*Tetrahedron* Vol. 47, No. 41, pp. 8753-8766, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00
Pergamon Press plc

# HIGH DIASTEREOFACIAL SELECTIVITY IN THE REACTION OF SILYL ENOL ETHERS WITH CHLOROSULFIDES

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(*Received in UK* 13 *August* 1991)

**Abstract** : The chlorosulfides 1 or 2 react with silyl enol ethers in presence of anhydrous zinc bromide to give mainly the corresponding syn products 4 or 6 respectively. The high syn selectivity of these reaction is explained by nucleophilic addition to a Chelated Chiral thioniun ion.

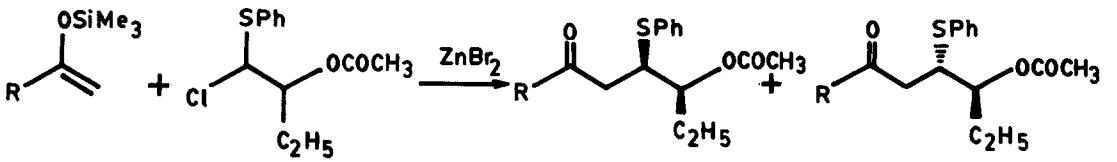
The Lewis acid mediated reaction of carbonyl compounds and the masked carbonyl compounds (e.g. acetals, thioacetals, dithioacetals etc.) with silyl enol ethers is an efficient method[1] for carbon-carbon bond formation. The addition of silyl enol ethers to chiral aldehydes (with an α-heteroatom substituted chiral centre) can be performed with high diastereofacial selectivity which may be explained due to the chelation[2] of the Lewis acid between the carbonyl oxygen and the heteroatom on the α-chiral centre. The reactions of chiral thioacetal and dithioacetal with allyl metals and silyl enol ethers have been shown to occur[3] with high syn selectivity, however, the thioacetals bearing an α-acetoxy group reacts[3i] via a intramolecular displacement rearrangement sequence involving a sulfenyl group. These results indicate the inferior ability of a sulfenyl group to stabilise an α-carbocation, relative to a methoxyl group. The high diastereofacial selectivity is also observed during the reaction of chiral dithioacetals with silyl enol ethers or allyl silane. These nucleophilic additions were shown to proceed via thioniun ion and the high selectivity during these reactions was attributed[3b] to the bulkiness of aromatic ring attached to the sulphur atom. In the context of our studies[4] on phenylthioalkylation of silyl enol ethers with chlorosulfides, we have observed that the reaction of 2-acetoxy--1-chloro-1-phenylthiobutane 1 and methyl (3-chloro-2-methyl-3-phenylthio) propionate 2 with various silyl enol ethers is highly diastereoselective. A detailed account of our findings are given below.

## RESULTS AND DISCUSSIONS

The chlorosulfides 1 and 2 were prepared from the corresponding sulfides as shown in Scheme 1. The opening of 1, 2-epoxybutane

with benzenethiol was catalysed by cobalt(II)chloride to give β-hydroxy-sulfides 1a. Acetylation of 1a followed by treatment of 1b with N-chloro-succinamide gave the chlorosulfides 1 in quantitative yields. On the

**Table 1. $ZnBr_2$ Catalysed reaction of 1 with Silyl enol ethers**




3 1 4 5

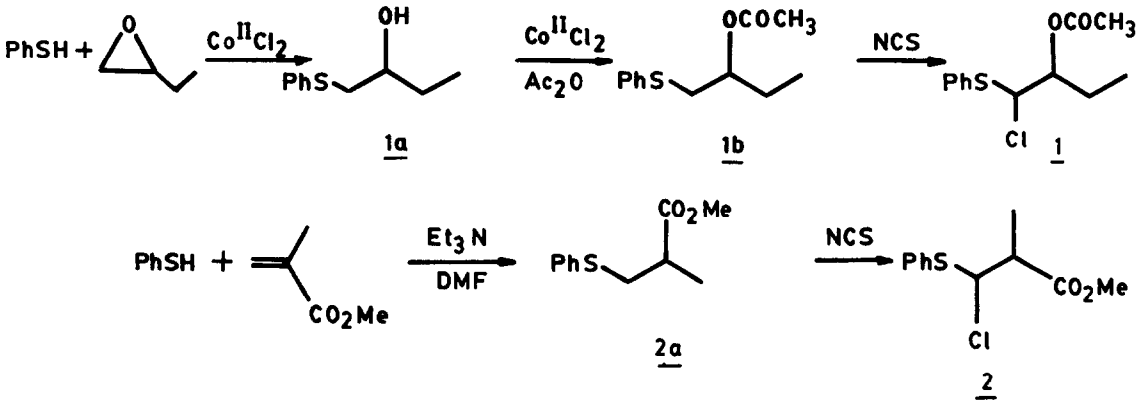
| Entry | R | Reaction condition (Time, Temperature) | Ratio (4:5)[a] | Yield (%)[b] |
|---|---|---|---|---|
| 1. | $CH_3$ (3a) | 20min, 25°C | 4a:5a (95:5) | 91 |
| 2. | $C_2H_5$(3b) | 20min, 20°C | 4b:5b (92:8) | 87 |
| 3. | $C_6H_5$ (3c) | 15min, 25°C | 4c:5c (97:3) | 79 |
| 4. | $Bu^t$ (3d) | 25min, 25°C | 4d:5d (91:9) | 75 |

