Pergamon

Tetrahedron 54 (1998) 531–540

TETRAHEDRON

Lewis Acid Induced Tandem Carbocationic Ring Opening and Cyclizations of α-[Bis(methylthio)methylene]ethyl-2-styrylcyclopropyl Ketones and Carbinols: Novel Approach to Bicyclo[3.3.0]octene and Cyclopent[a]indene Frameworks

Pranab K. Patra,[a] V. Sriram,[b] H. Ila*[a] and H. Junjappa*[b]

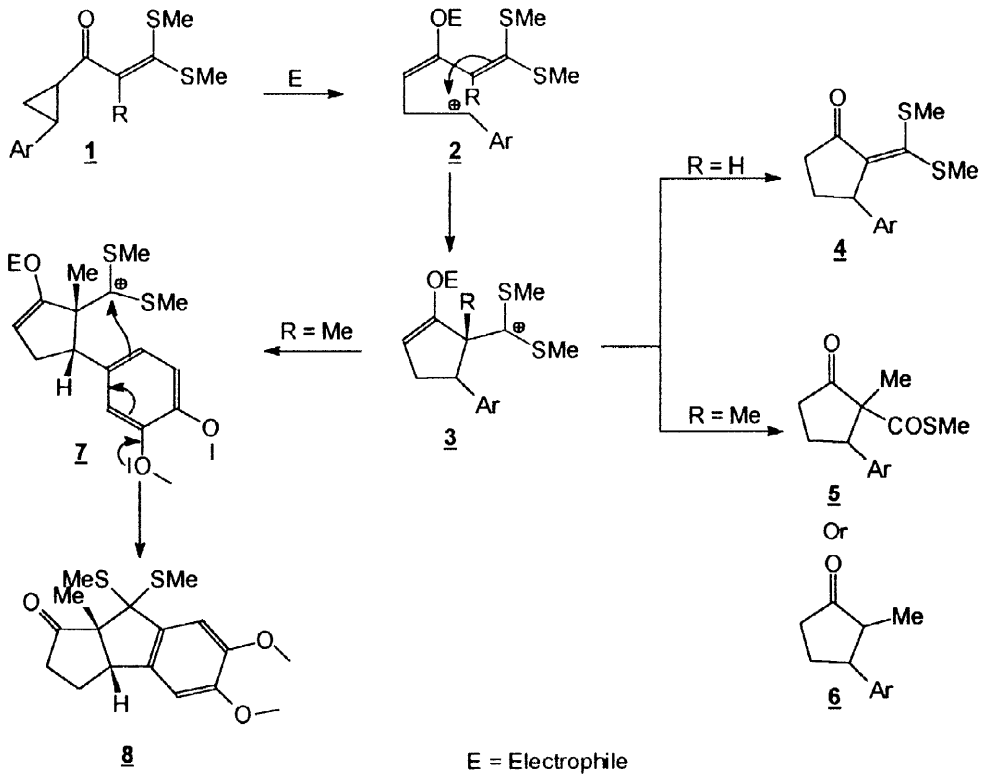
[a]Department of Chemistry, Indian Institute of Technology, Kanpur-208 016, U.P., India.
[b]Department of Chemistry, North-Eastern Hill University, Shillong-793 003, Meghalaya, India.

Received 16 July 1997; revised 4 November 1997; accepted 6 November 1997

Abstract: α-[Bis(methylthio)methylene]ethyl-2-styrylcyclopropyl ketones **12a-d** and the corresponding carbinols **19a-c** have been examined under $SnCl_4$ induced ring opening and tandem carbocationic cyclizations to afford bicyclo[3.3.0]octene and cyclopent[a]indene derivatives in highly stereoselective manner.

As a part of our ongoing programme on α-oxoketenedithioacetals,[1] we have reported that the cyclopropyl ketones[2] of general formula **1** (Scheme 1) undergo a facile acid assisted rearrangement to afford either ketenedithioacetal **4** (R = H), carboxythioate **5** or the cyclopentanone **6** (R = Me) depending on the reaction conditions and nature of the substituents. Interestingly when the aryl ring was oxygenated, the cations **7** (Scheme 1) and **10** (Scheme 2) are intramolecularly trapped by the aryl ring to afford the corresponding cyclopent[a]indenes **8** (Scheme 1) and **11** (Scheme 2) involving novel tandem carbocationic cyclization.[3] The 11-oxosteroids were similarly prepared following the described protocol.[4] In an another set of experiments the carbinols obtained either by 1,2-reduction ($NaBH_4$) or by addition of alkyl Grignard reagents, were shown to afford the corresponding cyclopentenes or open chain polyenes depending on the nature of substituents and reaction conditions.[2c] Thus this reactivity pattern has been successfully exploited for their use as excellent cationic cyclization initiators as well as terminators providing an effective method for the formation of five membered rings.[5] Although there are several examples of polyolefinic cationic cyclizations[7] promoting the formation of two or more six membered rings,[6] the similar examples for the construction of two or more fused five membered rings[8] in one step are rare in the literature. Thus, we became interested to examine the behaviour of styryl cyclopropyl ketones **12a-d** and the corresponding carbinols **19a-c** under acidic conditions in polar medium. The cyclopropyl ketones **12** are expected to follow tandem two step reaction sequence to afford the corresponding bicyclo[3.3.0]octenones **13**. Similarly the cyclopropyl carbinols **19** are of interest to understand their behaviour under similar reaction conditions. We now present our results of these studies in this paper.

