3-SH \longrightarrow CH_3-S\cdot + H_2S$$

$$H\cdot + CH_3-SH \longrightarrow CH_3-S\cdot + H_2$$

SCHEME - 3

$$\underset{\underline{1}}{H_3CH_2CH_2SH} + CH_3CH{=}CH_2 \xrightarrow{h\nu} \underset{\underline{2}}{(CH_3CH_2CH_2)_2S}$$

Stacey and Harris have reported[5] Anti Markovnikov addition of thiols to olefins on irradiation. For example, photolysis of propanethiol (1) with propylene resulted in dipropyl sulphide[5] (2) (Scheme 3).

Upon UV irradiation allylic mercaptans, like crotonyl mercaptan has been reported[6] to undergo self addition by a free-radical chain mechanism to give different products.

It has also been reported that unsaturated thiols undergo intramolecular reaction to give a bicyclic compound[7] 4 and heterocyclic sulphur compounds[8] 6 and 7 (Scheme 4).

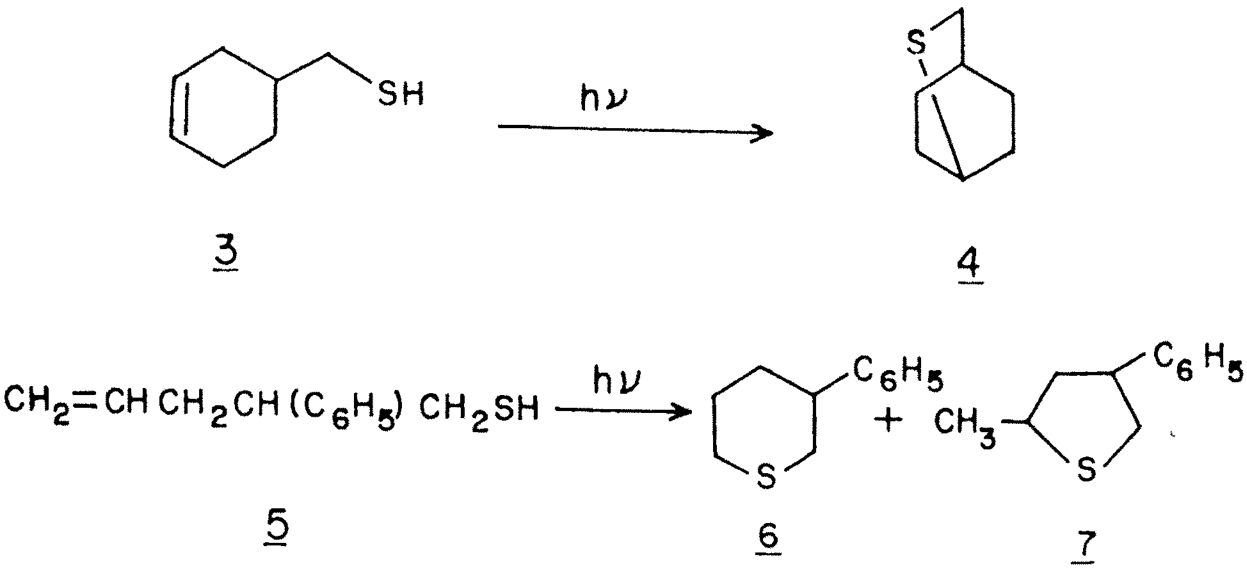
UV irradiation technique has been attempted by Baba Yoshio[9] to remove sulphur from mercaptans and sulphides present in crude naphtha.

1.2 Sulfides

(A) Simple sulphides

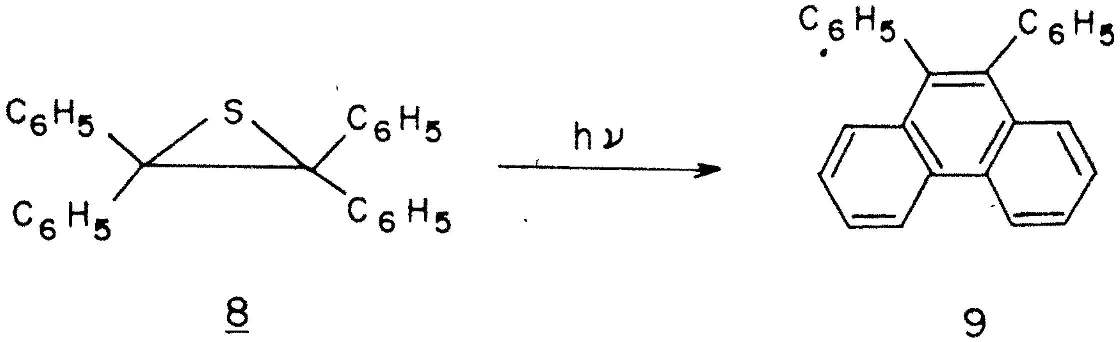
Simple dialkyl sulphides have been shown to undergo fragmentation through the initial homolysis of the C-S bond, leading to radical intermediates. For example, the principle products in the photolysis of dimethyl sulphide vapour observed[10] were methane, ethane, dimethyl disulphide and methanethiol.

SCHEME - 4



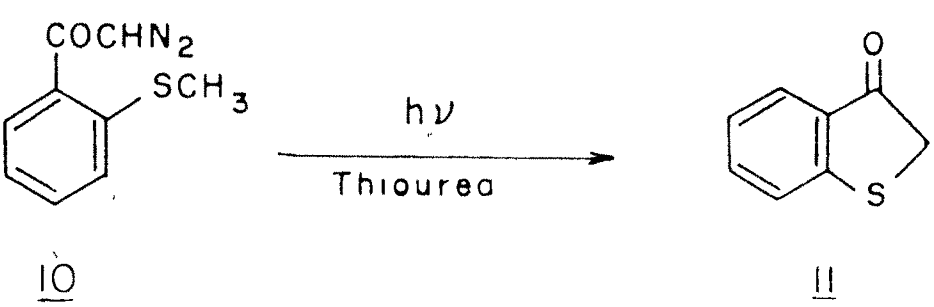
3 4 5 6 7

SCHEME -5



8 9

SCHEME-6



10 11

Photolysis of episulphides[11] and other cyclic sulfides[12] have been reported to give several interesting products. For example, the photolysis of tetraphenylethylene episulfide (8) has been reported to give 9,10-diphenylphenanthrene (9) (Scheme 5)[13].

The photolysis of Diazo(methylthio) acetophenone (10) in presence of thiourea gave 3-oxothionaphthene (11) (Scheme 6).[14]

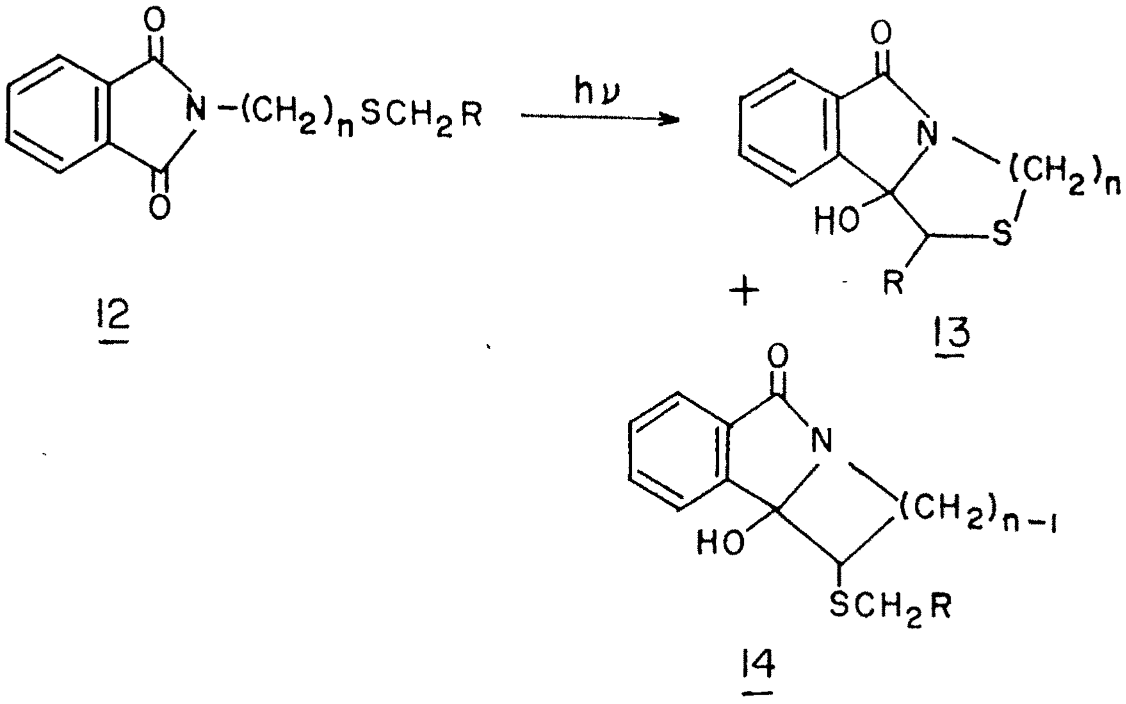
The photochemistry of phthalimide with a sulphide function in their N-alkyl side chain has been reported in literature.[15-17] For example, phthalimide 12 undergo facile and regio selective photocyclization to give corresponding azathiacyclos 13 and product 14 (Scheme 7).[17]

(B) Ketosulphides

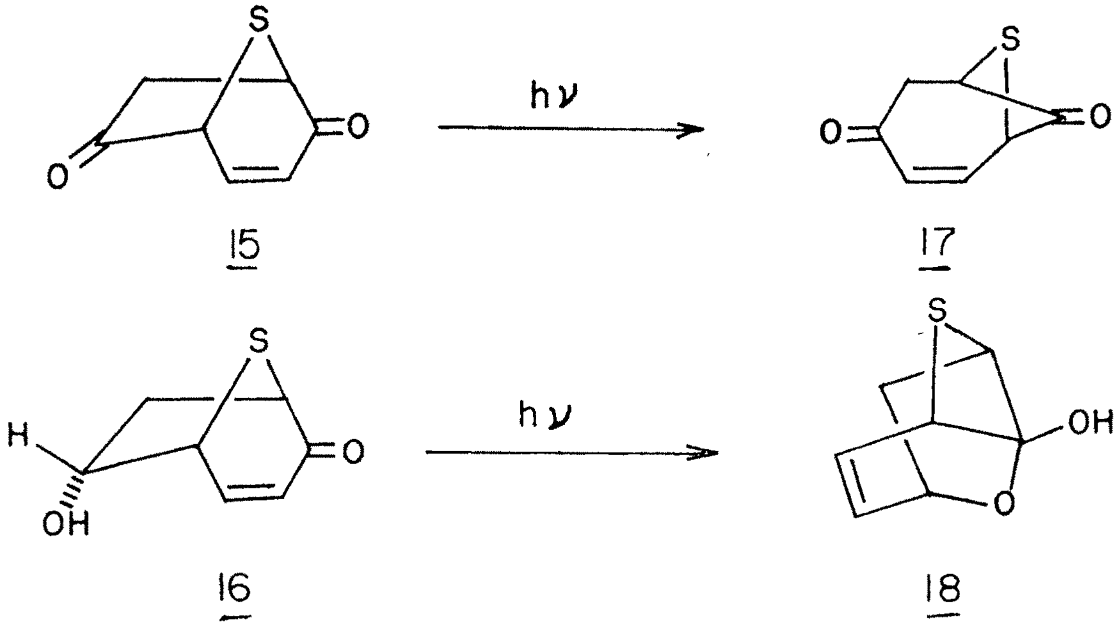
The photochemistry of β-ketosulphides have been studied by several group of workers,[18,19] who have shown that many interesting products have formed in these reactions.

Tsuruta and co-workers[20] have shown formation of 3-thiethanone 17 and 18 on irradiation of β-ketosulphides 15 and 16 respectively (Scheme 8).

SCHEME-7



SCHEME-8



The photolysis of 3-thiacyclohexanone (19) in Freon 113 gave products such as thiacyclopentan-2-one (21) and thiacycloheptan-4-one (22) through the formation of intermediate ylide 20, whereas the product 23 in tert.butyl alcohol seems to result from a homolytic cleavage (Scheme 9)[21].

Pederson and co-workers reported[22] that the photolysis of 2-phenyl-3,1-benzoxathian-4-one (24) gave benzaldehyde and dibenzo-[c,g]-(1,2)-dithiocan-5,6-dione (26) through thioketone-ketene intermediate 25 (Scheme 10). Subsequent investigations carried out by Chapmann and McIntosh[23] revealed that 2-thiobenzpropiolactone (27) is formed from 24 which leads to the formation of Di(thiosalicylide) (28) and not 26 (Scheme 10).

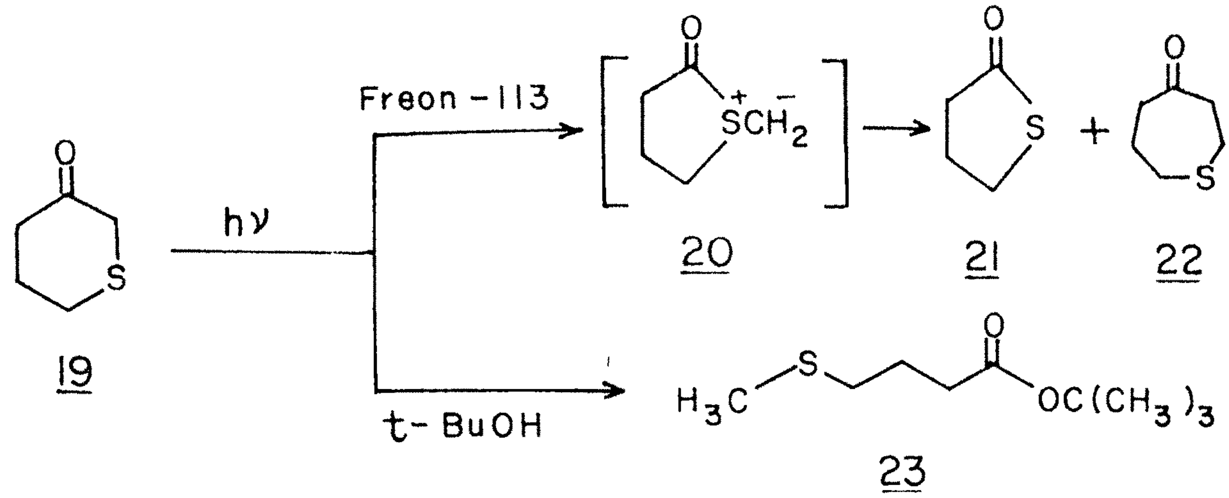
(C) Disulphides and polysulphides

Disulphides have been reported to undergo exchange reaction as well as fragmentation reaction on photolysis.

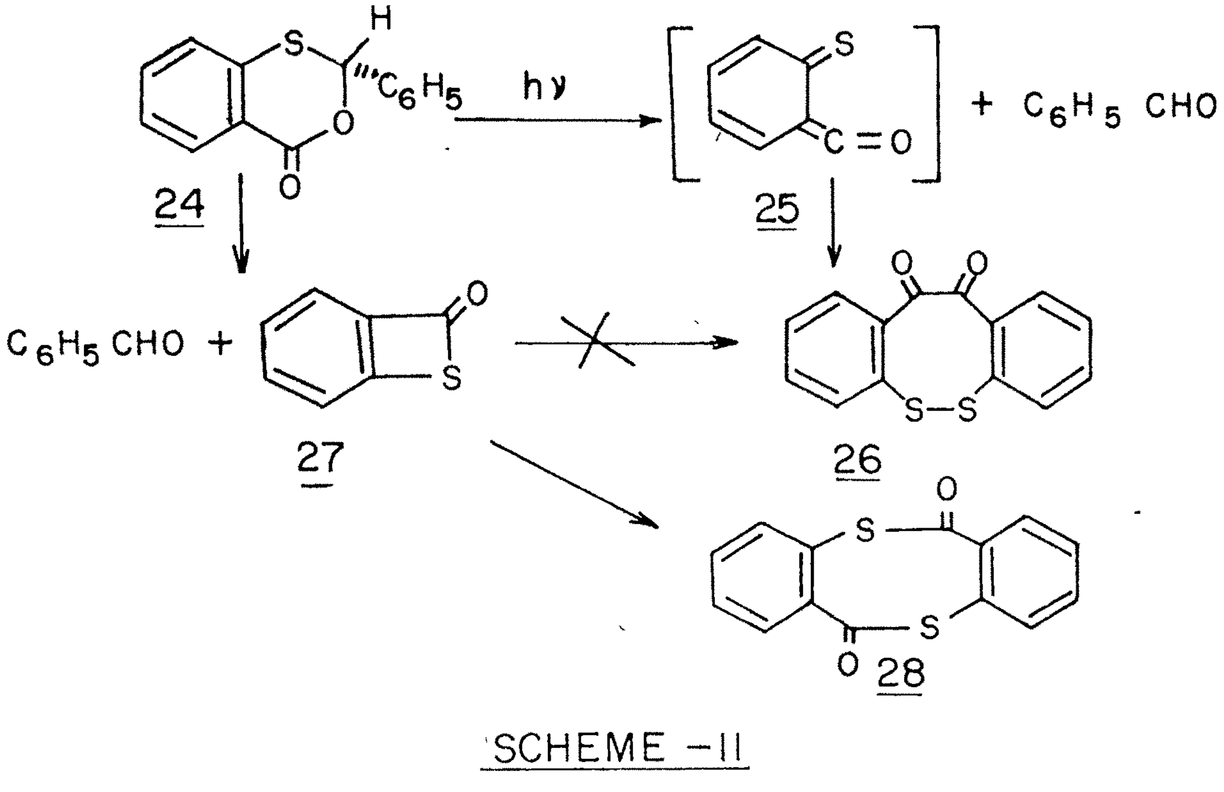
$$\text{R-S-S-R} + \text{R'-S-S-R'} \longrightarrow 2(\text{R-S-S-R'})$$

$$\text{R-S-S-R} \longrightarrow \text{R-S-R} + \text{R-S}_3\text{-R} + \text{R-S}_4\text{-R}$$

SCHEME - 9



SCHEME - 10



SCHEME - 11

$$(CH_3)_3C{-}S{-}S{-}C(CH_3)_3 \xrightarrow{h\nu} (CH_3)_3C-S-S\bullet + (CH_3)_3C\bullet$$

29

The former reaction involves the cleavage of S-S bond giving rise to mercaptyl radical which may participate in chain reaction. The fragmentation reaction on other hand, is unique for di- and polysulfides and involves C-S bond cleavage resulting in the formation of alkyl and R-S-S radical.

