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A NEW ENE REACTION MEDIATED ACCESS TO CYCLOHEPTATRIENE ENOL THIO-ETHERS

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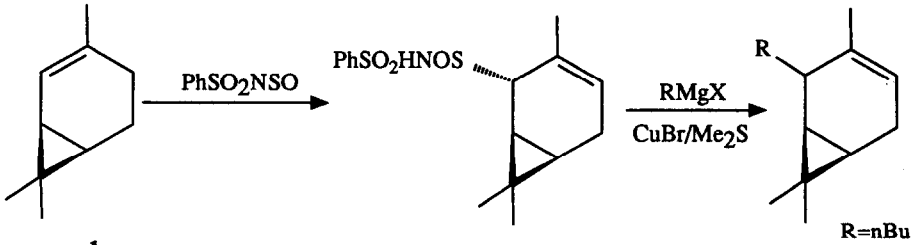
Abstract :
The sequence, ene reaction with N-sulfinylbenzene sulfonamides, treatment with reductive Grignard reagents has been shown, when performed on Δ_3-carene, to be a straightforward synthetic approach towards functionalized cycloheptatrienic enol thio-ethers.

We had previously shown that N-sulfinyl arene sulfonamides were among the most potent chemically stable enophiles ever described. Ene reactions of these derivatives are a convenient way to introduce at allylic positions various functions such as thiols (1), amines (2) or silylated moieties (3) from which ketones (4) or nitriles could be obtained.

As ene reaction is a metal free scheme allowing selective allylic activation of olefines we decided to use this property as a way for hydrocarbon, especially terpene, homologation. Thus treatment of ene adducts (scheme 1), by Grignard reagents in the presence of catalytic amounts of $CuBr/Me_2S$ allowed the alkylation of olefines (5).



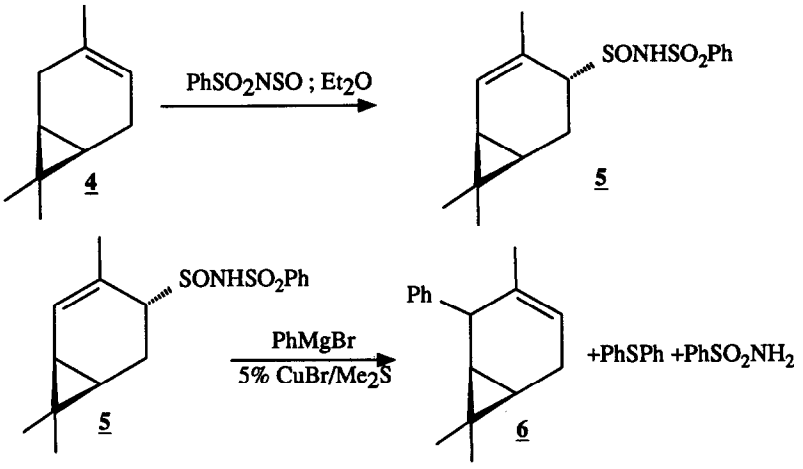
1 2 3

R=nBu yield=47%
R=Ph yield=40%
R=Et yield=46%

SCHEME 1

During the course of our studies we investigated the behaviour of Δ_3 carene. When treated with phenyl magnesium bromide in the presence of catalytic amounts of Cu^{I} its ene reaction adduct yields a single aryl

derivative embodying a Δ_3 structure (20% yield), the phenyl group being presumably trans to cyclopropane (5).

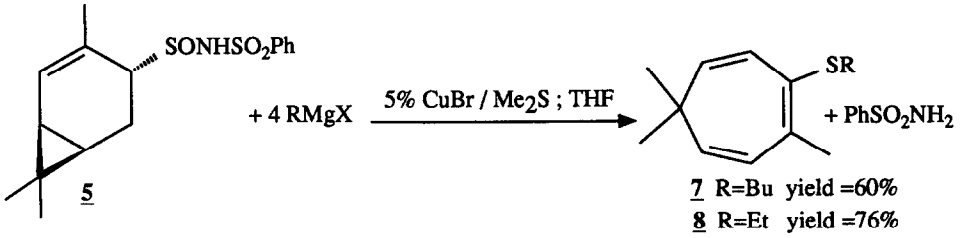


SCHEME 2

As observed for the adduct of Δ_2 carene(5), the only isomer is the 2-phenyl-Δ_3 carene. The regioselectivity of the phenyl Grignard reagents in this kind of reaction had already been uncovered by Normant and al. (6).

