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Reaction of Benzyl Phenacyl Sulphide with Ethanolic Sodium Hydroxide

تفاعل بنزيل فينسيل كبريتيد مع هيدروكسيد الصوديوم الايثانولي

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R.M. Scrowston (School of Chemistry,
University of Hull, HU6 7RX, U.K.),
Elageed Elnazeer H. M.
Nawal M.Suleman
Department of Chemistry, Faculty of
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Elnazeer H. M. Elageed (elnazeerhamid @hotmail.com),
Nawal M.Suleman
Department of Chemistry, Faculty of Education, University of Khartoum, Sudan.

مستخلص

تفاعل بنزيل فينسيل كبريتيد مع هيدروكسيد الصوديوم الايثانولي اعطي نواتج اطمحلال (خسف). تم تحديد الصيغ البنائية للحمض الهيدروكسيلي واستره الميثيلي بناءً على التحليل بواسطة طيفالاشعة تحت الحمراء (I.R)، طيف الرنين النووي المغناطيسي (^{1}H NMR ، ^{13}C NMR) طيف الكتلة (MS) والتحليل العنصري. التحلل المائي القلوي للا ستر الميثيلي بهيدروكسيد الصوديوم المائي اعطى ملح الصوديوم للحمض الهيدروكسيلي ، والذي اعطى عند معالجته بحمض الهيدروكلوريك المخففالحمض الهيدروكسيلي الأصل.

Abstract

The reaction of benzyl phenacyl sulphide with ethanolic sodium hydroxide gave degradation products. The structures of the hydroxy - acid and its methyl ester were elucidated based on their infra red spectra (IR) , nuclear magnetic resorance (^{13}C NMR , ^{1}HNMR) , mass spectra(MS) and elemental analysis. The alkaline hydrolysis of the methyl ester with aqueous sodium hydroxide gave the sodium salt of the hydroxy - acid, which on treatment with dilute hydrochloric acid gave the original hydroxy - acid.

Keywords: Keto -sulphides,benzyl phenacyl sulphide, ethanolic sodiumhydroxide, hydroxy - acid, methyl ester, and lactone.

Introduction

Organic sulphides are normally very stable towards acids and alkalis, but if the sulphide contains a strong electron- releasing group, the sulphide undergoes acidic hydrolysis *via* the protonated sulphide. On the other hand, if the sulphide contains an electron-withdrawing group, the sulphide readily undergoes alkaline fission(Iskander,1948, Iskander andTewfik,1961). Although simple alkyl sulphides are generally stable towards alkalis, the presence of a carbonyl group β - to the sulphide bond renders the sulphide labile towards alkalis (Billheimer and Reid ,1930 ; Nicolet,1931). There are some examples in the literature in which keto- sulphides are found to be very sensitive towards the action of alkalis (Tarbell and Harnish,1951). Keto-sulphides undergo CO-CH bond fission when treated with alkalis,the reason for the lack of carbon –sulphur bond cleavage in these compounds is probably that the thiolate ion which would be formed cannot be stabilized by the formation of a conjugated enolate anion. The action of alkali on a keto -sulphide could take any of the following routes :(a) C-S bond fission, (b) CO-C bond fission, (3) Combination of (a) and (b), (d) No bond fission (Mogan, 1959 ; Teich, and Curtin , 1950) . The reaction of benzyl phenacyl sulphide (1) with 30% aqueous sodium hydroxide gave benzoic acid and benzyl mercaptan, , probably *via* CH-S bond fission, whereas the action of 20% aqueous sodium hydroxide gave acetophenone, probably *via* CO-CH bond fission (David and Herman,1966) ,(Schemes 4,5 and 6). Reduction of β- keto - sulphides afforded β- hydroxy-sulphides (Cho*etal.,*2003). The anti-mycobacterial activity of phenacyl aryl/cyclohexylsulfides(Ramaiyan*etal.* 2010) and 3-Thioxo-1, 2,4-triazin-5-ones and their derivatives (Mohammad *et al.,* 2019) were studied.In the present study the reaction of benzyl phenacyl sulphide with ethanolic sodium hydroxide is investigated.

Experimental

Melting - points are uncorrected . ^{1}H and ^{13}C NMR spectra were derermined at 270 and 68 MH$_Z$ respectively on a JEOL JNM-GX-FT-NMR

Deuteriochloroform was used as a solvent in NMR spectroscpoy (unless otherwise stated) . Chemical shifts are recorded in parts per million (ppm) downfield from tetramethylsilane ; coupling constants are in H$_Z$. The abbreviations used are : s = singlet , d = doublet t = triplet , q = quartet , dd = doublet of doublet , dt = doublet of triplet , br = broad and m = unresolved multiplet. IR were obtained on a Perkin –Elmer sPE783 spectrometer ; samples were perpared as KBr or KCl or as liquid films . Mass spectra were performed on Finnigan-MAT 1020 automated GC/Ms . Ether refers to diethyl ether and light petroleum refers to to the fraction wth bp 60-80°C.

4-(benzylthio)-5-hydroxy-3,5-diphenylpentanoic acid (2)

A stirred mixture of benzyl phenaacyl sulphide (1) (10g , 0,041mol),sodium hydroxide (30g , 0.75 mol) , distilled water (20ml) and ethanol (130ml) was heated under reflux for 4h ,then cooled . The precipitated solid was filtered off , washed successfully with distilled water, ethanol, and ether, then dried, to givethe sodium salt as white powder (3g) ,IR spectrum√max3340 cm^{-1}br (OH) ,1575 and

1420 cm^{-1}(COO^-) . It was treated with dilute hydrochloric acid and the free acid was extracted with ether. The combined ethereal extracts were dried with ($MgSO_4$) and the solvent was removed. The resulting solidwas then recrystallized from ethyl acetate to give the corresponding acid as microneedles.Yield 2.78g ,(17%) , mp: 143-144°C,IR spectrum √max:3320 cm^{-1}br (OH) and 1705cm^{-1} (C═O) ,m /z 374 (M^+-H_2O) . (Found : C, 73.6 ;H, 6.0 . $C_{24}H_{24}O_3S$ requires C, 73.45; H, 6.15 %). ^1H and ^{13}C NMR spectral data are recorded in Tables (1) and (2).