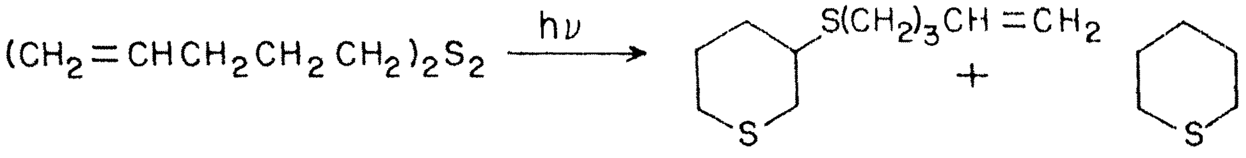
The photolysis of di-tert. butyl disulphide (29) has been shown by photo-CIDNP studies to give C-S bond fission via the triplet excited state of the disulfides (Scheme 11).[24]

Fission of the S-S bond in primary and secondary dialkyl sulphide leads to radical which readily recombine and thus the compounds are comparatively photostable.[25]

Photolysis of alkenyl disulphide has been reported[26] to give cycloalkyl alkenyl sulphides and a trace of thiacycloalkanes. For example, di-4-pentenyl disulphide (30) gave mainly 3-(4-pentenylthio) thiacyclohexane (31) and a trace of thiacyclohexane (32) (Scheme 12).[26]

The photochemical disproportionation reaction of a mixture of disulphide such as dimethyl and diethyl

SCHEME -12



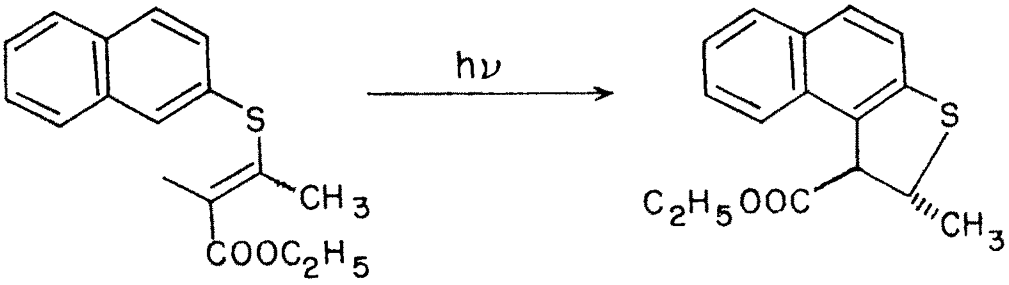
30 31 32

SCHEME - 13

$$CH_3-S-S-S-CH_3 \xrightarrow{h\nu} CH_3-S-S-CH_3 + (CH_3-S-S\cdot)_2$$

33 34 35

SCHEME - 14



36 37

$$C_2H_5OCH{=}CH-S-C_2H_5 \xrightarrow{h\nu} (C_2H_5O)(C_2H_5S)\,CHCHO$$

cis 38 39

$$+$$

$$C_2H_5SH$$

$$+$$

$$C_2H_5O\,(C_2H_5S)\,CH\,CH_2S-C_2H_5$$

40

disulphides gives methylethyl disulphide[27] as a major product. A number of investigators have studied the photolysis of polysulphides. Thus, for example, Dimethyl trisulphide (33) on irradiation gives the disulphide 34 and the tetrasulphide 35 (Scheme 13).[27]

The photolysis of Dibenzoyldisulphide[28] and Bis-trifluoromethyl disulphide[29] have also been studied.

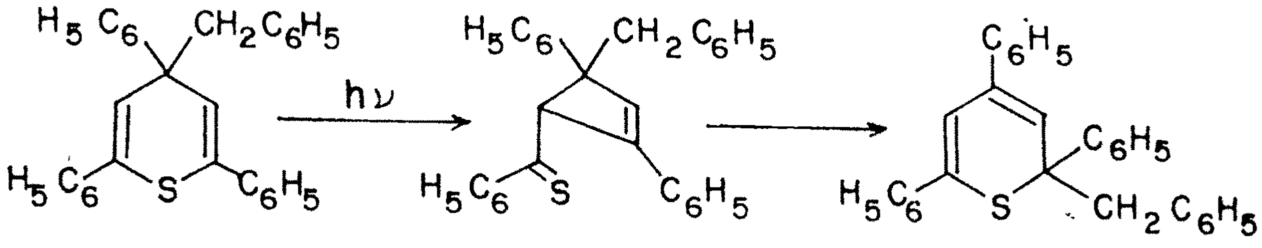
(D) Unsaturated sulphides

Photochemical transformation of unsaturated sulphides has been reported in the literature.[30,31] For example, naphthylsulphide 36 was irradiated to give naphtho-thiophene 37 as shown in Scheme 14.[31] Photolysis of 1-ethoxy-2-(ethylthio)ethene (38) resulted in formation of glyoxalmonothioacetal (39), ethanethiol and 1-ethoxy-1,2-di(ethylthio)ethane (40) (Scheme 14).[30]

An interesting example of photochemical isomerisation has been provided in the transformation of 4-benzyl-2,4,6-triphenyl-4H-thiopyran (41) to 2-benzyl-2,4,6-triphenyl-2H-thiopyran (43) (Scheme 15).[32]

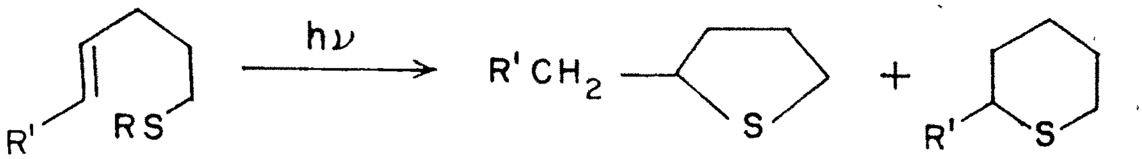
Bastein and co-workers[33] have reported the formation of monoalkylated heterocyclic compounds in

SCHEME-15



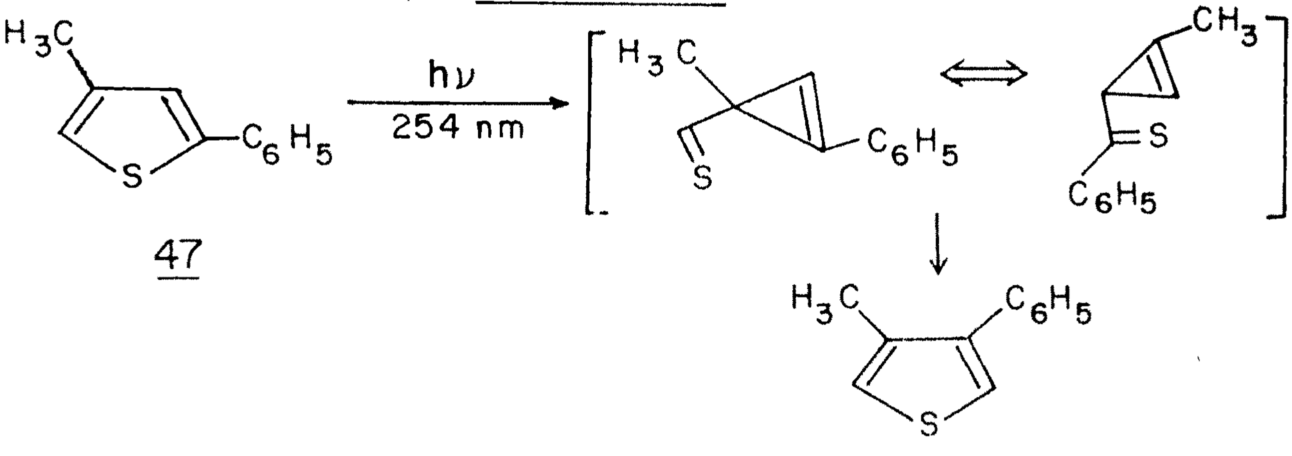
41 42 43

SCHEME-16



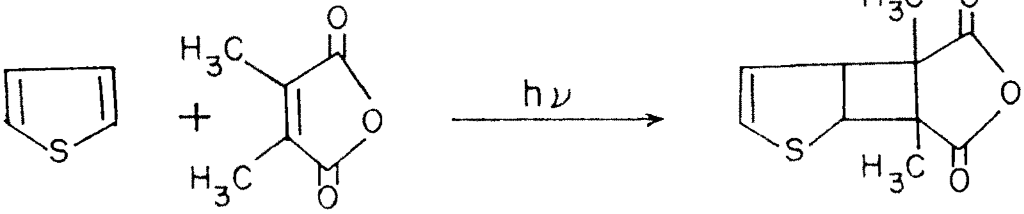
44 45 46

SCHEME-17



47 48

SCHEME-18



49 50 51

the photolysis of pent-4-en-1-yl sulfides 44 (Scheme 16).

(E) Thiophene derivatives

Thiophene and substituted thiophene have been shown to undergo variety of photochemical transformation.[34-36] An important type of reaction observed is interchange of substituent.[37] For example, 2-aryl or 2-alkyl thiophene (47) isomerises to 3-aryl or alkylthiophene (48) on photolysis (Scheme 17).[37]

It has been also shown that photochemical addition of dimethylmaleicanhydride to thiophene resulted in cyclobutane derivative 51 (Scheme 18).[38]

1.3 Sulfenyl compounds

The photolysis of a few sulfenyl compounds has been reported in the literature. Sulfenyl compounds can undergo either a homolytic or heterolytic cleavage under photochemical conditions giving rise to several products. The photolysis of trichloromethane sulfenyl chloride (52) in cyclohexane, for example, it has been reported to give a mixture of products consisting of hexachlorodimethyldisulfide (53), cyclohexyl chloride (54) and hydrogen chloride (Scheme 19).[39]

SCHEME -19

$$\underset{\underline{52}}{Cl_3CSCl} \xrightarrow{h\nu} Cl_3CS\cdot + Cl\cdot$$

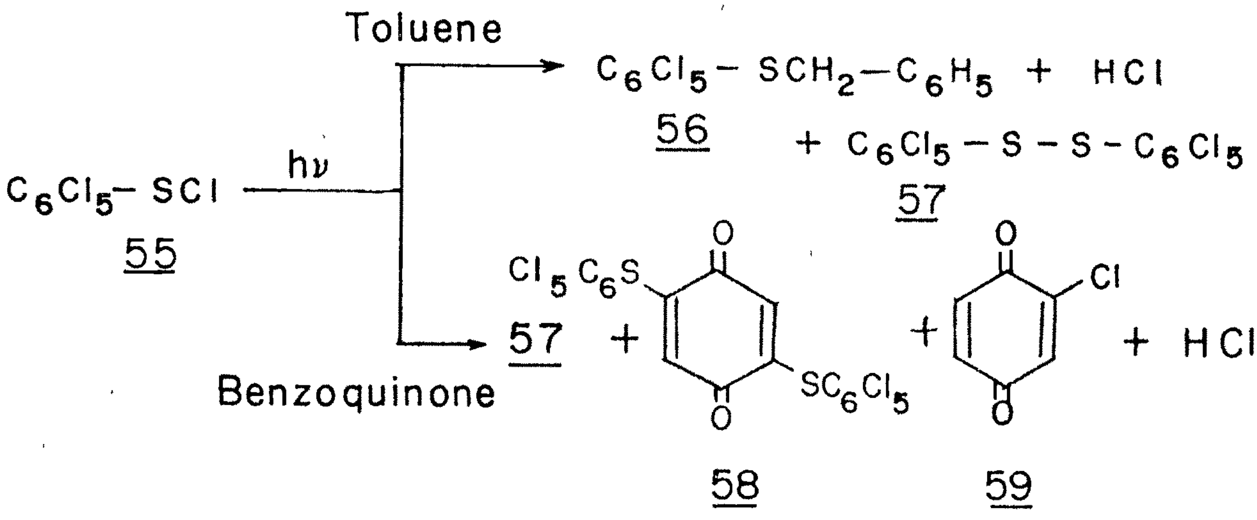
$$Cl\cdot + RH \longrightarrow R\cdot + HCl$$

$$R\cdot + Cl_3CSCl \longrightarrow RCl + \underset{\underline{54}}{Cl_3CS\cdot}$$

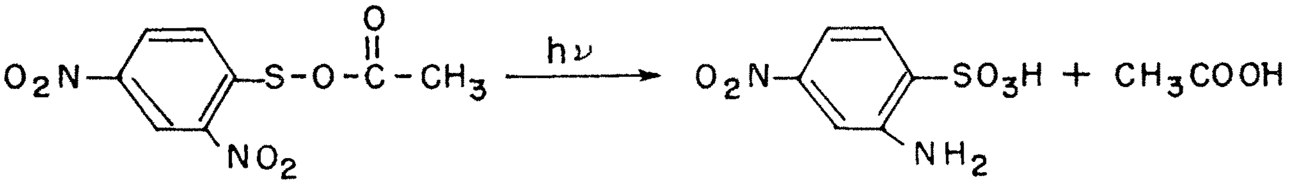
$$Cl_3CS\cdot + RH \longrightarrow R\cdot + Cl_3CSH$$

$$Cl_3CSH + Cl_3CSCl \longrightarrow \underset{\underline{53}}{Cl_3CSSCCl_3} + HCl$$

SCHEME -20



SCHEME -21



60

61

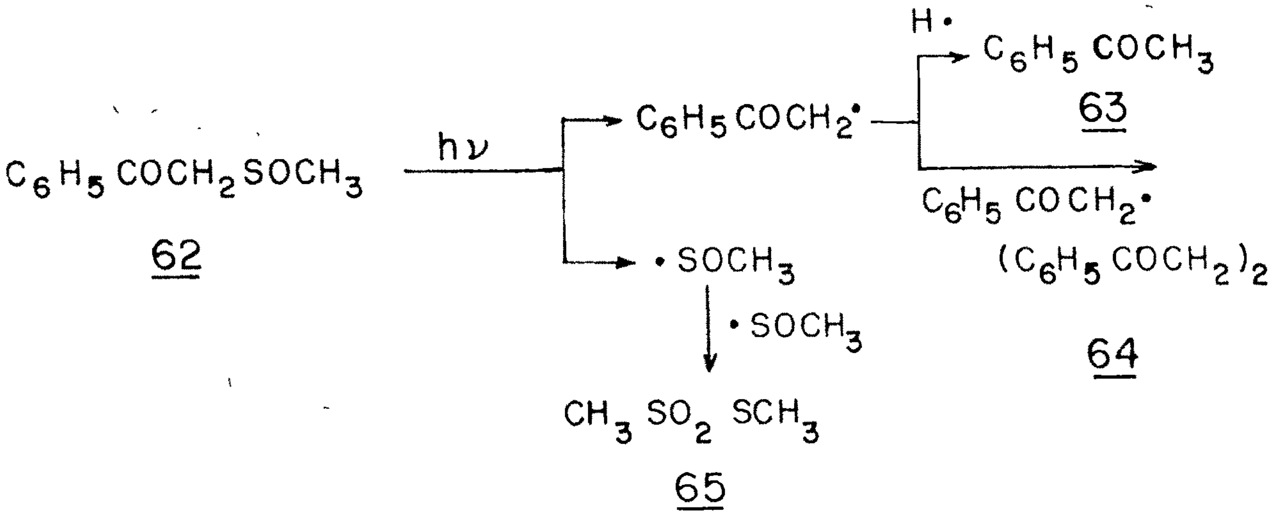
It has also been shown that sulfenyl halides can bring about substitution reactions in suitable substrates under photochemical conditions.[40,41] Thus, the photolysis of pentachlorobenzenesulfenyl chloride (55) in toluene yields pentachlorophenyl benzylsulfide (56) as the major product.[41] A small amount of dipentachlorophenyl disulfide (57) has also been observed in this reaction (Scheme 20). The photolysis of pentachlorophenyl sulfenylchloride (55) in the presence of benzoquinone gave a mixture of products such as 57, 58, 59 and hydrogen chloride (Scheme 20).

Barton and co-workers[42-44] have shown that the 2,4-dinitrophenylthiyl group can act as a photolabile protecting group for carboxylic acids. Thus, they have shown that the photolysis of a sulfenyl carboxylate 60 gives rise to a mixture of products consisting of acetic acid and 2-amino-4-nitrobenzenesulfonic acid (61) (Scheme 21).