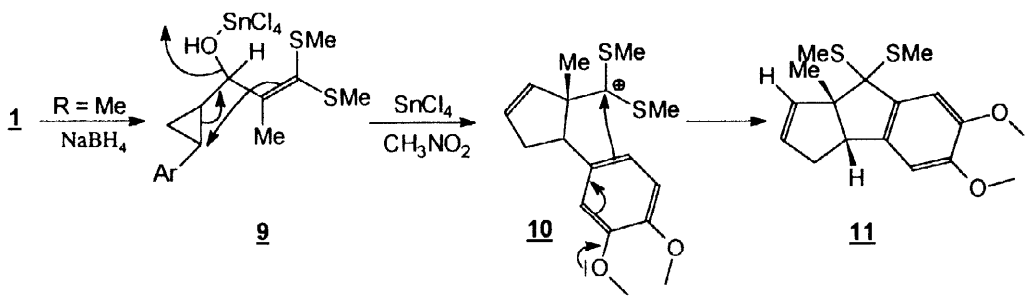
0040-4020/98/$19.00
PII: S0040-4020(97)10313-1



Scheme 1

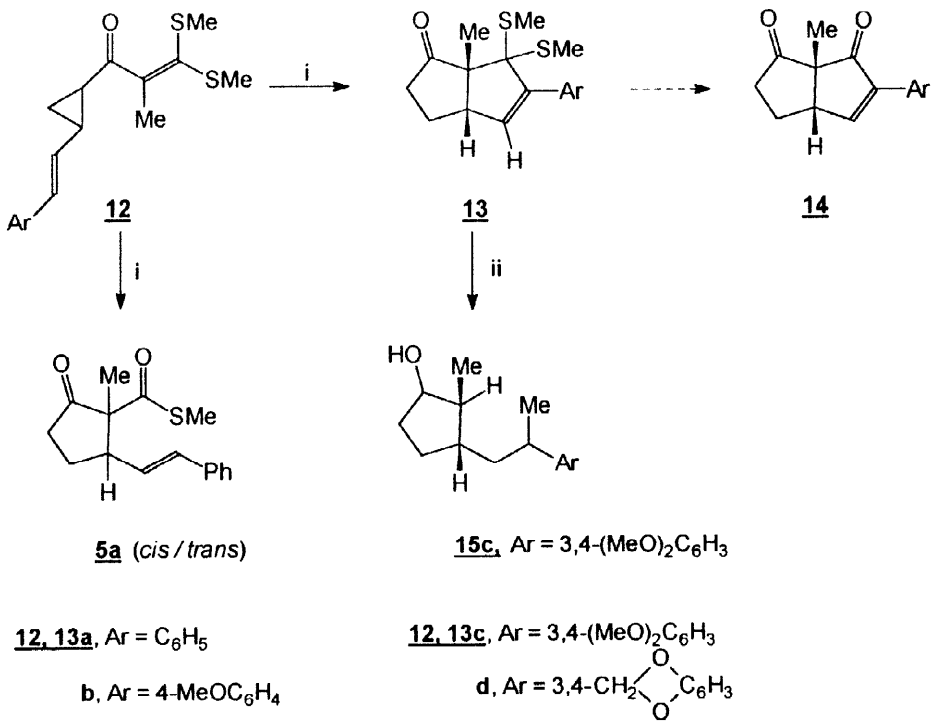
Results and Discussion

The required cyclopropyl ketones **12a-d** were prepared according to our reported procedure.[4] In a typical experiment the ketone **12a** was treated with $SnCl_4$ in nitromethane at room temperature, and the reaction mixture after work-up yielded a product which was characterized as **5a** (Scheme 3) on the basis of its analytical and spectral data. The expected bicyclo[3.3.0]octenone however was not



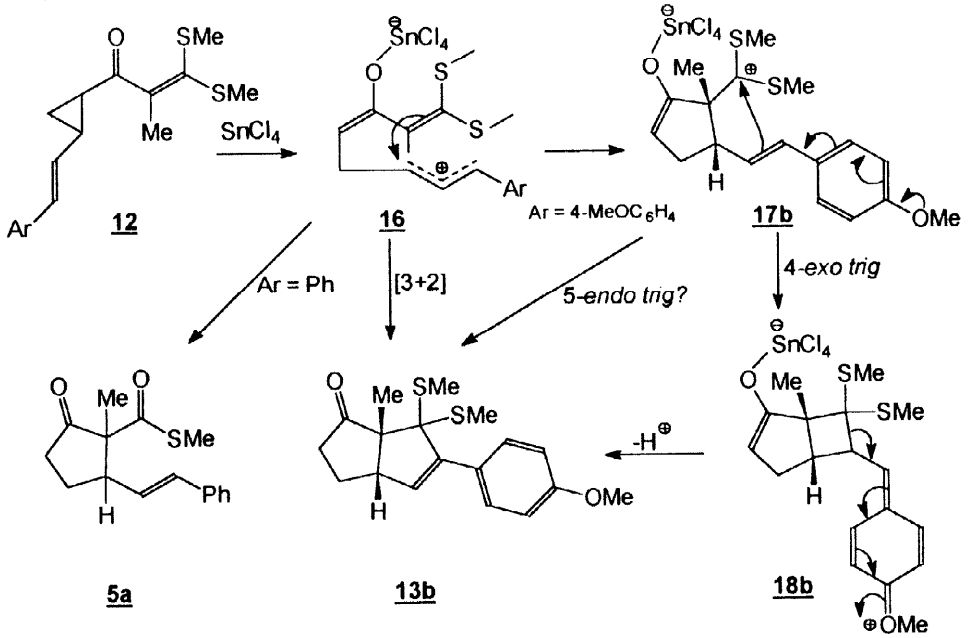
Scheme 2

detected even in traces in the reaction mixture. Apparently, the styryl double bond in **12a** is not sufficiently electron-rich to trap the carbocation **16** (Scheme 4) in the second step to afford the corresponding bicyclic system. It was therefore decided to examine the styryl systems with oxygenated aryl rings (**12b-d**), where the styryl double bond is further enriched with electron density. Thus **12b**, when treated under the described reaction conditions, the reaction mixture after work-up, yielded a single product (72%) which was characterized as bicyclo[3.3.0]octenone **13b**. Similarly the activated