The filtrate remaining after the removal of the white powder was diluted with an equal volume of distilled water and shaken with ether (50ml). The ethereal extract contained several components in minor quantities (TLC). The aqueous phase was acidified with concentrated hydrochloric acid, then shaken successively with light petroleum (3x25ml) and ether (3x25ml). The light petroleum extract contained benzyl mercaptan (0.9g, 17.5%), identical with an authentic sample.

Evaporation of the ethereal extract afforded benzoic acid (0.4g,8%), mp121-122°C (Lit. 122°C (Heilbron*etal.,* 1965*)*, the mp undepressed on admixture with an authentic sample of benzoic acid.

Methyl 4-(benzylthio)-5-hydroxy-3,5-diphenylpentanoate(3)

The hydroxy-acid (2) 2.4g, 0.006mol) was treated with ethereal diazomethane until the evolution of nitrogen has ceased. Evaporation of the solvent left a white solid, which was then recrystallized from ethyl acetate -light petroleum as white needles.Yield: 2.2g , 89% ,mp: 83-84°C , IR spectrum √max: 3485 cm^{-1}br and 1730 cm^{-1} (ester C=O) , m /z 389 (M^+-OH).(Found : C,73.75 ; H, 6.4 $C_{25}H_{26}O_3S$ requires C ,73.85 ; H, 6.45 %) . ^1H and ^{13}C NMR spectral data are recorded in Tables (3) and(4).

δ - Lactone (4)

A stirred mixture of the hydroxy-acid (2) (1g, 0.0026mol) and a catalytic amount of toluene- 4-sulphonic acid in dry toluene (20ml) was heated under reflux for 2h, then cooled. Water (20ml) was added, then the organic layer was separated and dried ($MgSO_4$). Removal of the solvent gave analytically pure oil (TLC).Yield : 0.65g ,68% ,IR spectrum√max: 1780 cm^{-1} (δ -lactone), M^+ 374. (Found : C, 76.95 ; H ,6.0 $C_{24}H_{22}O_2S$ requires C,77.0 ; H; 5.9) . ^1H and ^{13}C NMR spectral data are recorded in Tables (5) and (6).

Similar treatment of the methyl ester (3) gave the same δ -lactone (4).

δ - Lactone (5)

A stirred mixture of δ - lactone (4) (0.5g , 0.00135mol) and Raney nickel (0.4 g) ,in ethanol (15ml) was heated under reflux for 4h . The catalyst was filtered off (hyflo) and washed with hot ethanol. Evaporation of the solvent left analytically pure brown oil (TLC). Its IR spectrum indicated that the expected product (5) had been formed , IR spectrum √max: 1730 cm^{-1} (δ - lactone) ,(Scheme 3).

Hydrolysis of the methyl ester (3)

A mixture of the methyl ester (3) (0.5 g, 0.0012mol) and 10%w/v sodium hydroxide (2ml) in methanol was heated under reflux for 2h, then cooled and partially evaporated. The residue was poured into ice-cold water and acidified with hydrochloric acid to give a white precipitate. This was filtered off, washed thoroughly with distilled water, cooled, dried, and recrystallized from ethyl acetate, to give back the hydroxy - acid (2), identical with that already described. Yield :0.28g , 58% .

Methyl 5-acetoxy-4-(benzylthio)-3,5-diphenylpentanoate (6)

A mixture of the hydroxy-acid (2) (0.5g,0.0012mol), pyridine (2ml), and acetic anhydride (10 ml) was heated on a water-bath for 2h, the mixture was cooled and diluted with dilute hydrochloric acid, then the product was extracted into ether. The combined ethereal extracts were washed with aqueous sodium carbonate, dried with ($MgSO_4$) and evaporated, to give a white solid. Recrystallization from ethanol gave white microcrystals.Yield 0.4g ,73% ,mp; 116 -117 °C , IR spectrum√max: 1745($OCOCH_3$) and 1735 cm^{-1} (ester C=O) , M^+ 448).(Found : C,71.2 ; H, 6.15, $C_{25}H_{26}O_4S$ requires C ,71.05 ; H, 6.2 %) . ^1H and ^{13}C NMR spectral data are recorded in Tables (7) and(8).

Methyl 4-(benzylsulphinyl)-5-hydroxy-3,5-diphenylpentanoate (7)

A mixture of the hydroxy-acid (2) (0.5g,0.0012mol), 30% w/v hydrogen peroxide (2ml), and glacial acetic acid (10ml) were stirred at room temperature for 24h, then poured into ice-cold water. The precipitated solid was filtered off, washed thoroughly with water to remove traces of the acid and dried. Recrystallization from ethanol gave white microcrystals.yield 0.38g ,73% ,mp; 131-132 °C , IR spectrum √max: 3400 br (OH) and 1730 cm^{-1} (C=O) , M^+ 422).(Found : C,71.2 ; H, 6.15, $C_{25}H_{26}O_4S$ requires C ,71.05 ; H, 6.2 %) . ^1H and ^{13}C NMR spectral data are recorded in Tables (9) and(10).

Methyl-4-(benzoyl-4-(benzylsulphonyl)-3-phenylbutanoate (8)

Jones' reagent was prepared by the cautious addition of concentrated sulphuric acid(0.6ml) to a stirred, ice-cold solution of chromium oxide (Cr_2O_3), (0.7g) in water (5ml), was added dropwise to a stirred, ice-cold solution of the hydroxy-acid (2) (1g, 0.0025mol) in acetone (15ml), then stirring was continued for a further 3h. The green precipitate was filtered off (hylfo) and the filtrate was evaporated, to give a white solid. Recrystallization from ethanol gave a white impure product (0..8g) (probably the expected ketone, accompanied by material obtained by partial oxidation of the sulphur atom) This product was therefore subjected to further oxidation.

A stirred mixture of the foregoing product (0.7 g) and 30% w/v v hydrogen peroxide (2ml) and glacial acetic acid (10 ml) was kept 100 °C for 3h. the cooled mixture was poured into ice-cold water. The resulting white precipitate was filtered off, washed thoroughly, dried, and recrystallized from ethanol as white microcrystals.Yield 0.0.52g ,48% ,mp; 131-132 °C , IR spectrum√max: 1740 (ester C=O) and 1680 cm^{-1} (Keto\ C=O) , M^+ 436 .(Found : C,68.7 ; H, 5.5, $C_{25}H_{24}O_5S$ requires C ,68.8 ; H, 5.5 %) . ^{1}H and ^{13}C NMR spectral data are recorded in Tables (11) and(12).