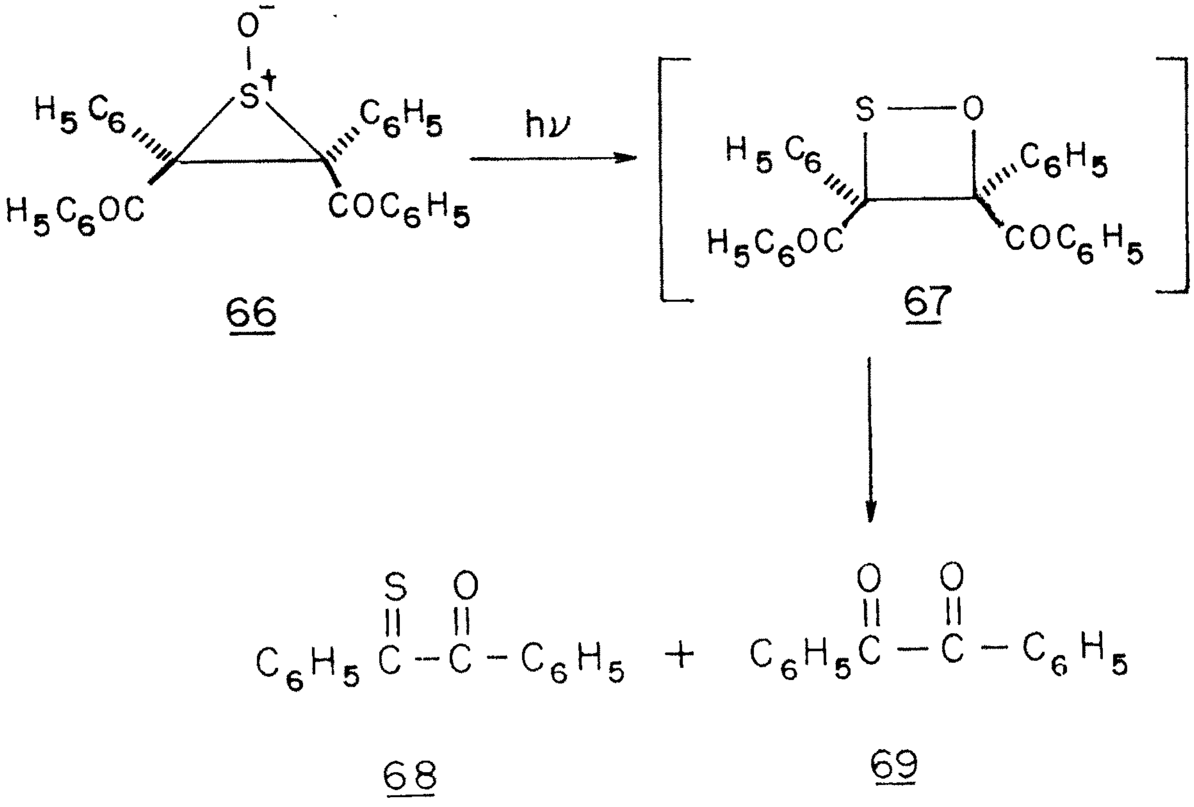
1.4 Sulfoxides

The photolysis of several sulphoxide has been studied in detail.[45-50] Irradiation of methyl phenacylsulfoxide (62) has been reported to give acetophenone (63), dibenzoylethane (64) and methane thiol sulfonate (65) (Scheme 22).[47]

SCHEME - 22



SCHEME - 23



Photolysis of episulfoxide 66 has been reported to yield monothiobenzil (68) and benzil (69) via ring expansion of the intermediate 67 (Scheme 23)[48,49]

An interesting type of photochemical reaction has been reported by Still and co-workers.[50] Photolysis of 3-methylthiochroman-4-one-1-oxide (70) proceeds via cyclization, β-H-abstraction and homolysis of S-O bond to give 71 (Scheme 24).[50]

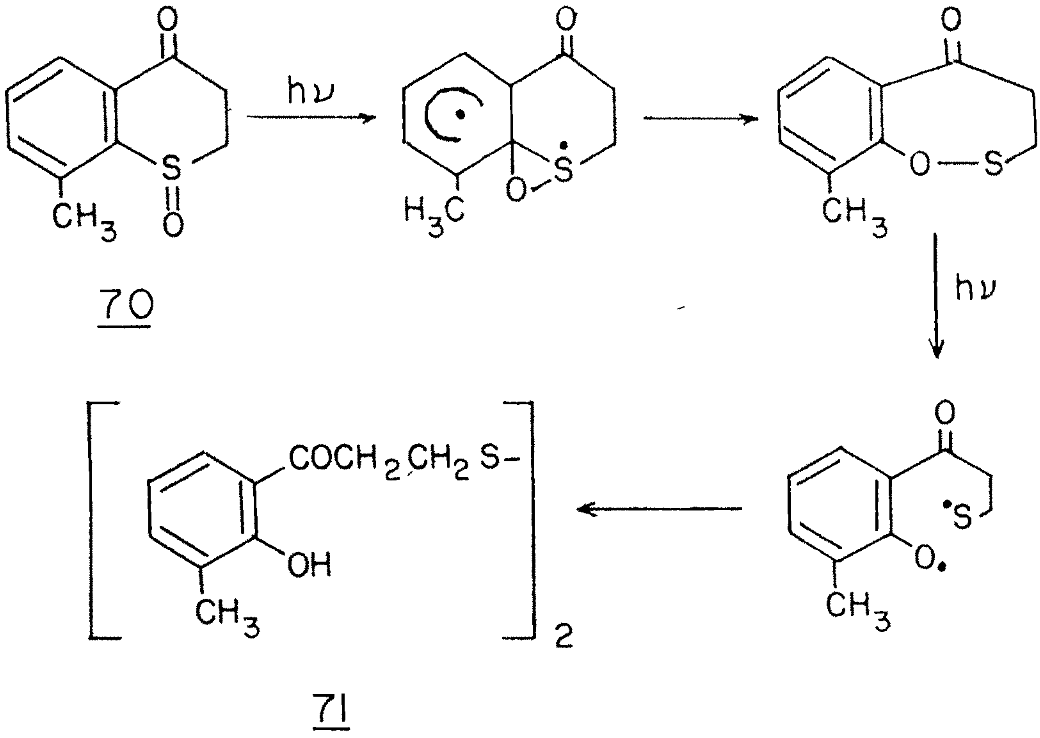
1.5 Sulphones

Extrusion of SO_2 and less frequently SO or sulphur itself by photochemical means has been attempted in a variety of compounds.[51-57] For example, photolysis of dihydrothienothiophene sulfone (72) affords primarily the thienocyclobutene (73) (Scheme 25).[57]

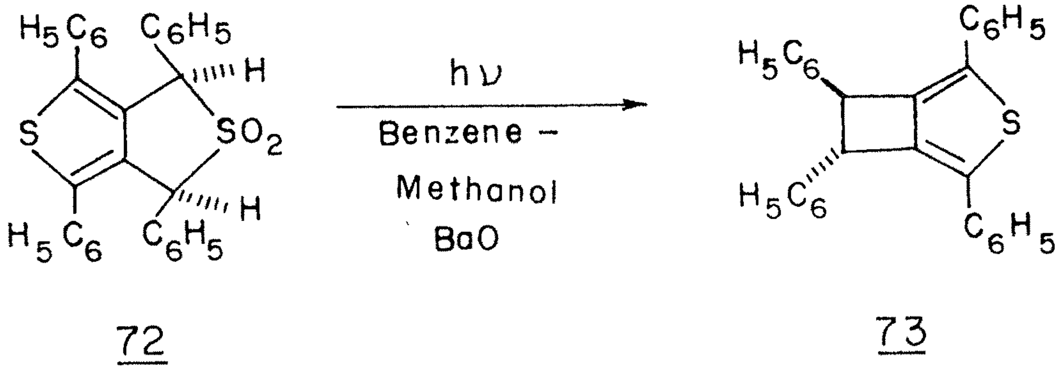
Photocyclo addition of sulphones gave interesting product.[58] Photolysis of 3-acetoxybenzo(b)thiophene 1,1-dioxide (74) in benzene-cyclohexene gave cyclohexene adduct (75) as shown in Scheme 26.

Photodecomposition[59] and phenylation[60] to sulphones were also studied by several group of workers. The photochemical reaction of aromatic sulphone has

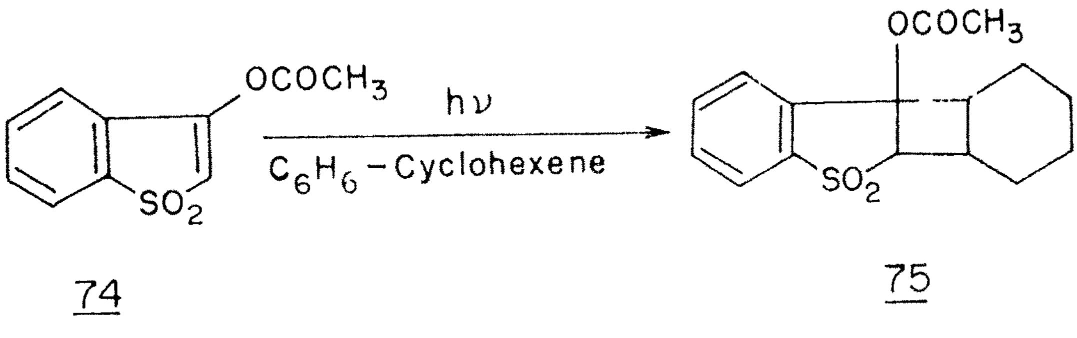
SCHEME - 24



SCHEME -25



SCHEME - 26



been reported to give variety of products.[61,62] For example, photolysis of diphenyldisulfone resulted in arenesulphonic acid, arenesulfonic anhydride, thiol sulfonate, diarylsulfone, biaryls and sulphurdioxide.[62] In the photolysis of mono-β-ketovinyl sulfone (76), SO_2 extrusion product combines with the solvent and results into products like 77 and arene 78 (Scheme 27).[63]

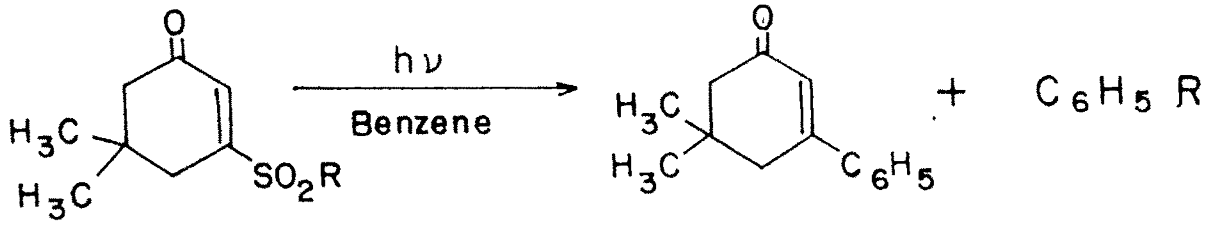
1.6 Sulfonic acid and their derivatives

Sulfonic acid and its derivatives have been reported to give variety of products.[64-70] For example, photolysis of α-toluenesulfonyliodide (79) in the presence of allene gave Benzyliodide (80) (Scheme 28).[70]

On irradiation, sulfonic acid and its derivatives involves reactions like desulfurization, desulfonation and extrusion of SO_2.[64,65]

Photolysis of alkylsulfinate and sulphites involves the fission of ArSO–OR bond, producing a sulfinyl radical and an alkoxy radical.[71] On irradiation, Benzyl sulphite (81) resulted into variety of products (Scheme 29) which involves homolysis of both C–O and S–O bond.[72]

SCHEME - 27



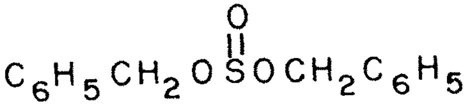
76 77 78

SCHEME - 28

$$C_6H_5CH_2SO_2I \xrightarrow[CH_2=C=C(CH_3)_2]{h\nu} C_6H_5CH_2I$$

79 80

SCHEME - 29



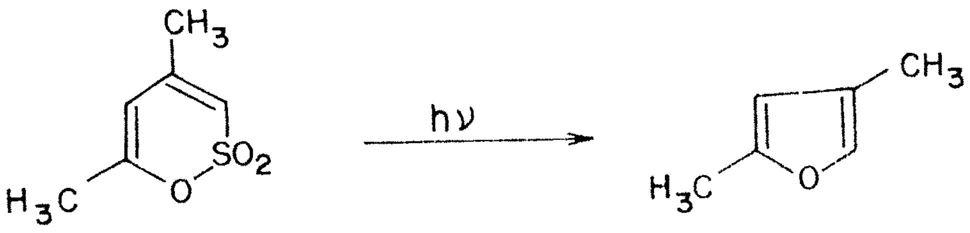
$$C_6H_5CH_2O\overset{O}{\overset{\|}{S}}OCH_2C_6H_5 \xrightarrow{h\nu} C_6H_5CH_2SO_3CH_2C_6H_5 +$$

81 82

$$C_6H_5CH_2OH + (C_6H_5CH_2)_2O$$

83 84

SCHEME-30



85 86

Photo cleavage of benzylic sulfonyl compounds yield products like sulfones and sulfinic acids.[73] Sulphonic acid sulfones has been reported to give interesting products.[74,75] For example, unsaturated sultone 85 resulted into 2,4-dimethylfuran (86) (Scheme 30).[75]

1.7 Sulphur-nitrogen compounds

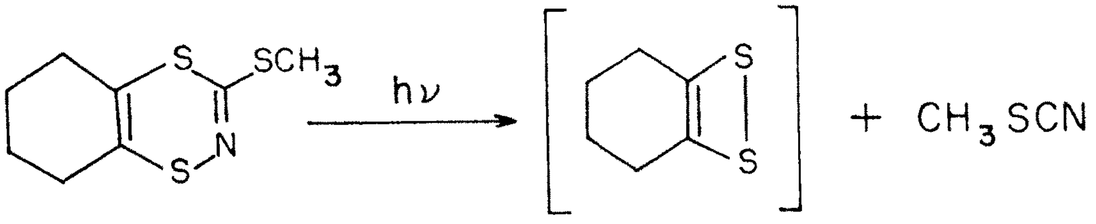
Organic compounds containing sulphur and nitrogen are reported to undergo degradation.[76-79] UV irradiation of the dithiazine (87) in methanol or dichloromethane resulted into methylthiocyanide (89) via the intermediate 88 (Scheme 31).[77]

Several interesting examples of the photochemical fragmentations of sulphur containing nitrogen heterocycles have been reported. The photolysis of 1,2,3-benzothiadiazole-1,1-dioxide (90), for example, has been shown to give a benzyne intermediate 91 (Scheme 32).[79]

1.8 Thioketones

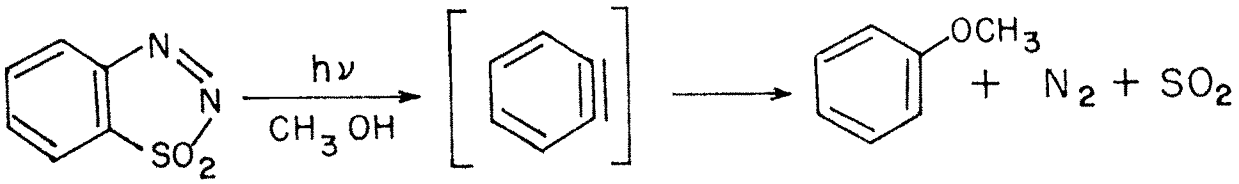
Photofragmentation reaction of thiocarbonyl compounds has been reported in variety of cases.[80-82] Cyclobutane thione 93 on irradiation afforded dithiolactone 94 and disulphide 95 (Scheme 33).[82]

SCHEME - 31



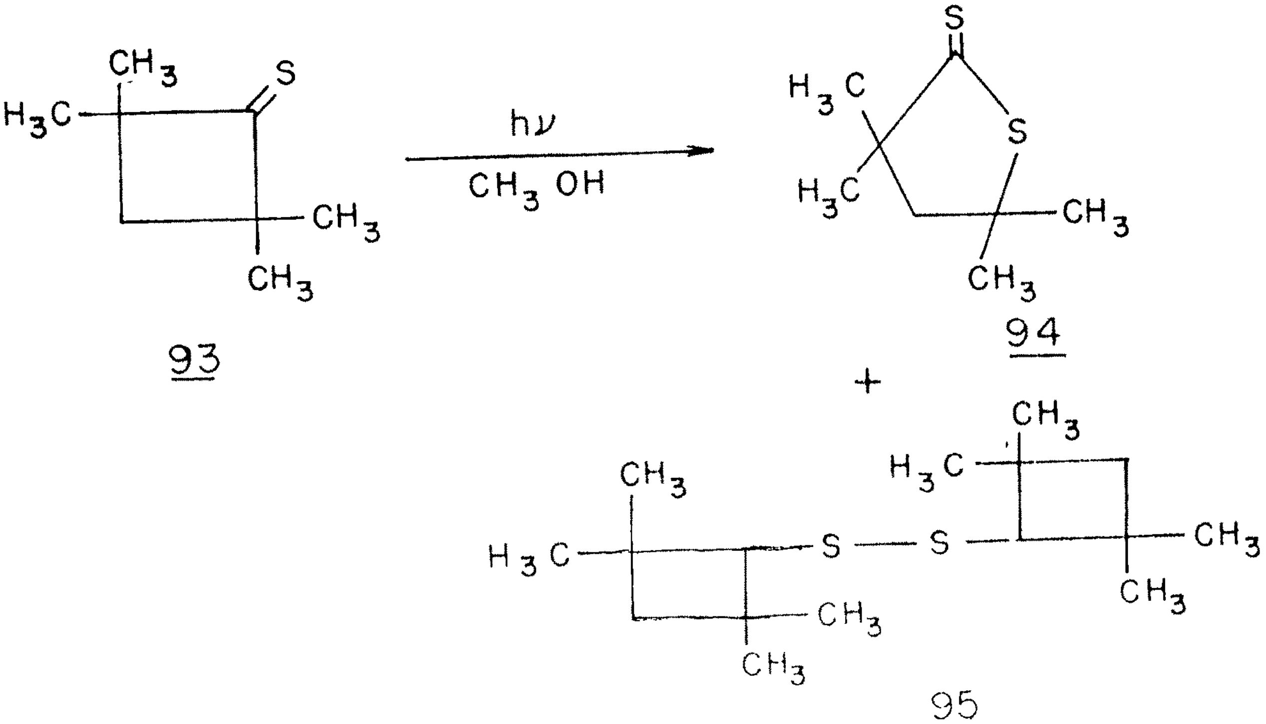
87 88 89

SCHEME - 32



90 91 92

SCHEME - 33



93 94 95

Irradiation of thiobenzophenone (96) in isopropanol was reported to give diphenylmethanethiol (97) through initial hydrogen abstraction. (Scheme 34)[83]

Thiocamphor[84] and thioketones[85,86] has been reported to give dimeric product. For example, alkylthiocarbonyl compound 98 resulted into 1,3-dithietans (99) on irradiation (Scheme 35).[86]

Thioketone also undergoes isomerisation to give thiol. For example, thione 100 gives the isomeric thiol 101 on irradiation.[87] (Scheme 36).

