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REVIEW
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Recent Progress in the Chemistry of 1, 3-Dithiolanes and Related Compounds

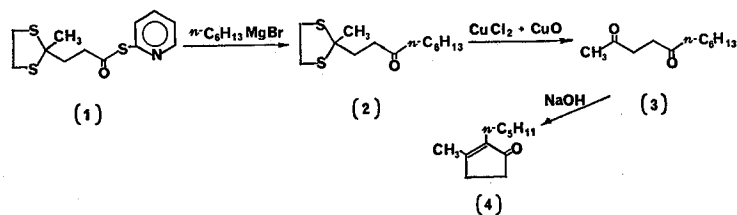Shigeo TANIMOTO*, Hiromu TERAO*,
Tatsuo OIDA*, and Hideyuki IKEHIRA*

This review deals with recent progress in the chemistry of 1,3-dithiolanes and related compounds. It consists of the following sections: introduction, the deprotonation at C-2 and the subsequent reaction, the deprotonation at C-4 or C-5 and the subsequent reaction, the attack to functional group at C-2 and the subsequent reaction, the attack to S-1 and/or S-3 and the subsequent reaction, and the other reactions.

KEY WORDS: 1,3-Dithiolanes/ 2-Substituted 1,3-dithiolanes/ Deprotonation/ Desulfurization/

I. INTRODUCTION

The synthetic usefulness of the umpolung of the reactivity of carbonyl compounds by reaction of sulfur-containing reagents is widely known.[1] Among the reagents employed for carbonyl umpolung, 2-lithio-1,3-dithianes have been most frequenlty employed since the 1,3-dithiane unit possesses high stability and hence it can be carried through a multistep synthesis.[1,2] Thus, the chemistry of 1,3-dithianes and related compunds have received much attention to say nothing of the chemistry of 2-lithio-1,3-dithianes. In contrast, the chemistry of 1,3-dithiolanes and related compounds is of practical significance with respect to the widespread use as the masked carbonyl compounds, and hence many efforts have been devoted to preparation and especially to desulfurization of such the compounds. For example, *S*-2-pyridyl ester (**1**) of 2-methyl-1, 3-dithiolane-2-propanethioic acid, prepared from levulinic acid, react with hexylmagnesium bromide in tetrahydrofuran to give the ketone **2** having a 1, 3-dithio-

lane unit. On treatment with $CuCl_2$ and CuO in 99% aqueous acetone **2** undergoes desulfurization, forming the 1,4-diketone **3**, which is cyclized to dihydrojasmone (**4**).[3,4] As is evident from the accompanying equation, the 1, 3-dithiolane unit of **1** is carried through the Grignard reaction without any change of the 1, 3-dithiolane moiety. As is described in the beginning of this section, the formation of 2-metalated 1, 3–dithianes from 1, 3-dithianes is clean and quantitative.[1] On the other hand, the five-membered homologues, 1, 3-dithiolanes, are reported[5] to undergo a variety of reactions upon treatment with strong base, including deprotonation, cycloreversion and elimination, depending on reaction conditions. Recently, several detailed reports in this area have been published in the literature. These results which seem to possess practical use in synthetic organic chemistry will be described in the latter sections. Thus, 1, 3-dithianes, 1, 3-dithiolanes, and their related compounds seem to fulfill the requirement for intermediates of synthetic organic chemistry. Concerning 1, 3-dithianes and related compounds, one or probably more parts of the chemstry of them have already been reviewed in a few articles.[1,6] To our knowledge, however, there has not been any collective information about the chemistry of 1, 3-dithiolanes and related compounds. In this article a survey is given of experimental results and some pertaining explanations in the area of synthetic reactions in which 1, 3-dithiolanes and related compounds participate with some emphasis on work conducted in our laboratory. However, the greater part of the previously reported reactions utilizing spiro-1, 3–dithiolanes is omitted due to its failure in generality.

## II. THE DEPROTONATION AT C-2 AND
THE SUBSEQUENT REACTION

2-Lithio-1, 3-dithiolanes have been reported[2] to undergo facile elimination to form ethylene. This hypothesis was apparently based on the work of Schönberg and his co-workers,[7] who showed that 4, 4, 5, 5-tetraphenyl-1, 3-dithiolane was cleaved with phenyllithium to tetraphenylethylene (**5**). Further, it has been found that several 2-aryl-1, 3-dithiolanes in *N*, *N*-dimethylformamide containing hexamethylphosphoric triamide undergo deprotonation by NaH at the ring C-2 to afford **6**, which are subsequently methylated by methyl iodide leading to the formation of the corresponding aromatic methyl dithiolates **7**.[8] Regarding 2-alkyl-1, 3-dithiolanes, only 2-methyl-1, 3-dithiolane has been found[9] to undergo the analogous deprotonation-methylation

(5)

(6)   (7)

R,R' = H,H ; H,Cl ; OCH₃,OCH₃ ; H,CHO ; -OCH₂O-

$$(8)$$
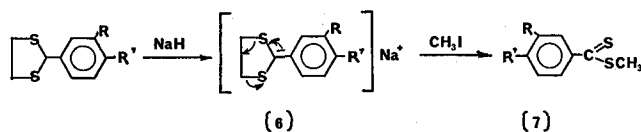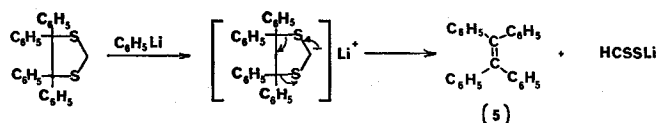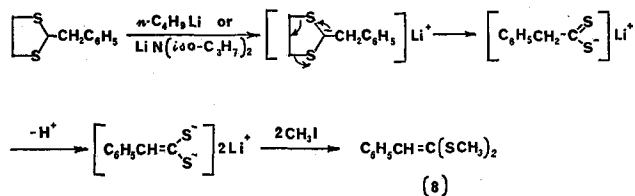
sequence to give methyl methyldithiolate, where lithium diisopropylamide is used instead of NaH. When 2-benzyl-1,3-dithiolane are treated with butyllithium or lithium diisopropylamide in ether, the reaction proceeds *via* a process involving deprotonation at the ring C-2 of 2-benzyl-1,3-dithiolane to afford preferentially β,β-bis(methylthio)styrene (**8**) upon treatment with methyl iodide.[10]