**(a) Ratio determined by $^1H$-NMR (400 MHz) of the crude mixture.**
**(b) Yield of the crude mixture**

other hand the benzenethiol addition to methylmethacrylate gave the β-phenylthioester 2a which on reaction with N-chlorosuccinamide gave 2 in quantitative yields. The chlorosulfides 1 and 2 were obtained as a mixture of diastereomers which could not be separated by column chromatography or any other techniques.

The reaction of 1 with various silyl enol ethers 3 in presence of anhydrous zinc bromide (catalytic) in $CH_2Cl_2$ at 20°C led to the formation of a mixture of sulfides 4 and 5 in which the syn product

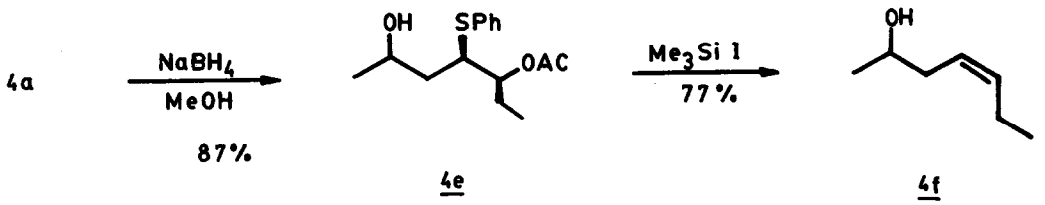
4 was obtained predominantly (Table 1). These reactions proceed under very mild conditions without affecting the acetoxy group. The stereo-




## SCHEME 1

chemistry of the diastereomers 4 and 5 were confirmed by the vicinal coupling constant in $^1$H-NMR and the coupling constant for the syn isomer was found to be higher than the anti isomer. In contrast to reactions[3i] with 2-acetoxy-2-phenylacetaldehyde thioacetals, the reaction with 1 does not involve any loss of the acetoxy group. The coupling with 1 can also be carried out in presence of other Lewis acids ($TiCl_4$, $SnCl_4$) however, the best selectivity is obtained only with zinc bromide catalysed reactions.

The syn stereochemistry in 4a was proved by its conversion to the homoallylic alcohol 4f by previously described procedure. The syn diastereomer 4a was reduced with sodium borohydride to the corresponding alcohol which on treatment with iodotrimethylsilane gave the (z)-olefin 4f as the sole product. The (z)-stereochemistry of the double bond in 4f clearly supports the syn relationship[9] between the acetoxy and phenylthio groups in 4a (Scheme 2).



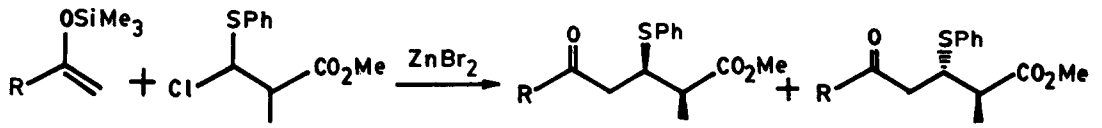

## SCHEME 2

The reaction of the chlorosulfide 2 with silyl enol ethers

3 in presence of anhydrous zinc bromide (catalytic) at 0°C yielded a mixture of keto esters 6 and 7 in which the syn isomer 6 was obtained as the major product (Table 2). However, the syn selectivity in this case was not as high as it is with chlorosulfide 1. The chlorosulfide 2 is quite prone to β-elimination, however the coupling reactions may be carried out from the freshly prepared 2 without any elimination.

The syn stereochemistry in 6a was confirmed by reducing ($NaBH_4$-MeOH) it to the corresponding lactone 10. The lactone 10 was transformed ($NaIO_4$-MeOH) into the sulfoxide 10a which on thermal elimination[11] gave β, γ-unsaturated lactone 10b as the only product (Scheme 3).

