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Desulfurization utilizing Sn(IV) hydrides.

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NL-339 (3/77)

DESULFURIZATION UTILIZING Sn(IV) HYDRIDES

BY

CALVIN K. SCHRAM

A THESIS

Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment
of the Requirements for the Degree
of Master of Science at the
University of Windsor

Windsor, Ontario
1977

To my mother and father

ABSTRACT

The desulfurization of various types of sulfur compounds, utilizing tributyltin hydride as the desulfurizing agent, was investigated. It was hoped that under these conditions 2,5-dihydrothiophenes and 3,6-dihydro(2H)thiopyrans would yield olefins. Reductive desulfurization of sulfides and dithioketals was attempted, anticipating totally desulfurized hydrocarbons as products.

The results show that acyclic sulfides undergo reductive desulfurization, but that cyclic ones give differing reactions, depending on the ring size.

ACKNOWLEDGEMENTS

I wish to express my gratitude to my research advisor, Dr. John M. McIntosh, whose wisdom, experience and patience were a great help in the completion of this undertaking.

The advice and encouragement rendered by my colleagues Mr. David Pillon, Mr. Bob Sieler, Dr. Richard Steevensz, Dr. Gary Masse and especially Mr. Hamdy Khalil, will long be remembered. I am also indebted to Dr. P.Y. Lau, Mr. Bob Charleton and Mr. Mike Fuerth for their technical assistance.

The author is deeply indebted to Miss Shirley Steevensz for her kindness and help in both the typing and editorial processes involved in the production of this thesis.

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CHAPTER I

INTRODUCTION

The synthesis of carbon-carbon double bonds in a regiospecific and stereospecific manner, has long been an object of interest for the organic chemist[1]. Wittig[2], Cornforth[3], and Julia[4] are names of well known chemists who have confronted this synthetic problem. Their solutions however, are complicated by problems such as incomplete regiospecificity or stereospecificity, low yields, long elaborate synthetic pathways or limited versatility in the types of olefins which can be synthesized.

An efficacious olefin synthesis was important to us, since much of the research in our laboratory is directed toward the synthesis of the sulfur heterocycles: 2,5-dihydrothiophenes, and 3,6-dihydro-(2H)thiopyrans~~, which we felt~~ could act as olefin precursors. Stereospecific and regiospecific reductive desulfurization of these two types of molecules, without concomitant reduction of the carbon-carbon double bond, would yield a synthesis of Z-olefins (Figure 1 and Figure 2)

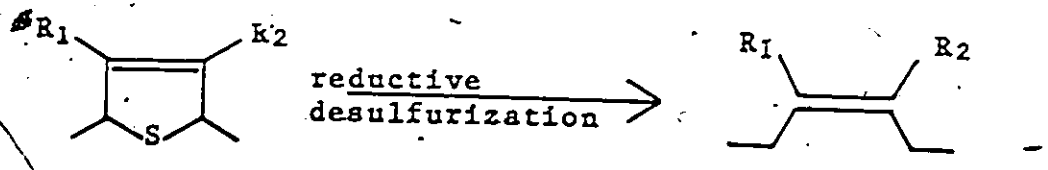
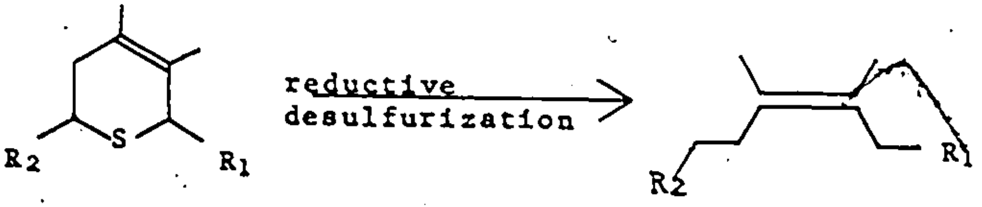
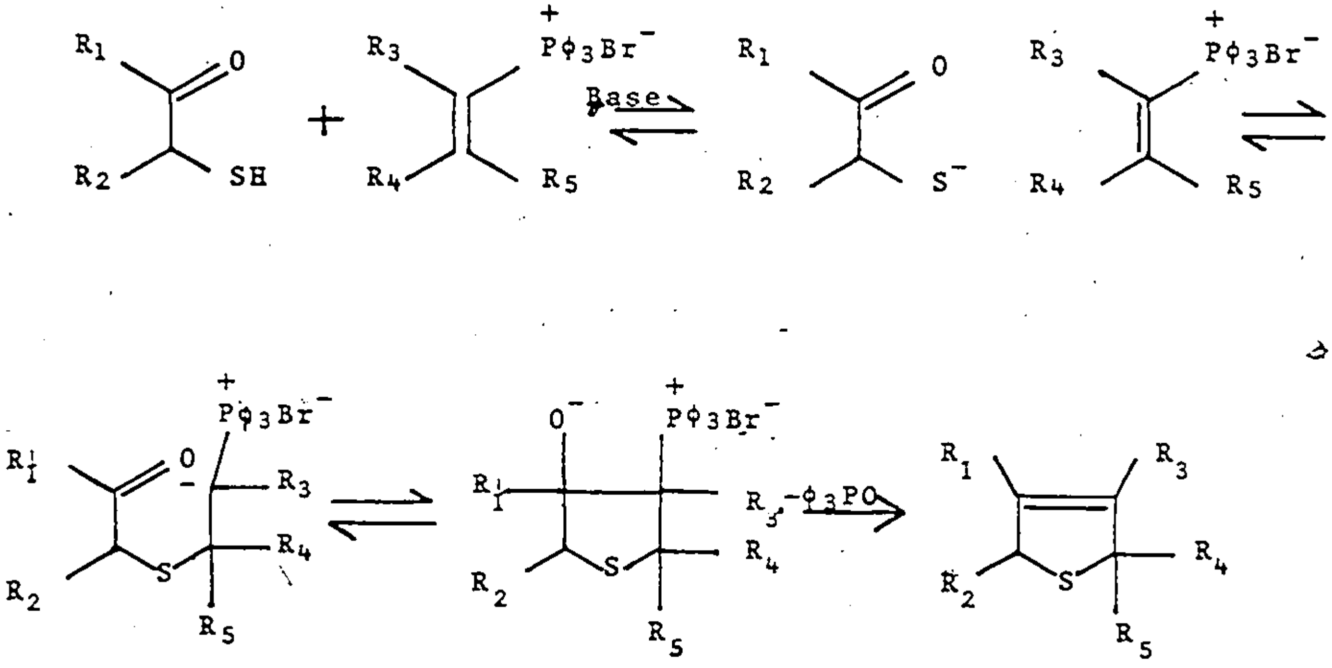


Figure 1 - Reductive Desulfurization of 2,5-Dihydrothiophenes



<u>Figure 2</u> - <u>Reductive Desulfurization of 3,6-(2H)thiopyrans</u>

The 2,5-dihydrothiophenes are synthesized by a combined Michael-Wittig reaction sequence using α-mercaptocarbonyl— compounds, and substituted phosphonium salts[5,6,7] (Figure 3).



<u>Figure 3</u> - <u>Synthesis of 2,5-Dihydrothiophenes</u>

It can be seen from this synthesis, that assuming the previously described reductive desulfurization is possible, one of the carbon atoms of the newly formed carbon-carbon double bond originates from the α-mercaptocarbonyl compound, and the other carbon atom originates from the phosphonium salt (Figure 4).