On the other hand, the generatisn of 1,2-ethanediylbis(trithiocarbonic acid) dianion (**10**) from 2,2′-[1,2-ethanediylbis(thio)]bis-1,3-dithiolane and its reaction with several electrophilic reagents have been investigated.[11,12] The dianion formation is readily accomplished by the addition of butyllithium in hexane to 2,2′-[1,2–ethanediylbis(thio)]bis-1,3-dithiolane under nitrogen. The initially formed dianion **9** is unstable and therefore undergoes ring opening leading to **10** with elimination of two moles of ethylene. The dianion **10** thus formed was subsequently treated with the trapping agents such as highly electrophilic alkyl halides, haloacetic esters, and chloromethyl alkyl ethers to produce mainly the corresponding **11**. With the trapping agents such as less electrophilic alkyl halides and chloromethyl alkyl sulfides, the reaction occurred only at one of the nucleophilic ends in **10** to give a monoanion **12**, which underwent fragmentation to afford the trithiocarbonate anions and 1,3–dithiolane-2-thione, and the former was then attacked by the same trapping agent to give the corresponding trithiocarbonates.
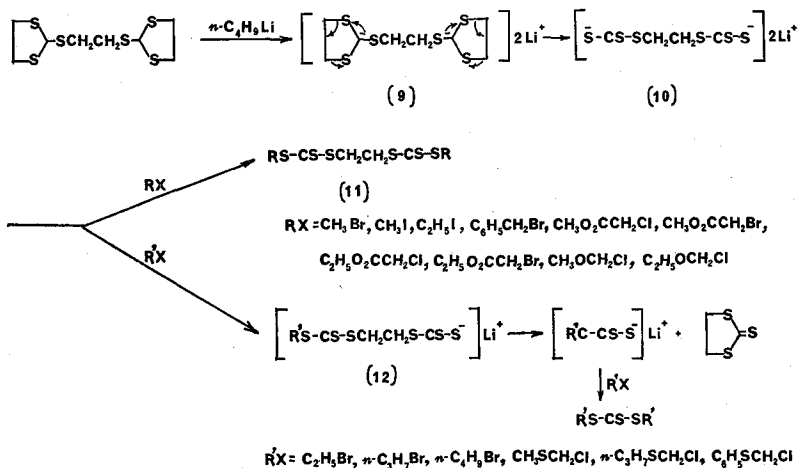

In the reaction of 2-alkylthio-1,3-dithiolanes with butyllithium, the initially formed anion is assumed to be **13**, which immediately decomposes to ethylene and alkyl trithiocarbonate anion, and the latter is subsequently alkylated by several alkyl

halides to afford the corresponding dialkyl trithiocarbonates.[13] In cases where 2-arylthio-1,3-dithiolanes were used instead of 2-alkylthio-1,3-dithiolanes, the similarly formed aryl trithiocarbonate anion undergoes further fragmentation to afford carbon disulfide and arenethiolate anion **14**, presumably due to the electron-withdrawing effect of the benzene ring. The anion **14** was then trapped by methyl iodide to afford the corresponding methyl sulfides.[13]
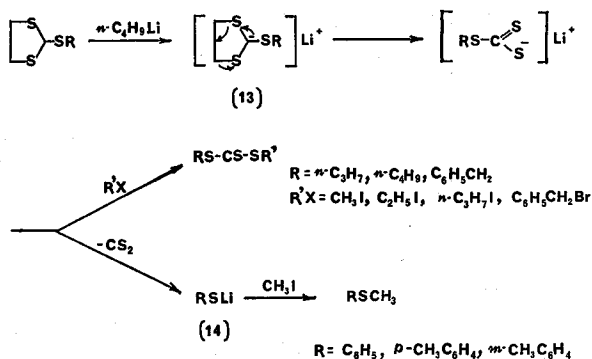

The reactions of 1,3-dithiolane derivatives having a typical electron-withdrawing group such as carbonyl or cyano group at the ring C-2 with strong bases have also been investigated. Especially, it is interesting that the initially formed anionic species in such the case is stable to the cycloreversion above mentioned. For example, the anion **15** generated from ethyl 1,3-dithiolane-2-carboxylate with lithium diisopropylamide at $-78°C$ was found[14] to be stable and does not undergo cycloreversion leading to **16** at that temperature. There are some instances relating to the reaction of **15** with several Michael receptors. Thus, **15** reacted with the unsaturated
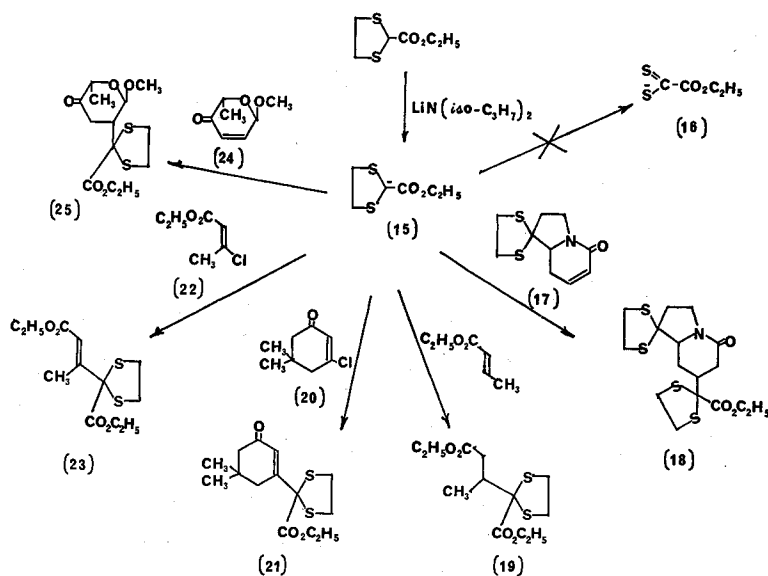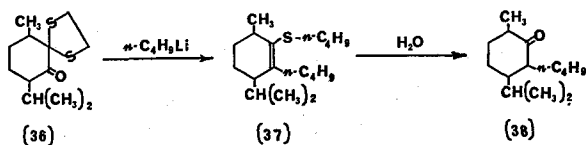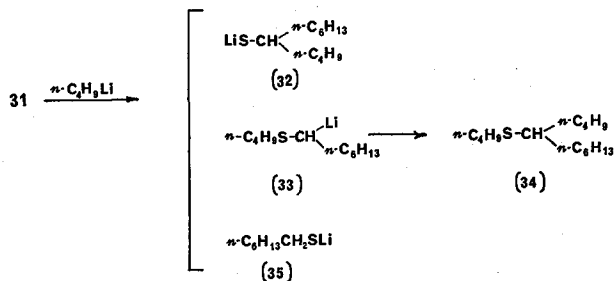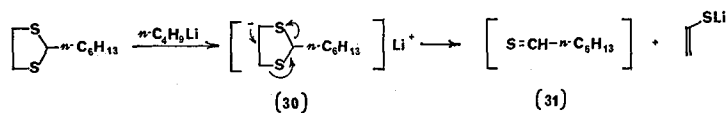
lactam **17** and ethyl crotonate to afford the adducts **18** and **19**, respectively. Also, the reaction of **15** with the β-chloro substituted Michael receptors such as **20** and **22** provides, after hydrolysis, a novel preparation of α,β-unsaturated 1,4-dicarbonyl compounds such as **21** and **23**.[15] In addition, **15** reacts cleanly with the pyranoside enone **24** to afford the adduct **25**.[16]

