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Reactions of 2-Phenylthio-2-Cycloalkenones and 2-[Phenyl(thiomethyl)]- 2-Cycloalkenones:[1] Synthesis of Some Useful Chiral and Achiral Intermediates

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Abstract: *The allyl acetates derived from 2-phenylthio-2-cyclopentenone, 2-phenylthio-2-cyclohexenone, 2-phenylthio-(methyl)]-2-cyclopentenone and 2-[phenylthio(methyl)]-2-cyclohexenone have been hydrolysed by pig liver acetone powder to obtain the corresponding alcohols in optically pure form. Palladium catalysed alkylations with diethyl malonate have been found to take place with the allyl acetates having a vinyl sulfide moiety whereas 2-phenylthio-2-cyclopentenone and 2-[phenylthio(methyl)]-2-cyclohexenone are transformed into some highly functionalised sulfur containing intermediates.*

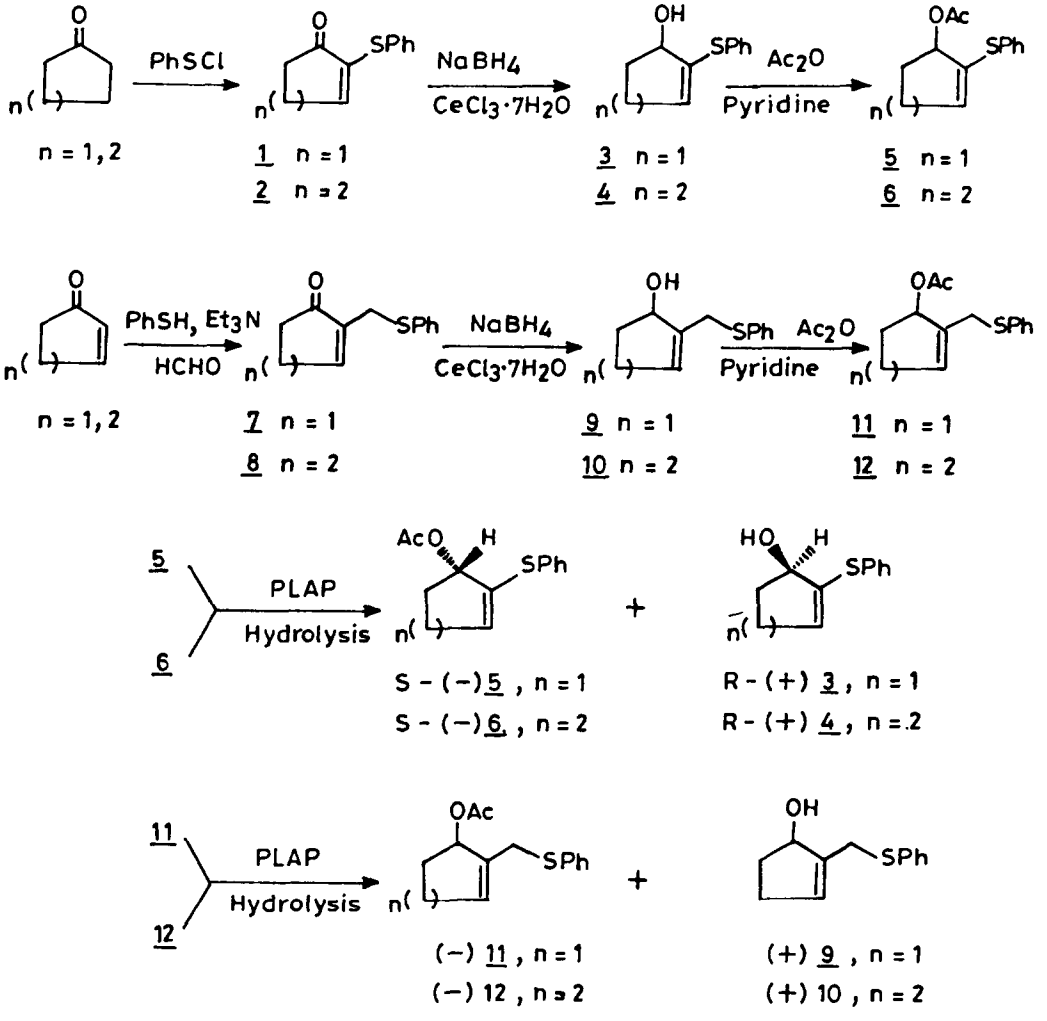
Vinyl[2]and allyl[3]sulfide derivatives are useful compounds in organic synthesis.In these molecules the rich chemistry offered by sulfur is further increased by the presence of a double bond and in the literature[4] exploration of this chemistry in the synthesis of useful compounds is well documented.