1.9 Thioacetals

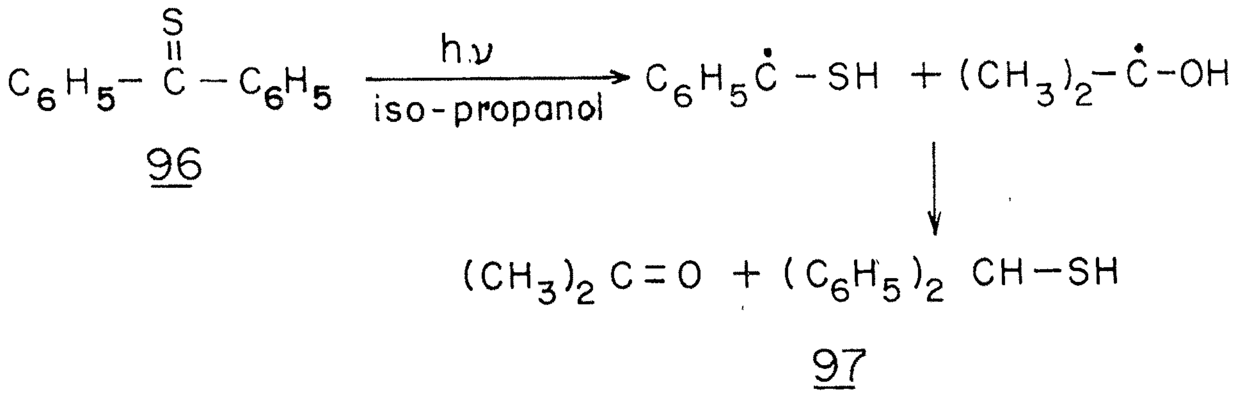
Photochemistry in multichromophoric system has been reported by Arad-Yellin and co-workers.[88] Thioacetal 102 on irradiation gave alkene 103 and ketone 104 through fission of C-S bond (Scheme 37).[86]

The major photo reaction of some spirodithiolanes 105 consists of elimination with formation of the corresponding thiones 106,[89] whereas the benzo derivatives 107 undergo rearrangements[90] (Scheme 38).

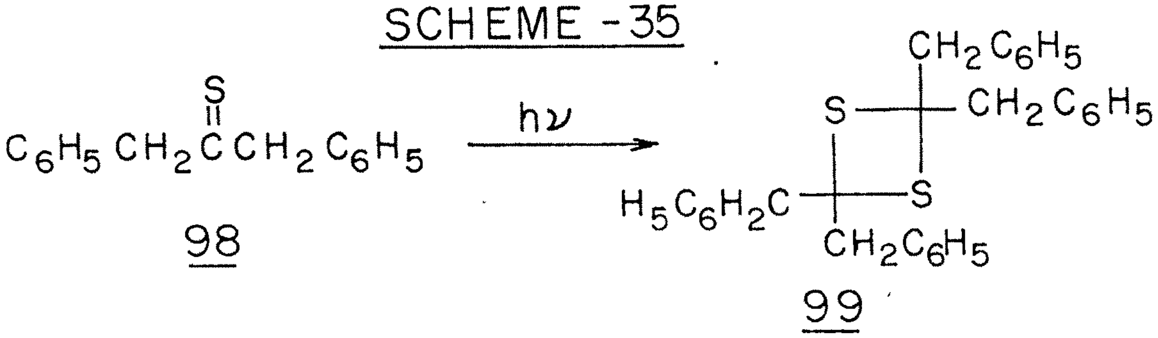
1.10 Acyl and Aroyl xanthates

The xanthate derivatives of aliphatic acids are

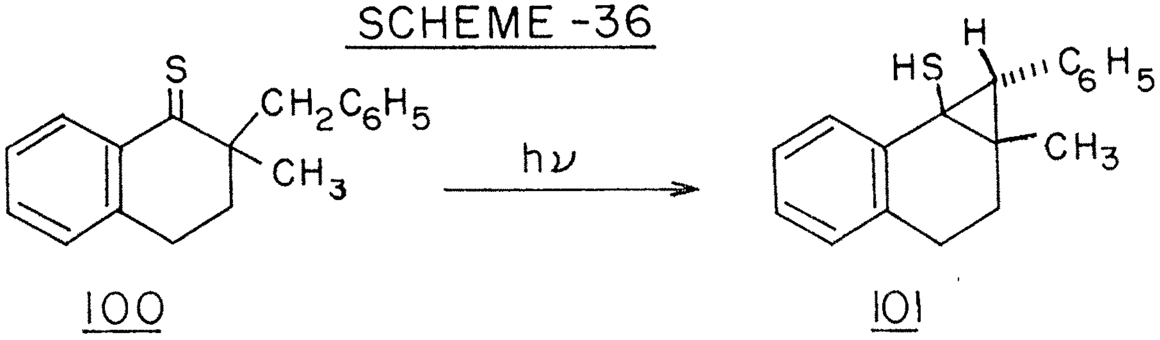
SCHEME -34



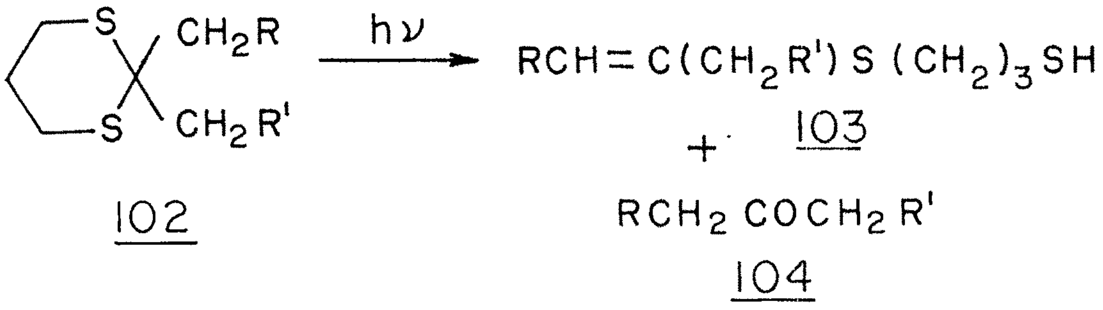
SCHEME -35



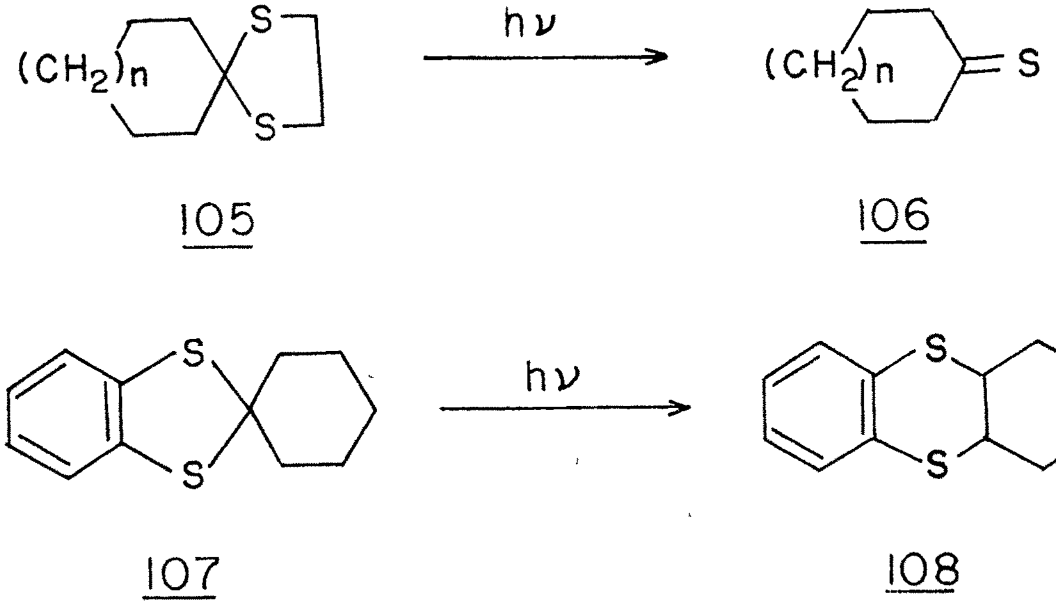
SCHEME -36



SCHEME -37



SCHEME-38



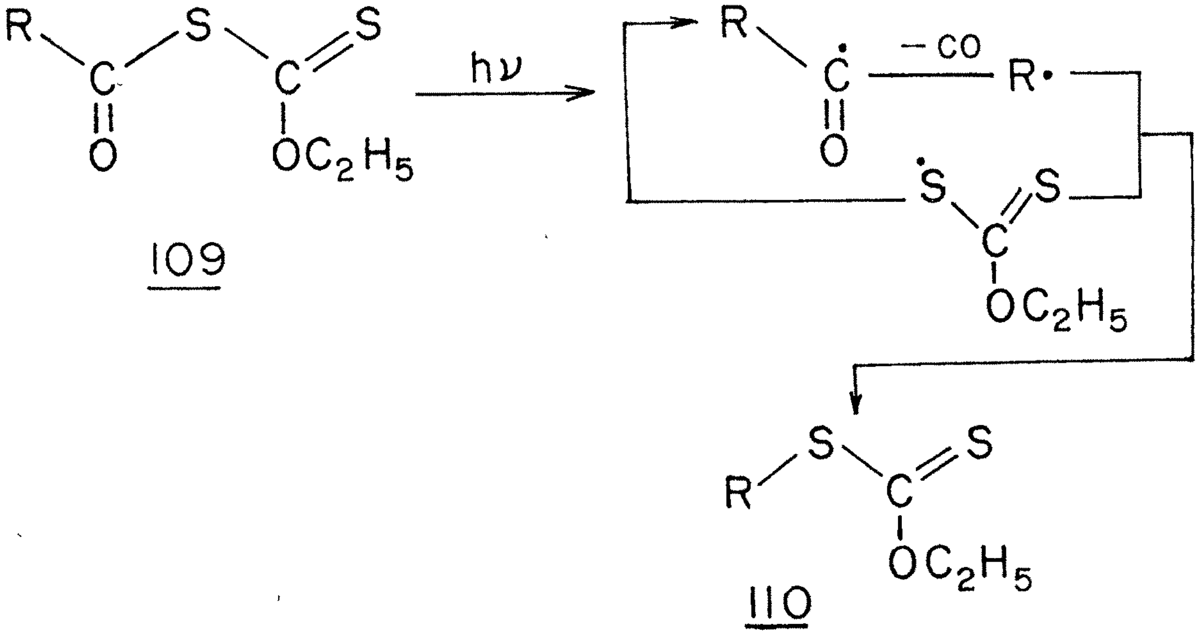
105

106

107

108

SCHEME-39



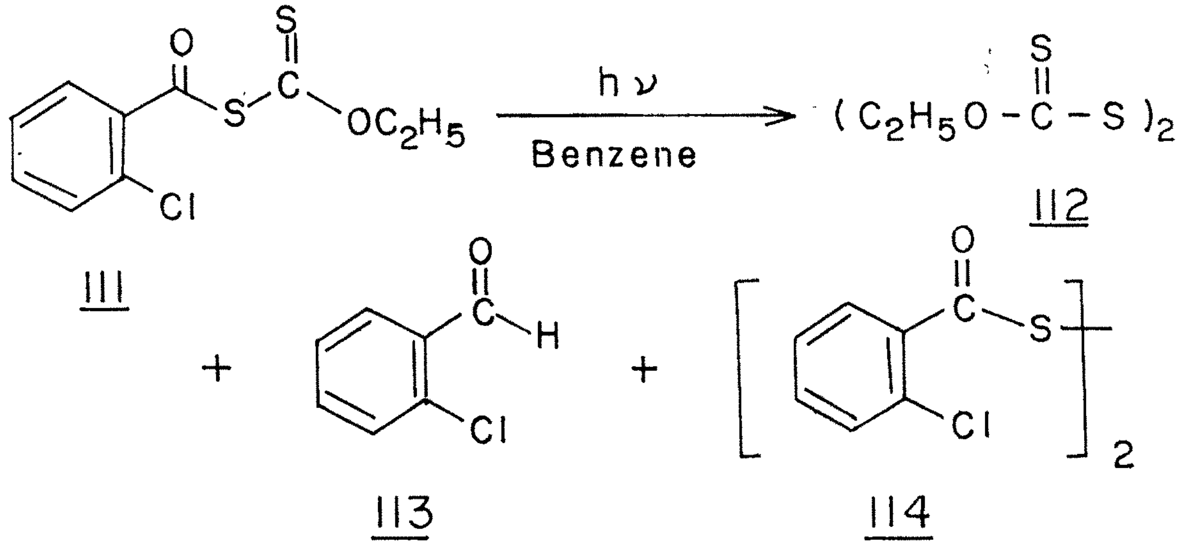
109

110

generally considered to be unstable. They undergo ready decomposition to ester and carbon disulphide.[91] A convenient method for synthesis of acyl and aroyl xanthate[92,93] have been reported. A detailed study concerning the photochemical transformation of acylxanthates has been reported by Barton et al.[93] It has been observed that acyl xanthates 109, in general, undergo homolytic fission of C-S bond giving rise to acyl and xanthate radicals[93,94] (Scheme 39). The acyl radicals lose carbonmonoxide and combine with xanthate radical to give O-ethyl S-alkylxanthate (110). They have reported that S-benzoyl and S-p-chlorobenzoylxanthate were resistant to photolysis in boiling benzene or toluene. O-Ethyl-S-o-chlorobenzoylxanthate (111) on prolonged photolysis in benzene was reported by Praefcke Klaus et al.[95] to give xanthic acid disulphide (112), o-chlorobenzaldehyde (113) and o-chlorobenzoyl disulphide (114) (Scheme 40).

George and co-workers[96,97] have reported the photochemical transformations of several phthaloyl dixanthates. For example, photolysis of O,S-dialkyl-S,S-phthaloyldixanthate (115) in benzene solution at room temperature gave trans-biphthalyl (116) as the only isolable product (Scheme 41).[97]

SCHEME -40



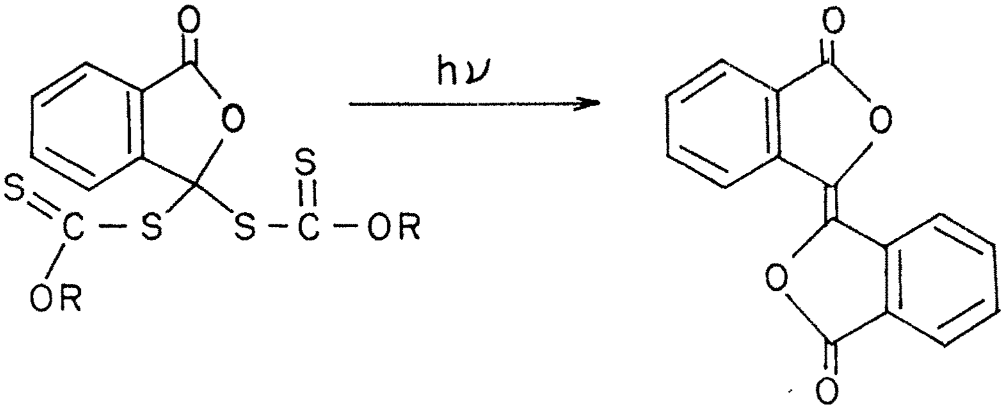
111

112

113

114

SCHEME - 41



115

116

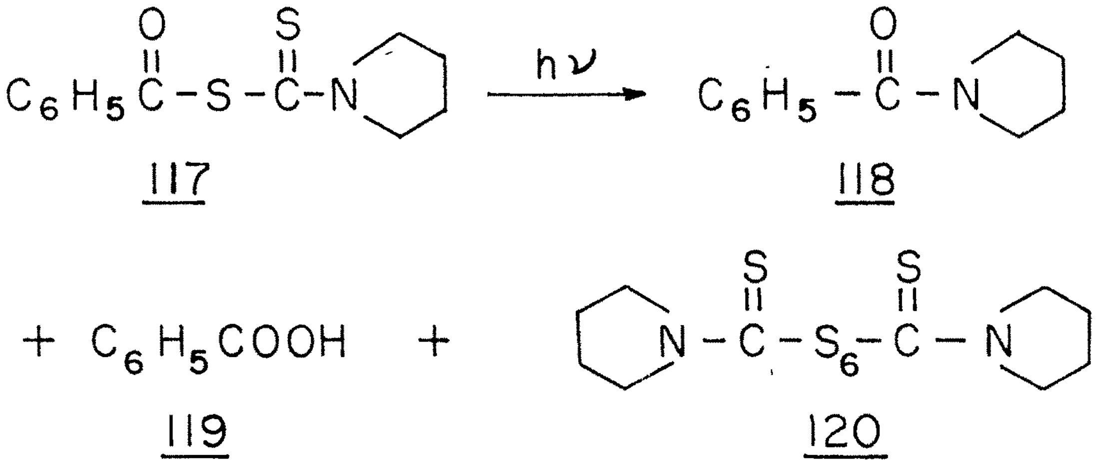
1.11 Carboxylic dithiocarbamic anhydride

Photochemical transformations of a few carboxylic-dithiocarbamic anhydrides have been reported by Hoffmeister and Tarbell.[98] They have observed that several products are formed in these reactions depending on the nature of starting materials. Thus, for example, the photolysis of benzoic pyrrolidine dithiocarbamic anhydride (117) gave rise to a mixture of products consisting of N-benzoyl pyrrolidine (118), benzoic acid (119) and pyrrolidyl thiuram hexasulphide (120) (Scheme 42).