However, when a crystalline sulfonium salt (**26**, R$=$OC$_2$H$_5$), prepared from ethyl 1,3-dithiolane-2-carboxylate and methyl fluorosufonate, was treated with K$_2$CO$_3$ in the presence of 2,3-dimethylbutadiene, the thiocarbonyl cycloadduct (**29**, R$=$OC$_2$H$_5$) was obtained[14] in good yeild. This means that a labile sufur ylide (**27**, R$=$OC$_2$H$_5$) was apparently formed as the intermediate which underwent cycloreversion to **28** (R$=$OC$_2$H$_5$) under nearly neutral conditions. Similar transformations leading to **29** (R$=$CH$_3$) and **29** (R$=$C$_6$H$_5$) were also achieved[14] with 2-acyl-1,3–dithiolanes such as 2-acetyl- and 2-benzoyl-1,3-dithiolane as representative examples. Batyrbaev and his co-workers have found[17] that the free-radical addition of 1,3–dithiolane and 2-methyl-1,3-dithiolane to 1-hexene in the presence of *tert*-butyl hydroperoxide at elevated temperature give 2-hexyl-1,3-dithiolane and 2-methyl-2–hexyl-1,3-dithiolane, respectively.
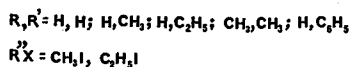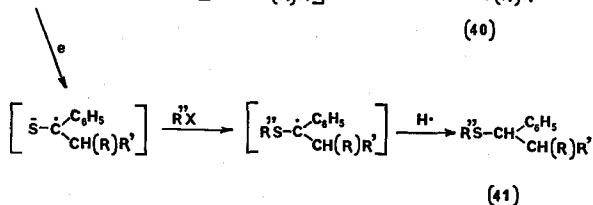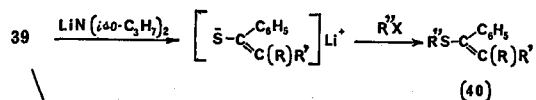

(26)   (27)

(28)

R$=$OC$_2$H$_5$,CH$_3$,C$_6$H$_5$ (29)
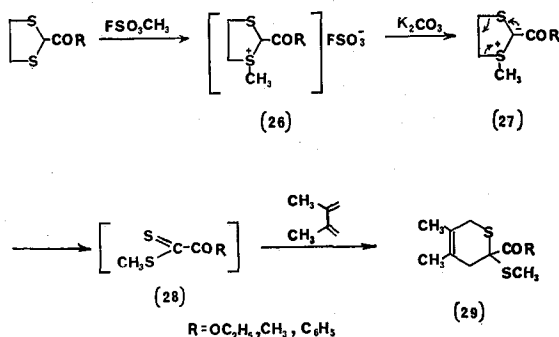
III. THE DEPROTONATION AT C-4 OR C-5
AND THE SUBSEQUENT REACTION

The successful deprotonation at the ring C-4 of 1,3-dithiolanes is initially found by Wilson and his co-workers[18] and independently by us.[19] The reaction of major part of 1,3-dithiolanes with butyllithium in an appropriate solvent results in fragmentation to the corresponding thiocarbonyl compound followed by further reaction with butyllithium. All four type of thiocarbonyl reactions such as reduction, *S*-addition, *C*-addition, and double addition have been observed in the reaction.[18] For example, an excess of butyllithium in ether at room temperature reacted with 2-hexyl-1,3-dithiolane to yield a product mixture consisting of **32** and **34** together with **33** and **35** in relatively low yields. All products obtained from this reaction can be explained[18] by involving initial deprotonation at the ring C-4 giving **30** and subsequent cleavage to the thiocarbonyl compound **31** followed by reaction with excess butyllithium. Such the new 1,3-dithiolane cleavage reaction offers a unique approach to 1,2-carbonyl transposition. Thus, when the α-ketodithiolane **36** was treated with an excess of

$$\left[\begin{array}{c} S \\ S \end{array}\right]\!-n\text{-}C_6H_{13} \xrightarrow{n\text{-}C_4H_9Li} \left[\ \overset{-}{\underset{S}{\left[\begin{array}{c} S \\ \ \end{array}\right]}}\!-n\text{-}C_6H_{13}\ \right]Li^+ \longrightarrow \left[\ S\!=\!CH\!-\!n\text{-}C_6H_{13}\ \right]\ +\ \left[\begin{array}{c} \\ \end{array}\right]^{SLi}$$

$$(30) \qquad\qquad\qquad (31)$$

$$31 \xrightarrow{n\text{-}C_4H_9Li} \left[\begin{array}{l} LiS\text{-}CH\!\!<\!\!\overset{n\text{-}C_6H_{13}}{\underset{n\text{-}C_4H_9}{}} \\ \quad (32) \\[2ex] n\text{-}C_4H_9S\text{-}CH\!\!<\!\!\overset{Li}{\underset{n\text{-}C_6H_{13}}{}} \longrightarrow\ n\text{-}C_4H_9S\text{-}CH\!\!<\!\!\overset{n\text{-}C_4H_9}{\underset{n\text{-}C_6H_{13}}{}} \\ \quad (33) \qquad\qquad\qquad (34) \\[2ex] n\text{-}C_6H_{13}CH_2SLi \\ \quad (35) \end{array}\right.$$

butyllithium, a vinyl sulfide **37** was formed in moderate yield. Hydrolysis of **37** in the presence of $TiCl_4$ in acetic acid gave the 1,2-transposed ketone **38**.[18]