However this reaction (scheme 2) is rather difficult (100h, 20°C, 20% yield) and we were unable to obtain any alkylation derivative when running it with trimethylsilylmethyl magnesium bromide.

We here report that, in the presence of Grignard reagents which embody a β-hydrogene, the ene adducts of Δ_3 carene show a very different behaviour. They undergo an unique ring enlargement yielding cycloheptatrienic enol thio-ethers according to scheme 3.



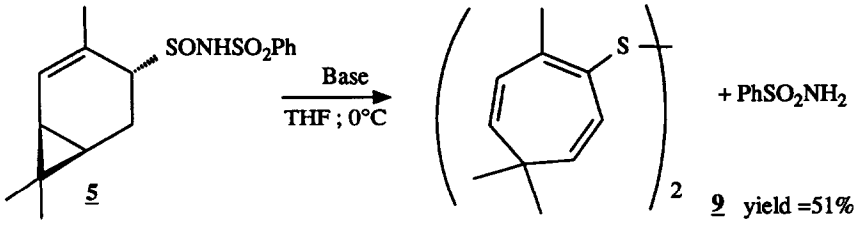
SCHEME 3

Conservation of the sulfur atom can be rationalized by the rapid formation of a vinylic sulfur moiety. Indeed Posner and Tang(7) showed that, when treated with Grignard reagents in presence of Cu^I catalyst, vinylic sulfoxides lead to vinyl sulfides without subsequent evolution.

One of the shortest ways to bring the sulfur atom on a vinylic position is H_4 abstraction ; so we studied the behaviour of **5** in presence of bases like tBuOK or LDA. Reaction occurs according to scheme 4 affording bis-cycloheptatrienyl disulfide **9**.

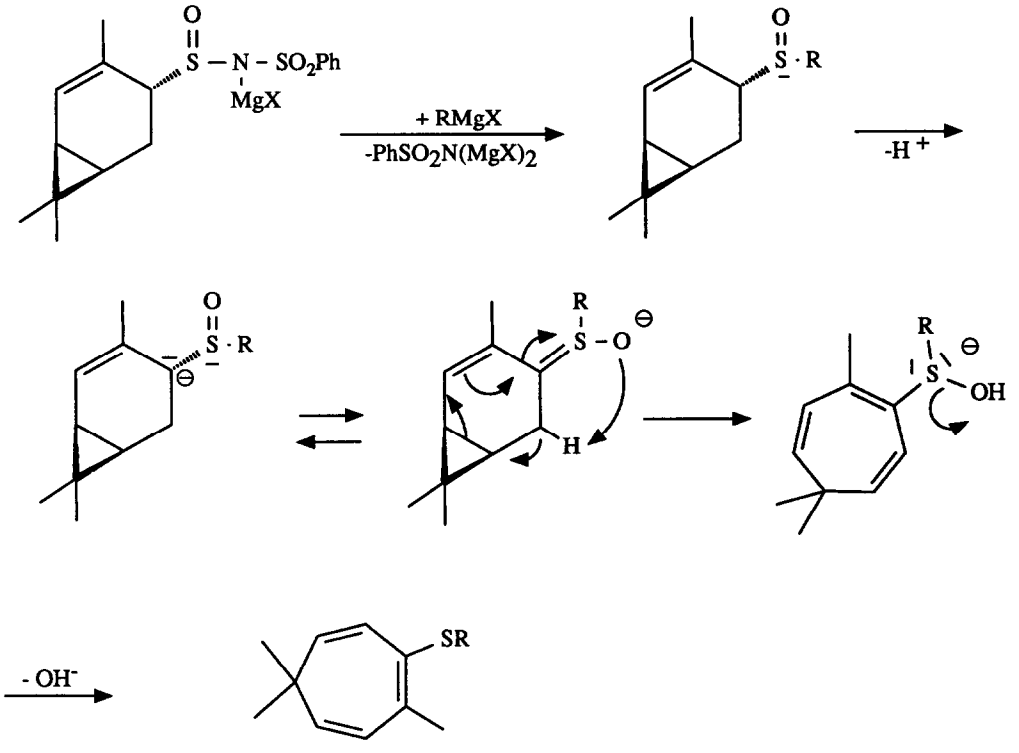
This result, although not a proof, constitutes an element towards the understanding of this reaction that gives an entry to these series of cycloheptatrienic enol thio-ethers.