Scheme 3

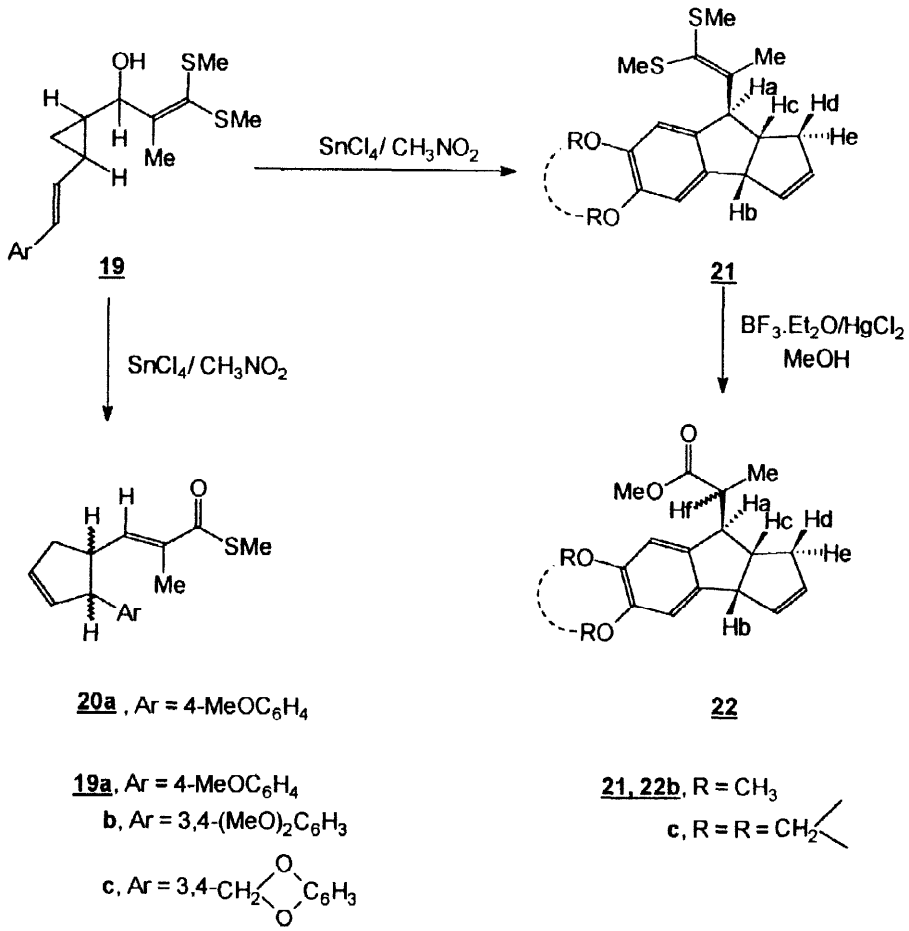
ketones **12c** and **12d** also yielded the expected bicyclo[3.3.0]octenones **13c** and **13d** in 65% and 66% yields respectively (Scheme 3). The formation of these bicyclic compounds **13b-d** was confirmed by their ^{1}H and ^{13}C NMR and analytical data. The presence of a single vinyl proton at δ 7.4 was indicative of the partcipation of styryl double bond in the ring formation. It was further confirmed by ^{13}C NMR data. Also DEPT experiments conducted on **13d** confirmed the ring closure in the tandem step with the formation of a new C-C bond.



Scheme-4

The plausible mechanism for the rearrangement is described in Scheme 4. The tandem step ring closure is observed only when the phenyl ring was activated by *p*-OMe group. The presence of OMe group in the phenyl ring will considerably increase the electron density at the styryl terminal carbon atom facilitating the allowed 4-*exo trig* ring closure, rather than disfavoured 5-*endo trig* process. The cation **18b** then undergoes ring expansion and proton loss to afford **13b**. The [3+2] cycloaddition ring closure[9] is another likely pathway to explain the observed rearrangement.

Our attempts to hydrolyse dithioketal moiety in **13b-d** using a range of reagents ($HgCl_2/CH_3CN$, DMSO, NBS, $AgNO_3$, $BF_3.Et_2O/HgO$ etc.) to afford the corresponding bicyclic enediones **14** were not successful and in most of the cases, only a complex product mixture was obtained. Similarly, the attempted reductive dethiomethylation of **13c** with Raney Ni resulted in concomitant ring cleavage to afford the corresponding cyclopentanol **15c** (Scheme 3).