**Table 2. $ZnBr_2$ Catalysed reaction of 2 with Silyl enol ethers**

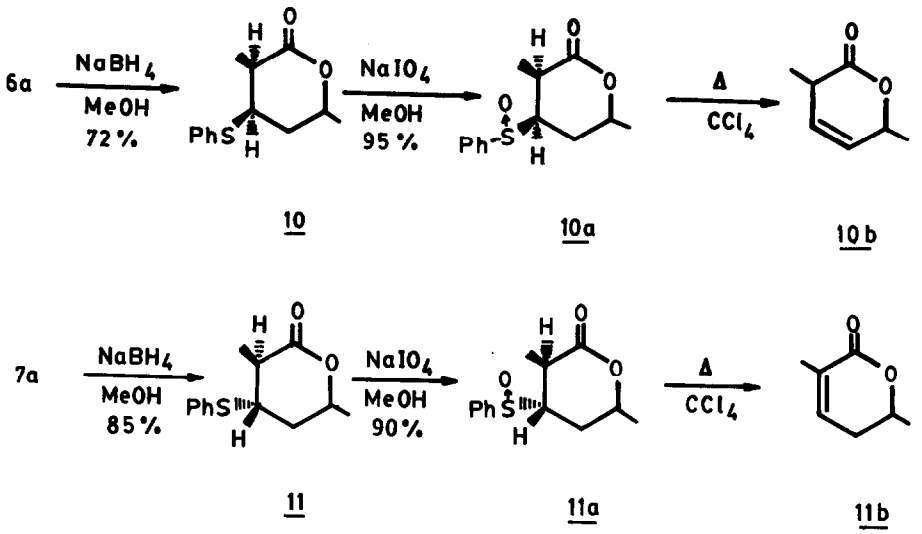



3 2 6 7

| Entry | R | Reaction condition ( Time ,Temperature) | Ratio (6:7)[a] | Yield (%)[b] |
|---|---|---|---|---|
| 1. | $CH_3$ (3a) | 1h ,15 °C | 6a : 7a (80:20) | 86 |
| 2. | $C_2H_5$(3b) | 45min ,20°C | 6b : 7b (77:23) | 81 |
| 3. | $C_6H_5$(3c) | 35min ,20°C | 6c : 7c (78:22) | 78 |
| 4. | $Bu^t$ (3d) | 45 min ,25°C | 6d : 7d (81:19) | 83 |

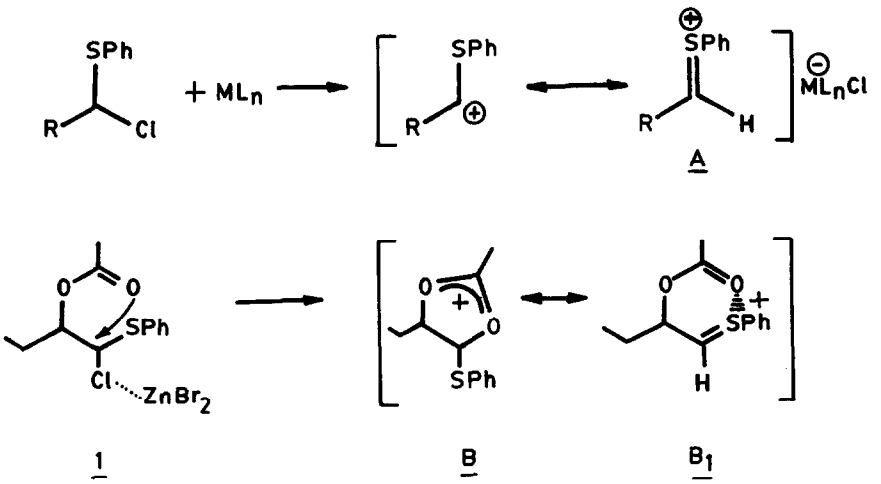
(a) Ratio determined by $^1H$-NMR and HPLC of the crude mixture
(b) Yield of the crude mixture

The formation of 10b clearly supports the anti relationship between α -H and β -SPh in 10. In a similar manner the anti-stereochemistry in 7a was shown by the elimination of the sulfoxide 11a from the corresponding lactone 11 to give the α , β -unsaturated lactone 11b. The formation of 11b unambiguously proves the syn relationship between α -H and β -SPh in 11.