One explanation we had proposed for the substitution of allylic sulfinamides (ene adducts) by Grignard reagents under Cu^I catalysis is : first the formation of an allylic sulfoxide by action of a cuprous derivative formed from organomagnesium compound and Cu^I salt, then evolution towards a π-allylic copper derivative yielding alkylated product. (5)



SCHEME 4

As carene adducts are very slow reacting substrates, they could let time to the cuprous derivative to decompose itself (8) towards copper hydride which could then perform H_4 proton abstraction leading to subsequent rearrangement to cycloheptatrienic enol thio-ethers (scheme 5).

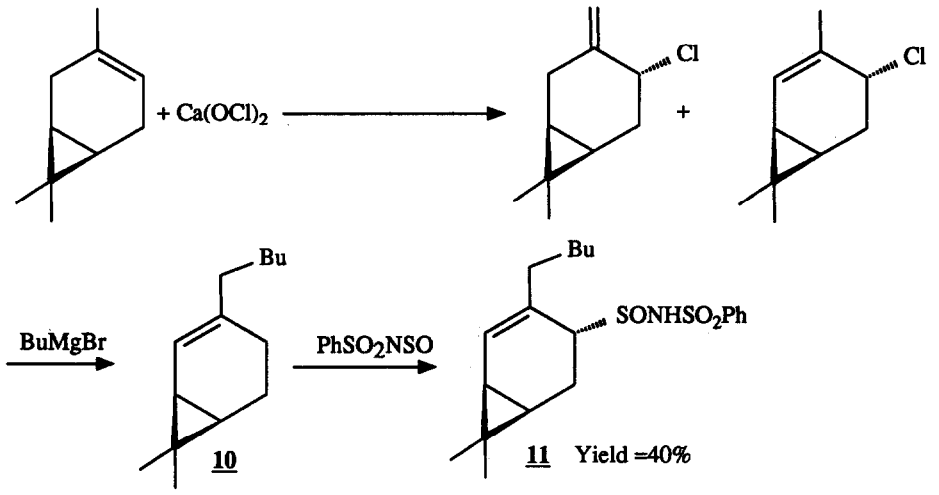


SCHEME 5

This short scheme enabled us to synthesize structures that gather an "hair pin" fixed configuration moiety and a strong electron donating element enol thio-ether.

This kind of structure could have a great importance if we consider results obtained by Corey (9) dealing with oxygenase inhibitors. So we have decided to undergo efforts to introduce various chains on the cycloheptatrienic enol thio-ether in a search to obtain oxygenase inhibitors.

For this purpose we introduced an alkyl chain in the C_{10} position of the Δ_3 carene by a chlorination-alkylation sequence (scheme 6). Treatment of the chlorinated compound with butylmagnesium bromide yielded the higher analog of Δ_3 carene. Then ene reaction was performed on this derivative to give adduct 11.