In this paper we wish to report chemistry of a few allylic and vinylic sulfide containing synthons in synthesising some useful chiral and achiral intermediates.For the synthesis of chiral compounds the process of enzymatic resolution using pig liver acetone powder (PLAP)[5] has been employed. Vinyl sulfide derivatives 5 and 6 chosen for this study (Scheme 1) are derived from cyclopentanone and cyclohexanone respectively.Thus,treatment[6] of cyclopentanone with benzenesulfenyl chloride gave 2-phenylthio-2-cyclopentenone 1 in 60% yield.Likewise, compound 2 was obtained in 62% yield.Reduction of 1 and 2 with $NaBH_4/CeCl_3.7H_2O$[7] in methanol gave the corresponding allyl alcohols 3 and 4 which were acetylated to obtain 5 and 6 in 92% and 95% yields respectively.On the other hand,the allylic sulfide derivatives 11 and 12 are derived

from cyclopentenone and cyclohexenone respectively.

Treatment[8] of cyclopentenone with thiophenol,formaldehyde and triethylamine gave 2-[phenylthio(methyl)]-2-cyclopentenone whose reduction with $NaBH_4/CeCl_3.7H_2O$ followed by acetylation led to the required precursor **11**.Cyclohexenone was converted into **12** in analogous manner.

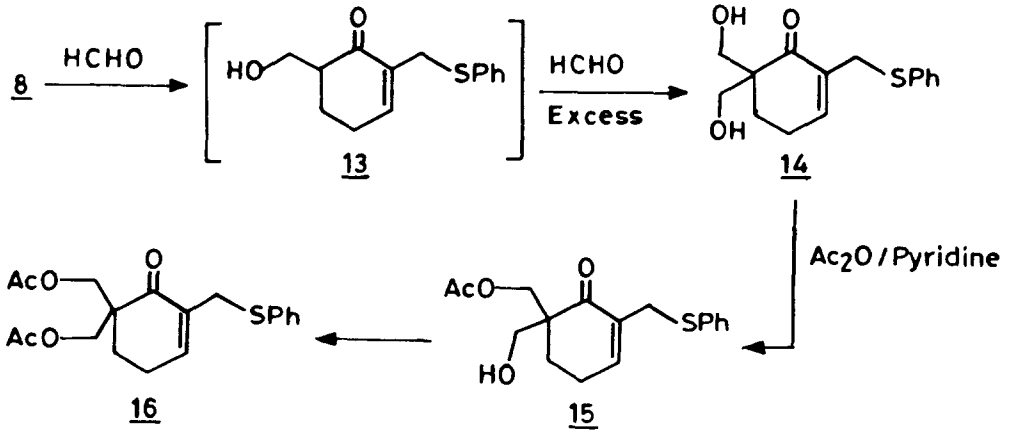
These vinylic sulfide derivatives **5** and **6** and allylic sulfide derivatives **11** and **12** were then subjected to enzymatic resolution studies with freshly prepared PLAP under standard reaction conditions



Scheme 1

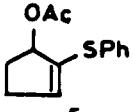
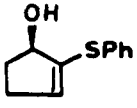
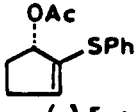
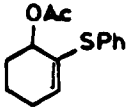
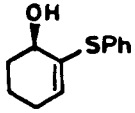
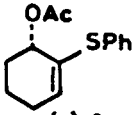
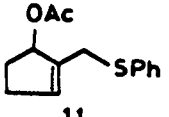
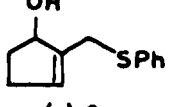
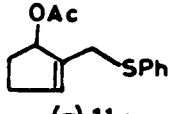
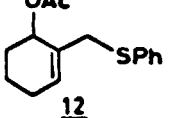
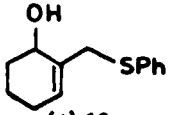
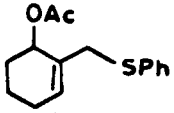
(cf. experimental part). Results of this study are summarised in Table 1. It is clear from the results that the resolved alcohols 3 and 4 from vinylic sulfides show higher optical purity than the ones viz. 9 and 10 derived from allylic sulfides. It is probable that farther the -SPh group goes from the asymmetric centre its influence on the enzymatic resolution decreases. These resolved alcohols (or the corresponding acetates), however, did not yield any clean product when treated with Raney'Ni' to effect desulfurisation so that the absolute configuration of these compounds could not be established. The assignment of absolute configuration to compounds 3, 4, 5 and 6 is on the basis of literature[9] comparison[10]. Work to determine the absolute configurations of compounds 9, 10, 11 and 12 via alternate routes is being carried out.