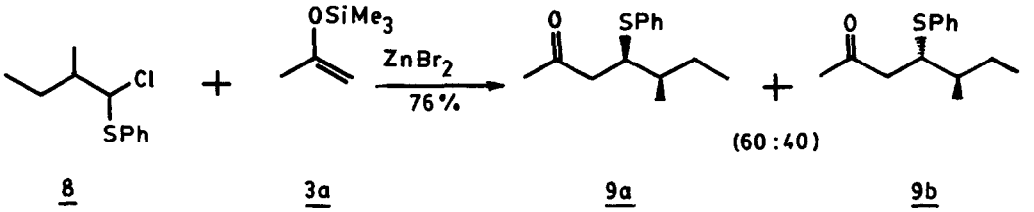

## SCHEME 3

The high diastereofacial selectivity in reaction with chlorosulfide 1 may be explained by considering an $S_N1$ type of mechanism. It is known from the previous studies that chlorosulfides can be activated with a Lewis acid to give a sulfur stabilised[4a,b] cation (Scheme 4) involving a thionium ion **A** and the latter have been shown to react like an aldehyde with allyl metals and silyl enol ethers. In an elegant study[3b] Heathcock and Batlett et.al. have shown that the chiral thionium ions undergo a high diastereoselective addition of allyl silane or silyl enol ethers to give predominantly the corresponding syn product. In view of their results, the reaction of silyl enol ethers with 1 can be explained by an $S_N1$ mechanism where the acetoxy group is providing an anchimeric assistance during the activation of the carbon chlorine bond with Lewis acid (Scheme 4). The role of acetoxy group as a neighbouring group participant in chlorosulfide **1** can be assessed by its unusually high rate of reaction (15 Min) compared to the reaction of the corresponding chlorosulfide 8 without an acetoxy group. Thus




## SCHEME 4

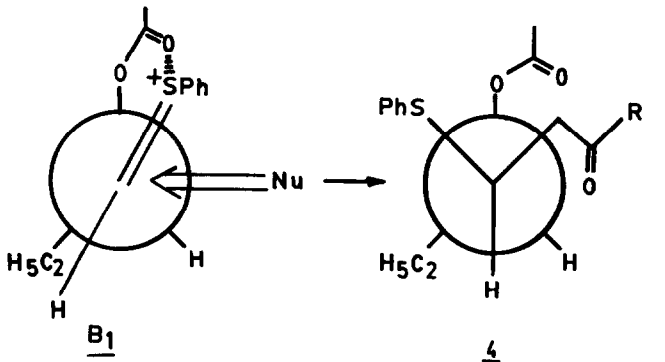
the reaction of 8 with silyl enol ethers is much slower (8h) compared to the reaction of 1 and it leads to the formation of a mixture of sulfides 9a and 9b (Scheme 5) in a ratio of 60:40 (76%). The stereochemical out come of the reaction with 1 can be explained by a nucleophilic attack of silyl enol ether on the chiral thionium ion via the eclipsed[10] conformation $B_1$ (Scheme 6). The electrostatic attraction between the oxygen of acetoxy group and the positive charge on sulfur will favour this reaction to proceed via conformation $B_1$. On the other hand such a high selectivity can not be expected to occur if the reaction is proceeding via the cyclic cation B. Moreover the thionium ion $B_1$, will be preferred over B due to the involvement of a six-membered cyclic intermediate as shown in Scheme 6. Therefore, the reason for high syn selectivity with 1 is mainly due to the presence of the acetoxy group at the α-carbon of the thionium $B_1$. The low syn selectivity




## SCHEME 5

obtained from chlorosulfide 8 also supports the involvement of the acetoxy group in the reaction with 1.

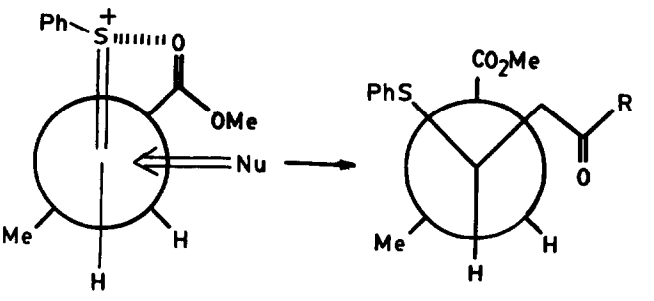
In a similar manner the selectivity with chlorosulfide 2 can be explained by an $S_N1$ reaction involving the nucleophilic attack




B1 4

SCHEME 6

of silyl enol ether on the eclipsed conformation of chiral thionium ion $B_2$ (Scheme 7). Once again, the electrostatic attraction between the carbonyl of ester and the positive charge on sulfur atom will be responsible for the high syn selectivity during these reactions. The role of methoxycarbonyl group in controlling the high selectivity during these reactions is quite clearly evident by comparing the results of the reactions from 2 and 8. Thus due to the absence of any chelating ligand in 8 the syn selectivity is low (Scheme 5) as compared to the selectivity observed in similar reaction with 2 (table 2). A similar charge attraction based model[11] was proposed between a carbonyl oxygen and sulfonium group during the hydride reduction of α-oxosulfonium salts.




B2 6

SCHEME 7

In conclusion, the zinc bromide catalysed reactions of silyl enol ethers with chlorosulfide 1 or 2 proceed in a highly diastereofacial manner to give the syn diastereomers 4 or 6 as the major product. The high diastereoselectivity can be explained by nucleophilic attack on the chelated chiral thionium ion $B_1$ or $B_2$.