The reaction of several 2,2-disubstituted 1,3-dithiolanes derived from saturated ketones with butyllithium under the same reaction conditions and subsequent quenching with methyl iodide leading to the corresponding methyl sulfides has also been reported by the same authors.[18] However, more interesting results have been observed[20] in the reaction of 1,3-dithiolane derivatives of several ketones having α-hydrogen with the less nucleophilic lithium diisopropylamide and the subsequent quenching with alkyl halides. Thus, similarly formed thiocarbonyl compounds **39** were further converted in a few steps to the other intermediate species which, on trap-

$$\left[\begin{array}{c} S \\ S \end{array}\right]\!\!\underset{CH(R)R'}{\overset{C_6H_5}{\diagdown}} \xrightarrow{LiN(iso\text{-}C_3H_7)_2} \left[\ S\!=\!C\!\!<\!\!\overset{C_6H_5}{\underset{CH(R)R'}{}}\ \right]\ +\ \left[\begin{array}{c} \\ \end{array}\right]^{SLi}$$

$$(39)$$

$$39 \xrightarrow{LiN(iso\text{-}C_3H_7)_2} \left[\ \overset{-}{S}\text{-}C\!\!<\!\!\overset{C_6H_5}{\underset{C(R)R'}{}}\ \right]Li^+ \xrightarrow{R''X} R''S\text{-}C\!\!<\!\!\overset{C_6H_5}{\underset{C(R)R'}{}}$$

$$(40)$$

$$\downarrow e$$

$$\left[\ \overset{-}{S}\text{-}\overset{\cdot}{C}\!\!<\!\!\overset{C_6H_5}{\underset{CH(R)R'}{}}\ \right] \xrightarrow{R''X} \left[\ R''S\text{-}\overset{\cdot}{C}\!\!<\!\!\overset{C_6H_5}{\underset{CH(R)R'}{}}\ \right] \xrightarrow{H\cdot} R''S\text{-}CH\!\!<\!\!\overset{C_6H_5}{\underset{CH(R)R'}{}}$$

$$(41)$$

R,R'= H, H; H,CH₃; H,C₂H₅; CH₃,CH₃; H,C₆H₅

R''X = CH₃I, C₂H₅I

ping with alkyl halides, lead to vinylic sulfides **40** and/or sulfides **41** bearing a secondary alkyl group depending on choice of the starting 2,2-disubstituted 1,3-dithiolanes. When 1,3-dithiolane derivatives of several diaryl ketones were submitted to the deprotonation with the same base and the subsequent quenching with alkyl halides, either one of **43, 44** and its mixture with **45** was produced depending on choice of the starting 2,2-diaryl-1,3-dithiolanes.[19]

The lithium diisopropylamide-induced hydrolysis of 2-aryl-2-methyl-1, 3–dithiolanes leading to the corresponding carbonyl compounds has also been reported.[21] The reaction may be assumed to proceed *via* deprotonation of the similarly formed intermediate thioketone **46** by lithium diisopropylamide to give a species **47** which finally converted into the corresponding ketone by added aqueous acetic acid.

A variety of alkyl vinyl trithiocarbonates **48** can be prepared[22] in synthetically useful yields by reaction of 1, 3-dithiolane-2-thione with lithium diisopropylamide in tetrahydrofuran followed by treatment with several alkyl halides. Some 1, 3-dithiolane–2-thione derivatives such as 4-methyl- (**49**), 4-phenyl- (**50**), and *cis*-4, 5-diphenyl-1, 3–dithiolane-2-thione (**51**) also receive[22] the same conversion to give the corresponding trithiocarbonates. The initial deprotonation involved in these reactions occurred at C-5 of **49** and at both C-4 and C-5 of **50**.[22] An example of the analogous conversion

is also seen in the reaction of 2-alkylidene-1, 3-dithiolanes with a strong base. Thus, a sequential reaction of 2-alkylidene-1, 3-dithiolanes with lithium diisopropylamide in tetrahydrofuran in the presence of hexamethylphosphoric triamide and aqueous HCl gave 52.[23] Besides, basic catalysts can effect a rapid polymerization of 1, 3-dithiolane-2, 4-dione to yield polyester (53) of 2-mercaptoacetic acid. The catalytic effect of aprotic bases such as N-methylmorpholine and triethylamine increases with their increasing basicity because the initiation consists of the deprotonation at C-5 of the monomer.[24]

$$RX = CH_3I, C_2H_5I, C_2H_5Br, C_6H_5CH_2Br$$

(52)   R = H, CH₃

(53)
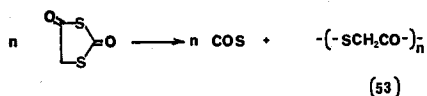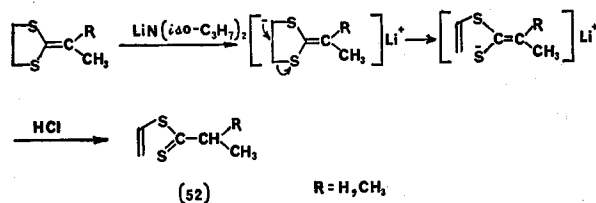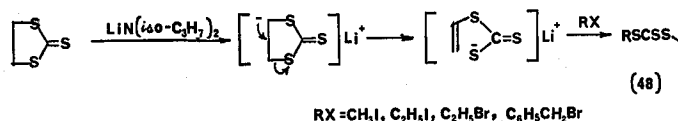
IV. THE ATTACK TO FUNCTIONAL GROUP AT C-2
AND THE SUBSEQUENT REACTION

When the reaction mixture of 1, 3-dithiolane-2-thione with butyllithium in tetrahydrofuran is quenched with methyl and ethyl iodides, butyl methyl trithiocarbonate and butyl ethyl trithiocarbonate are obtained, respectively, together with ethylene.[25] It seems reasonable that the reaction involves direct attack of the nucleophile on the sulfur of thiocarbonyl leading to an intermediate anion 54 and subsequent fragmentation of 54 to ethylene and butyl trithiocarbonate anion. Prior to this report, it has already been reported by Corey and Märkl[26] that the reaction of 1, 3-dithiolane-2-thione derivatives with trimethyl phosphite leads to the formation of the corresponding olefins by cis-elimination. If the objective product in these reactions is only the olefin, the former reaction using butyllithium seems to exhibit more advantages because it can be more easily visualized. More important from the synthetic point of view is the discovery that the former reaction constitutes, together with the reaction proposed by Overberger and Drucker,[27] a new process of the interconversion of cis- and trans–olefins. For example, cis- and trans-stilbene are converted to trans-4, 5-diphenyl-1, 3-dithiolane-2-thione (55) and its cis-isomer (56), respectively. Thus, the compound 55 was treated with butyllithium in tetrahydrofuran to afford trans-stilbene in 100% yield. Similarly, cis-stilbene was obtained free of isomeric impurity in 99% yield from