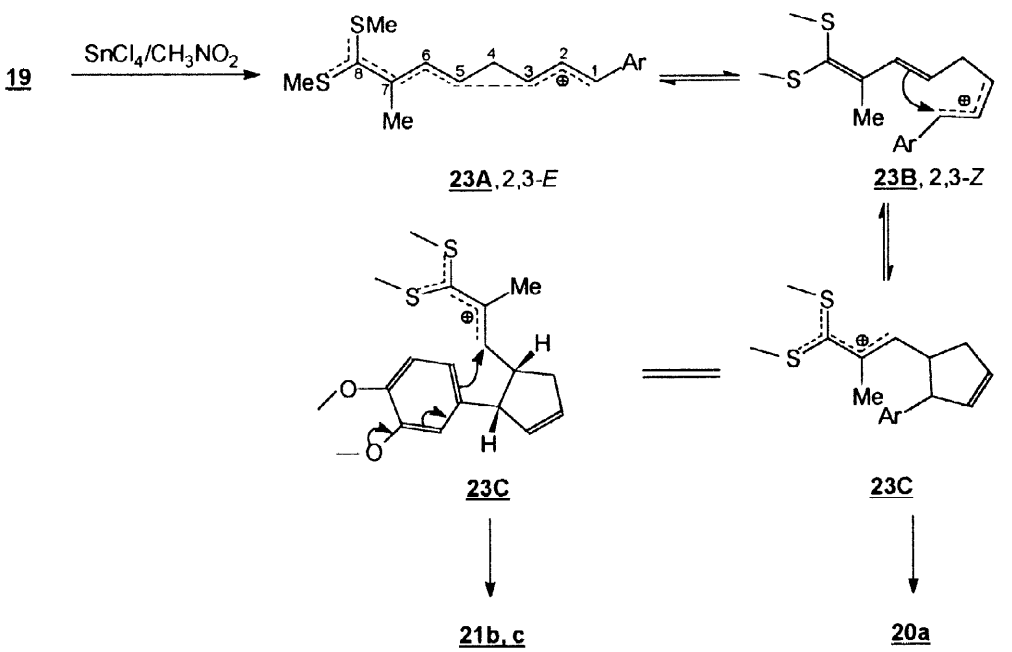
Scheme 5

We next investigated the ring opening and carbocationic rearrangement of the cyclopropyl carbinols **19a-c** obtained by sodium borohydride reduction[13] of the respective cyclopropyl ketones **12b-d**. When **19a** (Scheme 5) was treated with $SnCl_4$ in nitromethane, the reaction mixture after work-up and purification afforded only one product, which was characterized as cyclopentene enecarboxythioate **20a** (42%). Apparently, the aryl ring was not sufficiently electron rich to attack the sulfur stabilized carbocation, which suffered hydrolysis to yield **20a**. We therefore decided to examine dioxygenated styryl cycloproyl carbinols **19b** and **19c** in the next experiments. Thus, **19b** on treatment with $SnCl_4$ in

nitromethane, the reaction mixture after work-up yielded a single product in 71% yield, which was characterized as cyclopent[a]indene **21b**. Similarly **19c** yielded the corresponding **21c** in 79% yield. On the basis of ^{1}H and ^{13}C NMR data, the compounds **21b** and **21c** were found to be single diastereomers. The n.O.e. experiment conducted on **21b** confirmed the *cis* stereochemistry of the ring junction on the basis of a strong n.O.e. between the bridgehead protons H_b (δ 4.16) and H_c (δ 2.97). The absence of n.O.e. between H_a (δ 4.85) and H_c (δ 2.97) confirmed their *trans* stereochemistry. Additional n.O.e. correlations were in support of the structure **21b**. Further confirmation of the structures **21b** and **21c** was obtained by $BF_3.Et_2O$ assisted methanolysis of their bis(methylthio)propylidene side chains to the corresponding methyl esters **22b** and **22c** in high yields (Scheme 5). The structures of **22b** and **22c** were also confirmed on the basis of their spectral and analytical data.

The probable mechanism for the formation of cyclopent[a]indenes **21b** and **21c** from **19b** and **19c** is shown in the Scheme 6. The stannic chloride assisted formation of highly stabilized homotrienylic carbocation **23A** appears to equillibriate with 2, 3 - *Z* isomer **23B** having a favourable geometry for 5-*exo trig* cyclization to afford the corresponding cyclopentenyl carbocation **23C** which either yields hydrolyzed product **20a** (Ar = 4-$OMeC_6H_4$) or undergoes tandem cyclization involving dioxygenated aryl ring to afford **21b** and **21c** as shown in scheme 6.

In summary, we have demonstrated that the electron rich styryl cyclopropyl ketones undergo a



Scheme 6

facile Lewis acid assisted tandem carbocationic rearrangement to yield a novel bicyclic system. The overall bisannulation observed in one pot process may follow ambident pathways as described in scheme 4. Similarly the functionalized tricyclic cyclopent[a]indene framework can be readily assembled from the carbinols **19b-c** through tandem carbocationic process in good yields involving the formation of three stereogenic centres. Based on our results, both the cyclopropyl and ketenedithioacetal moieties should find further applications as initiators and terminators in cationic cyclization reactions for

assembling novel polycyclic structural frameworks of natural origin. Our efforts in this direction are in progress and will be published in due course.

Experimental Section

Melting points were obtained on a "Thomas Hoover" melting point (capillary method) apparatus and are uncorrected. IR spectra were recorded on an Bomem DA8 FT spectrophotometer. ^{1}H NMR (300 MHz), ^{13}C NMR (75.43 MHz) spectra were recorded on Bruker ACF-300 spectrometer. The chemical shifts (δppm) and the coupling constants (*J*) were measured in the standard fashion with reference to either TMS as internal standard (for ^{1}H NMR) or the central line (77.1 ppm) of $CDCl_3$ (for ^{13}C NMR). Mass spectra (MS) were obtained on a Jeol JMS-D 300 Mass spectrometer. Masses are reported in units of mass over charge (m/z). Elemental analyses were carried out on a Heraeus CHN-O-Rapid analyzer.

All reactions were conducted in oven-dried (120°C) glassware under a dry argon/nitrogen atmosphere. All reactions were monitored by analytical TLC on glass plates precoated with silica gel (Acme) containing 13% calcium sulfate as binder and visualization of spots was accomplished by exposure to iodine vapour or potassium permanganate (acidic) solution. All columns were packed using Acme's silica gel (60-120 mesh) and eluted with mixtures of hexane and ethylacetate.

The commercial samples of 3,4-dimethoxybenzaldehyde, 3,4-methylenedioxybenzaldehyde and 4-methoxybenzaldehyde were used as such for the preparation of corresponding cinnamaldehydes as per the reported procedure.[10] Cinnamaldehyde was distilled prior to use. Solvents used for the reaction were dried prior to use. Stannic chloride and nitromethane were purchased from Spectro-Chem and used without purification. Trimethylsulphoxonium iodide was prepared by reported method[11] and the phase transfer catalyst (tetrabutylammonium bromide) was purchased from Aldrich.

General Procedure of the Synthesis of Cyclopropyl Ketones 12a-d.