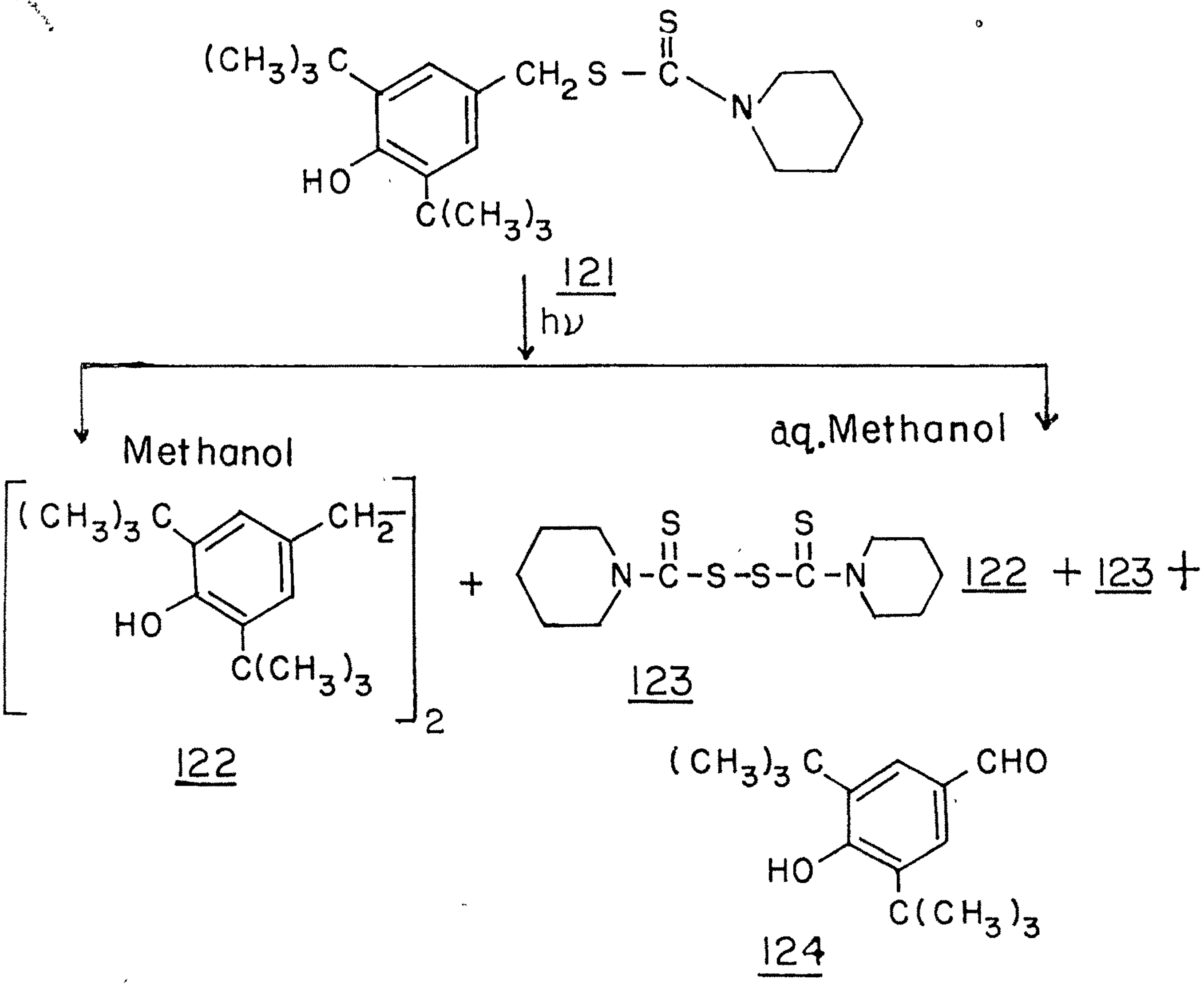
Thompson and co-workers[99] have studied the photodecomposition of several substituted 4-hydroxybenzyldithiocarbamates. Thus, for example, 4-hydroxybenzildithiocarbamate (121), on irradiation in dry and wet methanol give different products which include diphenylethane (122) N,N,N',N'-bis(tetramethylene) thiuram disulfide (123) and 4-hydroxy-3,5-ditert. butyl benzaldehyde (124) (Scheme 43).

George and co-workers[94,97,100] have reported the formation of various products in the photolysis of several acyl and aroyl carboxylicdithiocarbamic anhydrides. Thus, for example, photolysis of

SCHEME - 42



SCHEME - 43



3-(dimethylaminodithiocarbamyl)phthalide (125) gave meso-3,3'-dihydrobiphthalide (126), as the only isolable product (Scheme 44).[100]

1.12 Thiocarbonates, Thiocarboxylate and Dithiooxalates

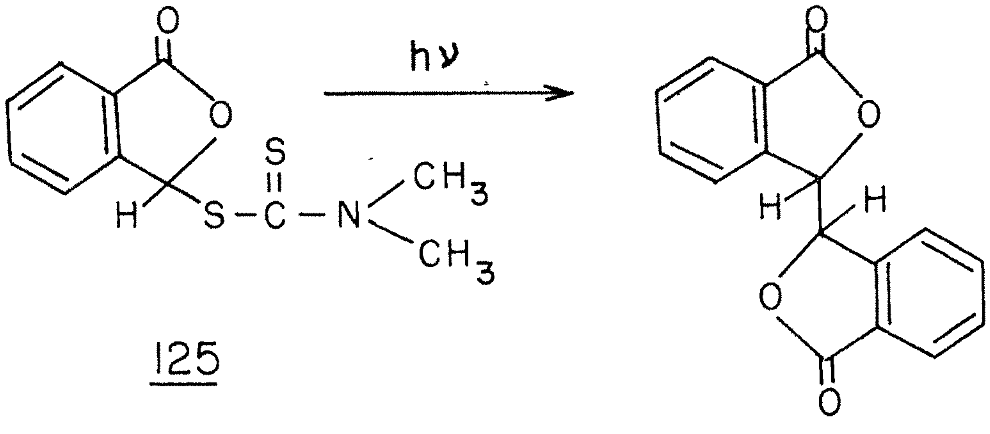
Photolysis of thiocarbonates are reported to result into the formation of decarbonylated product.[101-103] Thus, for example, photolysis of thiocarbonate 127 gave tetrathiooxalic acid ester (128) which in solution, is in equilibrium with its [4+2] dimer 129. Tetrathiooxalates are probably unstable at room temperature (Scheme 45).[102]

Hein and Metzer[104] have reported the photo fragmentation of 1,2-dithiooxalates, dithio and trithiocarbonates which involve elimination of carbon monoxide and carbon monosulphide. Photochemical addition accompanied by rearrangement has been reported for thiono compound (130) (Scheme 46).[105]

Photolysis of thio and dithio acid esters has been extensively studied.[106-113] For example, photolysis of O-1-Benzyl-Z-methylthiobenzoate (133) gave thioketone (134) and trans alkene (135) (Scheme 47).[109]

UV irradiation of 3,3-bis(arylthio)phthalides

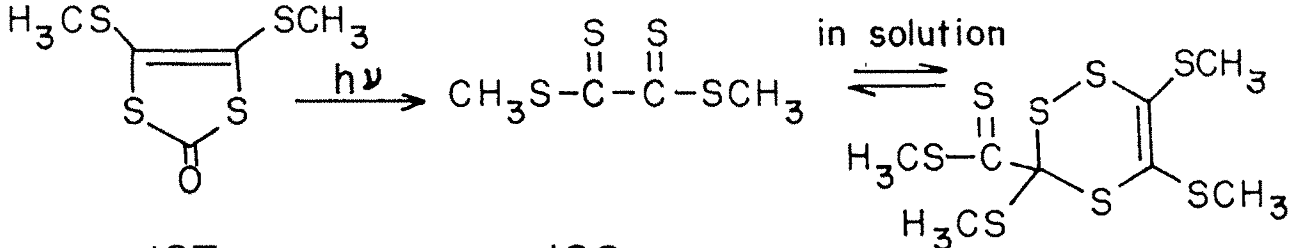
SCHEME - 44



125

126

SCHEME - 45

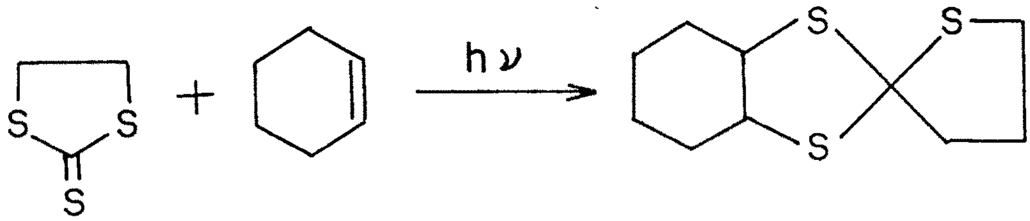


127

128

129

SCHEME - 46

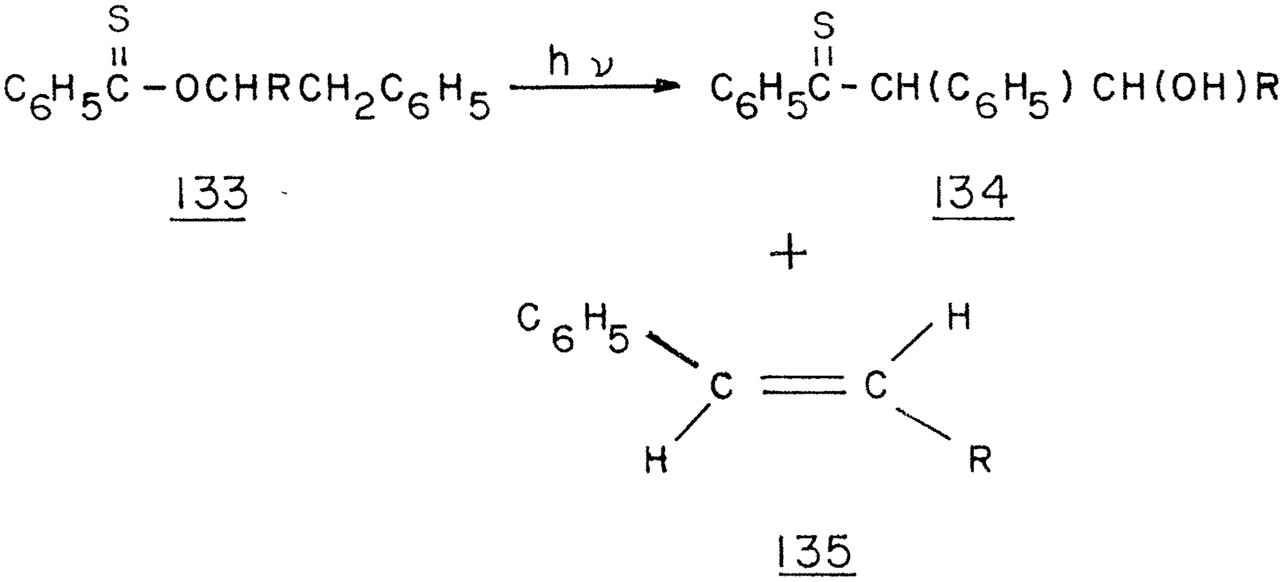


130

131

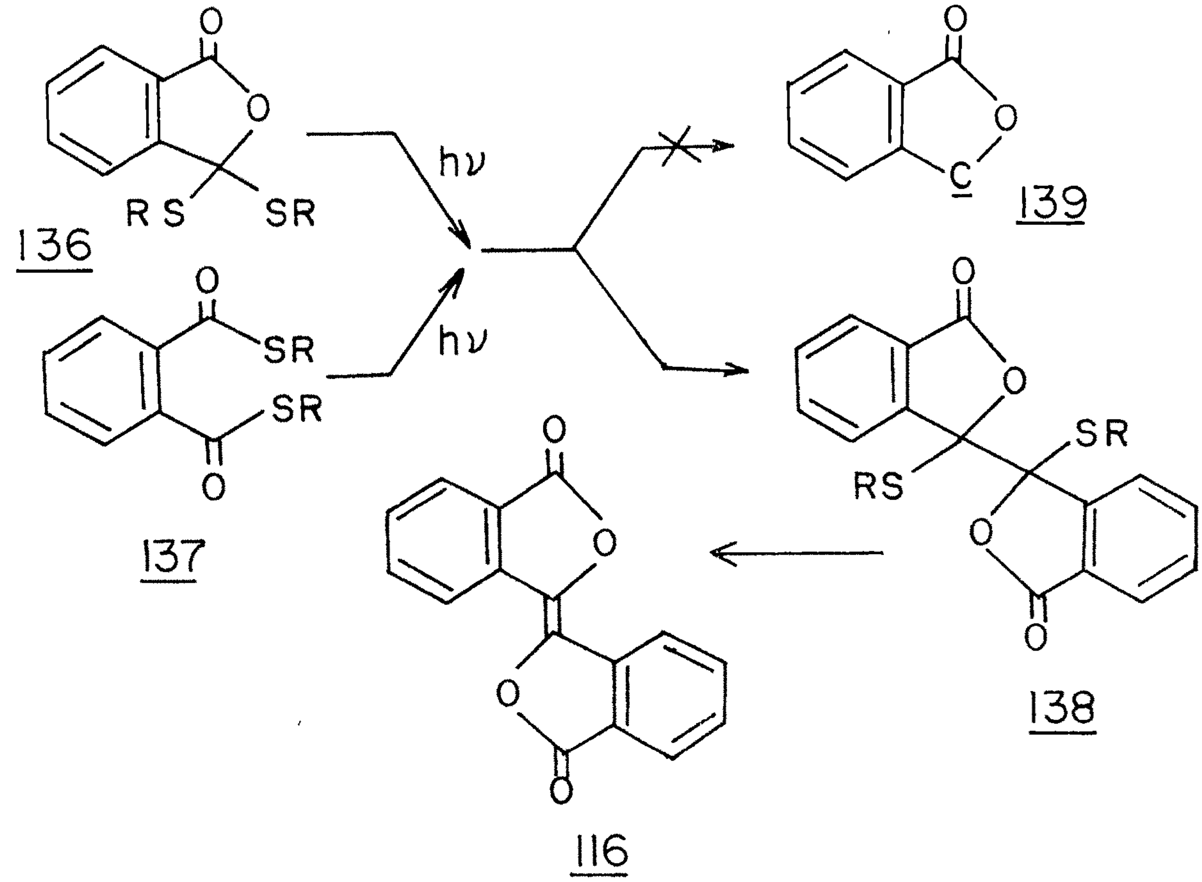
132

SCHEME-47



$$C_6H_5\overset{S}{\overset{\|}{C}}-OCHRCH_2C_6H_5 \xrightarrow{h\nu} C_6H_5\overset{S}{\overset{\|}{C}}-CH(C_6H_5)CH(OH)R$$

SCHEME - 48



(136) and S,S'-diaryldithiophthalate (137) yields trans-biphthalyl (116) via photolabile intermediate (138) and not from a phthalydyl carbene 139 (Scheme 48).[112]

2. Thermal Decomposition of Organic Sulphur Compounds

Thermal decomposition of a variety of organic sulphur compounds have been investigated in detail. A brief survey of the decomposition of a few organic sulphur compounds are described below :

2.1 Sulfides, sulfites, sulphates, sulphone and sulphoxylate

The pyrolysis of several types of sulphides have been studied. Some of these substrates include dibenzoyl disulfide,[114] dialkyl sulphides,[115] dialkoxy sulphides,[116] allyl sulfides,[117] dibenzyl sulphides,[118] azosulphide[119] and thiuramdisulphides.[120]

Thermolysis of dialkoxy disulphide[116] 140 above 120° was reported to give aldehyde 141, alcohol 142 and free sulphur (Scheme 49).

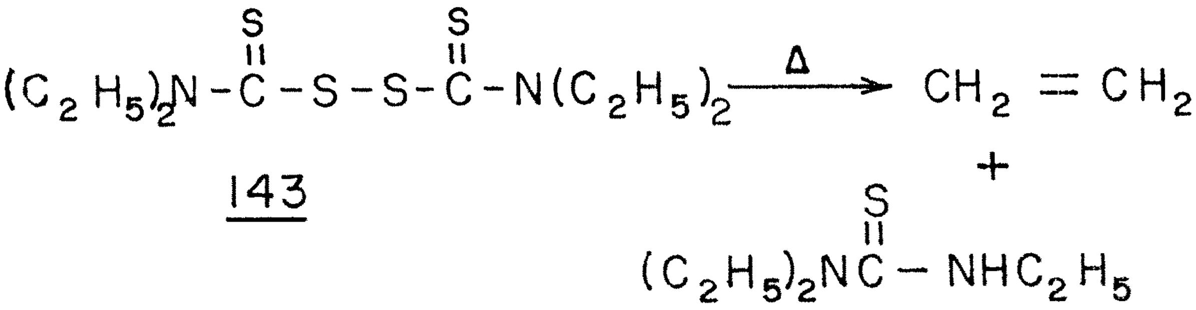
A mixture of products have been reported in the thermolysis of benzylsulphides. The products included hydrogen sulphide, toluene, benzaldehyde, dibenzyl,

SCHEME-49

$$R^1CH_2O-S-S-OR^2 \xrightarrow{\Delta} R^1CHO + R^2-OH + 2S$$

140 141 142

SCHEME-50

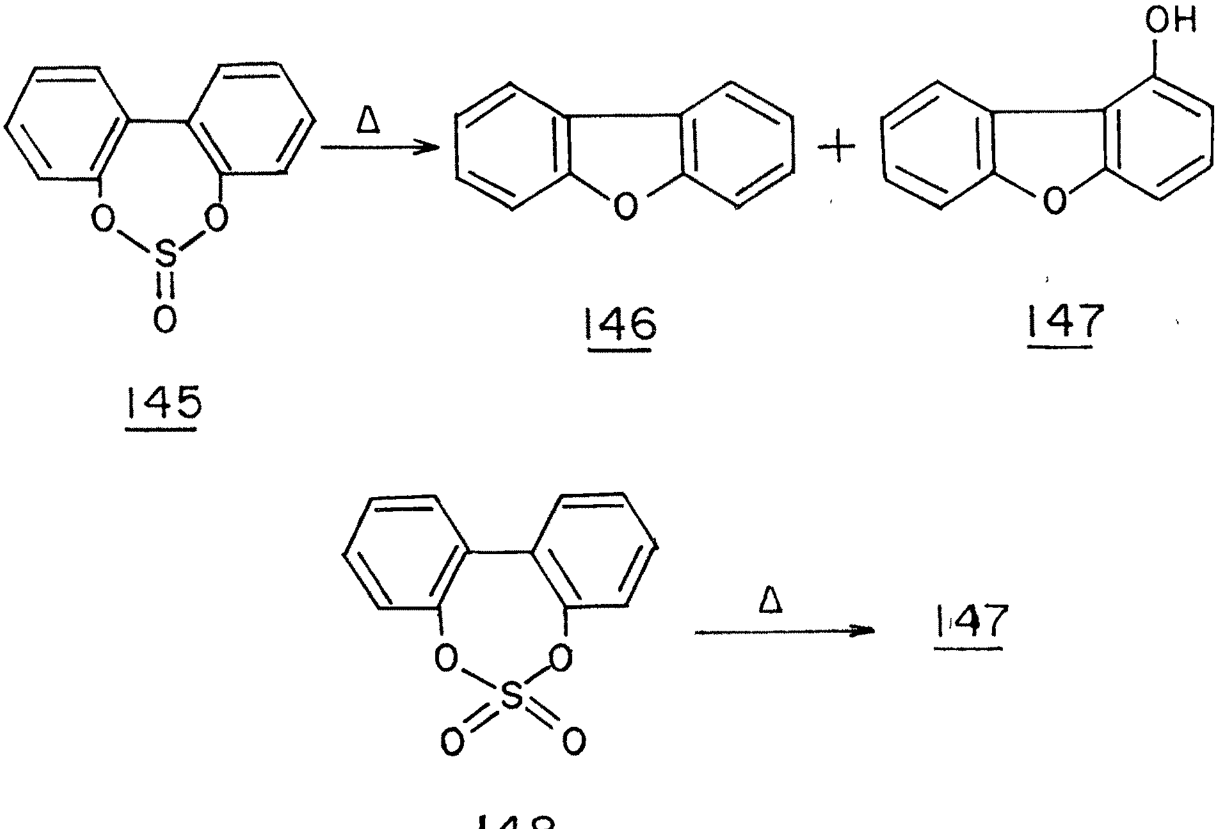


$$(C_2H_5)_2N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-N(C_2H_5)_2 \xrightarrow{\Delta} CH_2=CH_2 + (C_2H_5)_2N\overset{S}{\overset{\|}{C}}-NHC_2H_5$$

143

144

SCHEME-51



145 146 147

148 147

stilbene and tetraphenyl thiophene.[118] The probable mechanism involves the initial cleavage of C-S bond and a series of hydrogen abstraction, coupling, dehydrogenation and cyclization processes.