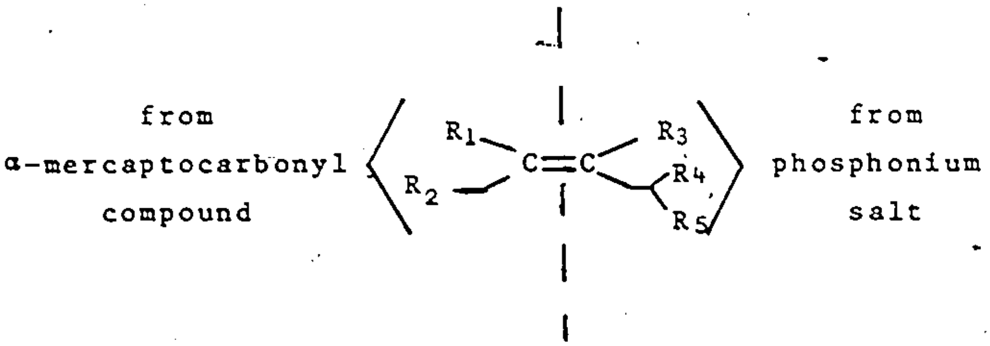


Figure 4 - Substitution Pattern in Proposed Olefin Synthesis

Since it is possible to use various α-mercaptoketones and aldehydes[5,6,7], and phosphonium salts substituted in the α or β position[5,6,7], it would be theoretically possible to synthesize mono-, di-, tri-, or tetrasubstituted olefins. This would represent an extremely versatile olefin synthesis.

One of the more classical methods of desulfurization is reduction using Raney nickel saturated with hydrogen[8]. When this procedure was performed on 2,5-dihydrothiophenes, total reductive desulfurization occurred (i.e. reduction of the sulfur function as well as reduction of the carbon-carbon double bond)[9] (Figure 5).

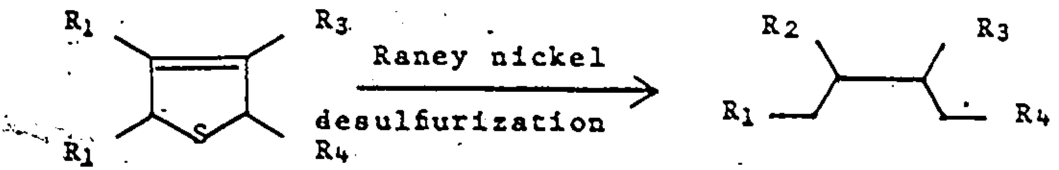


Figure 5 - Raney Nickel Desulfurization of 2,5-Dihydrothiophenes

Another widely used method of desulfurization utilizes an alkali metal in liquid ammonia. When this method was attempted on 2,5-dihydrothiophenes, polymeric products resulted[10].

Thiopyrans can be synthesized in essentially the same manner as dihydrothiophenes[11]. The major difference in the syntheses is that β-mercaptocarbonyl compounds are used in synthesizing thiopyrans, whereas α-mercaptocarbonyl compounds are used in the synthesis of dihydrothiophenes (Figure 6).

It is possible to use β-mercaptoketones as well as aldehydes, so only one substitutent may be placed on the double bond. However, the use of α-substituted phosphonium salts causes the reaction to follow a different course[11], and as a result no substitutent may be placed on the double bond, originating from the phosphonium salt component of the reaction.

The alkali metal in ammonia reduction of thiopyrans has been accomplished by different groups. Biellmann et al

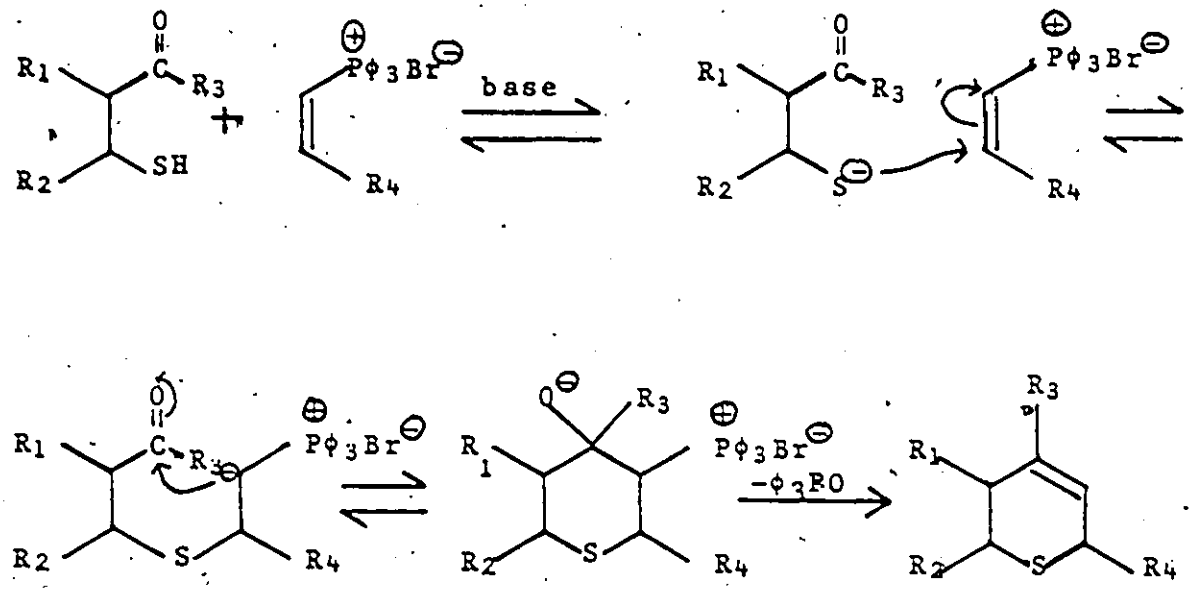


Figure 6 - Synthesis of 3,6-Dihydro-(2H)thiopyrans

showed that allylic carbon-sulfur bonds could be cleaved by lithium in ethylamine[12]. Kondo *et al*[13] showed that thiopyrans could be desulfurized using lithium in ethylamine alone, or by lithium in ethylamine (to cleave the allylic carbon-sulfur bond) followed by Raney nickel (to cleave the aliphatic carbon-sulfur bond). Stotter[14] also used the lithium in ethylamine, Raney nickel process to desulfurize thiopyrans. His results show that the two step procedure affords no isomerized products and also suppresses reduction of the carbon-carbon double bond, presumably because the sulfur deactivates the Raney nickel.

Desulfurization with Raney nickel is not without limitations. Reduction of other functional groups present in the molecule has often been a problem[8]. Other side reactions involving oxidations, reductions, rearrangements and condensations diminish the applicability of this method.

The desulfurization of sulfur compounds with Raney nickel is usually thought to involve a radical mechanism[15]. Mechanistically the reaction can be classified as an S_H2 process (i.e. a bimolecular homolytic substitution, which involves attack on the sulfur atom by an incoming radical to bring about replacement of a second radical originally bound to the sulfur)[15]. The first step in the reduction is considered to be a homolytic substitution by nickel, accompanied by, or followed by, scission of the nickel alkyl sulfide to give a second free radical (Figure 7).

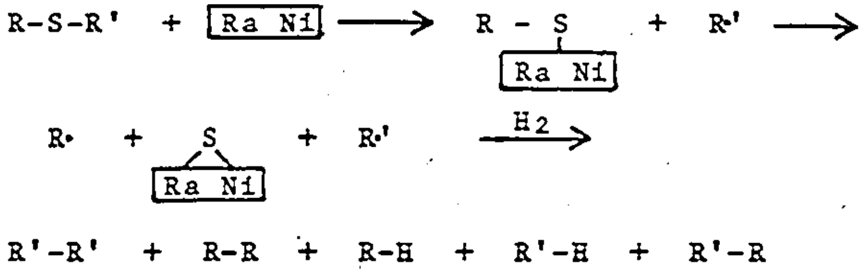


Figure 7 - Raney Nickel Desulfurization of Sulfides

It was thought that if some agent could be found which would act in a manner similar to Raney nickel, another method of desulfuization could be introduced. Organotin hydrides are generally thought to react by a radical mechanism[16] and the tin-sulfur bond is a strong one[17]. This led us to believe that organotin hydrides could act as desulfurizing agents.