The cyclopropyl ketones **12a-d** were prepared according to our earlier reported procedure[4] by cyclopropanation of the corresponding 1,1-bis(methylthio)-2-methyl-7-arylhepta-1,4,6-trien-3-ones with dimethyloxosulphonium methylide generated in the presence of phase transfer catalyst.[12] The spectral and analytical data for the known **12a-b** have been reported earlier,[4] while those of the unknown **12c-d** are given below.

1-[2-[Bis(methylthio)methylene]propanoyl]-2-(3,4-dimethoxystyryl)cyclopropane (12c).
Viscous liquid; yield 82%; IR (CCl_4): 1658 cm^{-1}; ^{1}H NMR (CCl_4): δ 0.91-1.13(m, 1H, CH_2), 1.40-1.61 (m, 1H, CH_2), 1.98-2.24(m, 2H, CH), 2.00 (s, 3H, CH_3), 2.15 (s, 3H, SCH_3), 2.26 (s, 3H, SCH_3), 3.70 (s, 6H, OCH_3), 5.55 (dd, *J* = 8, 16Hz, 1H, =CH), 6.40 (d, *J* = 16Hz, =CH), 6.68-6.77(m, 3H, ArH). Anal. Calcd. for $C_{19}H_{24}O_3S_2$ (364.5): C, 62.60; H, 6.63%. Found: C, 62.92; H, 6.50%.

1-[2-[Bis(methylthio)methylene]propanoyl]-2-(3,4-methylenedioxystyryl)cyclopropane (12d).
Viscous liquid; yield 86%; IR (CCl_4): 1660 cm^{-1}; ^{1}H NMR (CCl_4): δ 0.94-1.3(m, 1H, CH_2), 1.5-1.82(m, 1H, CH_2), 2.15 (s, 3H, CH_3), 2.14-2.4(m, 2H, CH), 2.20 (s, 3H, SCH_3), 2.30 (s, 3H, SCH_3), 5.68 (dd, *J* = 8, 16Hz, 1H, =CH), 5.98 (s, 2H, methylenedioxy), 6.43 (d, *J* = 16Hz, 1H, =CH), 6.75 - 6.90 (m,

3H, ArH). Anal. Calcd. for $C_{18}H_{20}O_3S_2$ (348.46): C, 62.03; H, 5.78%. Found: C, 62.29; H, 5.67%.

Cyclization of Cyclopropyl Ketones (12a-d) in the Presence of Stannic Chloride in Nitromethane: General Procedure.

To a stirring ice cold solution of appropriate cyclopropyl ketones **12a-d** (10 mmol) in nitromethane (25 mL), $SnCl_4$ (3.9 g, 15 mmol) was added and the reaction mixture was further stirred at room temperature for 6-12 h (monitored by TLC). It was then poured into cold saturated $NaHCO_3$ solution (200 mL), extracted with chloroform (3x60 mL), washed with water (3x100 mL), dried (Na_2SO_4) and solvent evaporated to afford crude products, which were purified by column chromatography over silica gel using EtOAc-hexane (1:99) as the eluent.

(1*R*,*S*,5 *S*,*R*)-2-Bis(methylthio)-3-(4-methoxyphenyl)-1-methylbicyclo[3.3.0]oct-3-en-8-one (13b). Viscous liquid; yield 72%;IR (CCl_4): 1740, 1620 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.60 (s, 3H, CH_3), 2.14 (s, 3H, SCH_3), 2.18-2.50(m, 4H, CH_2), 2.35 (s, 3H, SCH_3), 3.75 (s, 3H, OCH_3), 4.96 (ddd, J = 3, 5, 6Hz, 1H, H-5), 6.75 (d, J = 9Hz, 2H, ArH), 7.30 (d, J = 9Hz, 2H, ArH), 7.40 (d, J = 3Hz, 1H, =CH); ^{13}C NMR ($CDCl_3$): δ 16.65, 16.81, 18.32, 24.96, 29.47, 36.71, 45.76, 55.13, 67.02, 113.63, 113.83, 132.41, 134.66, 147.06, 160.61, 207.25; MS (m/z, %): 334 (M^+, 8.4), 287 (84.12), 239 (100). Anal. Calcd. for $C_{18}H_{22}O_2S_2$ (334.48): C, 64.63; H, 6.63%. Found: C, 64.95; H, 6.47%.

(1*R*,*S*,5 *S*,*R*)-2-Bis(methylthio)-3-(3,4-dimethoxyphenyl)-1-methylbicyclo[3.3.0]oct-3-en-8-one(13c). Colourless solid (hexane); mp. 105°C; yield 65%; IR (KBr): 1740, 1623 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.70 (s, 3H, CH_3), 2.26 (s, 3H, SCH_3), 2.27-2.61(m, 4H, CH_2), 2.40 (s, 3H, SCH_3), 3.76 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.82 (ddd, J = 3, 5, 6Hz, 1H, H-5), 6.75 (d, J = 9Hz, 1H, ArH), 6.81 (d, J = 3Hz, 1H, ArH), 7.04 (dd, J = 3, 9Hz, 1H, ArH), 7.43 (d, J = 3Hz, 1H, =CH); MS (m/z, %): 364 (M^+, 9.2), 317 (33.5), 269 (69.2). Anal. Calcd. for $C_{19}H_{24}O_3S_2$ (364.5): C, 62.60; H, 6.63%. Found: C, 62.98; H, 6.44%.