During the preparation of compound 8, as per the literature procedure, a small amount of a very polar compound was observed to form. If a large excess of formaldehyde was used, this polar compound 14 was obtained as the main product which was charaterised as an acetate 15 after its acetylation under standard conditions. Further acetylation of 15, however, was found to be sluggish at room temperature and at higher temperatures the reaction was not clean. It is clear that under slightly basic conditions and in the presence of excess of HCHO double hydroxymethylation took place with both the reactive methylene hydrogens (cf. Scheme 2).

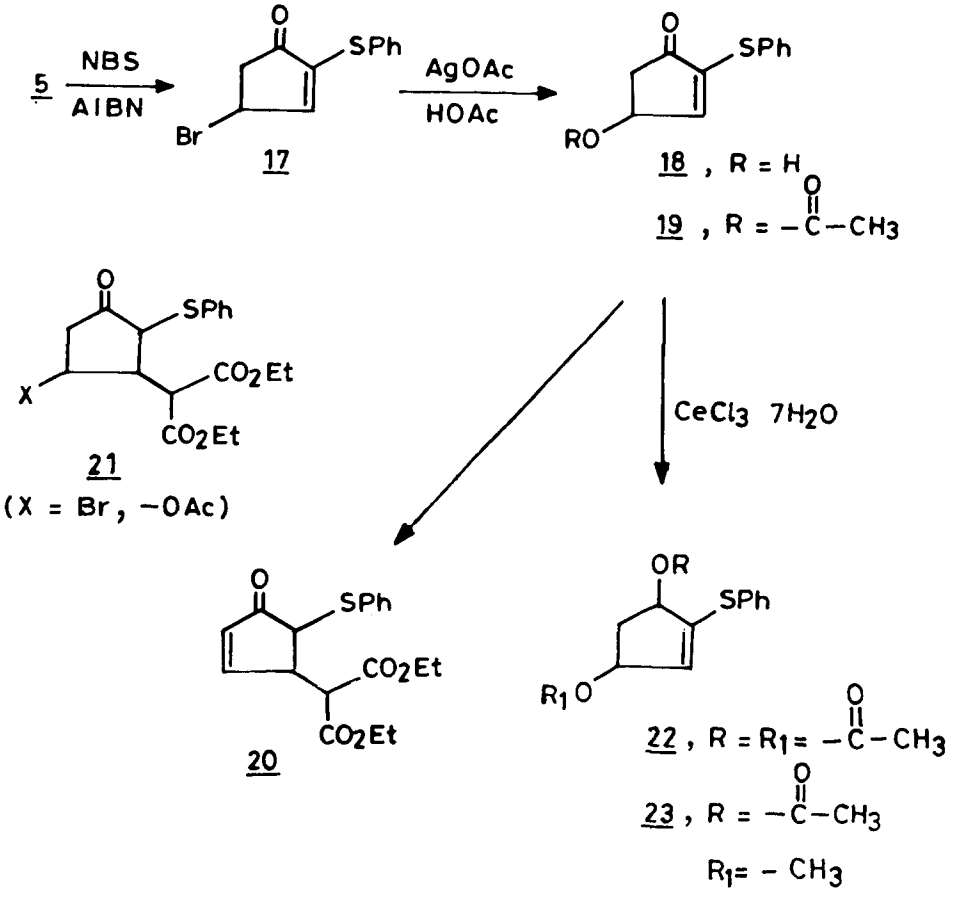


Scheme 2

Table -1
PLAP Catalysed Hydrolysis

Entry	(±) Acetate	Chiral Allylic Alcohol			Chiral Allylic Acetate		
		Compound (% yield)	$[\alpha]_D^{25}$	e.e.	Compound (% yield)	$[\alpha]_D^{25}$	e.e.
1	 5	 (+) 3 (26)	(+) 46.279 (C1, $CHCl_3$)	70%	 (-) 5 (54)	(-) 17.475 (C1, $CHCl_3$)	53%
2	 6	 (+) 4 (39)	(+) 93.750 (C1, $CHCl_3$)	81%	 (-) 6 (55)	(-) 58.733 (C1, $CHCl_3$)	34%
3	 11	 (+) 9 (17)	(+) 18.226 (C1, $CHCl_3$)	34%	 (-) 11 (50)	(-) 8.428 (C1, $CHCl_3$)	30%
4	 12	 (+) 10 (40)	(+) 26.017 (C1, $CHCl_3$)	62%	 (-) 12 (44)	(-) 15.019 (C1, $CHCl_3$)	40%

Further exploration of the potential of these highly functionalised sulfur containing compounds involved treatment[11] of 1 with N-bromosuccinimide in the presence of AIBN at 80°C followed by solvolysis with AgOAc/AcOH to form 19 which readily reacted with the sodium salt of diethyl malonate in 1,2-dimethoxyethane at 25°C to give compound 20 (Scheme 3) instead of a simple Michael adduct 21.This was,however ,not surprising as literature precedent[12] does exist for such type of addition-elimination reactions.Unfortunately both the compounds viz. 19