56.[25] The treatment of 1, 3-dithiolane-2-thione with dimethyl sulfate provides **57** which is further converted to a variety of compounds such as **58, 59, 60, 61,** and **62.**[28]
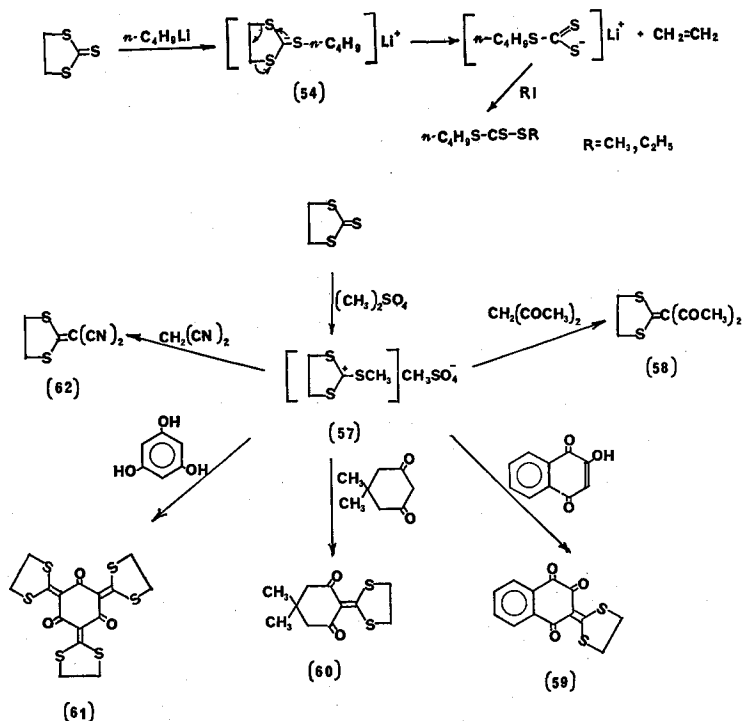

When *cis-* or *trans*-4, 5-diphenyl-1, 3-dithiolane-2-thione in ethanol was irradiated by a mercury arc lamp with Pyrex filter under nitrogen, the obtained product was phenanthrene (**63**) regardless of which starting material was chosen (*cis* and *trans*).[29] From the kinetic measurements which were made by monitoring the disappearance and appearance of the starting material and the product, respectively, in the presence of air and in degassed cells, and overview of the possible mechanistic paths operative in
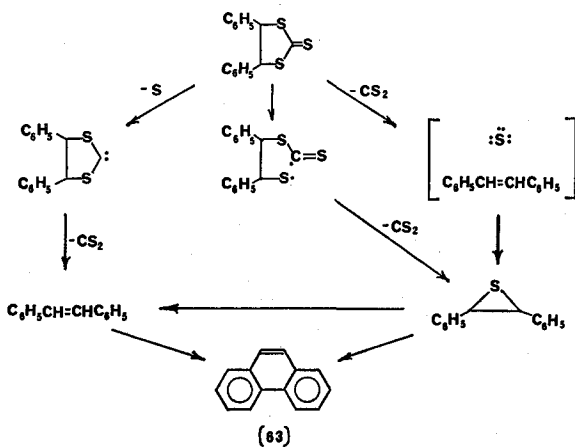
this system is proposed,[29] which is given as accompanying equations.

It has been found[30] that the reaction of enol silyl ethers **64** with 2-ethoxy-1,3-dithiolane proceeds smoothly in the presence of ZnCl$_2$ to give half-protected 1,3-dicarbonyl compounds **65**. A novel procedure to ketene S,S-acetals of general structure **68** has been proposed.[31] The procedure involves the initial formation of a phosphorus ylide **67** by base treatment of **66**, prepared from 2-ethoxy-1,3-dithiolane, triphenylphosphine, and HBF$_4$, and the subsequent Wittig reaction of **67** with aldehydes. The reaction of 2-ethoxy-1,3-dithiolane with a variety of active methylene compounds in the presence of ZnCl$_2$ leading to **69** was investigated. By this reaction the introduction of a 1,3-dithiolan-2-yl group into the active methylene compounds was achieved.[32] Also, the reaction of various phenols with 2-ethoxy-1,3-dithiolane in dichloromethane proceeded smoothly in the presence of BF$_3$·O(C$_2$H$_5$)$_2$ to afford 1,3-dithiolan-2-ylated phenols (**70** and **71**), which were readily hydrolyzed to the corresponding aldehydes.[33] This process for the fromylation of phenols could also be extended to N,N-dimethylaniline and indole.[33] Another example of the introduction of 1,3-dithiolan-2-yl moiety into methyl lysergate is also reported by Stütz and Stadler.[34]