Reductions by tin hydrides can be considered as displacements (Figure 8). Alternately when multiple bonds are involved, the tin hydride reduction can be considered as a two step process involving hydrostannylation (i.e. addition of the elements of R_3SnH across the double bond), followed by replacement of the organotin group by hydrogen (Figure 9).

$$R-X \;+\; R'_3SnH \longrightarrow R-H \;+\; R'_3SnX$$

Figure 8 - Tin Hydride Reductions Which are Considered Displacements

Structure reactivity correlation of organotin hydrides follow the order $RSnH_3 > R_2SnH_2 > R_3SnH$[18]. Triaryltin hydrides are more reactive than trialkyltin hydrides. The

$$A{=}B + R_3SnH \longrightarrow R_3Sn{-}A{-}B{-}H \xrightarrow{HY}$$

$$H{-}A{-}B{-}H + R_3SnY$$

(HY can be a protonic acid or R_3SnH)

Figure 9 - Tin Hydride Reductions of Multiple Bonds

dialkyltin dihydrides, triaryltin monohydrides, and trialkyltin monohydrides are the only groups with sufficient stability to be synthetically useful.

The two most widely studied reactions of tin hydrides are reduction of alkyl halides and hydrostannylation of multiple bonds[19]. The reduction of alkyl halides is a radical chain reaction[20] (Figure 10).

$$R_3SnH + \text{initiator} \longrightarrow R_3Sn\cdot + \text{H-initiator}$$

$$R_3Sn\cdot + R'{-}X \longrightarrow R_3SnX + R'\cdot$$

$$R'\cdot + R_3SnH \longrightarrow R_3Sn\cdot + R'{-}H$$

Figure 10 - Tin Hydride Reduction of Alkyl Halides

Increased reaction rates are observed for alkyl halides according to the order tertiary > secondary > primary[8]. The reactivity of different halides follows the usual order of iodide > bromide > chloride > fluoride[18].

Organotin hydrides also undergo noncatalysed addition to terminal olefins at 60°- 100°C[19]. This reaction enables a number of functionally substituted organotin compounds to be synthesized.

As well as these reactions, organotin hydrides add to alkynes (trans, polar addition)[18], reduce aldehydes and ketones[21], reduce the carbon-nitrogen double bond of isocyanates (by a polar mechanism)[22] and also reduce esters (by a free radical mechanism)[23].

Reports of the reactivity of organotin hydrides with sulfur-containing organic compounds have been sporadic. The first such report appeared in 1959 when Van Der Kerk and Noltes[24] reported the reduction of allyl mercaptan by triphenyltin hydride to yield propene and bis (triphenyltin) sulfide (Figure 11). In 1963, Lorenz and Becker[25] reported

$$CH_2{=}CHCH_2SH \xrightarrow{\phi_3SnH}$$

$$CH_2{=}CHCH_3 + (\phi_3Sn)_2S$$

<u>Figure 11</u> - <u>Triphenyltin Hydride Desulfurization of Allyl Mercaptan</u>

that 1-naphthyl- and phenyl- isothiocyanates are converted to the corresponding aryl isocyanides and N-methylarylamines.

In 1964, Becker and Pang[26] published a paper on the reduction of sulfur containing functional groups by triphenyltin hydride. They found that in some cases, the reductions occurred without free radical initiators, but in general higher yields of reduced products were obtained when the free radical initiators 2,2'-azobis (2-methylprorionitrile) (AIBN) or triphenyl borine were present. The carbon-sulfur bonds of benzyl disulfide, benzyl sulfide, and benzyl mercaptan were cleaved in the following manner (Figure 12):

$$(\phi CH_2)S \xrightarrow{\phi_3SnH}$$

$$(\phi_3Sn)_2S + \phi CH_3 + \phi CH_2SH \text{ (trace)} + H_2S$$

Figure 12 - Triphenyltin Hydride Reduction of Benzyl Sulfide

No aromatic carbon-sulfur bonds were cleaved by triphenyltin hydride. Thiobenzophenone was converted to diphenylmethane.

Some years later in 1974, Kozuka, Furami and Akasaka[27] reported the reduction of sulfoxides and sulfilimines with tributyltin hydride. These compounds were reduced to the corresponding sulfides, and in some cases carbon-sulfur bond cleavage occurred (Figure 13). In keeping with the

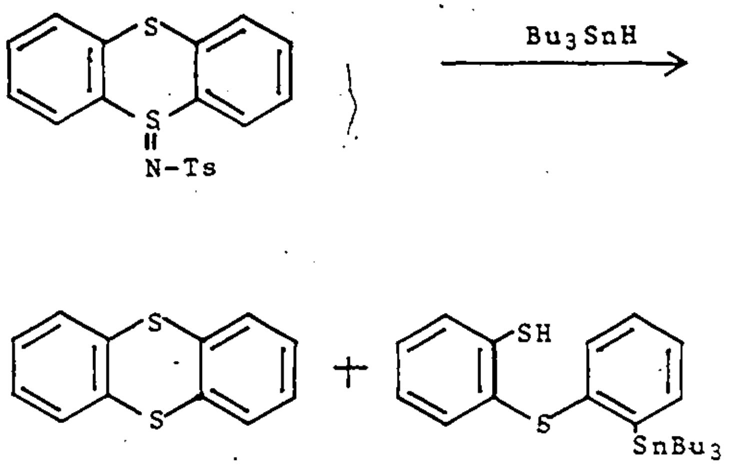
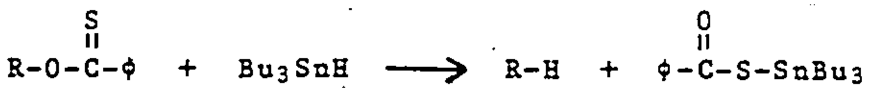


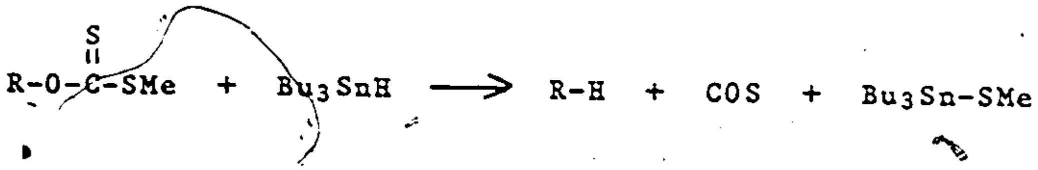
Figure 13 - Tributyltin Hydride Reduction of Sulfilimines

results of Pang and Becker[26], these authors found that the reactions would not proceed in the absence of a free radical initiator. Starting materials were quantitatively recovered when AIBN was not present.

In 1975 Barton et al utilized tributyltin hydride for the removal of a sulfur-containing function. They reacted O-cycloalkylthiobenzoates and O-cycloalkyl-S-methyl dithiocarbonates with tributyltin hydride and obtained good yields of the corresponding hydrocarbons (Figure 14).



$$R\text{-}O\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}\phi + Bu_3SnH \longrightarrow R\text{-}H + \phi\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}S\text{-}SnBu_3$$



$$R{-}O{-}\overset{\overset{S}{\|}}{C}{-}SMe + Bu_3SnH \longrightarrow R{-}H + COS + Bu_3Sn{-}SMe$$

Figure 14 - Tributyltin Hydride Reduction of Thiobenzoates and Dithiocarbonates

In 1976, Barton et al reported the reduction of dithiocarbonates of deoxysugars and deoxynucleosides with tributyltin hydride (Figure 15). Opening of the thiocarbonate ring yields the more stable secondary radical.