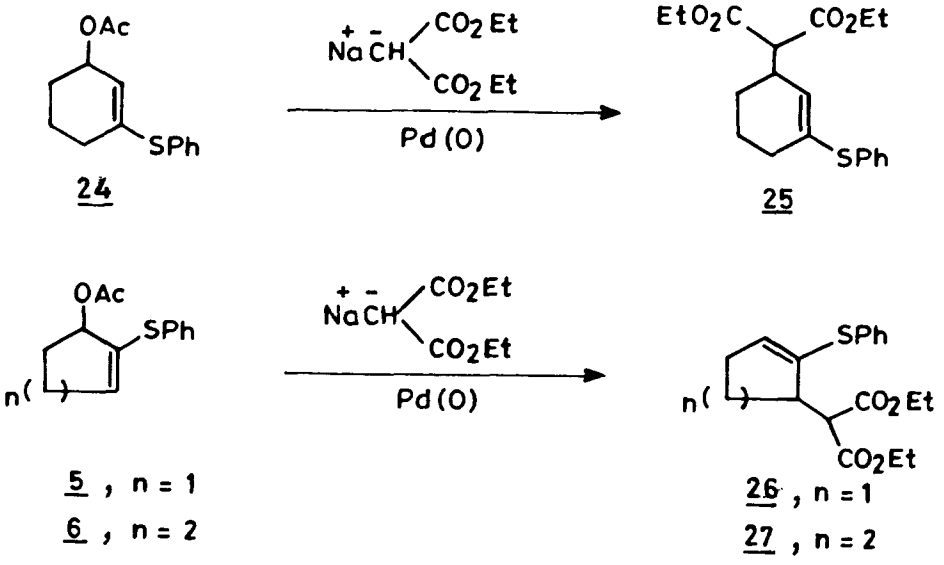


Scheme 3

and 20 did not undergo clean hydrolysis with PLAP.It appears that all those allyl acetates and diesters, at least under present studies,which possess an enone moiety are not suitable substrates for hydrolysis with PLAP.

In an attempt to convert compound **19** into the diacetate **22**, which could be subjected for PLAP hydrolytic studies,its reduction with $NaBH_4/CeCl_3.7H_2O$ in methanol followed by acetylation was attempted.However,surprisingly, it gave compound **23**, presumably through solvent (methanol) participation. Since the diacetate **22** could not be obtained in this manner ,further studies on PLAP hydrolysis were not carried out.

Godelski et al[13]have reported that 3-phenylthio-1-acetoxycyclohexene **24** smoothly undergoes palladium catalysed alkylation to give **25** (Scheme 4) a derivative of which has been further used in the synthesis of an indole alkaloid, alloyohimbone.This reaction and a few others[14] clearly suggest that the metal is not poisoned by sulfur.The vinyl sulfide group can be transformed into a carbonyl group which can be further elaborated.Such palladium catalysed alkylations were attempted,in our study,on **5** and **6** which are analogues of **24**.The reactions proceeded smoothly in DMSO to yield **26** and **27** from **5** and **6** in 66% and 73% yields respectively.