(63)
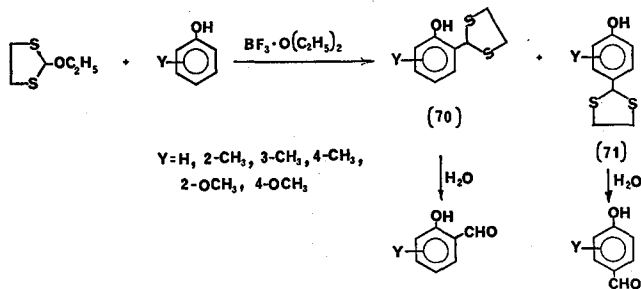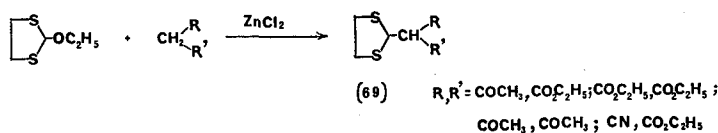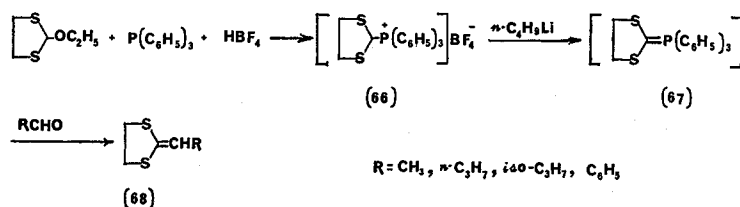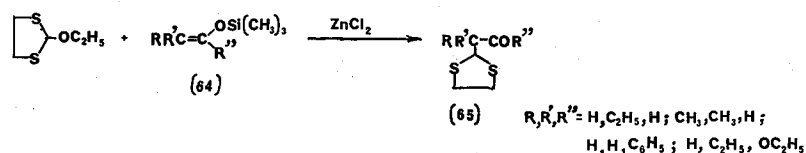
2-Propyl-1, 3-dithiolane itself undergoes formylation with N-chloromethylene-N, N-dimethylammonium chloride in dichloromethane in the presence of a catalytic amount of p-toluenesulfonic acid to afford 2-(1, 3-dithiolan-2-yl)butanal.[35] Ueno and Okawara[36] reported on the reaction of 2-methylthio-1, 3-dithiolan-2-ylium iodide, prepared[37] from 1, 3-dithiolane-2-thione and methyl iodide in nitromethane, with ethyleneimine to produce 72, which was easily converted into the conjugated N-vinyl monomer 73. Further, it has been reported by the same authors[36] that 2-methylthio-1, 3-dithiolan-2-ylium iodide reacts with NaN_3 in N, N-dimethylformamide with evolution of nitrogen to give 74. Another interesting examples which should be involved in this section may be the reaciton of 1, 3-dithiolane-2-thione with diphenylketene in dichloromethane leading to 75 as well as the reaction with bromocyanoacetylene in xylene to give 76.[38,39] The compound 76 was further converted to 77.
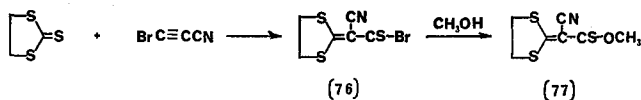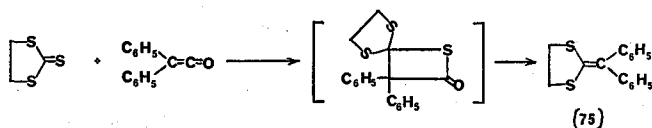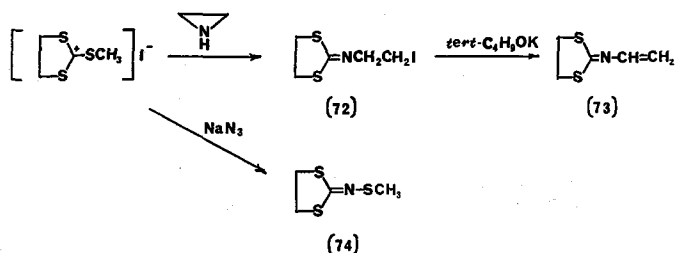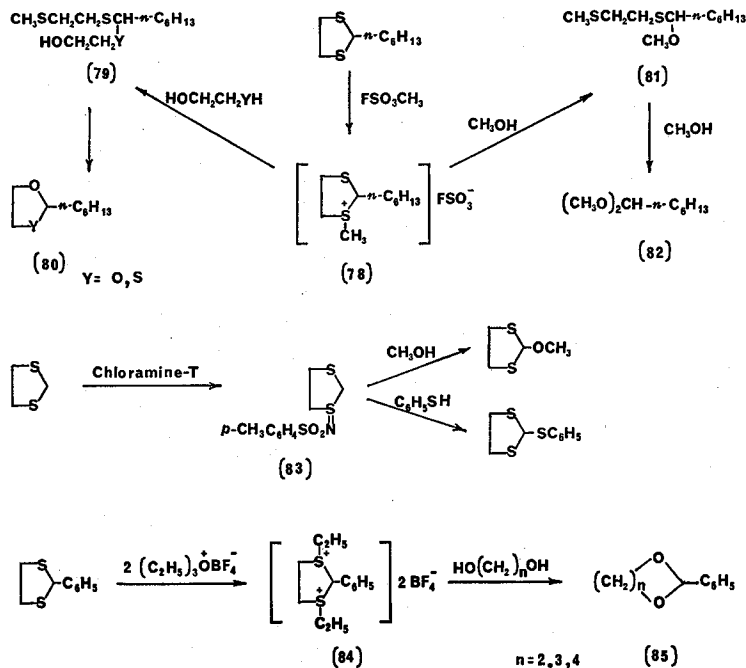

V. THE ATTACK TO S-1 AND/OR S-3 AND THE SUBSEQUENT REACTION

As described in the introduction of this review, the research upon the hydrolysis of 1, 3-dithiolanes and related compounds affording the corresponding carbonyl compounds is of practical significance with respect to the widespread use as the masked carbonyl compounds. Thus, a variety of simple, mild, and effective techniques for hydrolyzing 1, 3-dithiolanes and related compounds based on the use of easily available reagents have been investigated by many chemists. Almost all of these techniques have been accomplished by the following two methods.[40] One is the acidic or transition-metal hydrolysis and the other is the oxidative or alkylative hydrolysis. A number of procedures using reagents such as methyl iodide[41] or benzyl bromide[42] in aqueous methanol, dimethyl sulfate in aqueous methanol,[42] a combination of triethyloxonium tetrafluoroborate in dichloromethane and aqueous $CuSO_4$ (the

latter reagent is employed for hydrolysis of the intermediate sulfonium salt produced by action of the former reagent),[43] methyl fluorosulfonate in benzene and aqueous NaOH (both of which are employed in the same significance),[44] sulfuryl chloride fluoride in ether and water required for hydrolysis,[45] tert-butyl bromide or iodide in dimethyl sulfoxide and water required for hydrolysis,[46] $(NH_4)_2Ce(NO_3)_6$ in aqueous acetonitrile,[47] ice cold concentrated H_2SO_4,[48] O-(mesitylenesulfonyl)hydroxylamine in dichloromethane and water required for hydrolysis,[49] trichloroisocyanuric acid in aqueous acetonitrile in the presence of $AgNO_3$,[50] concentrated HCl plus H_2O_2 in methanol,[40] benzeneseleninic anhydride in tetrahydrofuran and water required for hydrolysis (this works well for hindered spiro-1,3-dithiolanes),[51] a combination of HgO and BF_3 as well as water required for hydrolysis (this works well for 2-hydroxyalkyl-1, 3-dithiolanes and ketene S, S-acetals of 1, 3-dithiolane series),[52,53] $Tl(NO_3)_3$ in methanol and co-solvents and water required for hydrolysis,[54] aqueous HBF_4 plus HgO in tetrahydrofuran,[55] $NO^+HSO_4^-$ in dichloromethane and water required for hydrolysis,[56] $NaNO_2$ or $NaNO_3$ in trifluoroacetic acid and water required for hydrolysis,[56] $NO_2^+BF_4^-$ in dichloromethane and aqueous $NaHCO_3$ for hydrolysis,[56] bromodimethylsulfonium bromide in dichloromethane and water required for hydrolysis,[57] SO_2Cl_2 in dichloromethane in the presence of wet silica gel,[58] chloramine–T in aqueous methanol,[59] aqueous $Hg(OCOCH_3)_2$,[60] as well as polystyryl-mercury trifluoroacetate in dichloromethane and water required for hydrolysis,[61] are currently known. Most of these reagents seem to be also effective even if one substituent at the ring C-2 of 1, 3-dithiolanes and related compounds is alkoxy, alkoxycarbonyl, alkenyl, or hydroxyalkyl group. It can be assumed that in the presence of these reagents 1, 3-dithiolanes and related compounds undergo electrophilic attack on S-1 and/or S-3 followed by cleavage of the C-S bond in the first step of the reaction. Another type of dethioacetalization of a spiro-1, 3-dithiolane is accomplished[62] by its interchange reaction (transacetalization) with glyoxylic acid hydrate in acetic acid in the presence of concentrated HCl.