Reaction with Raney Nickel:

A mixture of the hydroxy-acid (2) (3g,0.0074 mol)and Raney Nickel (3g) in ethanol (80ml) was heated under reflux for 3h The catalyst was filtered off (hyflo) and washed with hot ethanol. Removal of the solvent left a pale brown oil, which was chromatographed on silica.

Elution with ethyl acetate – light petroleum (9:1) afforded pure samples of component (9), (10), and a slightly impure sample of component (11). Component (11) was further purified by chromatography over silica; elution with ethyl acetate – light petroleum (19:1) gave a pure sample of component (11).

Component(9) , was identified as methyl 4- benzoyl -3 - phenylbutanoate , was obtained as a colourless oil , yield (0.23g , 13%) ,IR spectrum√max:1730 (C= O ester) and 1680 cm^- (C= O keto) , M^+ 282. ^{1}HNMR spectral data is recorded in Table (13).

Component(10), was identified as methyl 5-hydroxy-3,5-diphenylpentanoate, was obtained as a colourless oil, ,IR spectrum √max:3440 (OH) and 1730 cm^{-1} (C= O ester), M^+ 284. ^{1}HNMR spectral data is recorded in Table (14).

Component(11), was identified as methyl -3,5- diphenylpentanoate, was obtained a colourless oil , yield (0.22g , 9%), IR spectrum √max: 1730 cm^{-1} (C= O ester), M^+ 282..(Found : C ,80.45 ; H, 7.35 , $C_{25}H_{24}O_5S$ requires C ,80.56 ; H, 7.5 %) .^{1}HNMR spectral data is recorded in Table (15).

From the second column. Elution with dichloromethane - light petroleum (1: 1), gave toluene identical with authentic sample (IR and GLC).

Results and Discussion

By the use of a combination of spectroscopic and chemical methods, the structures of the hydroxy - acid (2) and its methyl ester (3), (Schemes 1and 2), were elucidated.

(a) Spectroscopic Evidence:

Examination of the ^{1}HNMR spectra of the hydroxy- acid (2) and its methyl ester (3), Tables (1) and (3), showed that the chemical shifts and coupling constants are nearly the same for the hydroxy - acid (2), the methyl ester (3), the acetoxy derivative (6), the sulphoxide derivative (7) and the keto -sulphone derivative (8) Tables (1), (3), (7),(9), and (11), ((Harwood and Claridge , 1996,Silverstein and Webster,1998 ;Pavia, *etal.*,2001).

In the methyl ester (3), H_a appeared at δ =4.56 ppm as pseudotripletwith coupling constants *j*(ab)=6.2Hz and *j*(ah)=4.9 Hz, while in the lactone (4), H_a appeared at δ =3.77 ppm as a doublet, *j*(ab)=3..5Hz.

The variation in the values of the chemical shifts could be attributed to the change from the open-chain structure of the methyl ester (3) to the strained cyclic structure of the lactone (4), Tables (5) and (6). showed clearly that the structures (2) and (3) were correct. This deduction was confirmed by ^{13}CNMR spectroscopy.

Examination of the ^{13}CNMR spectra of the hydroxy - acid (2) and its methyl ester (3) showed that the chemical shifts and coupling constants are approximately the same for the hydroxy - acid (2), the methyl ester (3), the acetoxy derivative (6), the sulphoxide derivative (7) and the keto -sulphone derivative (8)Tables (2), (4), (8),(10), and (12).Carbon atom C_a appeared at δ = 74.60ppm and C_b, at δ = 58.48 in the methyl ester (3), whereas in the lactone (4) C_a, appeared at δ =89,32ppm and C_b, at δ =51.17ppm, Table (6), (Harwood and Claridge , 1996 ,Silverstein and Webster,1998 ,Pavia, *etal.*,2001).

The variation in the values of the chemical shifts could be due to the same reason given in the discussion of the ^{1}HNMR spectra.

However, the correct structures could not be deduced with certainty without additional chemical evidence '

(b) Chemical Evidence:

To confirm the structures of the hydroxy - acid (2) and its methyl ester (3) several chemical reactions were carried out.

(1) Hydrolysis:

The alkaline hydrolysis of the methyl ester (3) with aqueous sodium hydroxide gave the sodium salt of the hydroxy - acid. Treatment with dilute hydrochloric acid afforded the original hydroxy - acid (2) .this experiment confirm that the esterification of the hydroxy –acid (2) with diazomethane had not accompanied by a rearrangement reaction.

(2) Acetylation:

Acetylation of the methyl ester (3) was achieved by using acetic anhydride in pyridine to give the acetoxy derivative (6)

(3) Oxidation with Peroxyacetic acid:

Oxidation of the methyl ester (3) with hydrogen peroxide in acetic acid yielded the sulphoxide derivative (7).

(4) Oxidation with Jones′ Reagent:

Oxidation of the methyl ester (3) with Jones′ reagent (CrO_3/H_2SO_4 in acetone) was carried out in the hope that the keto - derivative might be obtained. However, although the product showed the expected ketonic absorption in the IR. It was to contain some impurities, which perhaps resulted from the oxidation of the sulphur atom. However, when the crude mixture was further oxidized with hydrogen peroxide in glacial acetic acid, the corresponding crystalline keto-sulphone derivative (8) was obtained.

(5) Hydrodesulphurization with Raney Nickel:

Hydrodesulphurization of sulphur –containing compounds using Raney nickel has been employed for synthetic and degradative purposes (Hauptmann and Walter,1962 ; Petti and Tamelen van 1962) .

The methyl ester (3) was subjected to catalytic hydrodesulphurization with Raney nickel in ethanol. toluene (from the -SCH_2Ph group) was detected by Gas-Liquid Chromatography (GLC) and three other products (9), (10) and (11), were isolated by HighPressure Liquid Chromatography (HPLC). The major component was the expected hydroxy-ester (10), which as a result of hydrodesulphurization of the methyl ester (3). Surprisingly, one of the minor components had arisen by dehydrogenation of the hydroxy-ester (10) to the corresponding keto- ester (9).

The same keto- ester (9) was obtained by oxidation (Jones′ reagent) of the hydroxy-ester (10), thus the structure was confirmed. It is unusual for alcohol to be oxidizedin the presence of a strong reducing agent. However, hydrodesulphurization of several substituted mercaptoethanol with Raney nickel yielded sulfur-free alcohol, accompanied by the corresponding ketone and sometimes by the corresponding saturated or unsaturated hydrocarbon, depending on the solvent used for the reaction (Hauptmann and Walter,1962 ; Petti and Tamelen van 1962) .