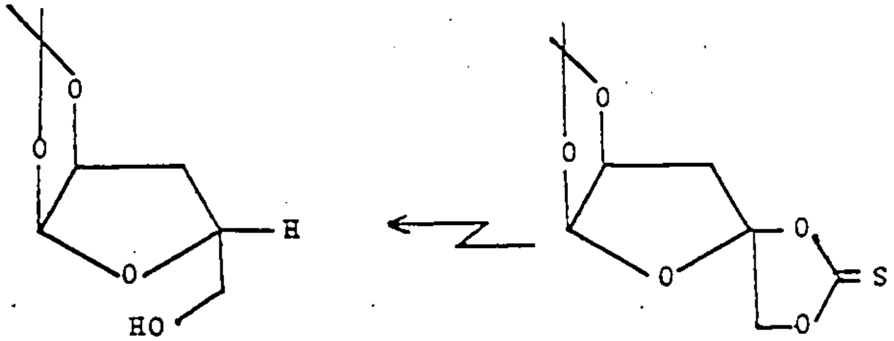


Figure 15 - Tributyltin Hydride Reduction of a Deoxysugar

In view of the number of reports of reduction of sulfur compounds with tin hydrides, the possibility of using tin hydrides to desulfurize dihydrothiophenes and dihydrothiopyrans looked promising. The possibility that tin hydrides could become a widely used reagent for desulfurization comparable to Raney nickel or lithium in liquid ammonia, was another reason which prompted us to investigate this problem.

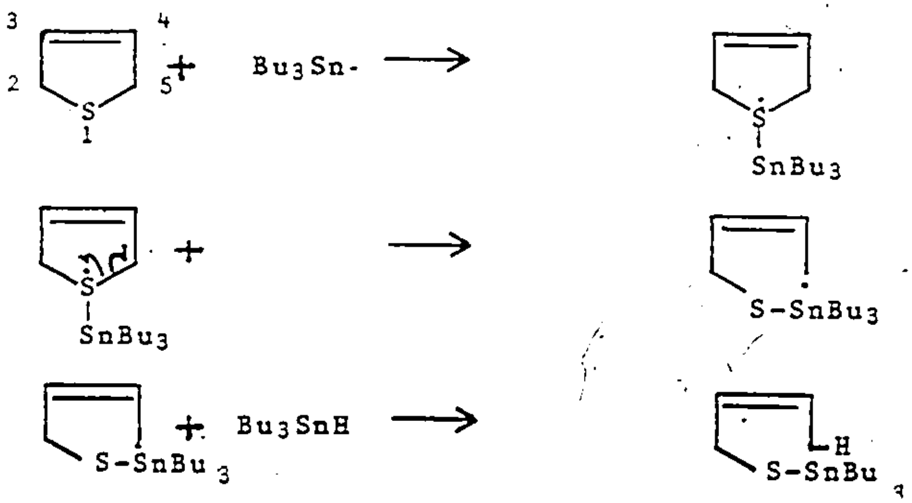
CHAPTER II

RESULTS AND DISCUSSION

Before any desulfurizations were attempted, a decision was required on the particular organotin hydride which would be used. Triphenyltin hydride and tributyltin hydride are the two most commonly used. Tributyltin hydride was chosen because of its greater thermal stability and its ease of preparation.

The initial attempt at desulfurization was made on a 2,5-dihydrothiophene. The synthesis of 2,5-dihydrothiophenes has been previously outlined in this thesis[5,6,7].

A great deal of evidence suggests that organotin hydride reductions involve a radical chain mechanism[16]. On this basis we envisaged that the following reaction might occur, which would lead to the formation of olefins from dihydrothiophenes (Figure 16). Closer examination of



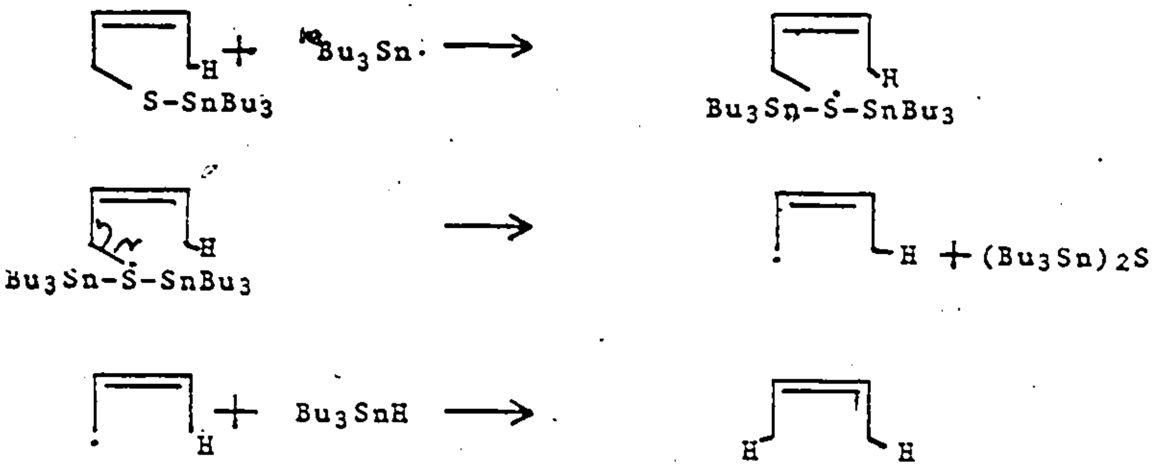
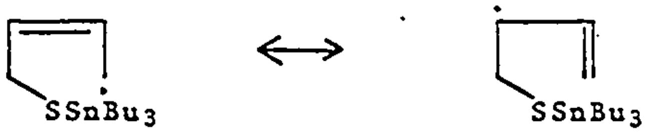


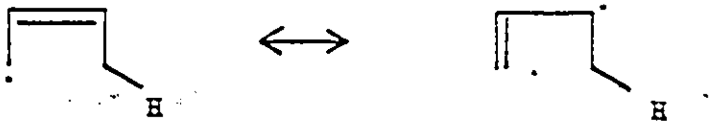
Figure 16 - Proposed Mechanism of Olefin Formation from Dihydrothiophenes

this mechanism revealed two undesirable side reactions. It is known that tin hydrides reduce various functional groups[18]. For our purposes, reduction of the sulfur moiety only, was desirable. Also, as was previously mentioned, one of the most widely studied reactions in tin hydride chemistry is the addition of the elements of the tin hydride across a carbon-carbon double bond, a reaction known as hydrostannylation[19]. If hydrostannylation of the dihydrothiophene occurred, a tetrasubstituted organotin compound would be formed, rendering the proposed olefin synthesis useless.

The other problem which was foreseen involves possible isomerization of the carbon-carbon double bond. In Figure 16, both steps 2 and 5 involve allylic radicals. Two resonance forms can be drawn for these allylic radicals. In such cases, reduction can occur at two sites leading to a mixture of olefins. Furthermore, rotation about the C_3-C_4 bond of the partially reduced heterocycle would lead to isomerization of the double bond. The overall scheme is shown in Figure 17. The deciding factor here is which reaction takes place more rapidly, hydrogen abstraction by the initially formed



For Figure 16 Step 2



For Figure 16 Step 5

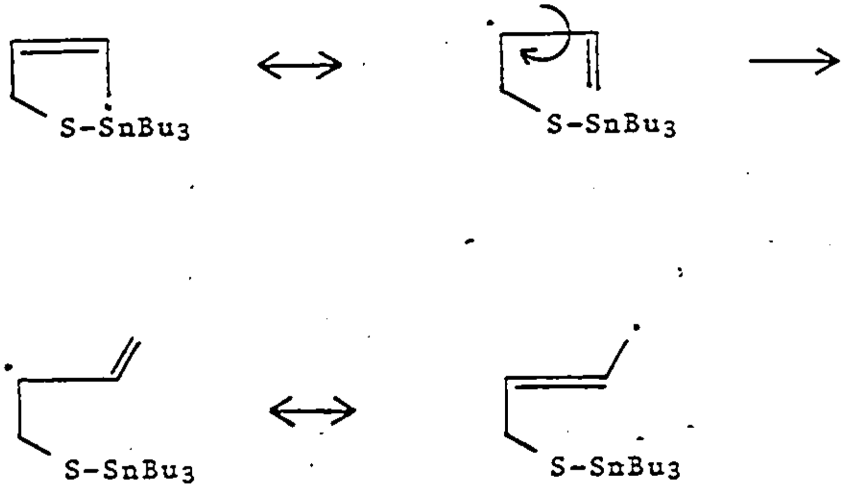


Figure 17 - Mechanism of Isomerization of Double Bond of Dihydrothiophene

allylic radical or isomerization or stereomutation of the initially formed allylic radical.