Scheme 4

This indicates that irrespective of the position of the -SPh group these Pd catalysed reactions proceed easily. We are currently exploring the utility of these sulfur containing synthons in the synthesis of useful natural products.

EXPERIMENTAL:

General

^{1}H NMR spectra were recorded on Jeol PMX 60, Bruker WP 80 and Bruker WM 400 spectrometers with Me_4Si as internal standard. IR spectra were recorded on Perkin-Elmer 1320 spectrophotometer. Mass spectra were recorded at 70 ev on a Jeol MS-300 D mass spectrometer.Elemental analysis were carried out using Coleman automatic analyser.Optical rotations were recorded using Autopol II Rudolph polarimeter.

AIBN and NBS were recystallised from aqueous ethanol (85%) and water respectively prior to use. Cyclopentenone and cyclohexenone were prepared as per the literature procedure[15].

2-Phenylthio-2-cycloalkenones 1 and 2

Compound 1 was prepared according to a literature procedure[6]. The same procedure was also adopted to obtain 2 from cyclohexenone (490 mg, 5 mmol) and benzenesulfenyl chloride (2.2 g,15.3 mmol) in 58% yield (600 mg).

Compound 2:IR(neat):1670 cm^{-1};^{1}H NMR(CCl_4):δ 7.36-7.03 (5H,m,aromatic), 6.18 (1H,t,vinylic), 2.5-1.94 (6H, m,methylenes); Mass spectrum (m/z): 204(M^+).

Reduction of 1 and 2 followed by acetylation

2-Phenylthio-2-cycloalkenone (1.5 mmol) and $CeCl_3.7H_2O$ (582 mg, 1.56 mmol) were dissolved in methanol (5 ml) and sodium borohydride (60 mg,1.56 mmol) was added in one portion at 0^0C.After 10 min.of stirring methanol was removed under vacuum and the residue treated with satd.aq. NH_4Cl (3 ml),extracted with ether (25 ml) and it was followed by standard work up.The crude hydroxy compound was then immediately acetylated using acetic anhydride (1.6 mmol) and dry pyridine (1.56 mmol) in dry CH_2Cl_2 at room temperature.The reaction mixture was stirred for 5 hr followed by usual work up with ether.Purification of the crude acetate by column chromatography [eluent,pet.ether:ethyl acetate(95:5)] gave pure acetate.

1-Acetoxy-2-phenylthio-2-cyclopentene 5

Yield: 92% ;IR(neat): 1725cm^{-1};^{1}H NMR(CCl_4): δ 7.77-7.0 (5H,m,aromatic) 5.9-5.73 (1H,t,J = 3 Hz,olefinic), 5.73-5.33(1H,m, methine),2.7-1.7(4H, m,methylenes),1.87 (3H,s,-$OCOCH_3$); Mass spectrum: m/z 235(M+1)$^+$,174(M^+-CH_3COOH). Anal. Calcd. for $C_{13}H_{14}O_2S$: C,66.67; H,5.98; S,13.67. Found: C,66.08; H,5.53; S,13.98.

1-Acetoxy-2-phenylthio-2-cyclohexene 6

Yield 95% ;IR(neat):1720 cm^{-1}; ^1H NMR(CCl_4) δ 7.27 (5H,m,aromatic),6.21 (1H,t,J=3Hz,olefinic),5.15 (1H,br s,methine),2.2-1.5 (6H,m,methylenes), 1.8 (3H,s,-$OCOCH_3$).Mass spectrum: m/z 248(M^+),188 (M^+-CH_3COOH). Anal. Calcd. for $C_{14}H_{16}O_2S$: C,67.74;H,6.45; S,12.90. Found: C,67.01; H,6.92; S,12.21.

Reduction of 7 and 8 followed by acetylation

An analogous procedure as followed for 1 and 2 (vide supra) was adopted for 7 and 8.

1-Acetoxy-2[(phenylthio)methyl]cyclopent-2-ene 11

yield 78% ; IR(neat):1570 ,1720 cm^{-1}; ^1H NMR (CCl_4): δ 7.3- 6.93 (5H,m, aromatic), 5.87-5.5 (2H,m, methine and vinylic), 3.5 (2H,d,J=3 Hz,-CH_2-SPh), 2.5-1.3 (4H,m, methylenes), 1.93 (3H,s,-$OCOCH_3$);Mass spectrum:m/z 248 (M^+), 249 $(M+1)^+$,189 [$(M+1)^+$-CH_3COOH]; Anal. Calcd.for $C_{14}H_{16}O_2S$:C, 67.74; H,6.45; S,12.90. Found: C,67.21; H,5.98; S,12.16.