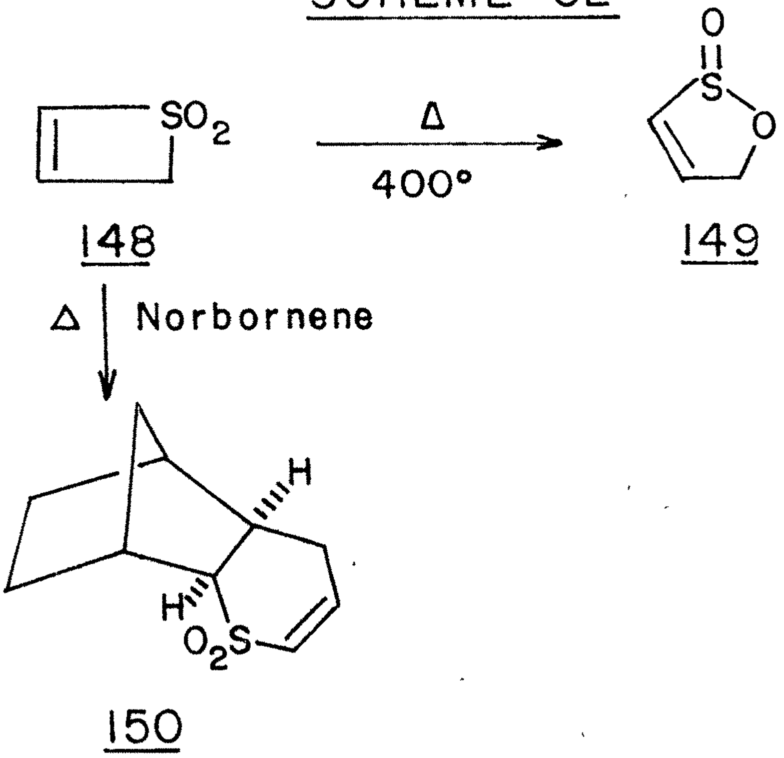
Thiuramdisulphide 143 on heating decomposes to give products like ethylene and 1,1,3-triethylthiourea (144) (Scheme 50).[120]

The pyrolysis of biphenylene-2,2'-sulfite (145) has been reported to give dibenzofuran (146) and 1-hydroxydibenzofuran (147) through the loss of sulphur monoxide and sulphur dioxide.[121] Similarly, the pyrolysis of biphenylene 2,2-sulfate (148) results in the formation of 1-hydroxydibenzofuran (147) (Scheme 51).[122]

A number of sulphones have been reported to exclude sulphur dioxide on pyrolysis.[123-125] Paul de Mayo and co-workers[126] have reported that theit-1,1-dioxide (148) do not lose sulphur dioxide on heating upto 750° and forms sulfines (149) (Scheme 52).

Thiet 1,1-dioxide (148) in the presence of norbornene has been reported[127] to give cycloadduct 150 of the Diels-Alder type (Scheme 52).

SCHEME-52

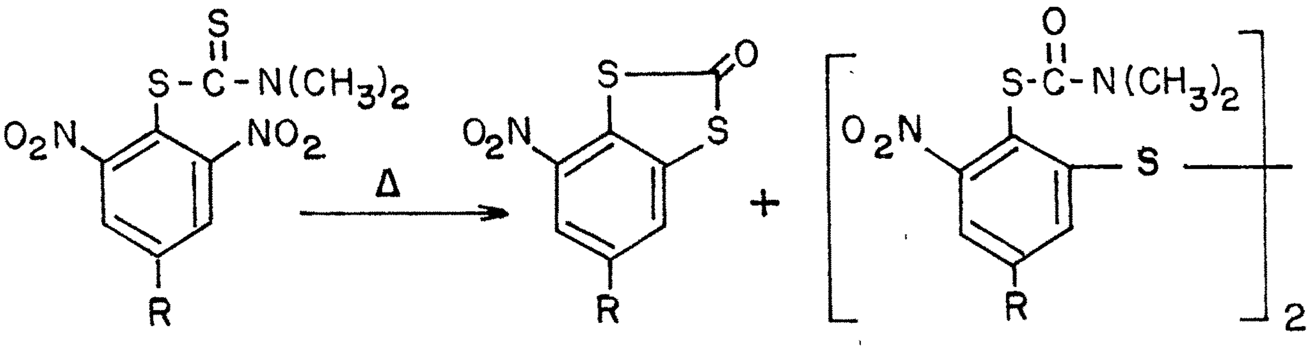


SCHEME-53

$$(C_4H_9O)_2S \xrightarrow[130^\circ]{\Delta} C_4H_9OH + SO_2 + S + C_2H_5CH{=}CH_2$$

151

SCHEME-54



152 153 154

Pyrolysis of sulphonic acid esters have also been studied by several workers. The pyrolysis of di-n-butylsulfoxylate (151) at 130° gave variety of products which include n-butyl alcohol, sulphur dioxide, sulfur and 1-butene (Scheme 53).[128]

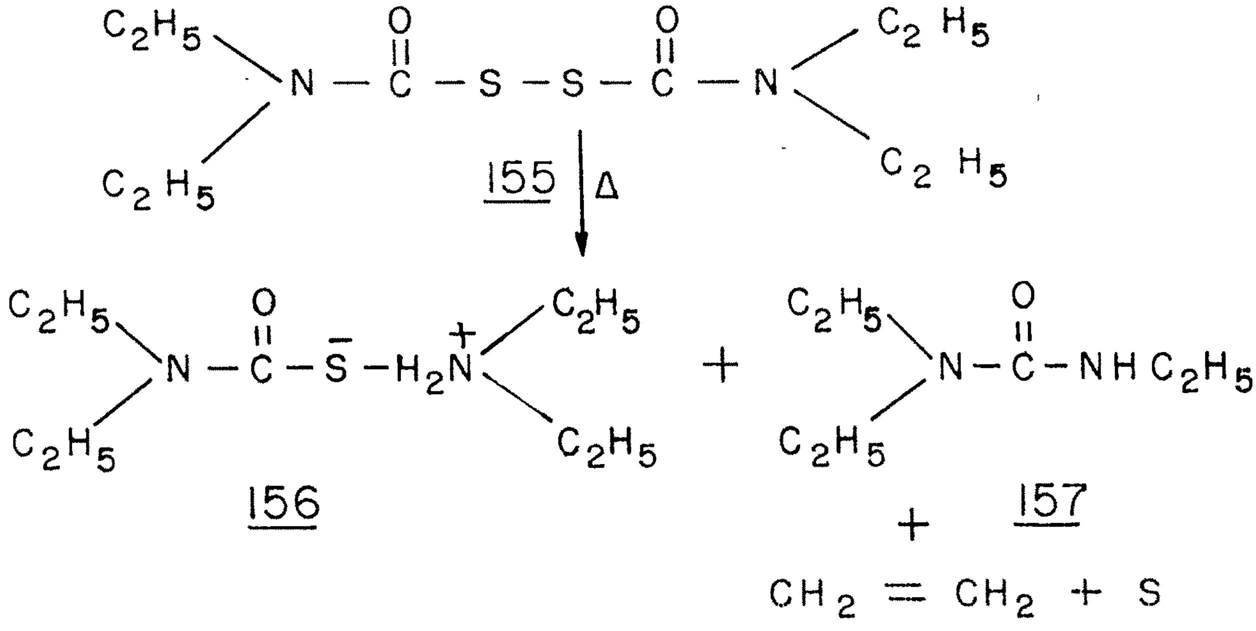
2.2 Thiocarbamates and thiocarbonates

The pyrolytic decomposition of dithiocarbamate and related substrates have been studied by several workers.[129-134] Thus, for example, alkyl substituted dinitrophenyl N,N-dimethyldithiocarbamate (152) on pyrolysis gave variety of nitro 1,3-benzodithiol-2-one (153) and disulphide 154 (Scheme 54).[133]

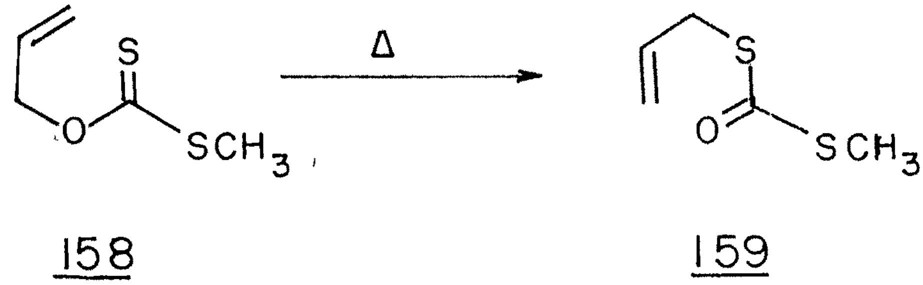
Chande and Kulkarni[134] studied the pyrolytic decomposition of carbamyl disulphide. Bis(N-diethylcarbamyl) disulphide (155) which has been found to afford diethylammonium diethylthiocarbamate (156), 1,1,3-triethylurea (157), ethylene and elemental sulphur (Scheme 55).[134]

The formation of olefin is reported[135] in the thermolysis of alkylthiol and thionoacetates. Nakai et al.[136] have reported [3,3] sigmatropic rearrangements on pyrolysis of allylic thionesters (158) (Scheme 56).

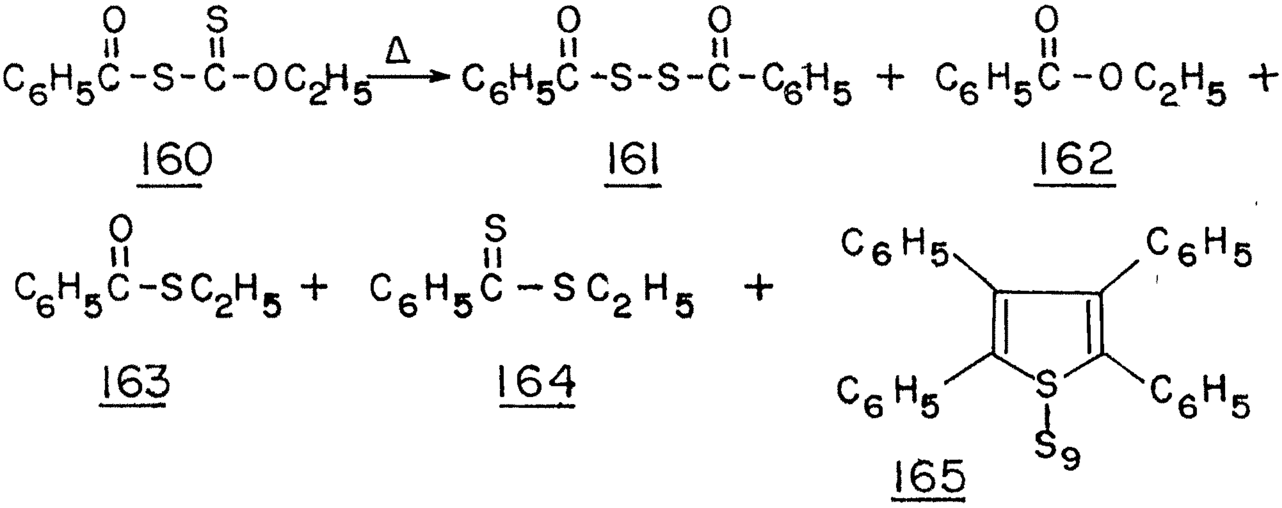
SCHEME -55



SCHEME - 56



SCHEME - 57



2.3 Acyl and Aroylxanthates

Thermal decomposition of acyl and aroylxanthates has been studied by different group of workers.[91-93] Thus, for example, when O-ethyl S-benzoylxanthate[92] (160) was pyrolysed under vacuum, a mixture of products consisting of dibenzoyldisulphide (161), ethyl benzoate (162), ethyl thiobenzoate (163), ethyldithio benzoate (164) and 2,3,4,5-tetraphenyl thiophenenonasulphide (165) were formed. (Scheme 57).[92] It has also been shown by these workers that nonasulphide 165 is not a direct product of the thermal decomposition of xanthate 160 but it arises f from dibenzoyl disulphide (161).[114] Barton and co-workers[93] have also studied the thermolysis of several aroylxanthates and they have shown that esters and carbon disulphide are formed in these reactions. Similar observation has been reported by George and co-workers[94] in the thermal decomposition of substituted acetylxanthate.

Thermal decomposition of phthalyl and unsymmetrical phthaloyl dixanthate has been reported by George and co-workers.[96,97,100] For example, dimethylphthaloyldixanthate (166) when heated around 230°-240° for

30 minutes gave a mixture of products which include thiophthalic anhydride (168) O,S-dimethylxanthate (169) and carbonyl sulphide. The formation of thiophthalic anhydride is through the formation of thionophthalic anhydride (167) (Scheme 58).[97]

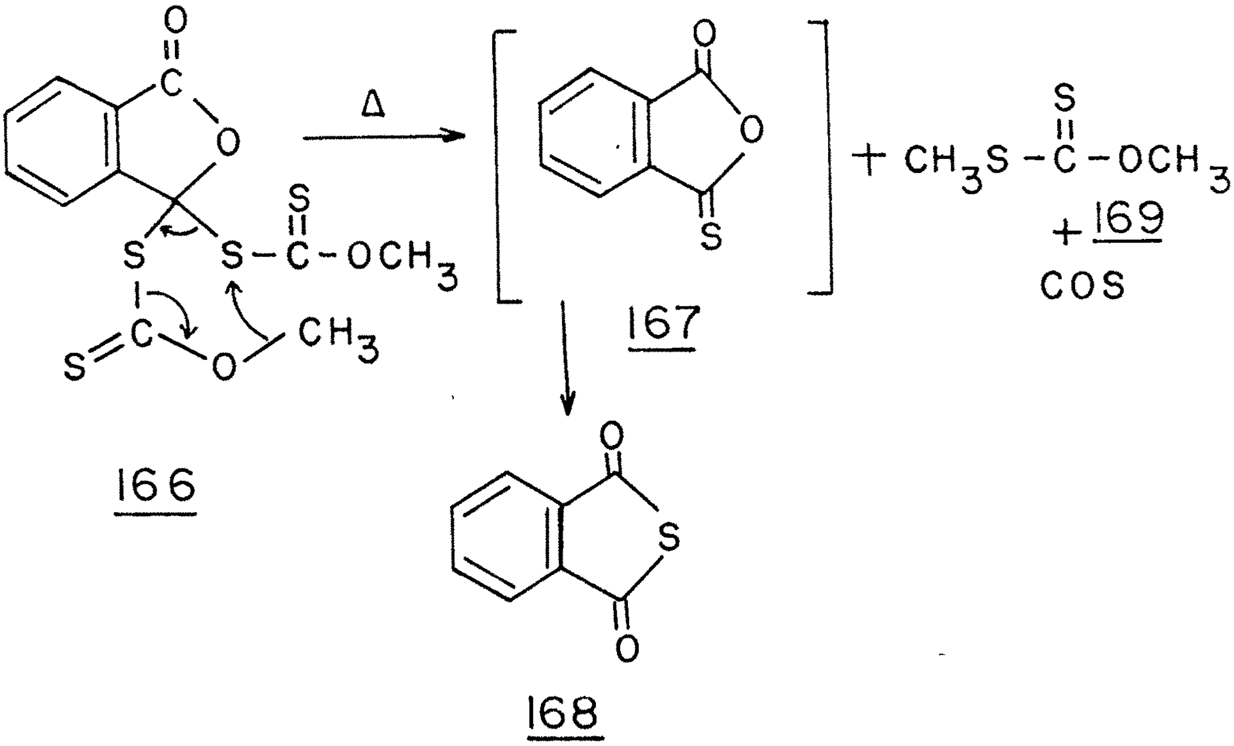
2.4 Carboxylic dithiocarbamic anhydride

Thermal decomposition of carboxylicdithiocarbamic anhydrides are shown to give the corresponding amides and carbon disulphide.[97,98,137,138] Thermal decomposition of 3-(aminedithiocarbamyl)phthalides has been reported[100] to give interesting products. Thus, for example, thermal decomposition of 3-(dimethylaminedithiocarbamyl)phthalide (125) gave a mixture of products consisting of 2-thio-3,3'-biphthalide (170), iso-coumarino [4,3-c] thioisocoumarin (171) and 3,3'-dithiobiphthalide (172) (Scheme 59).[100]