A comparable situation occurs in the reduction of allylic chlorides with tributyltin hydride. Denney et al[30] found that isomerization of the intermediate allylic radical resulted in a loss of the stereochemical integrity of the starting material.

When the reduction of 2-methyl-2,4,5,6,7,7a-hexahydrobenzo[b]thiophene (entry 1, Table I) was attempted, spectral data suggested that the desired olefin was not formed. Instead, the diene previously obtained from sulfone pyrolysis and identified as 1-(1-cyclohexenyl) propene, was the sole product. An authentic sample was prepared by meta-chloroperbenzoic acid oxidation of the dihydrothiophene to the dihydrothiophene sulfone and subsequent pyrolysis of the sulfone to the 1,3 diene[31] (Figure 18).

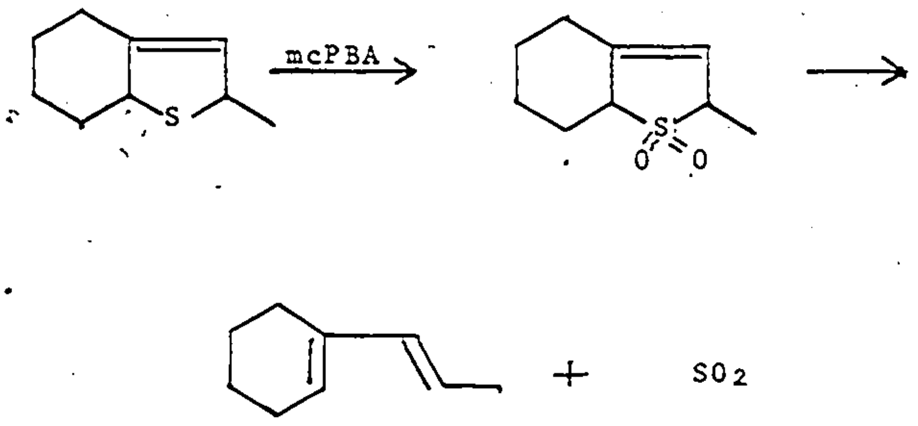
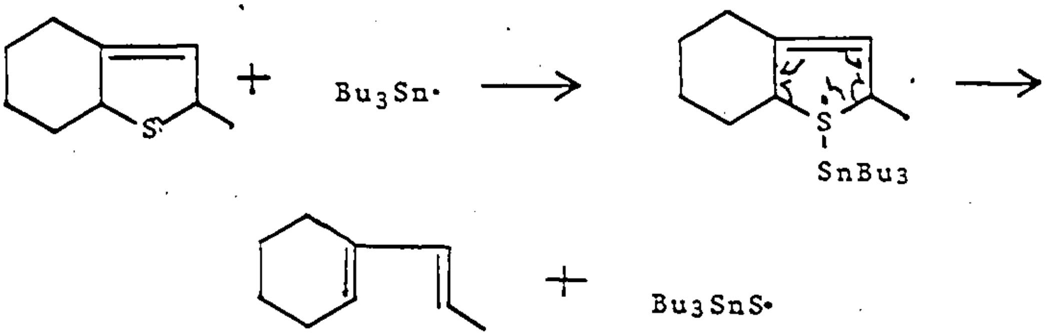


Figure 18 - Method of Preparation of Authentic 1-(1-Cyclohexenyl)propene

The formation of the diene, from the tributyltin hydride reduction of the dihydrothiophene may take place by a concerted or a stepwise mechanism. If the mechanism is concerted, the following steps may be involved (Figure 19):

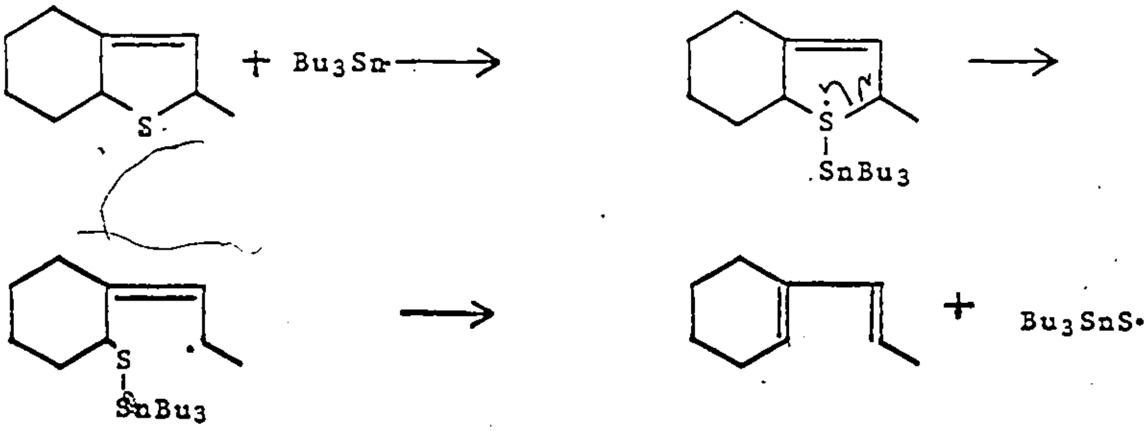


$$Bu_3SnS\cdot + Bu_3SnH \longrightarrow (Bu_3Sn)_2S + H\cdot$$

$$H\cdot + Bu_3SnH \longrightarrow Bu_3Sn\cdot + H_2$$

Figure 19 - Concerted Mechanism of Diene Formation from Dihydrothiophenes

The stepwise mechanism differs basically in the timing of the movement of the electrons (Figure 20).



$$Bu_3SnS\cdot + Bu_3SnH \longrightarrow Bu_3SnSH + Bu_3Sn\cdot$$

$$Bu_3SnSH + Bu_3Sn\cdot \longrightarrow (Bu_3Sn)_2S + H\cdot$$

Figure 20 - Stepwise Mechanism of Diene Formation from Dihydrothiophenes

Spectral data shed some light on the mechanism. The propenyl double bond of 1-(1-cyclohexenyl) propene was found to exist as the E isomer[31] (NMR vinyl proton coupling constants). Thus, if the mechanism is concerted, it must occur in a disrotatory fashion. Since the starting dihydrothiophene was known to possess the cis configuration[31], formation of the E isomer via a conrotatory mode would require the formation of a trans-double bond in the cyclohexene ring.

If the mechanism does not involve disrotatory motion of the orbitals to form the diene, then the stepwise mechanism must be in operation. The stepwise mechanism would allow for free rotation about single bonds and therefore would yield the thermodynamically more stable E isomer of the propenyl double bond. We are unable to distinguish between these possibilities at present.

The reduction of 2,2-dimethyl-2,4,6,7,7a-hexahydrobenzo[b]thiophene was also attempted (entry 2, Table I). Spectral data suggest that the desired olefin was not formed, but again the product was the analogous diene (Figure 21).