1-Acetoxy-2[(phenylthio)methyl]cyclohex-2-ene 12

Yield 95% ;IR(neat):1570 ,1710 cm^{-1}; ^1H NMR(CCl_4):δ 7.33-6.97 (5H,br s, aromatic), 5.77-5.53 (1H,br t,olefinic), 5.47-5.17 (1H,m,methine),3.37, 2H, s, -CH_2SPh), 2.1-1.47 (6H, m,methylenes), 1.92 (3H,s,-$OCOCH_3$) Mass spectrum : m/z 262 (M^+), 263 $(M+1)^+$ 202 (M^+ - CH_3COOH). Anal.Calcd. for $C_{15}H_{18}O_2S$: C, 68.70; H,6.87; S,12.21. Found: 69.03; H,6.91; S,12.08.

General Procedure for PLAP hydrolysis of 5, 6, 11 and 12

The pig liver acetone powder (PLAP) was freshly prepared by following a procedure reported by Ohno et al[5(i)].

To 0.5 M ,pH 8.0 KH_2PO_4 / K_2HPO_4 buffer (20 ml),racemic acetate (500 mg) dissolved in ether (10 ml) was added with stirring at 10-15^{0}C. To this mixture was added PLAP (600 mg) and stirring continued.Progress of the hydrolysis was followed by thin layer chromatography and when an appropriate degree of hydrolysis took place the reaction was quenched with 2N HCl (5 ml) so that the pH of the reaction mixture was 6.5. Sodium chloride and ethyl acetate were added to the reaction mixture and the resulting suspension was vigorously stirred for 0.5 hr.The enzyme was filtered and the layers separated.Usual work up thereafter gave a crude product whose purification by column chromatography [eluent, 6: 94,ethyl acetate:pet.ether)] gave optically active alcohol and enantiomerically enriched unhydrolysed acetate.

(+) 2-Phenylthiocyclopent-2-ene-1-ol 3

Yield:110 mg (26%); IR (neat):1580,1600,3540 cm^{-1}; ^1H NMR(CCl_4):δ 7.4-7.06 (5H,m,aromatic),5.7 (1H,br t,olefinic), 4.59-4.32 (1H,br m,-CHOH), 2.9-1.66 (5H,m,-OH and methylenes); $[\alpha]_D^{25}$: +46.279 (C1, $CHCl_3$).e/e: 70% determined through ^1H NMR (400 MHz) analysis of its Mosher's ester.

(+) 2-Phenylthiocyclohex-2-ene-1-ol 4

Yield:(166 mg) (39%);IR(neat):1580,1620,3560 cm^{-1}; ^1H NMR(CCl_4):δ 7.29-6.95 (5H,m,aromatic),6.03 (1H,t,J= 6Hz,olefinic),3.85 (1H,br s,-CHOH), 2.5-1.3 (7H,m,-OH and methylenes);$[\alpha]_D^{25}$:+ 93.750(C1,$CHCl_3$).e/e:81% determined through ^1H NMR analysis of its Mosher's ester.

(-) 1-Acetoxy-2-phenylthio-2-cyclopentene 5

Yield:270 mg (54%) $[\alpha]_D^{25}$:-17.475 (C1,$CHCl_3$).e/e:53% [determined through $Eu(hfc)_3$ based ^1H NMR analysis].

(-) 1-Acetoxy-2-phenylthio-2-cyclohexene 6

Yield: 273 mg (55%);$[\alpha]_D^{25}$:-58.733 (C1,$CHCl_3$).e/e:34% [determined through $Eu(hfc)_3$ based ^1H NMR analysis].

2-[Phenylthio(methyl)]-2-cyclopentene-1-ol 9

Yield: 69 mg (17%);IR (neat):1575,1610, 3550 cm^{-1}; ^1H NMR (CCl_4):δ 7.3-6.97 (5H,m,aromatic),5.51 (1H,br s,olefinic),4.95-4.85 (1H,m,-CHOH), 3.52 (2H,br s,-CH_2SPh),2.6-1.5 (5H,m,-OH and methylenes);$[\alpha]_D^{25}$:+18.226 (C1, $CHCl_3$).e/e: 34%[determined through ^1H NMR analysis of its Mosher's ester].