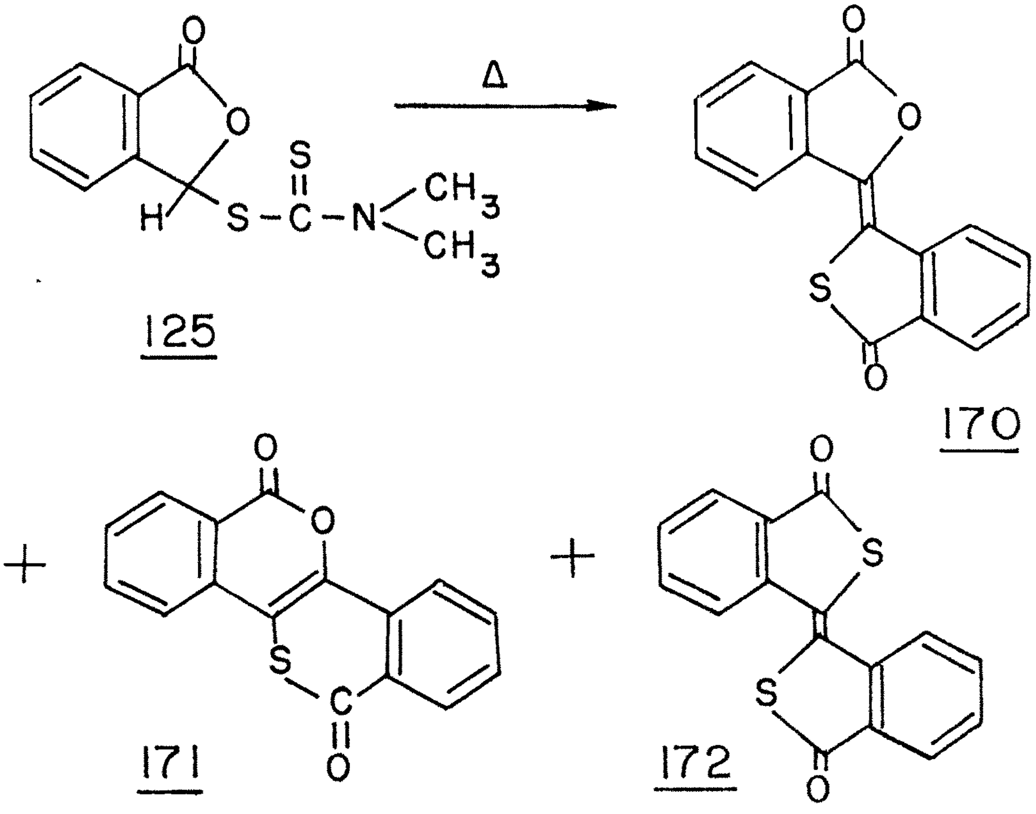
2.5 Gemdixanthylmethanes

It has been reported that gem dixanthylmethanes are formed in the reaction of potassium-O-alkyl xanthates with dichloromethanes. Thus, in the reaction of diphenylchloromethane (173) with excess of potassium-O-ethylxanthate, the gemdixanthylmethane (174)

SCHEME-58



SCHEME-59



was obtained.[139] The same dixanthylmethane **174** was formed in the reaction of diphenyldiazomethane (**175**) with diethylxanthogen disulfide (**112**). The thermal decomposition of **174** gave thiobenzophenone (**96**) (Scheme 60).[139] The reaction of diphenyldiazomethane (**175**) with anhydrosulphide of ethylxanthic acid (**176**) gave a substituted thiirane[140] (**177**). It has been shown that thiirane **177** undergoes decomposition to **178** on heating (Scheme 60).[140]

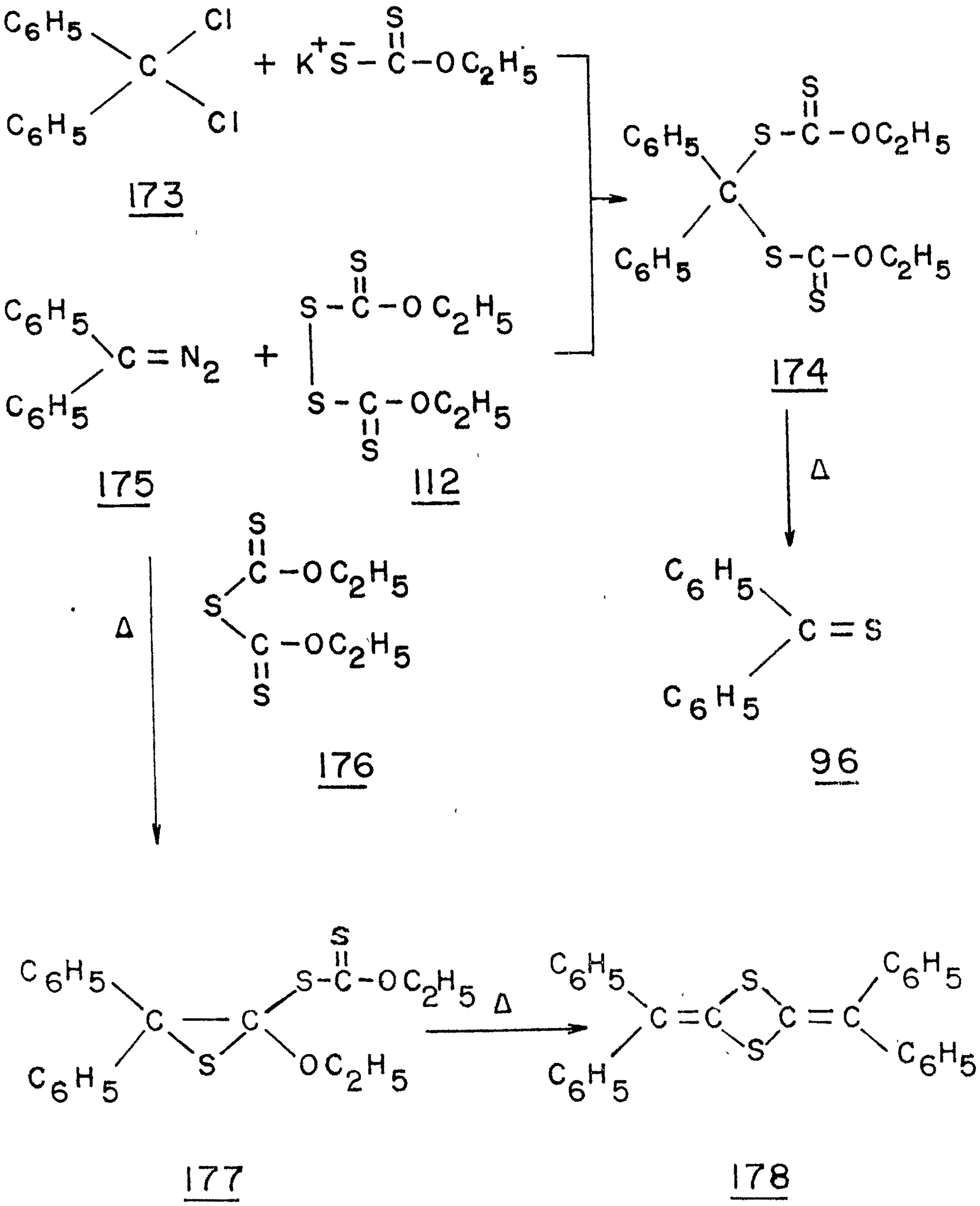
Schonberg and Frese[141] have reported that an interesting 1,3-diphenyl-1,3-dithio-1,2,3-triketone (**181**) is formed by the treatment of symmetrical diphenyl tetrabromoacetate (**179**) with potassium-O-ethylxanthate (Scheme 61).

2.6 Pyrolysis of xanthates

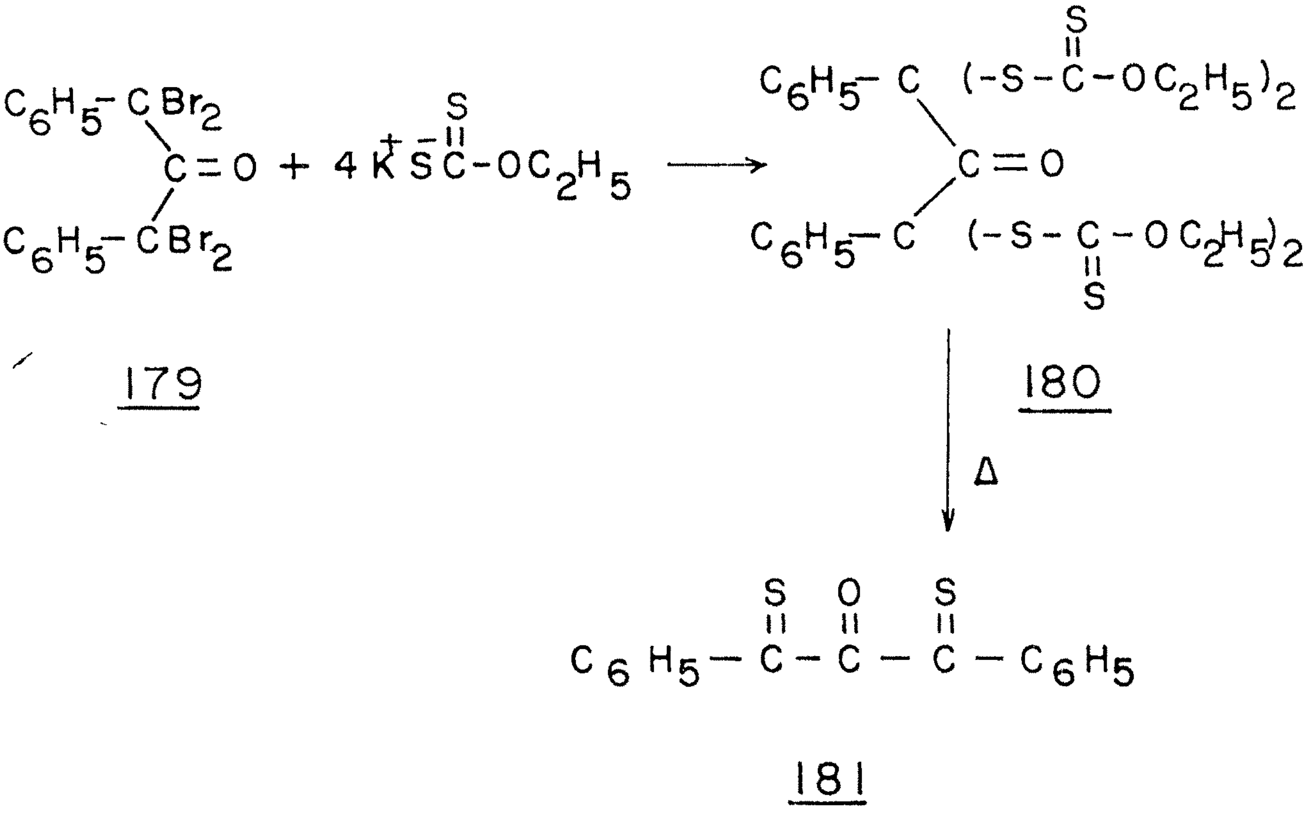
Formation of olefins through the pyrolysis of xanthates has been well documented in literature.[142,143] This is a useful method for preparing unsaturated hydrocarbon from alcohols particularly in the terpene group (Scheme 62).

Catalytic rearrangement[144-146] of xanthate to dithiolcarbonate was studied. Study of the crossover

SCHEME -60



SCHEME - 61

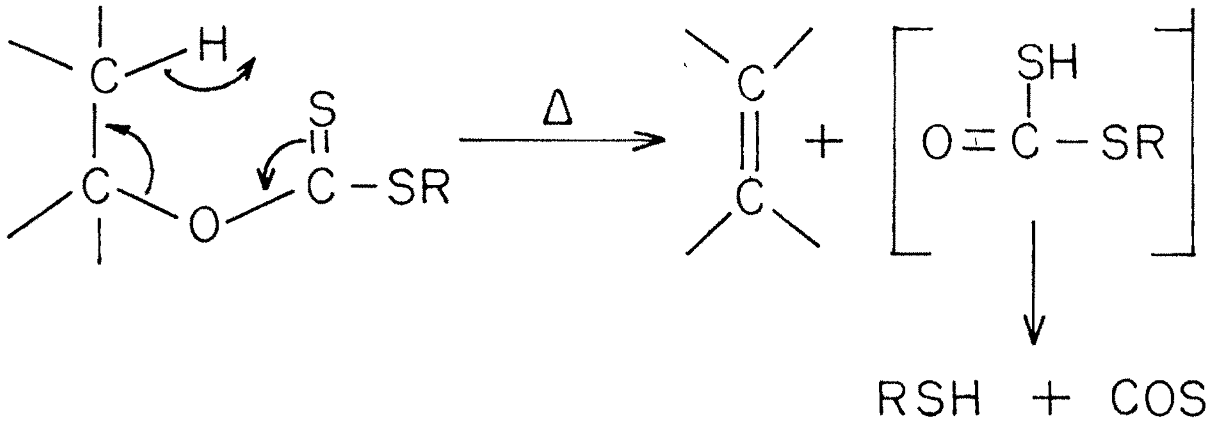


179

180

181

SCHEME - 62

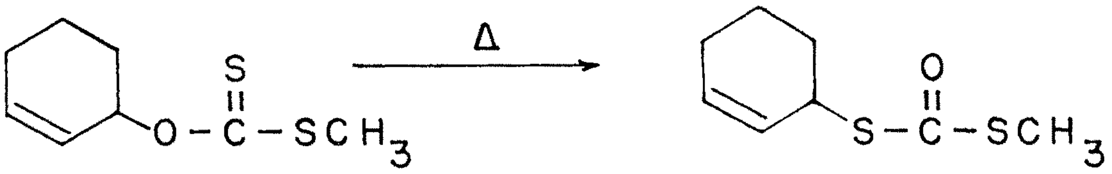


reaction showed that this rearrangement might be intermolecular. For example, 2-cycloalkenyl-S-methylxanthate (182) on pyrolysis gave corresponding dithiolcarbonate (183) (Scheme 63).[145]

2.7 Thioncarbonates

Diarylthionocarbonates rearranges intramolecularly to the corresponding thiolocarbonates on heating upto range of 200-300° (Schonberg rearrangement).[147,148] A similar rearrangement has been found to take place also for O,S-diphenyl dithiocarbonate (184) (Scheme 64).[149] The arrangement that takes place when ethylphenyltrithiocarbonates (186) are heated above their melting points provides a convenient method of preparing aromatic thioloesters.[150] (Scheme 64).

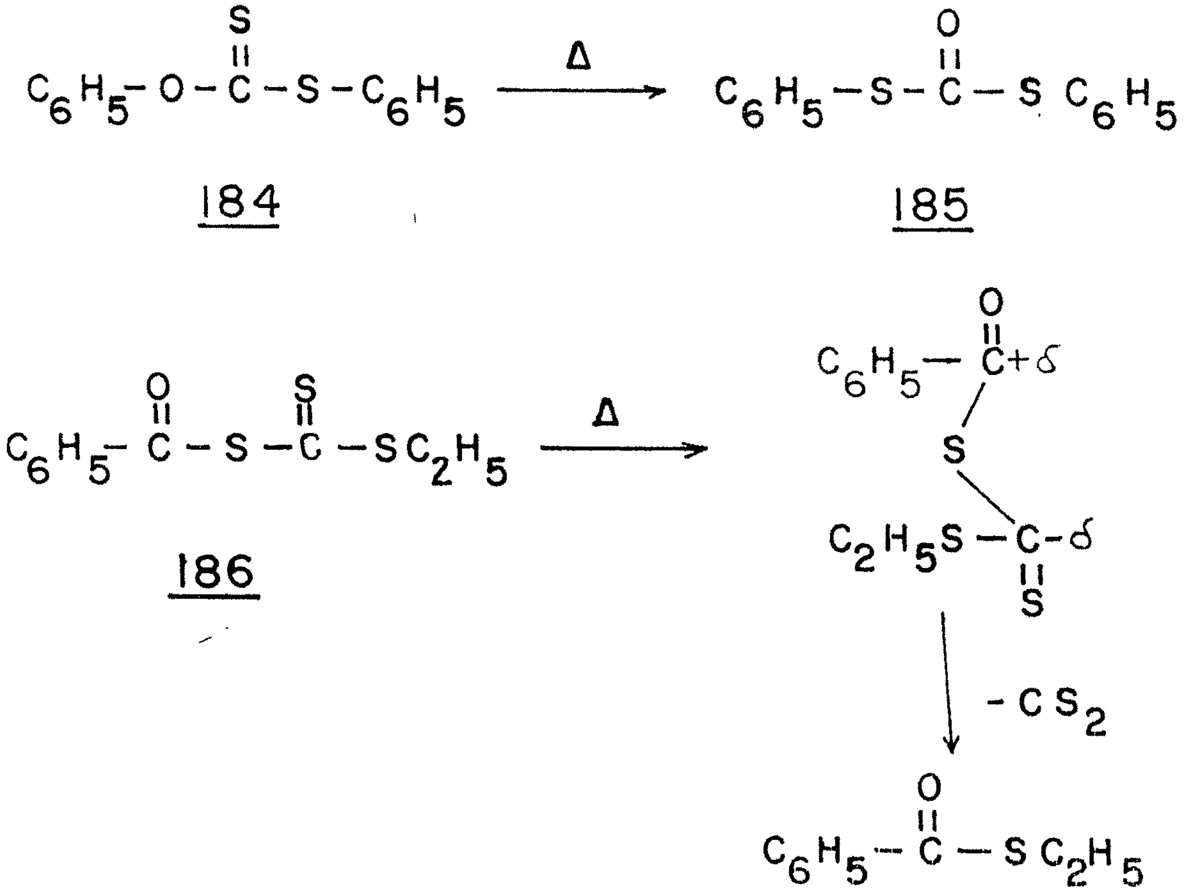
SCHEME-63



182

183

SCHEME - 64



184

185

186

163

REFERENCES

1. A.D. Clements, Chem. in Brit., 16, 466 (1980).
2. J.M. White and G.P. Sturm, Jr. Can. J. Chem., 47, 357 (1969).
3. C.L. Steven and J.C. French, J. Am. Chem. Soc., 75, 657 (1953).
4. L. Bridges and J.M. White, J. Phys. Chem., 77, 295 (1973).
5. F.W. Stacey and J.F. Harris, Org. reactions, 13, 150 (1963).
6. K. Takabe, A. Kajikawa, T. Katagiri and J. Tanaka, Nippon Kagaku Kaishi, 7, 1366 (1973) ; Chem. Abstr., 79, 78760 (1973).
7. J.M. Surzav, R. Nouguier, M.P. Crozet and C. Dupuy ; Tetrahedron Letters, 2035 (1971).
8. V.P. Krivonogov, V.I. Dronov and N.K. Pokoneshchikova, Khim. Geterotsikl. Soedin 9, 1204 (1975) ; Chem. Abstr., 84, 59113 (1976).
9. Y. Baba, Bull. Chem. Soc. Jap., 47, 204 (1974).
10. P.M. Rao and A.R. Knight, Can. J. Chem., 50, 844 (1972).
11. A. Padwa, Int. J. Sulfur Chem., Part B. 7, 331 (1972) ; Chem. Abstr. 80, 42850 (1974).