TABLE I

YIELDS OF DESULFURIZED PRODUCTS FROM VARIOUS SULFUR COMPOUNDS

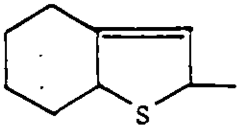
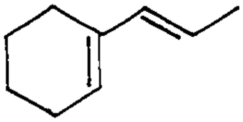
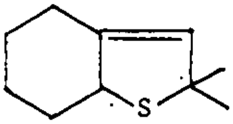
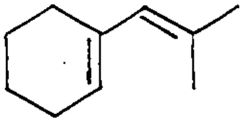
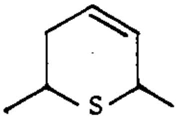
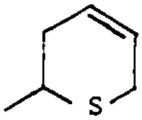
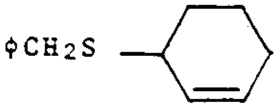
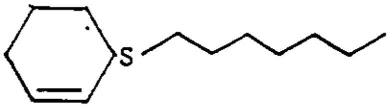
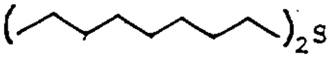
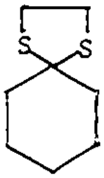
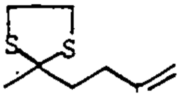
Entry	Starting Material	Product(s)	(Yield(s))
1			(<15%)
2			(44%)
3		no reaction	
4		no reaction	
5	$(\phi CH_2)_2S$	ϕCH_3	(76%)
6	$\phi CH_2S(CH_2)_6CH_3$	ϕCH_3 $CH_3(CH_2)_5CH_3$	(85%) (49%)

TABLE I (continued)

YIELDS OF DESULFURIZED PRODUCTS FROM VARIOUS SULFUR COMPOUNDS

Entry	Starting Material	Product(s)	(Yield(s))
7		ΦCH$_3$	(63%)
			(46%)
8			(62%)
			(33%)
9			(8%)
			(90%)*
10			(44%)
11		no isolable product	

* based on unreacted starting material

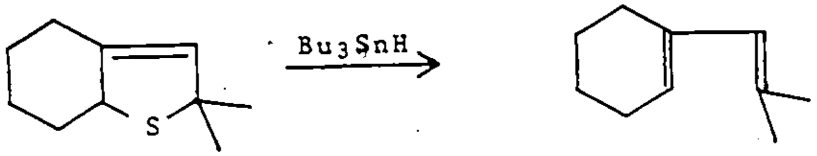


Figure 21 - Tributyltin Hydride Reduction of 2,2-Dimethyl-2,4,5,6,7,7a-hexahydrobenzo[b]thiophene

From these two examples it appears that tributyltin hydride is not an effective reagent for transforming dihydrothiophenes into olefins. However, this method does represent a one step synthesis of dienes from dihydrothiophenes. The yields are moderate to poor but no attempts were made to maximize them.

Since dihydrothiophenes did not prove to be effective olefin synthons, the six membered ring analogues dihydrothiopyrans were utilized. As outlined previously, these compounds were synthesized from β-mercaptocarbonyl compounds and substituted phosphonium salts[11]. As Table I entries 3 and 4 indicate, no reduction products of any sort were detected when 3-methyl-3,6-dihydro(2H)thiopyran and 3,6-dimethyl-3,6-dihydro(2H)thiopyran were reacted with tributyltin hydride at temperatures up to 140° C. Starting material was recovered almost quantitatively.

Hydrostannylation of the carbon-carbon double bond of the thiopyran cannot explain why no desulfurization products were detected, since the starting material is recovered. Consideration of the proposed mechanism for the desulfurization of dihydrothiopyrans with tributyltin hydride reveals no intermediates which appear to be energetically or sterically unfavourable (Figure 22). We are at a loss

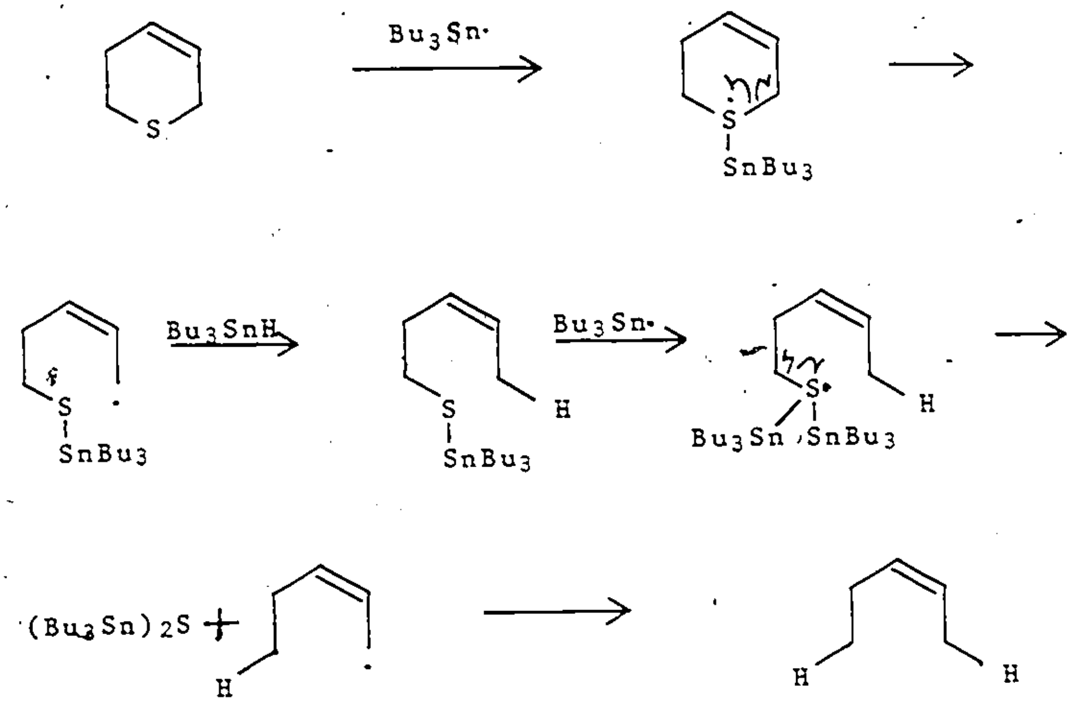


Figure 22 - Proposed Mechanism of Dihydrothiopyran Desulfurization

to explain the lack of reactivity of dihydrothiopyrans in these reactions.

Sulfides were the next class of compounds which were reacted with tributyltin hydride. Table I entries 5 to 9 list the starting materials and yields of desulfurized products obtained. Table II lists the characteristics of the new sulfides prepared.

The general method of synthesis for these sulfides, adapted from the procedure of de la Mere and Vernon[32], was as follows (Figure 23):

$$R{-}SH \xrightarrow{NaOEt} RS^{\ominus}Na^{\oplus} + EtOH$$

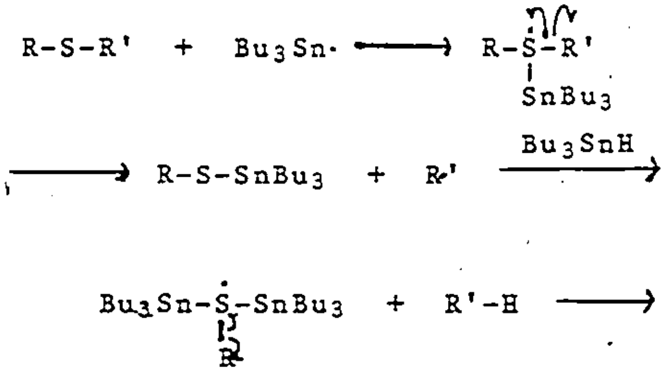
$$RS^{\ominus}Na^{\oplus} + R'{-}X \longrightarrow R{-}S{-}R' + NaX$$

$$X = \text{halide}$$

Figure 23 - General Method of Preparation of Sulfides

In the case of entries 7 and 8, the mechanism of the reaction may be S_N2' in nature[33].