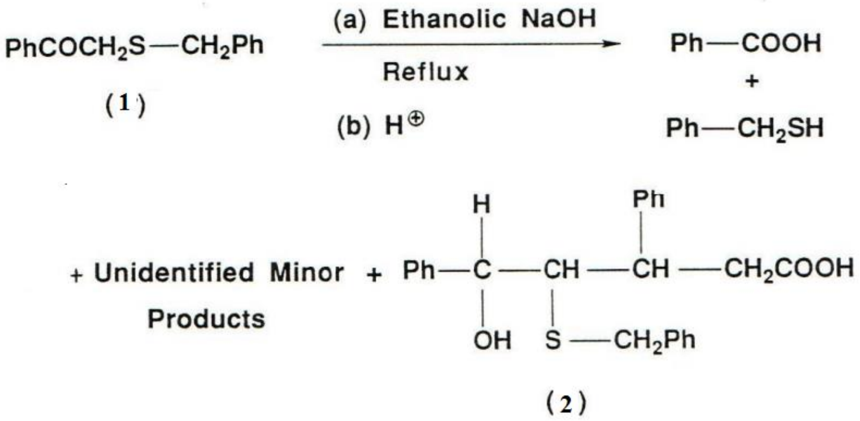
.(6) Formation of δ - lactone (4)

The hydroxy – acid (2) and its methyl ester (3) each formed the same oily δ - lactone (4) when warmed with a trace of toluene -4-sulphonic acid.

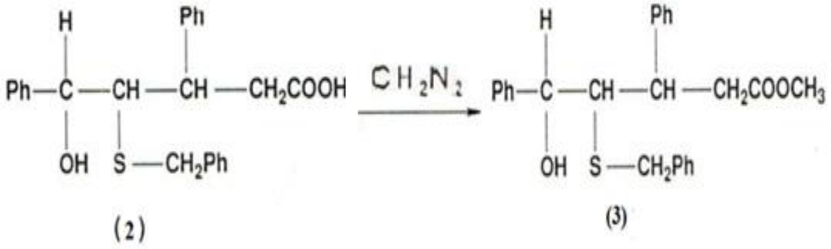
The lactone showed $\surd_{C=O}$ 1780 cm^{-1}, which can be interpreted as the carbonyl absorption of a γ lactone (usual $\surd_{C=O}$ range 1760-1780 cm^{-1}),(Harwood and Claridge , 1996,Silverstein and Webster *1998*,Pavia, *etal.*,2001) . However, if the structures (2) and (3) are correct and the lactone (4) should be a δ - lactone, for which $\surd_{C=O}$ falls within the range 1735-1750 cm^{-1}

The NMR spectral data, Tables (5) and (6) supported structure (4), but more evidence was necessary to confirm this structure.

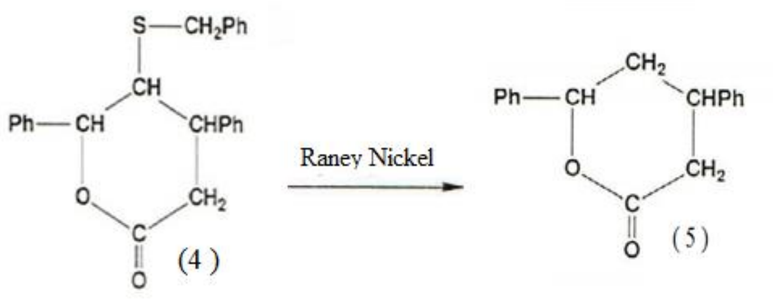
δ -lactone (4) was subjected to hydrodesulphurization with Raney nickel in ethanol. The IR spectrum of the resulting product δ -lactone (5) showed carbonyl absorption at 1735 cm^{-1} as expected for the lactone (5). The high $\surd_{C=O}$ value suggests that the lactone ring in (4) is considerably strained. Molecular models showed that the benzylthio group imparts considerable steric hindrance within the lactone (4). However, it appears possible to obtain strain-free conformations,(Scheme 3).



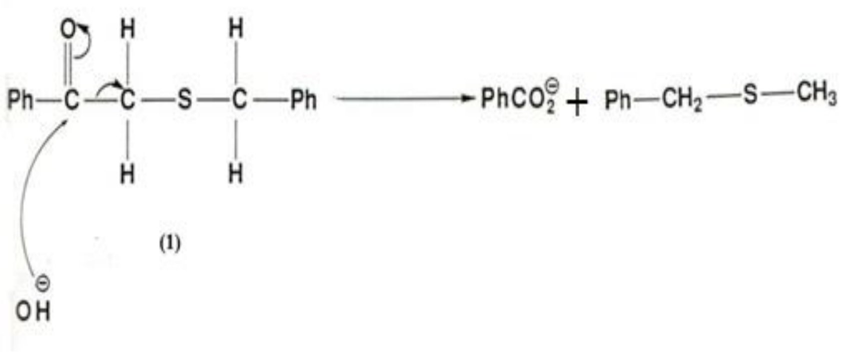
Scheme 1. The reaction between benzyl phenacyl sulphide and ethanolic sodium hydroxide



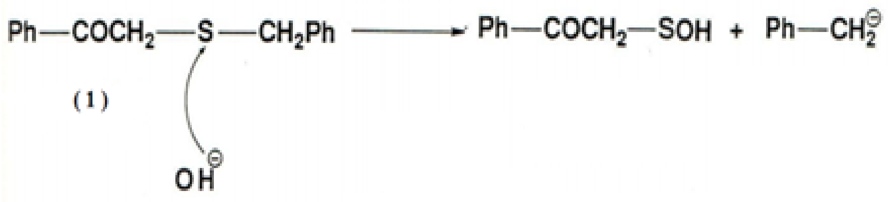
Scheme 2. The formation of the methyl ester



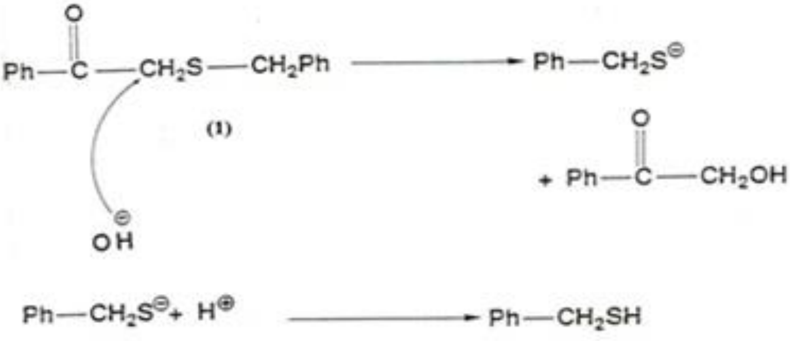
Scheme 3. Hydrodesulphurization of δ -lactone