## EXPERIMENTAL

**Methods and Materials** :

The infra red spectra were recorded on a Perkin Elmer 1320 spectrometer. The proton NMR spectra were recorded on Bruker WP-80, Jeol PMX-60, EM-390 and Bruker-400 spectrometer. Elemental analysis was conducted using coleman automatic C, H and N analyser. Analytical thin layer chromatography was performed on silica gel (Acme) coated glass plates. Column chromatography was performed using 100-200 mesh Acme silica gel. The ratio of diastereomers were checked by Shimadzu LC-6A HPLC systems.

Commercial grade solvents were distilled prior to use. Petroleum ether used were the fraction of 40°-60°C and 60°-80°C. Dichloromethane and carbontetrachloride were dried over $P_2O_5$. Zinc bromide was obtained from Aldrich Chemical Company and it was made anhydrous by boiling for five minutes over flame followed by cooling and powdering. N-chlorosuccinamide was purchased from Merck, Germany and used without purification. Silyl enol ethers were made by literature procedures[12]. Compound 1a was prepared by our procedure[5] as described earlier.

**2-Acetoxy-1-phenylthiobutane 1b** :

A catalytic amount of anhydrous cobalt(II)chloride (20 mg) was dissolved in dry acetonitrile (100 ml) and 1-phenylthiobutane-2-ol (9.1 gm, 50 mmol) and acetic anhydride (9.3 ml, 100 mmol) were added successively to this solution. The mixture was refluxed at 80°C for 2-3 hours. Acetonitrile was removed under vacuum and the residue taken into ether (2x200 ml). The ether layer was washed successively with saturated solution of sodium bicarbonate (2x50 ml) and water (2x50 ml). Drying ($MgSO_4$) and evaporation of ether gave a residue which on column chromatography ($SiO_2$, ether-pet. ether) yielded ester 1b in 92% yield. $^1$H-NMR ($CCl_4$) $\delta$ 7.5-7.1 (m, 5H), 5.0 (m, 1H), 3.15 (dd, J=6 and 3.5 Hz, 1H), 2.05 (S, 3H), 1.89 (m, 2H), 0.97 (t, J = 7 Hz, 3H). IR (thin film): 1735, 1650 $cm^{-1}$.

**2-Acetoxy-1-chloro-1-phenylthiobutane 1** :

2-Acetoxy-1-phenylthiobutane 1b (2.24 gm, 10 mmol) was

stirred with N-chlorosuccinamide (1.32 g, 10 mmol) in carbon-tetrachloride (30 ml) at 25°C for 30-40 minutes. The reaction mixture was filtered and the filterate evaporated to give 1 in 93% yield. $^1$H-NMR ($CCl_4$)δ 7.52-7.15 (m, 5H), 5.13 (m, 1H), 4.97 (m, 1H), 2.03 (S, 3H), 1.85 (m, 2H), 0.95 (t, J = 7 Hz, 3H).

**Methyl-2-methyl-3-phenylthiopropionate 2a** :

Methyl methacrylate (1.1 ml, 10 mmol) was added to a mixture of dimethylformamide (50 ml), triethylamine (1.3 ml, 10 mmol) and thiophenol (1 ml, 10 mmol). The mixture was stirred at 25°C for 1 hour and then poured into ether (200 ml). The ether layer was washed successively with saturated solution of sodium bicarbonate (2x50 ml) and water (2x50 ml). Drying ($MgSO_4$) and evaporation of ether gave a liquid which was purified by flash column chromatography to give 2a (90%). $^1$H-NMR ($CCl_4$)δ 7.2 (m, 5H), 3.67 (S, 3H), 3.5-2.75 (m, 3H), 1.05 (J = 6.8 Hz, 3H).

**Methyl-2-methyl-3-chloro-3-phenylthiopropionate 2** :

2a (2.1 gm, 10 mmol) was stirred with powdered N-chlorosuccinamide (1.32 gm, 10 mmol) in dry carbontetrachloride (30 ml) for 30-40 minutes at 25°C. The reaction mixture was filtered and the filterate evaporated to give 2 (93%) as an oil. This compound should be used immediately after its preparation. $^1$H-NMR ($CCl_4$)δ 7.9-1.0 (m, 5H), 5.5 (d, J = 6.5 H, 1H), 3.73 (S, 3H), 3.02 (m, 1H), 1.20 (d, J = 7 Hz, 3H).

**General procedure for the reaction of silyl enol ether and chlorosulfide 1, 2 and 8** :

A catalytic amount of powdered anhydrous zinc bromide (20 mg) was added to a solution of silyl enol ethers 2 (5 mmol) and the chlorosulfide (1, 2 or 8) (5 mmol) in dry dichloromethane (30 ml) at 25°C under nitrogen atmosphere. The reaction mixture was stirred for 2-4 hours and the progress of reaction was monitored by TLC. The mixture was poured into dichloromethane (20 ml) and the organic layer washed successively with saturated solution of sodium bicarbonate and brine. Drying ($MgSO_4$) and evaporation of dichloromethane gave a residue which on flash column chromatography yielded the products 4-7 and 9-10.