The mechanism of the desulfurization of sulfides is basically similar to the mechanism proposed for the desulfurization of dihydrothiophenes and dihydrothiopyrans. Outlining this mechanism for sulfides, will facilitate an explanation of the various yields obtained (Figure 24).



$$R{-}S{-}R' + Bu_3Sn\cdot \longrightarrow \underset{SnBu_3}{R{-}\dot{S}{-}R'}$$

$$\longrightarrow R{-}S{-}SnBu_3 + R'\cdot \xrightarrow{Bu_3SnH}$$

$$\underset{R}{Bu_3Sn{-}\dot{S}{-}SnBu_3} + R'{-}H \longrightarrow$$

TABLE II

CHARACTERISTICS OF NEW SULFUR COMPOUNDS PREPARED

Compound	Yield	b. p.	n_d^{25}	ir	nmr	Analysis			
						Calculated		Found	
						C(%)	H(%)	C(%)	H(%)
benzyl heptyl sulfide	85%	174-180 @ 17 mm	1.5204	a	7.30-7.25 s(5), 3.60-3.55 s(2), 2.45-2.18 t(2), 1.65-1.05 m(12), .95- .65 t(3).	75.67	9.99	75.77	9.88
cyclohexenyl heptyl sulfide	76%	92-96	1.4951	a	5.90-5.80 m(2), 3.62-3.30 m(1), 2.84-2.52 t(2), 2.30-1.75 m(6), 1.65-1.15 m(12), 2.05-1.85 t(3).	73.51	11.39	73.35	11.55
5-hexene-2-one thioketal	80%	b	1.5408	a	6.05-5.50 m(1), 5.15-4.75 m(2), 3.40-3.30 s(4), 2.45-1.85 m(4), 1.90-1.80 s(3).	55.12	8.10	55.33	8.19

[a] featureless

[b] purified by column chromatography, no boiling point obtained

$$R\cdot \quad + \quad (Bu_3Sn)_2S \xrightarrow{Bu_3SnH} R\text{-}H$$

Figure 24 - Proposed Mechanism of Desulfurization of Sulfides

Table I reveals yields of desulfurized products which correspond to the stability of the intermediate organic radicals. The factors affecting stability here are structure (where the usually found radical stability order is followed: tertiary > secondary > primary) and degree of resonance stabilization (where the usually found order of stability is also followed: benzyl > allyl > alkyl). The resonance stabilization of radicals is a more important factor in determining the radical stability than is the structure of the radicals[34].

Bearing these facts in mind, the yield of toluene from dibenzyl sulfide being the highest overall yield is not unexpected. The benzyl radical is presumably the most stable radical which can be formed from any of the sulfides listed. As well, the reduction product toluene, is stable to the reaction conditions.

In the desulfurization of benzyl 1-cyclohexenyl sulfide, toluene is formed in higher yield than cyclohexene. This is to be expected since benzyl radicals are more stable than allylic radicals. In this particaular case, some of the cyclohexene may be lost due to hydrostannylation.

Desulfurization of benzyl heptyl sulfide produces toluene in a much higher yield than heptane. The stability of benzyl vs alkyl radicals is again demonstrated.

In the case of 1-cyclohexenyl heptyl sulfide, the yield of cyclohexene realized is almost twice that of heptane. The fact that alkyl radicals are less stable than allylic radicals is illustrated.

That n-octyl sufide provides the lowest yield of a hydrocarbon of any of the sulfides listed, is not surprising. Primary alkyl radicals are the least stable of any radicals which could be formed from the sulfides used. The reduction of n-octyl sulfide was the only case in the sulfide series in which a significant amount of starting material was recovered. Based on unreacted starting material, the yield of octane from n-octyl sulfide is 90%. The much higher yield of heptane from benzyl heptyl sulfide, than octane from n-octyl sulfide suggests that the tributyltin radical ($Bu_3Sn\cdot$) cleaves the intermediate organotin sulfide ($R-S-SnBu_3$) faster than the starting sulfide ($R-S-R$).

Dithioketals were the last class of compounds examined. These thioketals were synthesized following the general procedure of Jones[35] (Figure 25). Table I entries 10 and

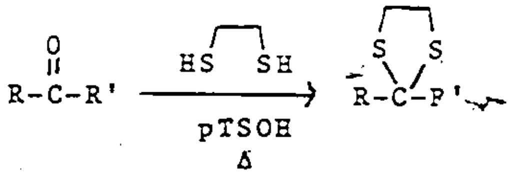
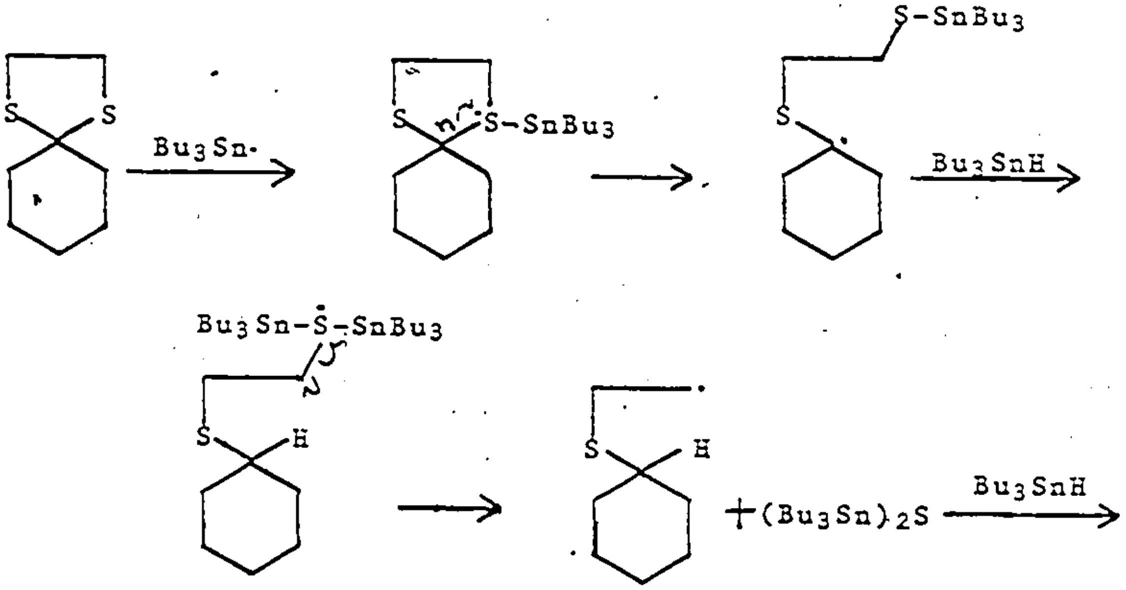


Figure 25 - Method of Synthesis of Thioketals

11 list the thioketals used. The thioketal of cyclohexanone yields cyclohexane upon reduction with tributyltin hydride but no 1-hexene could be isolated from the reaction of the thioketal of 5-hexene-2-one. Hydrostannylation of the terminal double bond of the starting material is a possible reason for no reduction products being isolated in the latter case. As was previously stated tributyltin hydride will undergo noncatalysed addition to terminal double bonds at temperatures analogous to those used here[19]. The proposed mechanism for the desulfurization of cyclohexanone thioketal is shown in Figure 26.