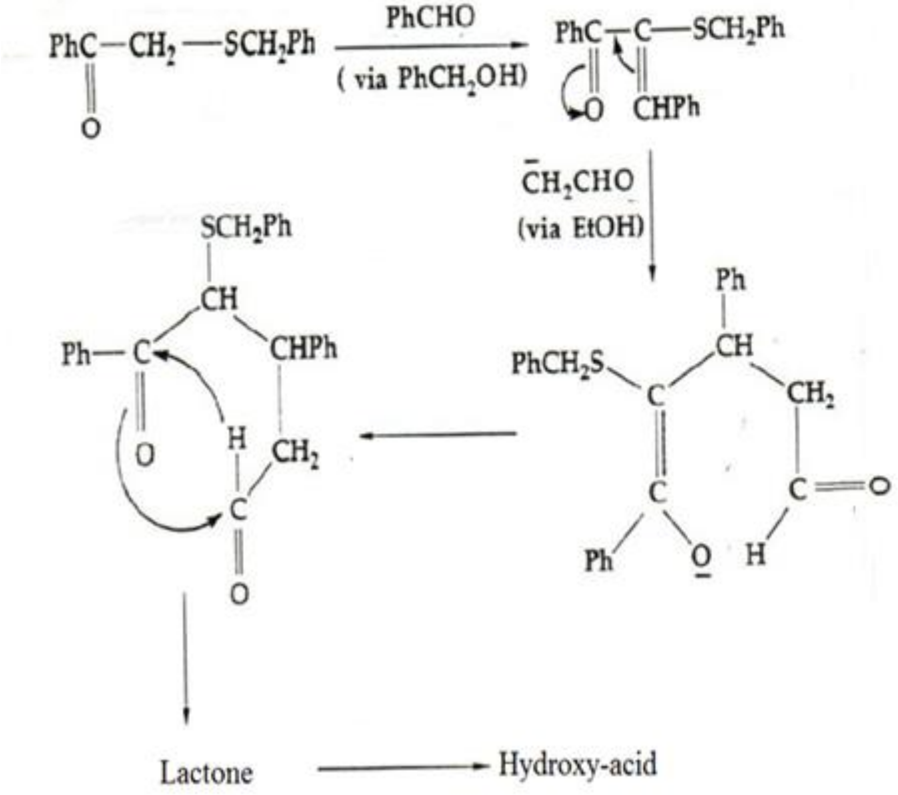
Scheme 4. Attack by the hydroxyl ion at the carbonyl group



Scheme 5. Attack by the hydroxyl ion at the sulphur atom



Scheme 6. Attack by the hydroxyl ion at the carbon atom α - to the carbonyl group



Scheme 7. Theproposed mechanism for the reaction of benzyl phenacyl sulphide with ethanolic sodium hydroxide

Conclusion

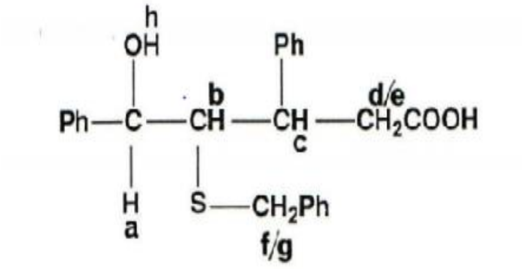
The reaction of benzyl phenacyl sulphide with ethanolic sodium hydroxide gives 4-(benzylthio)-5-hydroxy-3,5-diphenylpentanoic acid,when treated with ethereal diazomethane Methyl-4-(benzylthio)-5-hydroxy-3,5-diphenylpentanoate resulted. The structures of these compounds were elucidatedby the use of a combination of spectroscopic and chemical methods.

Acknowledgement

The authors would like to thank the goverment of Sudan (University of Khartoum) for financial support and the School of Chemistry (University of Hull) for providing the appropriate facilities for experiments and instrumental analysis.

Supplementary Material

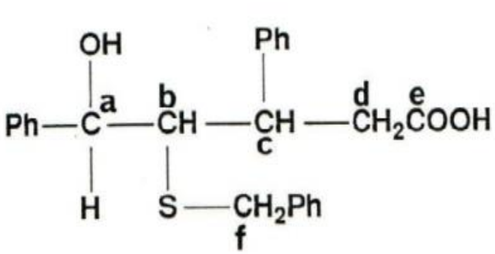
Table (1): ^{1}HNMR Spectral Data of compound (2)



$Ph-C(OH)(H)-CH(SCH_2Ph)-CH(Ph)-CH_2COOH$

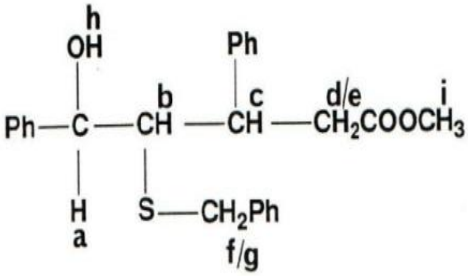
Chemical Shifts (ppm)	Relative Number of Protons	Assigment
7.40-7.00 (complex)	15	3xPh
4.64 (d)	1J(ab) =4.9H_Z	H_a
3.58-5.50(br)	1	OH_h
3.42 (d)	1J(fg) =13.0H_Z	H_f or H_g
3.35(d)	1J(fg) =13.0H_Z	H_g or H_f
3.34 (m)	1	H_c
3.13(pseudotriplet)	1J(ab) =4.9H_Z , J(bc) =4.9H_Z	H_b
2.82	2J(cd) =7.0H_Z	H_d and H_c

Table (2): ^{13}CNMR Spectral Data of compound (2)