4a : Yield (81%); IR (thin film): 1731, 1725, 1662 $cm^{-1}$. $^1$H-NMR ($CCl_4$)δ 7.82-7.05 (m, 5H), dt, J = 8.05), 2.21 Hz, 1H), 3.78 (dt, J = 8.05, 2.2 Hz, 1H), 2.55 (d, J = 7 Hz, 2H), 2.0 (S, 3H), 1.91 (S, 3H), 1.80 (m, 2H), 0.92 (t, J = 7 Hz, 3H). Anal. Calcd. for $C_{21}H_{24}O_3S$ : C, 70.78; H, 6.74. Found : C, 70.79; H, 6.93.

**4b** : Yield (85%); IR (thin film) : 1733, 1729, 1665 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.78-7.0 (m, 5H), 4.85 (dt, J = 8.05, 2.4 Hz, 1H), 3.80 (dt, J = 8, 2.2 Hz, 1H), 2.53 (d, J = 7 Hz, 2H), 1.97 (S, 3H), 1.85 (m, 4H), 0.97 (t, J = 6.8 Hz, 3H), 0.92 (t, J = 6.8 Hz, 3H), Anal. Calcd. for $C_{16}H_{22}O_3S$ : C, 65.30; H, 7.48. Found : C, 65.95; H, 7.90.

**4c** : Yield (79%); IR (thin film): 1730, 1700, 1650 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.73-6.80 (m, 10H), 4.87 (dt, 2.1 Hz, 1H), 3.90 (dt, J = 8 and 2.2 Hz, 1H), 2.94 (d, J = 6.5 Hz, 2H), 1.89 (S, 3H), 1.78 (m, 2H), 0.82 (t, J=6.8 Hz, 3H). Anal.Calcd. for $C_{20}H_{22}O_3S$: C, 70.17; H, 6.43. Found : C, 69.45; H, 5.78.

**4d** : Yield (75%); IR (thin film): 1731, 1727, 1660 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.75-7.0 (m, 5H), 4.79 (dt, J = 7.9, 2.5 Hz, 1H), 3.80 (dt, J = 8, 2.5 Hz, 1H), 2.59 (d, J = 6.5 Hz, 2H), 1.91 (S, 3H), 1.78 (m, 2H), 1.05 (S, 9H), 0.90 (t, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{18}H_{26}O_3S$ : C, 67.08; 8.07. Found : C, 66.87; H, 7.76.

**5a** : Yield ( 5%); IR (thin film) : 1730, 1729, 1665 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.80-7.11 (m, 5H), 4.89 (dt, J = 7.72, 2.15 Hz, 1H), 3.81 (dt, J = 7.57, 2.20 Hz, 1), 2.52 (d, J = 6.8 Hz, 2H), 2.0 (S, 3H), 1.75 (m, 2H), 0.95 (t, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{12}H_{24}O_3S$ : C, 64.28; H, 7.14. Found : C, 64.85; H, 7.92.

**5b** : Yield (7%); IR (thin film) : 1732, 1725, 1660 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.80-7.0 (m, 5H), 4.95 (dt, J = 7.35, 2.33 Hz, 1H), 3.78 (dt, J = 7.43, 2.27 Hz, 1H), 2.55 (d, J = 7 Hz, 2H), 1.95 (S, 3H), 1.80 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{16}H_{22}O_3S$ : C, 65.30; H, 7.48. Found : C, 66.05; H, 8.17.

**5c** : Yield (8%); IR (thin film): 1733, 1705, 1655 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.8-6.77 (m, 10H), 4.98 (dt, J = 7.55, 2.4 Hz, 1H), 3.96 (dt, J = 7.37, 2.35 Hz, 1H), 2.90 (d, J = 6.7 Hz, 2H), 1.85 (S, 3H), 1.81 (m, 2H), 0.92 (t, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{20}H_{22}O_3S$ : C, 70.17; H, 6.43. Found : C, 70.95; H, 7.38.

**5d** : Yield (5%); IR (thin film): 1728, 1720, 1655 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.70-7.08 (m, 5H), 4.85 (m, 1H), 3.87 (m, 1H), 2.52 ((d, J = 6.5 Hz, 2H), 1.87 (S, 3H), 1.80 (m, 2H), 1.0 (S, 9H), 0.85 - (t, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{18}H_{26}O_3S$ : C, 67.08; H, 8.07. Found : C, 68.23; H, 9.15.

**6a** : Yield (72%); IR (thin film): 1735, 1728, 1660 $cm^{-1}$. $^1$H-NMR($CCl_4$) $\delta$ 7.15 (m, 5H), 3.80 (dt, J = 5.85, 2.13 Hz, 1H), 3.58 (S,

3H), 2.70 (m, 3H), 2.0 (S, 3H), 1.12 (d, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{14}H_{18}O_3S$ : C, 63.15; H, 6.76. Found : C, 67.78; H, 7.23.