SCHEME 6

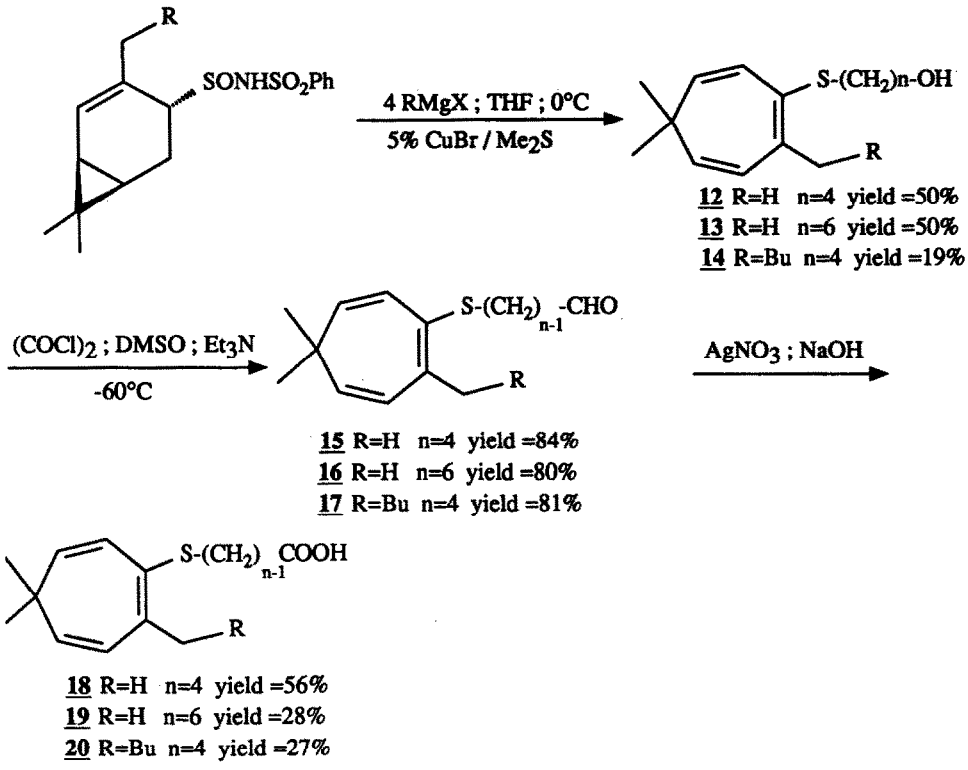
Δ_3 carene adducts 5 as well as 11 were then reacted with Grignard reagents derived from 4-chloro 1-butanol or 6-chloro 1-hexanol. In every case hydroxyl function was protected as a magnesium alcoholate obtained by reaction of the ω-halogeno-alcohol with ethyl magnesium bromide (10). Then condensation of Grignard reagent catalysed by Cu^I salt led to enol thio-ethers (scheme 7). Alcohols were oxidized to aldehydes according to Swern's method (11). Then aldehydes were oxidized in acids by action of silver oxide (12).

In conclusion, this successfull scheme constitutes a very easy way towards the synthesis of a whole series of lipidic substrates which incorporate a vinylic sulfur atom in a conformationnally restricted structure.

Everyone knows the importance of such structures as inhibitors of enzymes involved in infectious and inflammatory processes. Thus biological tests are actually in progress.

AKNOWLEDGEMENTS

We are grateful to Rhône-Poulenc for financial support and to Miss Christel Guillot for technical assistance.



SCHEME 7

EXPERIMENTAL PART

General

All reactions were performed under Argon.

THF was distilled from potassium benzophenone ketyl, diethylether was distilled upon $LiAlH_4$, dichloromethane was used as received from the vendors. ^1H NMR spectra were recorded at 60 or 90 MHz, ^{13}C spectra were recorded at 22.63 or at 62.9 MHz in $CDCl_3$ solution and expressed in ppm (δ) downfield from TMS. Mass spectra were performed at 70 eV.

Ene-reaction with N-sulfinylbenzensulfonamide:

A solution of $PhSO_2NSO$ (8.12g, 40 mmol)in anhydrous diethylether (40 mL) was cooled to 0°C and ene (1.2 eq.) was added dropwise. The medium was stirred at 0°C for a time variable with the ene. At the end of the reaction the precipitation of adduct was completed by hexane addition (40mL). The reaction mixture was filtered and the precipitate was washed several times with hexane and dried under vacuum. Products 5 and 11 obtained by this way were spectroscopically pure and stable in the dark under argon as they are sensitive to light and moisture.