2-[Phenylthio(methyl)]-2-cyclohxene-1-ol 10

Yield:166 mg (40%);IR(neat):1580,1615,3560 cm^{-1};^1H NMR (CCl_4):δ 7.25-6.9 (5H,m,aromatic),5.35 (1H,s,olefinic),4.15 (1H,br s,-CHOH),3.39 (2H, br s,-CH_2-SPh),2.3-1.3 (7H,m,-OH and methylenes); $[\alpha]_D^{25}$: +26.017 (C1,$CHCl_3$). e/e:62% [determined through ^1H NMR analysis of its Mosher's ester].

1-Acetoxy-2-[phenylthio(methyl)]-2-cyclopent-1-ene 11

Yield:240 mg (50%) $[\alpha]_D^{25}$:-8.428(C1,$CHCl_3$); e/e 30% [determined through $Eu(hfc)_3$ based ^1H NMR analysis].

1-Acetoxy-2-[phenylthio(methyl)]-2-cyclohex-1-ene 12

Yield:220 mg (44%) $[\alpha]_D^{25}$:-15.019(C1,$CHCl_3$); e/e 40% [determined through $Eu(hfc)_3$ based ^1H NMR analysis].

6-Acetoxymethyl-6-hydroxymethyl-2-phenylthiomethyl-2-cyclohexene-1-one 15

While adopting the procedure for the preparation of compound 2 excess of formaldehyde was added and refluxing continued for additional 24 hr. Usual work up gave a crude product which was acetylated using pyridine, acetic anhydride and 4-dimethylamino pyridine to obtain 15 in 52% yield.IR(neat):1570,1720 cm^{-1}; ^1H NMR(CCl_4):δ 7.4-6.83 (5H,m,aromatic), 6.6(1H ,br t,olefinic), 4.17(2H,s,-CH_2OAc), 3.6(2H,s,-CH_2SPh), 3.13 (2H,s,-CH_2OH), 2.5-1.83 (5H, m, -OH, and methylenes), 1.93 (3H, s, -$OCOCH_3$); Mass spectrum: m/z 320 (M^+).

Preparation of 4-acetoxy-2-phenylthiocyclopent-2-ene-1-one 19

A mixture of compound 5 (1g,5.2 mmol),NBS (1.125g,6.3 mmol) and AIBN (100 mg) were taken in CCl_4 (10 ml) and the reaction mixture was refluxed for 2.5 hr.It was then cooled in freezer for 0.5 hr.The solid residue was filtered and washed thoroughly with cold CCl_4 (10 ml) and the filtrate was worked up in the usual manner to obtain a crude product after removing CCl_4 under vacuum below 45°C.This crude product was then treated with acetic acid (17 ml) and silver acetate (0.97g, 5.8 mmol) and the mixture stirred at room temperature for 12 hr. Precipitated AgBr was filtered and acetic acid removed under reduced pressure. Purification of the crude product by column chromatography(eluent,pet. ether :ethyl acetate:92,8) gave 767 mg of pure 19.Yield :59%.IR (neat): 1720,1740 cm^{-1}; ^1H NMR (CCl_4):δ 7.32 (5H,m,aromatic),6.27 (1H,d,J=3Hz, olefinic), 5.5 (1H,m,-CHOAc),2.9 (1H,dd,J = 9Hz,16 Hz,one of the methylene hydrogens),2.26 (1H,dd,J=3 Hz,16 Hz,the other methylene hydrogen), 1.93 (3H, s,-$OCOCH_3$); Mass spectrum:m/z: 248 (M^+),206 (M^+-CH_2=C=O),189 (M^+-CH_3COOH).Anal.Calcd.for $C_{13}H_{12}O_3S$: C,62.90; H,4.84; S,12.90. Found: C,63.43; H,4.38; S,13.61.