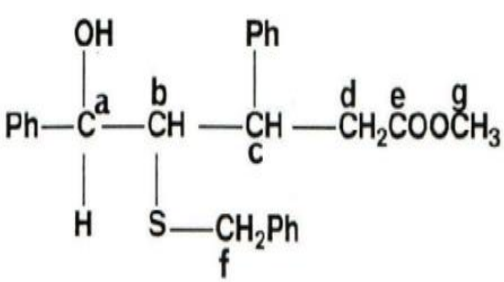
Chemical shifts (ppm)	Relative Number of Carbons	Assigment
173.99	1	C=O (ester)
142.50 , 140.88,137.50	3	Ipso carbons
128.77,128.39,128.05,127.84,127.14 ,126.65,126.47	9	0,m,p carbons
73.29	1	C_a
58.38	1	C_b
43.88	1	C_c
37.65	2	C_d and C_f

Table (3): ^{1}HNMR Spectral Data of compound (3)



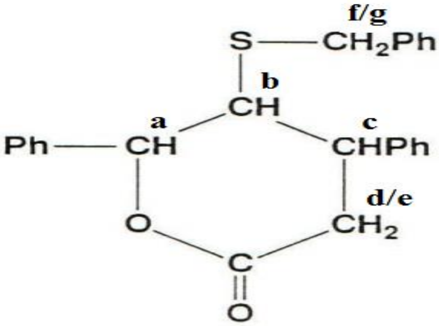
Chemical Shifts (ppm)	Relative Number of Protons	Assigment
7.42-7.09 (complex)	15	3xPh
4.56 (3.13(pseudotriplet)	1*J*(ab) =6.2H$_Z$, *J*(ah) =4.9H$_Z$	H$_a$
3.53(d)	1*J*(fg) =13.0H$_Z$	H$_f$ or H$_g$
3.47(s)	3	COOCH$_3^f$
3.37(d)	1*J*(fg) =13.0H$_Z$	H$_g$or H$_f$
3.19-3.35 (m)	2	H$_b$, H$_c$
2.88 (d)	1 *J*(ah) =4.9H$_Z$	OH^h
2.76 (dd)	1*J*(de) =17.0H$_Z$, *J*(cd) =7.0H$_Z$	H$_d$ or H$_e$
2.70(dd)	1*J*(de) =17.0H$_Z$, *J*(ce) =7.0H$_Z$	H$_e$ or H$_d$

Table (4): ^{13}CNMR Spectral Data of compound (3)



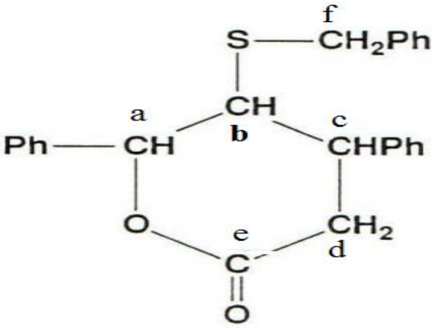
Chemical Shifts (ppm)	Relative Number of Carbons	Assigment
172.57	1	C^e =O (ester)
142.04 ,140.42 ,137.85	3	Ipso carbons
129.26,128.74.128.60 ,128.55, 128.31 ,128.01 127.27 .127 .22 ,127.16	9	o,m,p carbons
74.60	1	C_a
S8,48	1	C_b
51.60	1	C_g
43.57	1	C_c
38.38 ,38.05	1	C_d and C_f

Table (5): ^{1}HNMR Spectral Data of compound (4)



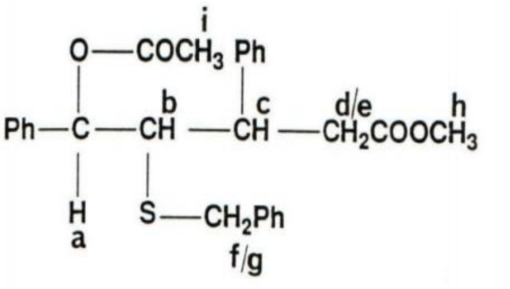
Chemical Shifts (ppm)	Relative Number of Protons	Assigment
7.37-7.18 and6.89-6.84 (complex)	15	3xPh
4.71(dd)	1*J*(ab) = 3.5Hz , J(bc) =7.0Hz	H_b
3.77(d)	1*J*(ab) =3.5Hz	H_a
3.74(d)	1 *J*(fg) =13.5Hz	H_f or H_g
3.56(d)	1*J*(cd) =3.5Hz , J(bc) =7.0Hz	H_c
3.44(d)	1*J*(fg) =13.5Hz	H_g or H_f
2.68(dd)	1*J*(de) =18.0Hz , J(cd) = 9.0Hz	H_d or H_e
2.59(dd)	1*J*(de) =18.0Hz , J(ce) = 9.0Hz	H_e or H_d

Table (6): ^{13}CNMR Spectral Data of compound (4)



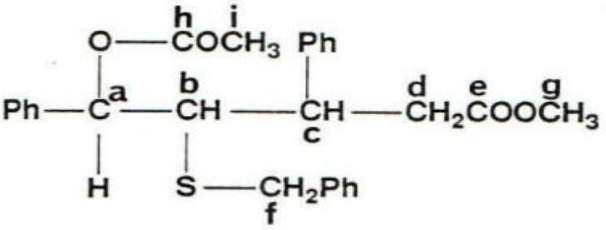
Chemical Shifts (ppm)	Relative Number of Carbons	Assigment
175.36	1	C^e = O
139.79 ,138.34 137.76	3	Ipso carbons
129.21 ,129.03 , 128.83 ,128.71 ,128.63 ,127.99,127.50 ,127.27 ,127.02	9	o,m,p carbons
89.32	1	C$_a$
51.17	1	C$_b$
44.27	1	C$_c$
36.54	1	C$_d$
36.54 and 35.21	2	C$_d$ and C$_f$

Table (7): ^{1}HNMR Spectral Data of compound (6)



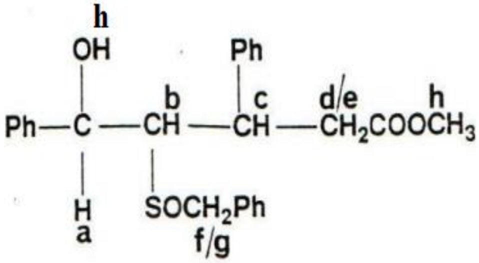
Chemical Shifts (ppm)	Relative Number of Protons	Assigment
7.40-7.09 (complex)	15	3xPh
5.79(d)	1J(ab) = 6.0Hz	H_a
3.54(d)	1	H_f or H_g
3.47 (s)	3	$COOH^h_3$(ester)
3.40(d)	1J(fg) = 13.0Hz	H_g or H_g
3.30-3.20 (m)	2	H_b or H_c
2.88(dd)	1J(de) =16.0Hz , J(cd) =7.0Hz	H_d or H_e
2.59(dd)	1J(de) =16.0Hz , J(ce) =7.0Hz	H_e or H_d
1.59(s)	3	$OCOCH^i_3$(acetoxy)