The intermediate adducts formed from a few 1, 3-dithiolanes and the electrophilic reagents such as methyl fluorosulfonate, chloramine-T, and triethyloxonium tetrafluoroborate are also capable of undergoing alcoholysis and thiolysis. For example, the reaction of 2-hexyl-1, 3-dithiolane with methyl fluorosulfonate in dichloromethane gave the sulfonium derivative **78**, which on reaction with ethylene glycol, 2–mercaptoethanol, and methanol in the same solvent gave **80** (Y=O), **80** (Y=S), and **82**, respectively.[63] If these reactions were carried out under milder conditions, only the corresponding precursors, **79** (Y=O), **79** (Y=S), and **81**, were obtained.[63] The treatment of 1, 3-dithiolane with chloramine-T in methanol gave the N-tosylsulfilimine **83**, which on reaction with methanol and benzenethiol in the presence of KOH, gave 2-methoxy- and 2-phenylthio-1, 3-dithiolane, respectively.[64] Also, the disulfonium salt **84**, prepared from 2-phenyl-1, 3-dithiolane with triethyloxonium tetrafluoroborate in dichloromethane, reacts with 1, 2-ethane-, 1, 3-propane-, and 1, 4-butanediol in the presence of either K_2CO_3 or tert-amine to afford the corresponding benzaldehyde acetals **85**.[65] The procedure provides a convenient method for the conversion of polyfunctional alcohols such as methyl α-D-glucopyranoside to the corresponding benzal-

CH₃SCH₂CH₂SCH-n-C₆H₁₃ HOCH₂CH₂Y (79)

HOCH₂CH₂YH

(80) Y= O,S

FSO₃CH₃

(78)

CH₃OH

CH₃SCH₂CH₂SCH-n-C₆H₁₃ CH₂O (81)

CH₃OH

(CH₃O)₂CH-n-C₆H₁₃ (82)

Chloramine-T p-CH₃C₆H₄SO₂N (83)

CH₃OH → OCH₃

C₆H₅SH → SC₆H₅

2 (C₂H₅)₃OBF₄⁻ (84) 2 BF₄⁻ HO(CH₂)ₙOH (CH₂)ₙ ... C₆H₅ (85) n=2,3,4

dehyde acetals under non-acidic conditions.[65)]

Dimethyl(methylthio)sulfonium tetrafluoroborate and methanesulfenyl chloride react rapidly with 2, 2-dimethyl-1, 3-dithiolane in nitromethane or dichloromethane to cleave both bonds between C-2 and the adjacent sulfur atoms. In the reaction, the product **89** has been obtained together with the polymer **90**.[66)] All of these events can be interpreted by the accompanying reaction sequence. The transformation of **86** to **88** amounts to a ring-expanding 1, 2-rearrangement whereupon C-2 migrates from S⁺ to S.

The reaction of several 1, 3-dithiolanes having two electron-withdrawing aryl substituents at C-2 with butyllithium in tetrahydrofuran can occur by a mechanism other than that involving deprotonation at C-4. Thus, when the 2, 2-diaryl-1, 3–

CH₃SY (86) (87) (88)

Y = S⁺(CH₃)₂BF₄⁻ , Cl

CH₃-C-SCH₃ (89)

CH₃⁺-C-SCH₃ + [S,S] → Polymer (90)
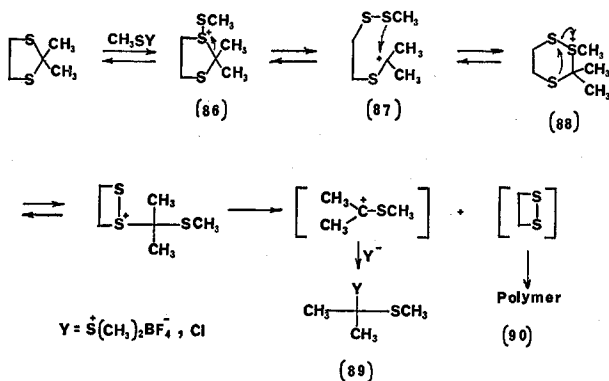
dithiolanes were treated with an excess of butyllithium in tetrahydrofuran solution followed by addition of an appropriate alkyl halide, the corresponding 1-butylthio-2–(1, 1-diarylalkylthio)ethanes **92** were obtained.[67] The process probably involves *S*-addition of an *n*-butyl anion with simultaneous cleavage of the bond between the sulfur atom and C-2 giving an intermediate anionic species **91**, which is then alkylated by the alkyl halide.


(91)   (92)
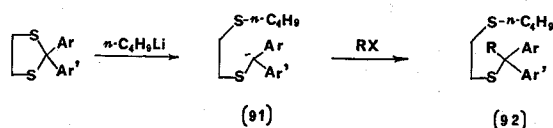
Ar, Ar$'$=C₆H₅, C₆H₅ ; C₆H₅ ; C₆H₅, *p*-CH₃C₆H₄ ; C₆H₅, 4-pyridyl

Ar⌢Ar$'$ = fluoren-9-ylidene

RX =CH₃I , C₂H₅I

Tributyltin hydride has been found to be an effective and selective agent for complete or partial desulfurization of some 1, 3-dithiolanes.[68] Thus, the reaction of the 1, 3-dithiolanes with 4 equivalents of tributyltin hydride in the presence of 2, 2′–azobis(isobutyronitrile) results in complete desulfurization, giving the corresponding hydrocarbons **96** in good yield, ethane, and bis(tributyltin) sulfide. Two equivalents of the hydride specifically cleave the two geminal bonds between C-2 and the adjacent sulfur atoms to give **96** and **95**. One equivalent of the hydride reduces the 1, 3-dithiolanes quantitatively to **94**. A reaction scheme consistent with these data obtained from the reaction of the 1, 3-dithiolanes with 1, 2, or 4 equivalents of tributyltin hydride is shown in the following equations.[68]
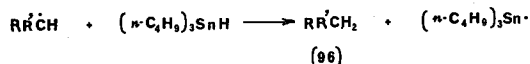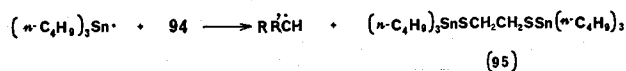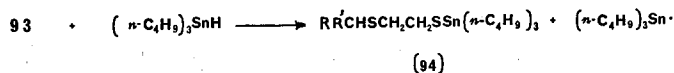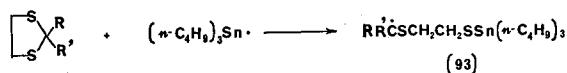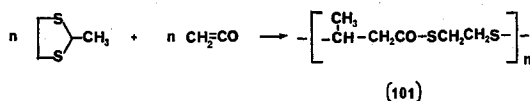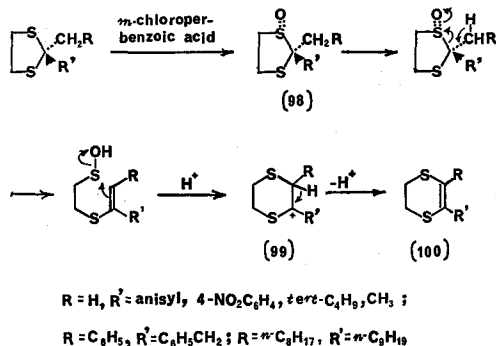