**6b** : Yield (75%); IR (thin film): 1730, 1725, 1655 $cm^{-1}$. $^1$H-NMR($CCl_4$) $\delta$ 7.20 (m, 5H), 3.77 (dt, J = 5.76, 2.23 Hz, 1H), 3.60 (S, 3H), 2.65 (m, 3H), 1.78 (m, 2H), 1.14 (d, J = 6.8 Hz, 3H), 0.89 (t, J = 7 Hz, 3H). Anal. Calcd. for $C_{15}H_{20}O_3S$ : C, 64.28; H, 7.14. Found : C, 64.92; H, 7.86.

**6c** : Yield (71%); IR (thin film): 1727, 1723, 1657 $cm^{-1}$. $^1$H-NMR($CCl_4$) $\delta$ 7.56-6.80 (m, 10H), 3.88 (dt, J = 6.12, 2.25 Hz, 1H), 3.55 (S, 3H), 2.87 (d, J = 6.8 Hz, 2H), 2.56 (m, 1H), 1.15 (d, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{19}H_{20}O_3S$ : C, 69.51; H, 6.09. Found : C, 70.38; H, 7.22.

**6d** : Yield (79%); IR (thin film): 1735, 1728, 1663 $cm^{-1}$. $^1$H-NMR($CCl_4$) $\delta$ 7.15 (m, 5H), 3.81 (dt, J = 5.88, 2.25 Hz, 1H), 3.61 (S, 3H), 2.62 (m, 3H), 1.16 (d, J = 6.80 Hz, 3H), 1.12 (S, 9H). Anal. Calcd. for $C_{17}H_{24}O_3S$ : C, 66.23; H, 7.79. Found : C, 67.05; H, 8.19.

**7a** : Yield (12%); IR (thin film): 1732, 1721, 1662 $cm^{-1}$. $^1$H-NMR($CCl_4$) $\delta$ 7.08 (m, 5H), 3.70 (dt, J = 7.66, 2.50 Hz, 1H), 3.50 (S, 3H), 2.62 (m, 3H), 2.05 (S, 3H), 1.10 (d, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{14}H_{18}O_3S$ : C, 63.15; H, 6.76. Found : C, 64.25; H, 7.37.

**7b** : Yield (10%); IR (thin film): 1733, 1725, 1657 $cm^{-1}$. $^1$H-NMR($CCl_4$) $\delta$ 7.12 (m, 5H), 3.61 (dt, J = 7.5, 2.5 Hz, 1H), 3.52 (S, 3H), 2.59 (m, 3H), 1.75 (S, 2H), 1.12 (d, J = 6.8 Hz, 3H), 0.85 (t, J = 7 Hz, 3H). Anal. Calcd. for $C_{15}H_{20}O_3S$ : C, 64.28; H, 7.14. Found : C, 64.86; H, 7.73.

**7c** : Yield (8%); IR (thin film): 1732, 1727, 1662 $cm^{-1}$. $^1$H-NMR($CCl_4$) $\delta$ 7.6-6.89 (m, 10H), 3.75 (dt, J = 7.20 2.71 Hz, 1H), 3.51 (S, 3H), 2.85-2.46 (m, 3H), 1.13 (d, J = 6.8 Hz, 3H). Anal. Calcd. for $C_{19}H_{20}O_3S$ : C, 69.51; H, 6.09. Found : C, 70.38; H, 7.22.

**7d** : Yield (14%); IR (thin film): 1732, 1726, 1659 $cm^{-1}$. $^1$H-NMR($CCl_4$) $\delta$ 7.15 (m, 5H), 3.70 (dt, J = 7.2, 2.5 Hz, 1H), 3.52 (S, 3H), 2.58 (m, 3H), 1.14 (d, J = 7 Hz, 3H), 1.10 (S. 9H). Anal. Calcd. for $C_{17}H_{24}O_3S$ : C, 66.23; H, 7.79. Found : C, 67.38; H, 8.69.

**1-chloro-2-methyl-1-phenylthiobutane 8** :

2-methyl-1-phenylthiobutane (1.8 g, 10 mmol) was stirred with N-Chlorosuccinamide (1.30 g, 10 mmol) in carbontetrachloride (30 ml) at 25°C for 10 hours. The reaction mixture was filtered and the filterate evaporated to give 8 in 95% yield. $^1$H-NMR ($CCl_4$) $\delta$ 7.10 (m,

10H), 2.05 (m, 1H), 1.65 (m, 2H), 1.0 (d, J = 7 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H).