12. E.J. Corey and E. Block, J. Org. Chem., 34, 1233 (1969).

13. R.C. Peterson, A.L. Hebert, G.W. Griffin, I. Sarkar, O.P. Strausz and J. Font, J. Heterocycl. Chem., 10, 879 (1973).

14. W. Hampel and J. Friedrich, Z. Chem. 10, 343 (1970) ; Chem. Abstr., 74, 3445 (1971).

15. Y. Sato, H. Nakai, H. Ogiwara and T. Mizoguchi, Tetrahedron Letters, 4565 (1973).

16. Y. Kanoka, Y. Hatanaka, Y. Sato, M. Wada and H. Nakai, Kokagaku Toronkai, Koen Yoshishu, 266 (1979) ; Chem. Abstr., 93, 70455 (1980).

17. Y. Sato, H. Nakai, T. Mizoguchi, Y. Hatanaka and Y. Kanaoka, J. Am. Chem. Soc., 98, 2349 (1976).

18. C. Ganter and J.F. Moser, Helv. Chim. Acta., 51, 300 (1968).

19. J.R. Collier and J. Hill, Chem. Commun, 700 (1968).

20. H. Tsuruta, M. Ogaswara and T. Mukai, Chem. Lett., 887 (1974).

21. K.K. Maheshwari and G.A. Berchtold, Chem. Commun., 13 (1969).

22. A.O. Pederson, S.O. Lawesson, P.D. Klemmensen and J. Kale, Tetrahedron, 26, 1157 (1970).

23. O.L. Chapman and C.L. McIntosh, J. Am. Chem. Soc., 92, 7001 (1970).

24. S.M. Rosenfeld, R.G. Lawler and H.R. Ward, J. Am. Chem. Soc., 94, 9255 (1972).

25. G.W. Byers, H. Gruen, H.G. Giles, H.N., Schott and J.A. Kampmeier, J. Am. Chem. Soc., 94 1016 (1972).

26. H. Morita and S. Oae, Heterocycles, 5, 35 (1976).

27. S.F. Birch, T.V. Cullum and R.A. Dean, J. Inst. Petrol, 39, 206 (1953).

28. A.L.J. Beckwith and Low Beng See, J. Chem. Soc., 2571 (1964).

29. G.A.R. Brandt, H.J. Emeleus and R.N. Haszeldine J. Chem. Soc., 2198 (1952).

30. R.I. Shekhtman, V.A. Krongauz and E.N. Prilezhaeva, Izv. Aked. Nahk, SSSR, Ser. Khim, 11, 2647 (1973), Chem. Abstr., 80, 42890 (1974).

31. A.G. Schultz, W.Y. Fu, R.D. Lucci, B.G. Kurr, K.M. Lo and M. Boxer, J. Am. Chem. Soc., 100 2140 (1978).

32. K. Dimroth, K. Wolf and H. Kroke, Ann., 678, 183 (1964).

33. G. Bastein and J.M. Surzur, Bull. Soc. Chim. Fr., 11, Part II, 601 (1979).

34. R.M. Kellogg, J.K. Dik, H. Van Driel and H. Wynberg, J. Org. Chem., 35, 2737 (1970).

35. H. Wynberg, M.B. Groen and R.M. Kellogg, J. Org. Chem., 35, 2838 (1970).

36. R.M. Kellogg, J. Am. Chem. Soc., 93, 2344 (1971).

37. H. Wynberg, R.M. Kellogg, H. Van Driel and G.E. Beekhnis, J. Am. Chem. Soc., 89, 3498, 3501 (1967).

38. G.O. Schenck, W. Hartmann and R. Steinmetz, Ber., 96, 498 (1963).

39. H. Kloosterziel, Rec. Trav. Chim., 82, 497, 508 (1963) ; Chem. Abstr., 60, 10523 (1964).

40. N. Kharasch and Z.S. Ariyan, Chem. & Ind., 929 (1964).

41. N. Kharasch and A.I. Khodair, " The Chemistry of Sulfides ", Ed., A.V. Tobolsky, Interscience, New York, 1968, p. 105.

42. D.H.R. Barton, Y.L. Chow, A. Cox and G.W. Kirby, Tetrahedron Letters, 1055 (1962).

43. D.H.R. Barton, Y.L. Chow, A. Cox and G.W. Kirby, J. Chem. Soc., 3571 (1965).

Smt. HANSA MEHTA

44. D.H.R. Barton, T. Nakano and P.G. Sammes, J. Chem. Soc., 322 (1968).

45. K. Gollnick and H.U. Stracke, Pure Appl. Chem., 33, 217 (1973) ; Chem. Abstr., 78, 110181 (1973).

46. R.G. Petrova and R.K.H. Friedlina, Bull. Acad. Sci. USSR, Div. Chem. Soc. (Eng Transl) 1797 (1966).

47. H. Nozaki, T. Shirufuji, K. Kuno and Y. Yamamoto, Bull. Chem. Soc. Jap., 45, 856 (1972).

48. D.C. Dittmer, G.C. Levy and G.E. Kuhlman, J. Am. Chem. Soc., 89, 2793 (1967).

49. D.C. Dittmer, G.E. Kuhlman and G.C. Levy, J. Org. Chem., 35, 3676 (1970).

50. I.W.J. Still, P.C. Arora, M.S. Chauhan, M.H. Khan and M.T. Thomas, Can. J. Chem., 54, 455 (1976).

51. M.P. Cava, R.H. Schlessinger and J.P. Vanmeter, J. Am. Chem. Soc., 86, 3173 (1964).

52. H.A.J. Carless, Chem. in Brit., 16, 458 (1980).

53. P.M. Weintraub, Chem. and Ind., 1296 (1970).

54. D.N. Harpp and D.F. Mullins, Can. J. Chem., 61, 757 (1983).

55. P.L. Wyllie, K.S. Prowse and M.A. Balill, J. Org. Chem., 48, 4022 (1983).

56. N. Kamigata, Bull. Chem. Soc. Jap., 57, 2325 (1984).

57. M.P. Cava, M.V. Lakshmikanthan and M. Behforouz, J. Org. Chem., 39, 206 (1974).

58. N.V. Kirby and S.T. Reid, J. Chem. Soc., Chem. Commun., 4, 150 (1980).

59. M. Nakai, N. Furukawa, S. Oae and T. Nakabayashi, Bull. Chem. Soc. Jap., 45, 1117 (1972).

60. T. Nakabayashi, Y. Nagata and J. Tsurugi, Int. J. Sulfur Chem. Part A, 1, 54 (1971) ; Chem. Abstr., 75, 97971 (1971).

61. A.I. Khodair, T. Nakabayashi and N. Kharasch, Int. J. Sulfur Chem., 8, 37 (1973) ; Chem. Abstr., 80, 120445 (1974).

62. M. Kobayashi, K. Tanaka and H. Minato, Bull. Chem. Soc. Jap., 45, 2906 (1972).

63. Y. Tamura, H. Kiyokawa and Y. Kita, Chem. Pharm, Bull., 27, 676 (1979).

64. O.P. Studzinskii, N.I. Rtishchev, N.N. Kravchenko and A.V. El'stov, Zh. Org. Khim., 11, 386 (1975); Chem. Abstr., 82, 111287 (1975).

65. C.W. Rees, D.L. Forster and T.L. Gilchrist, J. Chem. Soc. C, 5, 993 (1971).

66. T. Ohashi, M. Okhara and S. Komori, Bull. Chem. Soc. Jap., 44, 1141 (1971).

67. A. Abad, D. Mellier, J.P. Pete and C. Portella, Tetrahedron Letters, 4555 (1971).

68. J. Reisch and D.H. Niemeyer, Arch. Pharm., 305, 135 (1972).

69. N. Furukawa, M. Fukumara, T. Nishio and S. Oae, J. Chem. Soc. Perk. Trans. I, 2, 96 (1977).

70. W.E. Truce and D.L. Heuring, J. Org. Chem., 39, 245 (1974).

71. M. Kobayashi, H. Minato, Y. Miyaji, T. Yoshioka, K. Tanaka and K. Honda, Bull. Chem. Soc. Jap., 45, 2817 (1972).

72. R.J. Olsen, B.D. Maxwell and C.A. Ridgeway, J. Org. Chem., 48, 3847 (1983).

73. R.F. Langler, Z.A. Morini and J.A. Pincock, Can. J. Chem., 56, 903 (1978).

74. B. Gorewit and M. Rosenblum, J. Org. Chem., 38, 2257 (1973).

75. H. Itokawa, T. Tazaki and S. Mihashi, Heterocycles, 15, 1105 (1981).

76. M. Ohashi, A. Ezaki and T. Yonezawa, J. Chem. Soc. Chem. Commun., 15, 617 (1974).

77. E. Fanghaenel, R. Ebisch and B. Alder, Z. Chem., 13, 421 (1973) ; Chem. Abstr., 80, 70022 (1974).

78. N.I. Rtishchev, A.V. El'stov, I.Y. Kvitko, L.V. Alam and E.G. Bocharova, Zh. Obschch. Khim., 54, 152 (1984) ; Chem. Abstr., 100, 174109 (1984).

79. R.W. Hoffmann, W. Sleber and G. Guhn, Ber., 98, 3470 (1965).

80. M. Kayambu and R. Vaidhyanathan, J. Org. Chem., 45, 4532 (1980).

81. M. Kayambu and R. Vaidhyanathan, Chem. Lett., 1261 (1981).

82. M. Kayambu, B. Sundari and R. Vaidhyanathan, Indian J. Chem. Sect. B, 20, 797 (1981).

83. A. Ohno and N. Kito ; Int. J. Sulfur Chem., Part A, 1, 26 (1971).

84. D.S.L. Blackwell and P. de Mayo ; J. Chem. Soc. Chem. Commun., 130 (1973).

85. P. de Mayo and R. Suau, J. Am. Chem. Soc., 96, 6807 (1974).

86. J.J. Worman, M. Shen and P.C. Nichols, Can. J. Chem., 50, 3923 (1972).

87. A. Couture, M. Hoshino and P. de Mayo, J. Chem. Soc., Chem. Commun., 131 (1976).

88. R. Arad-Yellin and D.F. Eaton, J. Am. Chem. Soc., 104, 6147 (1982).

89. J.D. Willet, J.R. Grunwell and G.A. Berchtold, J. Org. Chem., 33, 2297 (1968).

90. R.E. Kohrman and G.A. Berchtold, J. Org. Chem., 36, 3971 (1971).

91. W. Willcox, J. Am. Chem. Soc., 28, 431 (1961).

92. G. Bulmer and F.G. Mann, J. Chem. Soc., 677 (1945).

93. D.H.R. Barton, M.V. George and M. Tomoeda ; J. Chem. Soc., 1967 (1962).

94. S.N. Singh and M.V. George, Tetrahedron, 2029 (1975).

95. K. Beelitz and K. Praefcke, Chem. Ztg. 102, 67 (1978) ; Chem. Abstr., 88, 189611 (1978).

96. A. Shah, S.N. Singh and M.V. George, Tetrahedron Letters, 3983 (1968).

97. S.N. Singh and M.V. George, J. Org. Chem., 36, 615 (1971).

98. E.H. Hoffmeister and D.S. Tarbell, Tetrahedron, 21, 35, 2857 (1965).

99. A.O. Fitton, J. Hill, M. Qutob and A. Thompson, J. Chem. Soc. Perkin Trans., I, 21, 2658 (1972)

100. S.N. Singh and M.V. George, J. Org. Chem., 37, 1375 (1972).

101. O.L. Chapman and C.L. McIntosh, Chem. Commun., 383 (1971).

102. K. Hartke, T. Kissel, J. Quante and R. Matusch, Chem. Ber., 113, 1898 (1980).

103. T. Kissel, R. Matusch and K. Hartke, Z. Chem. 16, 318(1976) ; Chem. Abstr., 86, 43146 (1977).

104. H.G. Heine and W. Metzer, Ann. Chem., 724, 233 (1969).

105. R. Okazaki, F. Ishii, K. Ozawa and N. Inamoto, Chem. Lett., 9 (1972).

106. Y. Ogata, K. Takegi and Y. Takayanagi, J. Chem. Soc., Perkin Trans, I, 12, 1244 (1973).

107. J. Wirz, J. Chem. Soc. Perkin Trans. II, 10, 1307 (1973).

108. D.H.R. Barton, M. Bolton, P.D. Magnus ; K.G. Marathe, G.A. Poulton and P.J. West., J. Chem. Soc. Perkin I, 15, 1574 (1973).

109. D.H.R. Barton, M. Bolton, P.D. Magnus and P.J. West, J. Chem. Soc., Perkin Trans. I, 15 1580 (1973).

110. J. Martens and K. Praefcke, Chem. Ber., 107, 2319 (1974).

111. R.R. Pillai and K.C. Eapen, Curr. Sci., 46, 75 (1977).

112. K. Praefcke and H. Simon, Chem. Ber., 109, 3915 (1976).

113. B. Kohne, K. Praefcke and C. Weichsel, Phosphorus Sulfur, 7, 211 (1979) ; Chem. Abstr., 93, 71732 (1980).

114. E. Fromm and P. Schmoldt, Ber., 40, 2863 (1907).

115. M.G. Voronkov, E.N. Deryagina, E.N. Sukhomazova, A.N. Mirskova and S.G. Seredkina, Zh. Org. Khim., 19, 1641 (1983) ; Chem. Abstr., 99, 194255 (1983).

116. O.E. Thompson, M.M. Crutchfield, M.W. Dietrich and E. Pierron, J. Org. Chem., 30, 2692 (1965).

117. H.G. Giles, R.A. Marty and P. de Mayo, Can. J. Chem., 54, 537 (1976).

118. A.A. Abdel-Wahab and A.E. Abdel-Rahman, Indian J. Chem., Sect. B ; 20B, 636 (1981).

119. D.H.R. Barton and B.J. Willis, J. Chem. Soc., Perkin Trans I, 3, 305 (1972).

120. M.S. Chande and S.W. Tanksale, J. Indian Chem. Soc., 55, 1062 (1978).

121. D.C. DeJongh, R.Y.V. Fossen and C.F. Bourgeois, Tetrahedron Letters, 271 (1967).

122. D.C. Jongh, R.Y.V. Fossen and A. Dekovich, Tetrahedron Letters, 5045 (1970).

123. F. Voegfle and L. Rossa, Tetrahedron Letters, 8577 (1977).

124. F. Voegfle and P.K.T. New, Angew. Chem., 90, 58 (1978).

125. M.G. Voronkov, E.N. Deryagina, E.N. Sukhomazova, V.Y. VitkovSkii, N.K. Gusarova and B.A. Trofimov, Izv. Akad. Nauk. SSSR, Ser. Khim., 4, 931 (1983) ; Chem. Abstr., 99, 21902 (1983).

126. J.F. King, P. De Mayo, C.L. Mc Intosh, K. Piers and D.J.H. Smith, Can. J. Chem., 48, 3704 (1970).

127. D.C. Dittmer, J.E. Mc Caskie, J.E. Babiarz and M.V. Ruggeri, J. Org. Chem., 42, 1910 (1977).

128. F. Mathey and J.P. Lampin, Tetrahedron Letters, 3121 (1972).

129. L.A. Kaluza ; Monatsh, 33, 363 (1912).

130. A. Andreasch, Monatsch, 27, 1211 (1906).

131. T.B. Johnson, A.J. Hill and E.B. Kelsey, J. Am. Chem. Soc., 42, 1711 (1920).

132. M.S. Chande, J. Indian Chem. Soc., 56, 386 (1979).

133. K. Rasheed and J.D. Warkentin, J. Org. Chem., 44, 267 (1979).

134. M.S. Chande and M.D. Kulkarni, J. Indian Chem. Soc., 58, 877 (1981).

135. P.C. Oele, A. Tinkelenberg and R. Louwy, Tetrahedron Letters, 2375 (1972).

136. T. Nakai and A. Ariizum ; Tetrahedron Letters, 2335 (1976).

137. J.V. Braun, Ber., 36, 3520 (1903).

138. D.S. Tarbell and R.P.F. Scharrer, J. Org. Chem., 27, 1972 (1962).

139. A. Schonberg and E. Frese, Ber., 101, 701, 716 (1969).

140. A. Schonberg and E. Frese, Ber., 103, 938, 949 (1970).

141. A. Schonberg and E. Frese, Tetrahedron Letters, 4063 (1969).

142. C.H. Depuy and R.W. King, Chem. Revs., 60, 431 (1960).

143. H.R. Nace, " Organic Reactions ", Ed., A.C. Cope, John Willey and Sons, Inc., New York, Vol. 12, 1962, p. 57.

144. K. Haruno and T. Taguchi, Tetrahedron Letters, 4479 (1947).

145. K. Haruno and T. Taguchi, Chem. Pharm. Bull., 20, 2348, 2357 (1972).

146. T. Kawata, K. Haruno and T. Taguchi, Chem. Pharm. Bull., 21, 604 (1973).

147. M.J. Janssen, in " The Chemistry of Carboxylic acids and Esters " Ed, S. Patai, Interscience, New York, 1969, Chapter 15, p. 705.

148. M. Bugemann, S. Petersen, O.E. Schultz and H. Soll, in " Methoden der organische Chemie ", ed., E. Muller, Houben-Weyl, Berlin, Vol. IX, 1955, p. 804.

149. Y. Araki, Bull. Chem. Soc. Japan, 43, 252 (1970).

150. H. Yoshida, T. Ogata and S. Inokawa, Bull. Chem. Soc. Japan., 44, 1949 (1971).