Table (8): ^{13}CNMR Spectral Data of compound (6)



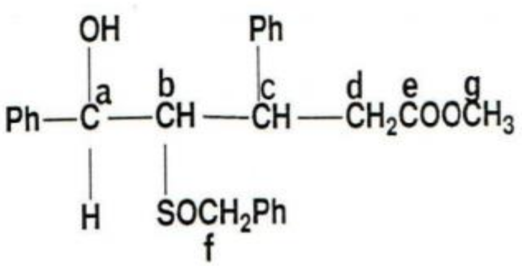
Chemical Shifts (ppm)	Relative Number of Carbons	Assigment
172.44	1	$C_e = O$ (ester)
169.71	1	OC^hOCH_3 ((acetoxy)
140.71 ,138.88 ,137.96	3	Ipso carbons
129.30 ,128.67 , 128.56 , 128.44,128 .35 ,127.27 ,127.16	9	o,m,p carbons
77.95	1	C_a
54.17	1	C_b
51.58	1	$COOC^gH_3$
43.44	1	C_c
38.40 and 37.89	2	C_d and C_f
21.13	1	$OCOC^f H_3$

Table (9): ^{1}HNMR Spectral Data of compound (7)



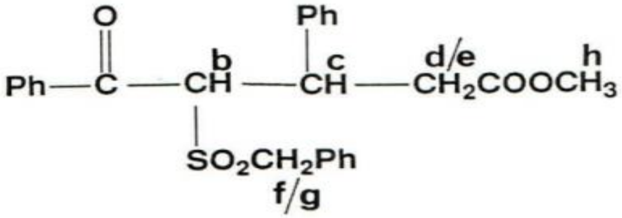
Chemical Shifts (ppm)	Relative Number of Protons	Assigment
7.50-7.20 and 7.12-7.04 (complex)	15	3xPh
5.02(d)	1*J*(ab) = 8,5Hz	H_a
4.29(d)	1*J*(fg) =12.0Hz	H_f or H_g
3.65 (dd)	1*J*(ab) =8.5Hz , *J*(bc) =4.9Hz	H_b
3.43(dt)	3	COOCH^{h}3
2.86(d)	1 *J*(ah) = 4.9H$_Z$	OH^h
2.22 (dd)	1*J*(cd) =7.5Hz , *J*(cd) = 4.9Hz	H_c
2.55(dd)	1*J*(de) =16.0Hz , *J*(cd) = 7.5Hz	H_d or H_e
2.29(dd)	1*J*(de) =16.0Hz , *J*(ce) = 7.5Hz	H_e or H_d

Table (10): ^{13}CNMR Spectral Data of compound (7)



Chemical Shifts (ppm)	Relative Number of Carbons	Assigment
171.37	1	C_e =O (ester)
130.10 ,129 .77 ,129.35,128.85 128 .71 , 128.64,128.06 .127.72	9	o,m,p carbons
140.10 ,138.57	3	Ipso carbons
74.14	1	C_a
63.83	1	C_b
59.87	1	C_g
51.69	1	C_c
40.73	1	C_f
38.32	1	C_d

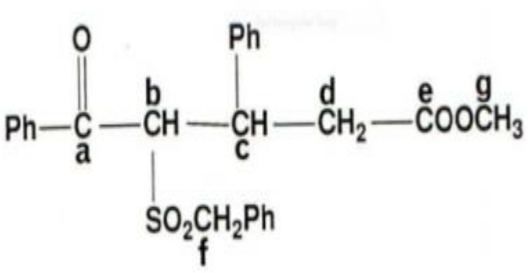
Table (11): ^{1}HNMR Spectral Data of compound (8)



$$Ph-C(=O)-CH(SO_2CH_2Ph)-CH(Ph)-CH_2COOCH_3$$

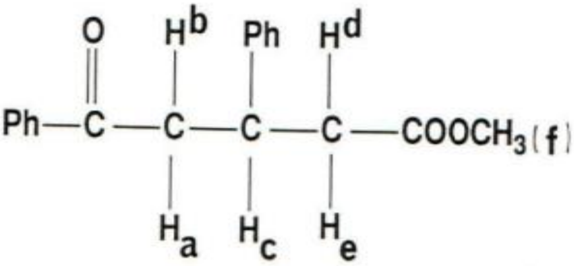
Chemical Shifts (ppm)	Number of Protons and coupling	Assigment
7.56-7.20 (complex)	15	3xPh
5.349(d)	1J(bc) = 9.0Hz	H_b
4.36 (dt)	1J(bc) = 9.0Hz , J(cd) = 5.0Hz	H_c
3.88 (dt)	1J(fg) = 14.0Hz	H_f or H_g
3.54(d)	1J(fg) = 14.0Hz	H_g or H_f
3.46 (s)	2	$COOCH^{h}_{3}$
2.89(dd)	1J(de) = 14.0Hz , J(cd) = 5.0Hz	H_d or H_e
2.759(dd)	1J(de) = 14.0Hz , J(cd) = 5.0Hz	H_e or H_d

Table (12): ^{13}CNMR Spectral Data of compound (8)



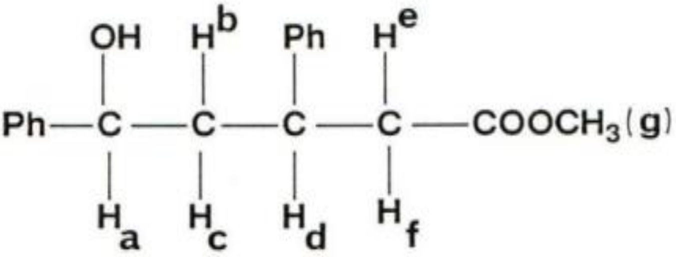
Chemical Shifts (ppm)	Relative Number of Carbons	Assigment
192.08	1	C_a= O (ketone)
192.08	1	C_a= O (ketone)
171.20	1	C_e=O(ester)
138.79,137.03,134.12	3	Ipso carbons
131.31,129.21,129.14,129.03,128.98 ,128.80 , 128.33 ,126.98	9	o,m,p carbons
69.00	1	Cb
60.21	1	$COOC^gH_3$
51.78	1	C_c
41.41	1	C_f
37.55	1	C_d