(1*R*,*S*,5*S*,*R*)-2-Bis(methylthio)-3-(3,4-methylenedioxyphenyl)-1-methylbicyclo[3.3.0]oct-3-en-8-one (13d). Viscous liquid; yield 66%; IR (CCl_4): 1740, 1620 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.68 (s, 3H, CH_3), 2.21 (s, 3H, SCH_3), 2.22-2.50(m, 4H, CH_2), 2.44 (s, 3H, SCH_3), 5.02 (ddd, J = 3, 5, 6Hz, 1H, H-5), 5.98 (s, 2H, OCH_2O), 6.77 (d, J = 8Hz, 1H, ArH), 6.88 (d, J = 3Hz, 1H, ArH), 6.96 (dd, J = 3, 8Hz, 1H, ArH), 7.40 (d, J = 3Hz, 1H, =CH); ^{13}C NMR ($CDCl_3$): δ 16.63, 16.98, 18.49, 26.56, 29.64, 36.81, 45.73, 67.79, 101.38, 108.26, 109.47, 127.21, 128.73, 135.04, 146.62, 147.64, 148.88, 207.20; MS (m/z, %): 348 (M^+, 26), 301 (100), 253 (88). Anal. Calcd. for $C_{18}H_{20}O_3S_2$ (348.46): C, 62.03; H, 5.78%. Found: C, 62.51; H, 5.58%.

S-Methyl 1-methyl-5-ß-styryl-2-oxocyclopentane-1-thiocarboxylate (5a). (*cis* and *trans* 33:66); Yellow oil; yield 56%; IR (CCl_4): 1740, 1660 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.15 (s, 0.99H, CH_3), 1.25 (s, 1.98H, CH_3), 1.59-1.87(m, 2H, CH_2), 2.13 (s, 1.98H, SCH_3), 2.28 (s, 0.99H, SCH_3), 2.38-2.42 (m, 2H, CH_2), 3.56-3.59 (m, 0.66H, CH), 3.75-3.78 (m, 0.33H, CH), 6.05 (dd, J = 8, 16Hz, 0.66H, =CH), 6.41-6.58 (m, 1.32H, =CH), 7.15-7.32 (m, 5H, ArH). Anal. Calcd. for $C_{16}H_{18}O_2S$ (274.384): C, 70.04; H, 6.61%. Found: C, 70.48; H, 6.46%.

Raney Nickel Desulphurization of 13c: 2-Methyl-3-[2-(3,4-dimethoxyphenyl)propyl]cyclopentanol(15c).

A suspension of **13c** (0.7 g, 2 mmol) and Raney Ni (2 g) in ethanol (15 mL) was refluxed for 6 h (monitored by TLC). The reaction mixture was filtered to remove Raney Ni and the filtrate evaporated to give a viscous residue which on column chromatography (silica gel) using EtOAc:hexane (1:90) as the eluent afforded pure cyclopentanol **15c**; viscous liquid; yield 0.28g (51%); IR (neat): 3350 (br), 2919, 1608, 1506, 1439cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.83 (d, J = 6Hz, 3H, CH_3), 0.94 (d, J = 6Hz, 3H, CH_3), 1.25-1.82 (m, 8H, CH_2, CH), 2.66-2.69 (m, 2H, benzylic, -CHO-), 3.85 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.03 (br s, 1H, -OH), 6.78 (s, 3H, ArH); ^{13}C NMR ($CDCl_3$): δ 16.93, 22.09, 23.47, 28.87, 33.56, 34.12, 47.27, 49.66, 55.78, 55.83, 74.40, 111.03, 111.95, 120.43, 134.36, 147.01, 148.72. Anal. Calcd. for $C_{17}H_{26}O_3$ (273.34): C, 73.35; H, 9.41%. Found: C, 73.73; H, 9.21%.

Stannic Chloride Induced Cyclization of the Cyclopropyl Carbinols (19a-c): General Procedure.

To a stirring ice cold solution of appropriate cyclopropyl carbinols **19a-c** (10 mmol) in nitromethane (25 mL), $SnCl_4$ (3.9 g, 15 mmol) was added and the reaction mixture was further stirred at room temperature for 6-12 h (monitored by TLC). It was then poured into cold saturated $NaHCO_3$ solution (200 mL), extracted with chloroform (3x60 mL), washed with water (3x100 mL), dried (Na_2SO_4) and solvent evaporated to afford crude products. Purification by column chromatography over silica gel using EtOAc-hexane (1:99) as the eluent afforded the cyclopent[a]indenes **21b-c** from **19b-c** and the carboxythioate **20a** from **19a** respectively.

(3a*S*,*R*,8 *S*,*R*,8a *R*,*S*)-8-[1-[Bis(methylthio)propen-2-yl]-5,6-(dimethoxy)cyclopent[a]ind-2-ene (21b).
Viscous liquid; yield 71%; IR (CCl_4): 1621, 1468, 1240 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.82 (s, 3H, CH_3), 2.34 (s, 3H, SCH_3), 2.37 (s, 3H, SCH_3), 2.46 (ddd, J = 1.5, 3, 17Hz, 1H, H_e), 2.67 (ddd, J = 1.5, 9, 17Hz, 1H, H_d), 2.95-3.04 (m, 1H, H_c), 3.80 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.25 (d, J = 9Hz, 1H, H_b), 4.92 (d, J = 6Hz, 1H, H_a), 5.69-5.75 (m, 1H, =CH), 5.75-5.83 (m, 1H, =CH), 6.38 (s, 1H, ArH), 6.78 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 16.97, 18.23, 39.06, 47.52, 56.06, 56.15, 57.39, 58.77, 107.02, 107.35, 128.64, 129.78, 132.31, 136.00, 137.26, 148.00, 148.66; MS (m/z, %): 348 (M^+, 52.3), 253 (89.7). Anal. Calcd. for $C_{19}H_{24}O_2S_2$ (348.5): C, 65.47; H, 6.94%. Found: C, 65.88; H, 6.73%.