Preparation of 3-(α,α'-dicarbethoxy methyl)-2-phenylthio-cyclopent-4-enone 20

To a mixture of diethyl potassiomalonate [prepared from diethyl malonate (203 mg,1.27 mmol and potassium t-butoxide (142 mg,1.27 mmol)] in dimethoxymethane (8 ml) was added compound 19 (315 mg,1.27 mmol).The resultant mixture was stirred at room temperature for 10 hr.Addition of

water followed by extraction with ether (3 x15 ml) gave a crude product which was purified by column chromatography [eluent, benzene].Yield:240 mg (54%).IR (neat):1730 cm^{-1};^1H NMR (CCl_4):δ 7.67-6.6(6H,m,aromatic and β vinylic),6.07 (1H, dd, J= 2 Hz,6 Hz, α-vinylic),4.13(4H, q,J=7 Hz,2x $-OCH_2CH_3$),3.6-3.13(3H,m,methines),1.23 (6H,t,J=7 Hz) Mass spectrum: m/z 348 (M^+),274 ($M^+-C_2H_5COOH$),188 [$M^+-CH_2(COOC_2H_5)_2$]. Anal.Calcd. for $C_{18}H_{20}SO_5$: C, 62.05;H;5.75.Found:C,62.12; H, 5.80.

Synthesis of 1-acetoxy-4-methoxy-2-phenylthiocyclopent-2-ene 23

Compound 23 was prepared by reduction of 19 followed by acetylation.The procedure adopted was similar to the one used for the preparation of compounds 5 and 6.Yield of 29 (30%).IR (neat):1720 cm^{-1}; ^1H NMR (CCl_4):δ 7.6-7.1(5H,m,aromatic),5.73-5.2 [2H,m,-CH(OAc),olefinic], 4.47-4.1(1H,m,-$CHOCH_3$),3.13 (3H,s,-OCH_3),3.0-1.75(2H,m,methylene), 1.93 (3H,s,-$OCOCH_3$).Mass spectrum :m/z 264 (M^+).

Preparation of 3-(α,α'-dicarbethoxy methyl)-2-phenylthiocyclopentene 26 and 3-(α,α'-dicarbethoxy methyl)-2-phenylthiocyclohexene 27

1-Acetoxy-2-phenylthiocyclopent-2-ene 5 (234 mg,1 mmol) in DMSO (0.5 ml) was added to a mixture of diethyl sodiomalonate [prepared from diethylmalonate (560 mg,3.5 mmol) and NaH (175 mg, 3.5 mmol)],triphenyl phosphine (78 mg,0.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (12 mg, 0.01 mmol) in DMSO (5 ml) at room temperature under ntrogen atmosphere.The reaction mixture was stirred for additional 30 hr at the same temperature.Addition of water (5 ml) followed by extraction with ether (3 x 15 ml) gave a crude product.Purification by column chromatography [eluent,pet.ether:ether(80:20)] gave pure 26.Yield 220 mg (66%). IR (neat):1730 cm^{-1};^1H NMR (CCl_4):δ 7.1(5H,m,aromatic),5.6 (1H,m,olefinic),4.03 (4H, q,J=7 Hz,2x-$COOCH_2CH_3$),3.53 [1H, d,J=5Hz,-CH($COOC_2H_5$)$_2$], 3.43-3.0 (1H, m,allylic methine),2.43-1.5 (4H, m,methylenes),1.2(6H,t, J=7Hz,-$COOCH_2CH_3$);Mass spectrum:m/z 334 (M^+),261 ($M^+-C_2H_5COOH$),225($M^+-C_6H_5$) Anal.Calcd.for$C_{18}H_{22}SO_4$:C,64.67;H,6.59. Found:C,64.75;H,6.52%.

1-Acetoxy-2-phenylthiocyclohex-2-ene was reacted with sodio diethyl malonate in the presence of Pd(0) in an analogous manner as above and 3-α,α'-(dicarbethoxymethyl)-2-phenylthiocyclohexene 27 was obtained in 73% yield whose spectral and analytical data are as follows:IR (neat): 1730 cm^{-1};^1H NMR ($CDCl_3$):δ 7.16 (5H,m,aromatic),6.23 (1H,m,olefinic), 4.13 (4H, q, J =7 Hz,2x-OCH_2CH_3),3.9 [1H,d,J=5 Hz,CH($COOC_2H_5$)], 3.2- 2.7 (1H,m,allylic methine),1.96-1.4 (6H,m, methylenes),1.23 (6H,t, J=7 Hz, 2x-OCH_2CH_3). Mass spectrum: m/z 348 (M^+), 239 ($M^+-SC_6H_5$). Anal. Calcd.for $C_{19}H_{24}SO_4$: C,65.52; H,6.90. Found:C,65.70;H,6.87%.

References and Notes:

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