9a : Yield (54%); IR (thin film): 1729, 1663 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.12 (m, 5H), 3.27 (dt, J = 5.5 and 3 Hz, 1H), 2.49 (d, J =6 Hz, 2H), 2.12 (m, 1H), 2.0 (S, 3H), 1.50 (m, 2H), 0.85 (t, J = 7 Hz, 3H). Anal. Calcd. for $C_{14}H_{20}O_1S$ : C, 71.18; H, 8.47. Found : C, 72.15; H, 9.27.

9b : Yield (12%); IR (thin film): 1732, 1657 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.20 (m, 5H), 3.18 (dt, J = 7.6 and 3.2 Hz, 1H), 2.50 (d, J = 6.5 Hz, 2H), 2.19 (m, 1H), 2.0 (S, 3H), 1.56 (m, 2H), 0.91 (t, J = 7 Hz, 3H).

**General procedure for the reduction with sodium borohydride :**

Ice-cooled methanolic solution of sodium borohydride (2.5 mmol) was added to the solution of 6a or 6b (8 mmol) in methanol (30 ml) at 0°C. The resulting mixture was stirred at 0°C for 1.5 h and the progress of reaction was monitored by TLC during this period. After the completion of reaction methanol was removed under vacuum and the residue taken into ether. The ether layer was wahsed with saturated solution of sodium bicarbonate and water. Drying ($MgSO_4$) and evaporation of ether gave a residue which on column chromatography yielded lactone 10 or 11.

10 : Yield (72%); IR (thin film): 1730, 1657 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.15 (m, 5H), 4.05 (m, 1H), 3.21 (m, 1H), 2.36 (m, 1H), 1.55 (m, 2H), 1.02 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 7 Hz, 3H). Anal. Calcd. for $C_{13}H_{16}O_2S$ : C, 52.88; H, 6.77. Found : C, 53.34; H, 7.23.

11 : Yield (72%); IR (thin film): 1732, 1665 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 7.19 (m, 5H), 4.12 (m, 1H), 3.19 (m, 1H), 2.41 (m, 1H), 1.59 (m, 2H), 1.07 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 7 Hz, 3H).

**General procedure for the oxidative removal of sulphur from 10 and 11 :**

Sodium metaperiodate (10 mmol) was added to a stirred solution of 10 or 11 (8 mmol) in methanol (20 ml) followed by the addition of distilled water (2 ml). The reaction mixture was stirred in dark for 16 hrs at 25°C and then diluted with dichloromethane (30 ml) and poured into water (40 ml). The aqueous layer was extracted with dichloromethane (2x15 ml) and combined organic extract were dried ($MgSO_4$) and evaporated in vacuum to give sulfoxide 10a or 11a. The sulfoxides were dissolved in carbon tetrachloride and heated to reflux (75°-80°C) for 8-12 hours. After complete disappearance of starting material the solution was concentrated and subjected to column chromatography to

give pure unsaturated lactone 10b or 11b.

**10b** : Yield (78%); IR ($CH_2Cl_2$): 1720, 1659 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 5.58 (m, 2H), 4.97 (m, 1H), 2.95 (m, 1H), 1.09 (d, J = 6.8 Hz, 3H), 0.98 (d, J = 7 Hz, 3H).

**11b** : Yield (87%); IR ($CH_2Cl_2$): 1705, 1668 $cm^{-1}$. $^1$H-NMR ($CCl_4$) $\delta$ 6.52 (m, 1H), 4.15 (m, 1H), 2.2 (m, 2H), 1.82 (S, 3H), 1.18 (d, J = 7 Hz, 3H).

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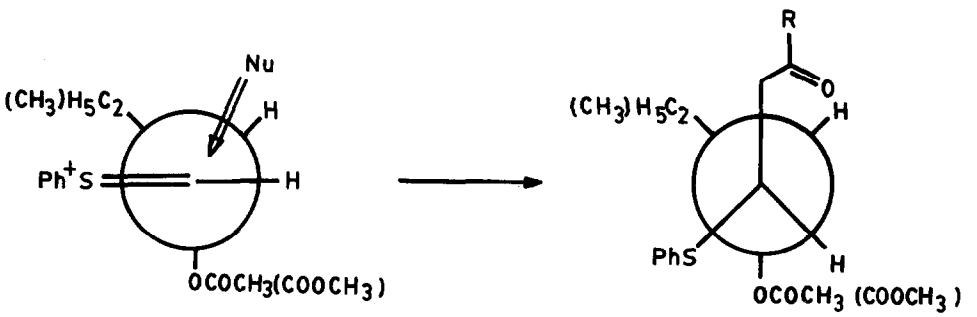
9. The syn hydroxy selenides have been shown[8] to undergo elimination without any loss of stereochemistry togive the corresponding (z)--Olefin.

10. The reaction is not proceeding via the Felkin-Anh model $B_4$ in which the α-heteroatom (acetoxy) substituted functional group is located anti to incoming nucleophile.




**$B_4$** **5(7)**

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