(3a*S*,*R*,8*S*,*R*,8a*R*,*S*)-8-[1-[Bis(methylthio)propen-2-yl]-5,6-(methylenedioxy)cyclopent[a]ind-2-ene (21c).
Colourless solid (hexane); mp. 59-60°C; yield 79%; IR (KBr): 1618, 1470, 1360 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 3H, CH_3), 2.27 (s, 3H, SCH_3), 2.31 (s, 3H, SCH_3), 2.42 (ddd, J = 1.5, 3, 16.8Hz, 1H, H_e), 2.59 (ddd, J = 1.5, 9, 16.8Hz, 1H, H_d), 2.94-3.01 (m, 1H, H_c), 4.16 (d, J = 9Hz, 1H, H_b), 4.85 (d, J = 6Hz, 1H, H_a), 5.70 (s, 2H, OCH_2O), 5.84 (d, J = 1.5Hz, 1H, =CH), 5.88 (d, J = 1.5Hz, 1H, =CH), 6.32 (s, 1H, ArH), 6.68 (s, 1H, ArH); ^{13}C NMR ($CDCl_3$): δ 16.85, 18.12, 38.91, 47.33, 57.05, 58.37, 100.92, 104.32, 104.53, 128.99, 129.65, 132.11, 137.16, 138.05, 146.93, 147.37; MS (m/z, %): 332 (M^+, 47.1), 286 (18.5), 269 (68.2), 237 (86.1). Anal. Calcd. for $C_{18}H_{20}O_2S_2$ (332.46): C, 65.02; H, 6.06%. Found: C, 65.39; H, 6.22%.

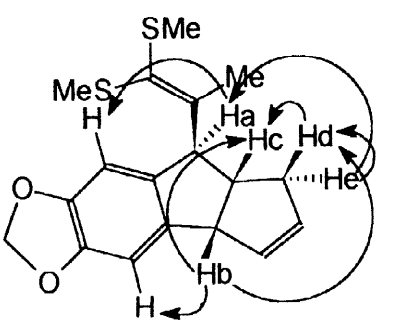


Fig. 1. Important n.O.e. correlations.

S-Methyl 3-[3-(4-methoxyphenyl)cyclopenten-4-yl]-2-methylthiopropenoate (20a).
Viscous liquid; yield 42%; IR (neat): 1653, 1608, 1557cm^{-1}; ^{1}H NMR (CCl_4): δ 1.78 (s, 3H, CH_3), 2.15 (s, 3H, SCH_3), 2.15-2.65 (m, 3H, CH_2, CH), 3.81 (s, 3H, OCH_3), 4.11 (dd, J = 3, 6Hz, 1H, CH), 5.71-6.40 (m, 3H, =CH), 6.90 (q, A_2B_2, J = 9Hz, 4H, ArH). Anal. Calcd. for $C_{17}H_{20}O_2S$ (272.414): C, 74.95; H, 7.40%. Found: C, 75.32; H, 7.25%.

Boron Trifluoride Etherate Assisted Methanolysis of Cyclopent[a]indenes 21b and 21c.

A suspension of either **21b** or **21c** (10 mmol) and $HgCl_2$ (2.7 g, 10 mmol) in anhydrous methanol (10 mL) was stirred at room temperature (10 min) followed by addition of $BF_3.Et_2O$ (1.5 mL). The reaction mixture was refluxed (3 h), cooled and filtered. The filtrate was poured into saturated $NaHCO_3$ solution (50 mL) followed by extraction with chloroform (3x30 mL). The combined extracts were washed with water (150 mL), dried (Na_2SO_4) and solvent evaporated to give a viscous residue which on column chromatography over silica gel (EtOAc/hexane, 2:98) afforded pure esters **22b-c** in nearly quantitative yields.

Methyl 2-[5,6-(dimethoxy)cyclopent[a]ind-2-en-8-yl]propanoate (22b).
Diastereomeric mixture (65:35); colourless viscous liquid; yield 91%; IR (CCl_4): 1733, 1604, 1497 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.01 (d, J = 7Hz, 1.05H, CH_3), 1.13 (d, J = 7Hz, 1.95H, CH_3), 2.16-2.24 (m, 1H, H_e), 2.70-2.82 (m, 2H, $H_{c,d}$), 2.95 (two overlapped quintets, J = 6Hz, 1H, H_f), 3.27 (dd, J = 1.5, 6Hz, 0.65H, H_a), 3.35 (dd, J = 1.5, 6Hz, 0.35H, H_a), 3.64 (s, 1.95H, OCH_3), 3.71 (s, 1.05H, OCH_3), 3.81 (s, 1.95H, Ar-OCH_3), 3.85 (s, 3.9H, Ar-OCH_3), 4.10 (d, J = 6Hz, H_b), 5.62-5.65 (m, 1H, =CH), 5.77-5.81 (m, 1H, =CH), 6.57-6.66 (m, 2H, ArH); MS (m/z, %): 302 (M^+, 29.9), 215 (100). Anal. Calcd. for $C_{18}H_{22}O_4$ (302.36): C, 71.49; H, 7.33%. Found: C, 71.78; H, 7.19%.

Methyl 2-[5,6-(methylenedioxy)cyclopent[a]ind-2-en-8-yl]propanoate (22c).
Diastereomeric mixture (65:35); colourless viscous liquid; yield 93%; IR (CCl_4): 1727, 1603, 1469 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.00 (d, J = 7Hz, 1.05H, CH_3), 1.13 (d, J = 7Hz, 1.95H, CH_3), 2.14-2.22 (m, 1H, H_e), 2.67-2.82 (m, 2H, $H_{c,d}$), 2.95 (two overlapped quintets, J = 6Hz, 1H, H_f), 3.24 (dd, J = 1.5, 6Hz, 0.65H, H_a), 3.33 (dd, J = 1.5, 6Hz, 0.35H, H_a), 3.64 (s, 1.95H, OCH_3), 3.71 (s, 1.05H, OCH_3), 4.09 (d, J = 6Hz, 1H, H_b), 5.63-5.65 (m, 1H, =CH), 5.75-5.78 (m, 1H, =CH), 5.86 (s, 0.65H, OCH_2O), 5.89 (s, 1.3H, OCH_2O), 6.53-6.62 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$): δ 11.85, 13.60, 40.19, 40.43, 43.45, 43.54, 44.02, 46.46, 51.56, 54.42, 55.82, 56.63, 100.98, 101.03, 104.29, 104.44, 105.67, 130.02, 130.19, 132.15, 132.21, 134.95, 135.81, 138.57, 146.58, 146.99, 147.26, 175.99; MS (m/z, %): 286 (M^+, 38.2). Anal. Calcd. for $C_{17}H_{18}O_4$ (286.31): C, 71.31; H, 6.33%. Found: C, 71.02; H, 6.21%.