R,R$'$ = -(CH₂)₅ ; H,C₆H₅ ; H, *n*-C₆H₁₃

1, 3-Dithiolane and several phenacyl bromides in *N*, *N*-dimethylformamide afford phenacyl-1, 3-dithiolanium bromides which, on treatment with aqueous NaOH, give **97** as stable crystals. By the following equations, several reactions of **97** with benzoic anhydride, phenyl isocyanate, and dimethyl acetylenedicarboxylate to afford

the corresponding carbonyl-stabilized sulfonium ylides having a 1, 3-dithiolane moiety are indicated.[69]   Similar research is also carried out by Kato and his co-workers.[70]


(97)
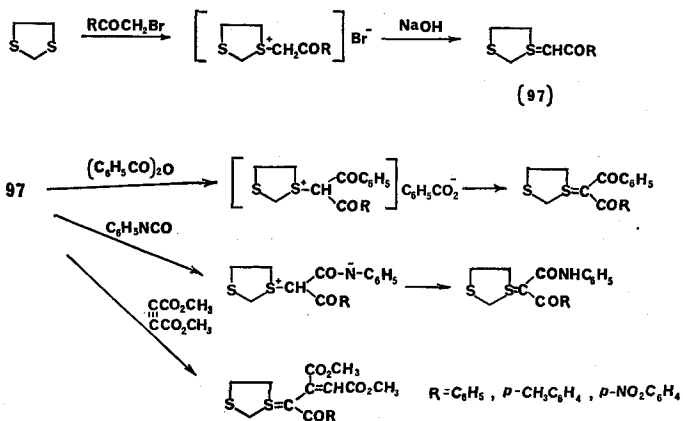
The oxidation of 1, 3-dithiolanes and related compounds affording the corresponding 1-oxides and/or 1, 3-dioxides may be included in this section.   For example, the stereoselectivity of oxidation of some 1, 3-dithiolanes such as 2-methyl-, 2-phenyl-, and 2-*tert*-butyl-1, 3-dithiolane with $NaIO_4$ and with *m*-chloroperoxybenzoic acid gives primarily the *trans*-1-oxide corresponding to attack from the less-hindered side.   The *trans/cis* ratio varies from 3/2 for oxidation of 2-methyl-1, 3-dithiolane to cleanly *trans* for 2-*tert*-butyl-1, 3-dithiolane.[71]   Thus, the some 1, 3-dithiolanes were oxidized in the analogous manner to the corresponding monosulfoxides **98** which, on heating in dimethyl sulfoxide or *N*, *N*-dimethylformamide, gave dihydro-1, 4-dithiins **100**.[72] The reaction involves [2, 3]sigmatropic rearrangement of the oxides to generate a sulfenic acid intermediate followed by ring closure through a *S*-stabilized carbonium ion **99**.   Similar conversion using some spiro-1, 3-dithiolanes is also achieved by


(98)

(99)   (100)

R = H, R' = anisyl, 4-NO$_2$C$_6$H$_4$, *tert*-C$_4$H$_9$, CH$_3$;

R = C$_6$H$_5$, R'=C$_6$H$_5$CH$_2$; R = *n*-C$_8$H$_{17}$, R'=*n*-C$_9$H$_{19}$

(101)

Janssen and Kwart.[73] Thus, the thermal β-*cis*-elimination reaction of cyclic sulfoxides and subsequent ring expansion reaction were achieved. HPF$_6$ catalyzes the copolymerization of 2-methyl-1, 3-dithiolane with ketene in dichloromethane at low temperature to afford the oily product 101.[74]

VI. THE OTHER REACTIONS

When the relatively labile methyl 4, 4, 5, 5-tetraphenyl-1, 3-dithiolane-2–carboxylate in toluene in the presence of a small amount of thiobenzophenone was kept at 100°C, the relatively stable methyl 2, 2, 5, 5-tetraphenyl-1, 3-dithiolane-4–carboxylate (105) and methyl 3, 3-diphenylacrylate (104) were formed. Kalwinsch and Huisgen[75] propose that the thiocarbonyl ylide 102 occurs in the 1, 3-dipolar cycloreversion of the starting ester. The cycloaddition of the 1, 3-dipole 102 to thiobenzophenone proceeds in both conceivable directions. The third competing reaction of 102 is the electrocyclic ring-closure to 103 which loses S to give 104.
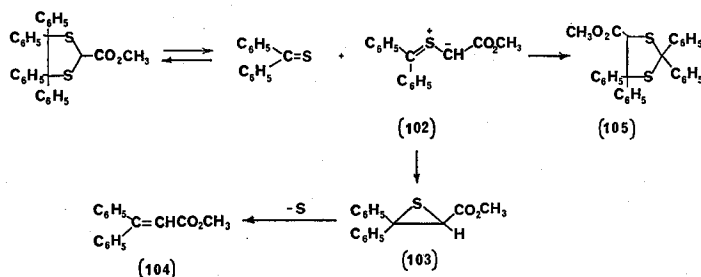
The irradiation of the acetylenes of the type 106 and 1, 3-dithiolane-2-thione with a low pressure mercury lamp under nitrogen yielded 107.[76] Selective excitation of the acetylenes 106 is essential to this reaction. Also, the irradiation of 1, 3-dithiolane-2–thione in dichloromethane and cyclohexene with a low pressure mercury lamp gave a pale yellow crystal 108.[77] Besides, the reaction of 1, 3-dithiolane-2-thione with dimethyl acetylenedicarboxylate to afford 109 has been reported.[78] The compound
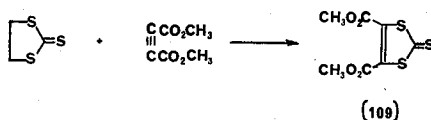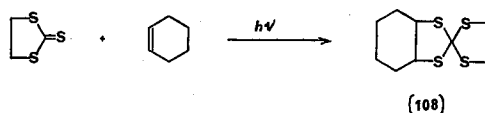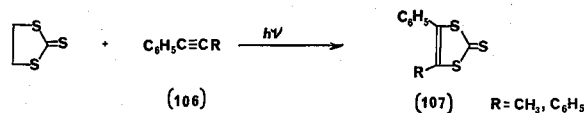
109 is useful for the preparation of tetrathiafulvalene.

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