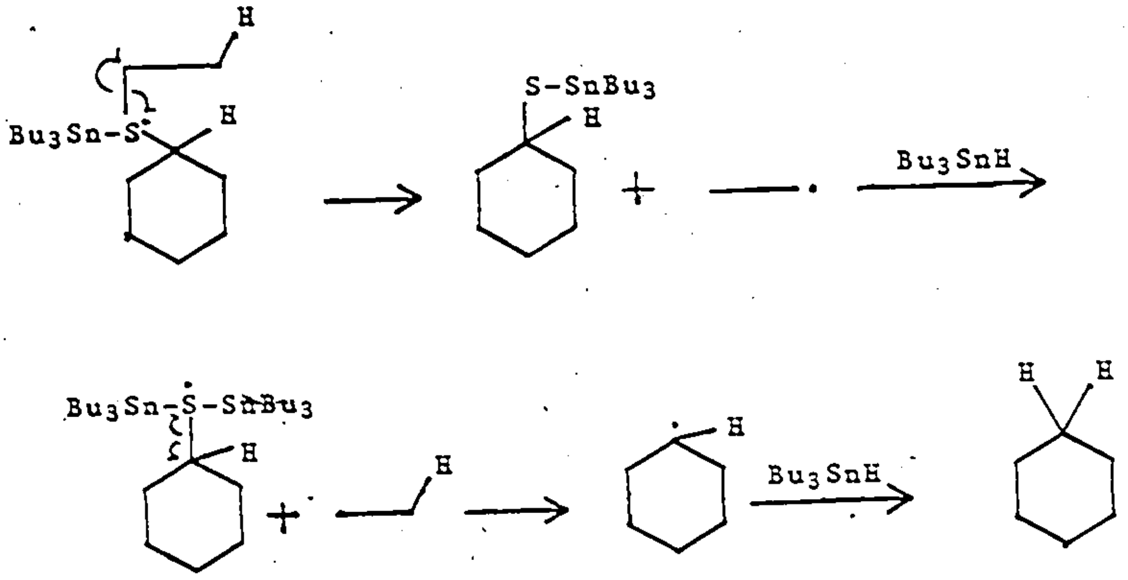


Figure 26 - Proposed Mechanism of Desulfurization of Thioketals

Support for this mechanism is given by the fact that cyclohexyl ethyl sulfide was isolated from one reaction mixture in which starting material had not totally reacted. The conversion of thioketals to the corresponding alkanes represents a method of transforming a ketone function to a methylene group, and is thus analogous to the Wolf-Kishner and Clemmensen reductions[36]. The transformation of dithioketals to methylene groups has also been accomplished with triethyl phosphite[37] with sodium in liquid ammonia[38] and with Raney nickel[39].

In general, it appears that with the exception of dihydrothiopyrans, tributyltin hydride will act as a desulfurization agent. Dihydrothiophenes do not yield olefins, but rather 1,3 dienes. This represents a method for the conversion of dihydrothiophenes to dienes in a one step process. Various types of sulfides yield the expected alkenes and alkanes.

One factor which makes tributyltin hydride appear attractive as a desulfurization agent, is that it is possible to regenerate it. Damle and Considine[40] have shown that bis(tri-n-butyltin) sulfide can be transformed into tri-n-butyltin hydride, in 72% yield, by the action of lithium aluminum hydride. Thus if desulfurization reactions are to be carried out on a large scale, or repeatedly, the hydride could easily be recycled.

From the results obtained in this project, it appears that tributyltin hydride has definite potential as a desulfurization agent.

CHAPTER III

EXPERIMENTAL

General Comments

Reagent grade chemicals were used without purification unless otherwise specified. Infrared (ir) spectra were recorded on a Beckman IR-12 instrument in 10% chloroform solution. Nuclear magnetic resonance (nmr) spectra were obtained on a JEOLCO C-60HL or Varian EM 360 spectrometer and are reported in parts per million (δ) downfield from tetramethylsilane as internal standard. The splitting pattern of each resonance is codified as follows: s = singlet, d = doublet, t = triplet, m = multiplet. Electron impact mass spectra were recorded at 70eV on a Varian MAT CH5 - DF spectrometer. GLC analyses were performed on a Hewlett-Packard 720 instrument with peak areas determined by disc integration. A Fisher-Johns melting point apparatus was employed to determine melting points. Indices of refraction were measured using a Carl Zeiss refractometer. Combustion analyses were performed by A. B. Gygli Microanalysis Laboratory, Toronto, Ontario.

Known Compounds

The following compounds were prepared by literature procedures (boiling points/melting points and experimental yields are listed): tributyltin hydride[42] (60° C @ 0.05 mm, 73%), dibenzyl sulfide[32] mp 42 C[43], 62%), 1-cyclohexenyl benzyl sulfide[44] (92° - 100° C @ 15 mm, 43%), 3-bromocyclohexene[45] (68° - 72° C @ 22 mm, 50%), 2-methyl-3,6-dihydro-(2H)thiopyran (35%)[11], 2,6-dimethyl-3,6-dihydro-(2H)thiopyran[11] (40%), 1,4-dithiaspiro [4.5] decane[35] (80%), β-mercaptobutyraldehyde[46] (71° C @ 17, 53%). Samples of 2-methyl-2,4,5,6,7,7a-hexahydrobenzo[b] thiophene and 2,5-dimethyl-2,4,5,6,7,7a-hexahydrobenzo[b] thiophene had been previously prepared.

Preparation of Benzyl Heptyl Sulfide and Cyclohexenyl Heptyl Sulfide

This procedure was adapted from the general procedure of de la Mere and Vernon[32]. n-Heptyl mercaptan (0.05 moles) was titrated to the phenolphthalein endpoint with a solution of 1.0 N NaOEt. The appropriate chloride (0.05 moles) was then added dropwise. A white precipitate began to form almost immediately. The mixture was stirred overnight at room temperature. The precipitate was filtered and the solvent evaporated under reduced pressure. The residual yellow oil was taken up in methylene chloride and dried over sodium sulfate. Evaporation of the solvent yielded a yellow oil, which upon distillation resulted in a colourless liquid. Yields and spectral data are reported in Table II.

Preparation of 5-Hexene-2-one Thioketal

This procedure was adapted from the general procedure followed by Jones[35]. Allyl acetone (10 g, 0.10 moles) was dissolved in 150 ml benzene. To this solution, ethanedithiol (15 g, 0.15 moles) and p-toluenesulfonic acid (1 g) were added. The mixture was refluxed in a 300 ml round bottom flask equipped with a Dean-Stark trap and reflux condenser. After refluxing for 8 hours, the mixture was cooled, washed once with an equal volume of 1 N KOH, once with an equal volume of water, then dried over sodium sulfate. The solvent was evaporated under reduced pressure. Chromatography on basic alumina with pentane as the solvent yielded 13.5 g (80%) of a clear liquid. Spectral data is listed in Table II.

General Desulfurization Procedure for Sulfides

These reactions were run on a 10 mM scale, using 10 mM of the sulfur compound and 22 mM tributyltin hydride (equivalent amount necessary for reduction plus ten percent excess). The sulfur compound and the tin hydride were added to a 25 ml round bottom flask equipped with a nitrogen inlet tube and a reflux condenser. AIBN (1.50 mole percent, 20 mg) was added at the start of the reactions. The flask was heated to 80° C by an oil bath. After heating for eight hours at 80°C, the reaction mixture was cooled and 15 ml diglyme was added to aid in distillation of the hydrocarbon. Distillation of the mixture was undertaken, and fractions were collected until diglyme started to distil (head temperature 160 C). The distillate was washed twice with 10 ml portions of water to remove diglyme. The hydrocarbon, usually contaminated with a small amount (∿5%) of diglyme, was then isolated. The identity of the samples was determined by comparison of spectral data with that obtained from authentic samples of the expected products.

General Desulfurization Procedure for Thioketals

The desulfurization procedure followed was basically the same as previously described, with differences occurring in the manner of addition of initiator and reagents. The reactions were run on a 10 mM scale. Initially 10 mM of the hydride was added to 10 mM of the thioketal along with 20 mg of AIBN. Equivalent additions of initiator and hydride were repeated at 2 hour intervals up to 8 hours. During this time the mixture was heated to 80° C using an oil bath preheated to that temperature. The work up procedure followed was identical to that previously described. For 5-hexene-2-one thioketal, when water was added to the distillate, only one layer was present. All attempts at isolation of a reduction product failed.

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