Acknowledgement: PKP thanks CSIR, New Delhi for a Senior Reseach Fellowship. Financial assistance under CSIR project is also acknowledged.

References and notes

1. Review: (a) Kolb, M. *Synthesis* **1990**, 171; (b) Junjappa, H.; Ila, H.; Asokan, C.V. *Tetrahedron* **1990**, *46*, 5423; (c) Junjappa, H.; Ila, H. *Phosphorous, Sulfur and Silicon* **1994**, *95-96*, 35.

2. (a) Deb, B.; Asokan, C.V.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1988**, *29*, 2111; (b) Deb, B.; Ila, H.; Junjappa, H. *J. Chem. Res.(S)* **1990**, 356; *J. Chem. Res.(M)* **1990**, 2728; (c) Patro, B.; Deb, B.; Ila, H.; Junjappa, H. *Tetrahedron* **1994**, *50*, 255; (d) Satyanarayana, J.; Rao, M.V.B.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1996**, *37*, 3565.
3. Patra, P.K.; Patro, B.; Ila, H.; Junjappa, H. *Tetrahedron Lett.* **1993**, *34*, 3951.
4. Patro, B.; Deb, B.; Ila, H.; Junjappa, H. *J. Org. Chem.* **1992**, *57*, 2257.
5. (a) Chamberlin, A.R.; Nguyen, H.D.; Chung, J.Y.L. *J. Org. Chem.* **1984**, *49*, 1682; (b) Chamberlin, A.R.; Chung, J.Y.L. *Tetrahedron Lett.* **1982**, *23*, 2619; (c) Chamberlin, A.R.; Chung, J.Y.L. *J. Am. Chem. Soc.* **1983**, *105*, 3658.
6. Ketenedithioacetals as cationic cyclization initiator and terminators, see: (a) Brinkmeyer, R.S. *Tetrahedron Lett.* **1979**, 207; (b) Semenovsky, A.V. *Tetrahedron Lett.* **1978**, 3603; (c) Andersen, N.H.; Yamamoto, Y.; Denniston, A.D. *Tetrahedron Lett.* **1975**, 4547; (d) Rigby, J.H.; Kotnis, A.S.; Kramer, J. *Tetrahedron Lett.* **1983**, *24*, 2939; (e) Rigby, J.H.; Kotnis, A.S. *Tetrahedron Lett.* **1987**, *28*, 4943.
7. (a) Review: Tietze, L.F. *Chem. Rev.* **1996**, *96*, 115; (b) Johnson, W.S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 9; (c) Johnson, W.S. *Bioorg. Chem.* **1976**, *5*, 51; (d) Van Tamelen, E.E.; Storni, A.; Hessler, E.J.; Schuartz, M. *J. Am. Chem. Soc.* **1963**, *85*, 3295; (e) Van Tamelen, E.E.; James, D.R. *J. Am. Chem. Soc.* **1977**, *99*, 950.
8. For successive formation of two cyclopentane rings see: (a) Transition Metal mediated cyclization: Agnel, G.; Negishi, E.-i. *J. Am. Chem. Soc.* **1991**, *113*, 7424; Dauben, W.G.; Dinges, J.; Smith, T.C. *J. Org. Chem.* **1993**, *58*, 7635; Veretenov, A.L.; Smit, W.A.; Vorontsova, L.G.; Kurella, M.G. *Tetrahedron Lett.* **1991**, *32*, 2109 and references therein; (b) Carbocationic cyclization: Angle, S.R.; Frutos, R.P. *J. Chem. Soc., Chem. Commun.* **1993**, 171; Balog, A.; Curran, D.P. *J. Org. Chem.* **1995**, *60*, 337; Corey, E.J.; Balanson, R.D. *Tetrahedron Lett.* **1973**, 3153; Gripper-Gray, A.C.; Kakihana, T.; Collins, P.M.; Hart, H. *J. Am. Chem. Soc.* **1967**, *89*, 4556; (c) Anionic route: Molander, G.A.; Harris, C.R. *J. Am. Chem. Soc.* **1995**, *117*, 3705; Danishefsky, S.; Dynak, J.; Hatch, E.; Yamamoto, M. *J. Am. Chem. Soc.* **1974**, *96*, 1256; (d) Radical cyclization: Little, R.D. *Chem. Rev.* **1986**, *86*, 875; (e) Wang, Y.; Mukherjee, D.; Birney, D.; Houk, K.N. *J. Org. Chem.* **1990**, *55*, 4509; Hatanaka, M.; Ueno, F.; Ueda, I. *Tetrahedron Lett.* **1996**, *37*, 89.
9. (a) Collins, M.P.; Mann, J.; Capps, N.; Finch, H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 239; (b) Collins, M.P.; Drew, M.G.B.; Mann, J.; Finch, H. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3211; (c) Barbey, S.; Mann, J. *Synlett* **1995**, 27.
10. Reddy, M.P.; Krishnarao, G.R. *Synthesis* **1980**, 815.
11. Corey, E.J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.
12. Merz, A.; Mark, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 845.
13. The carbinols **19a-c** were prepared from the corresponding cyclopropyl ketones in quantitative yields by our earlier reported procedure.[2c]