Table (13): ^{1}HNMR Spectral Data of compound (9)



Chemical shifts (ppm)	Relative number of Protons	Assigment
7.95-7.15 (c0mplex)	10	2xPh
3.84 (tt)	1/(ac)=7.0 , /(ce)=7.0	H_c
3,58 (s)	3	$COOH^f_3$
3.41(dd)	1/(ab)=12.0 , /(bc)=7.0	H_b
3.32 (dd)	1/(ab)=12.0 , /(ac)=7.0	Ha
2.84 (dd)	1/(ed)=15.0 , /(ce)=7.0	H_e
2.7(dd)	1/(ed)=15.0 , /(cd)=7.0	H_d

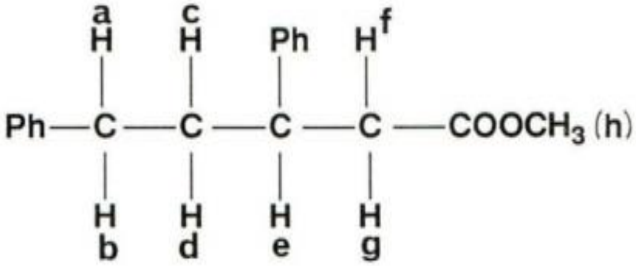
Table (14): ^{1}HNMR Spectral Data of compound (10)



$Ph{-}C(OH)(H_a){-}C(H^b)(H_c){-}C(Ph)(H_d){-}C(H^e)(H_f){-}COOCH_3(g)$

Chemical shifts (ppm)	Relative number of Protons	Assigment
7.35-7.1 (complex)	10	2xPh
4.43 (t)	1*J*(ac) =7.0	H_a
3.5(s)	3	$COOCH^{g}_{3}$
3.04 (tt)	1*J*(cd) =7.5 , *J*(fd) =7.5	H_d
2.68 (dd)	1 *J*(ef) =15 , *J*(ed) =7.5	H_e
2.58 (dd)	1*J*(ef) =15 , *J*(ed) =7.5	H_f
2.22 (dd)	1*J*(bc) =7.0 , *J*(bd) =7.0	H_b
2.1(dd)	1*J*(ac) =7.0 , *J*(ce) =7.0	H_c

Table (15): ^{1}HNMR Spectral Data of compound (11)



Chemical shifts (ppm)	Relative number of Protons	Assig ment
7.35-7.05 (complex)	10	2xPh
3.51 (s)	3	COOH $_{h}$ $_{3}$
3.2-3.06 (m)	1	H_e
2.65 (dd)	1 $J(fg)$ =7.5 , $J(ef)$ =4.0	H_f
2.57 (dd)	1 $J(fg)$ =7.5 , $J(eg)$ =4.0	H_g
.2.44 (t)	1	H_a
2.08-1.84 (m)	1	H_c and H_d

References :

Billheimer, E. C. and Reid, E. E. (1930) *The Decomposition of Mercaptans in Alkali Solutions . J. Am .Chem . Soc.*52 (11),4338-4344

Cho, B. , Choi, O. and Kim, D. (*2003*) *Facile Synthesis of Enantiopure 1,2-Diols and Terminal Epoxides from Chiral* β*-Hydroxy Sulfides . Bull. Korean Chem. Soc.* 24 (7) , 1023-1025

David , S. and Herman S. (1966) *Multi-Sulphur and Sulphur and Oxcygen Five and Six-Membered Hetrocycles.part 1.,Interscience Publisher,a divison of John Wiely and Sons.New york., 402*

Heilbron, I. , Cook, A. , Bunbury, H. and Hey, D. (1965) *Dictionary of Organic Compounds,* Eyre and Spottiswoode, London,4th edn., Vol.1 , 12.

Iskander,Y. (1948) *The Anionic Nature of Desyl and the* α *- Benzoylbenzhydryl Radical as compared with the Cationoid Reactivity of the Triphenyylmethyl* Radical ; *The Hydrolysis of Thioester . J.Chem . Soc.* 1549-1551

Iskander,Y .and Tewfik, R. (1961) *The Structural Factors Leading to either Carbanion-Sulphenium Fission or Benzoyl Elimination in (*α *- Benzoylmethylthio)acetic Acids by the Action of Alkalis . J.Chem . Soc.*2393-.2397

Harwood, L.M. and Claridge ,T.D.W (1996) *Introduction toOrganic Spectroscopy .* Oxford University Press,Oxford. UK

Hauptmann, H. and Walter .W.(1962) the Action of Raney Nickel on Organic Sulphur Compounds . *Chem. Rev.*,62, 351- 355

Mogan, K. J.(1959) *The Action of Alkali on o-nitrophenyl phenacyl Sulphide* ; *J.Chem . Soc.* 3502-3707

Mohammad, S.T. Makk , R M. Abdel-Rahman , Abdulrahman S. A,*(2019). Synthetic Strategies, Chemical Reactivities and Biological Activities of 3-Thioxo-1,2,4-triazin-5-ones and Their Derivatives .Mini-Reviews in Organic Chemistry , 16, 308-322*

Nicolet, B. (1931) *The Mechanism of Sulphur Liability in Cysteine and its Derivatives.1 Some Thioethers Readily Split by Alkali . J. Am .Chem . Soc.,53,3066.*

Pavia, D. , Lampman, G., and Kris, G. (2001) . *Introduction to Spectroscopy,* ThomsonLearning .U.S.A.

Petti, G. , Tamelen .V , and Eugene, E. (1962) Desulphurization with Raney Nickel . *Org. React. (NY)*12,356

RamaiyanVenkatesan , Shanmuga Muthususubramanian ,perumalYogeeswari , Dharmarajan Sriram (*2010*). *Bioorganic & Medicinal Chemistry Letters ; 20 , (23) ,6920-6924*

Silverstein, R.and Webster, F. (1998) *Spectroscopic Identification of Organic Compounds*. 6th edn . John Wiley &Sons , Inc., New York.

Tarbell, D. and Harnish, D. (1951) *Cleavage of Carbon-Sulphur Bond in DivalentSulphur Compounds . Chem. Rev.* 49(1), 31-45

Teich,S. and Curtin , D.Y . (1950) *The Alkaline Claevage of Desyl Thioether . J. Am.Chem . Soc.* 72 , 2481-2483