5:12.2g,(36 mmol)=90% yield, were obtained after 3 h. reaction time.
mp= 108 °C, dec. Rf= 0.1 (CH_2Cl_2/CH_3OH 9/1).
IR (KBr disk) cm^{-1} : 3200 (NH) ; 3080-3000 (Ph) ; 1650 (C=C) ; 1450 (CH_3) ; 1380, 1175 (SO_2).
^1H NMR: m(1H) 0.6-0.75: $C_{(6)}H$,s(3H) 0.8 and s(3H) 1.0: $C_{(8)}H_3$ or $C_{(9)}H_3$;m(4H) 1.8-1.95 with s at

1.8: $C_{(10)}H_3$ and $C_{(5)}H$ trans to $C_{(7)}$ and S; d-d(1H) 2.35 $J_{C5Ha-CH5e}$= 17.5Hz $J_{C4H-C5H}$= 6Hz $C_{(5)}H$ cis to $C_{(7)}$; d(1H) 3.3 J= 6Hz $C_{(4)}H$; broad s(1H) 5.9: $C_{(2)}H$; 2m(5H) 7.45-7.65 and 7.9-8.0: C_{ar}-H.

11: (6.32g, 16 mmol) 40% yield, were obtained after 12 h. reaction time.

mp= 74 °C, dec. Rf= 0.15 (CH_2Cl_2/CH_3OH 9/1).

IR (KBr disk) cm^{-1} : 3200 (NH) ; 3080, 3030 (Ph) ; 1440 (CH_3) ; 1360, 1160 (SO_2) ; 1090 (CH=).

^1H NMR : m(17H) 0.6-1.4 with s at 0.8 and 1.0: $C_{(1)}H$, $C_{(6)}H$, $C_{(8)}H_3$,$C_{(9)}H_3$, $C_{(14)}H_3$, $C_{(11)}H_2$, $C_{(12)}H_2$, $C_{(13)}H_2$; d of t(2H) 1.7-1.9 $J_{C5a-C5e}$=15 Hz, $J_{C4H-C5H}$=5.6 Hz: $C_{(5)}H$ cis to C_7; m(2H) 1.9-2.05: $C_{(10)}H_2$; d-d(1H) 2.4 $J_{C4H-C5H}$=11Hz: $C_{(5)}H$ trans to $C_{(7)}$; broad d(1H) 3.4 J= 5.6Hz: $C_{(4)}H$; s(1H) 5.8: $C_{(2)}H$; 2m(5H) 7.45-7.65 and 7.9-8.0: C_{ar}-H.

Reaction of ene adducts with Grignard reagents.

Preparation of the Grignard derivative.

A solution of ω-halogeno alcohol (59 mmol) in anhydrous THF (60 mL) containing a small amount of 1-10-phenanthroline was cooled to -20°C and isopropylmagnesium chloride was added dropwise. Addition was stopped when the color of the mixture became purple. The medium was allowed to warm up to room temperature. Then alcoholate (59 mmol) was added dropwise to magnesium (2.12 g, 88.5 mmol) in anhydrous THF and the mixture was stirred at reflux of THF for 2h30.

Condensation on adducts of ene reaction.

The dark solution yielded was added dropwise at 0°C to 14.75 mmol of adduct dissolved in anhydrous THF containing 5% molar $CuBr/Me_2S$. After addition was completed, mixture was allowed to warm up to room temperature,then stirred for 100 hours, hydrolised with a NH_4Cl solution and extracted with diethyl ether. Organic layers were washed with 2N HCl, then with a $NaHCO_3$ solution, and brine. They were dried over Na_2SO_4 and the solvent was evaporated. The crude product was purified on silicagel (eluent $CHCl_3$).

6 oil (0.63g, 2.95 mmol) 20 % yield.

IR cm^{-1} : 3030 (CH arom.) ; 1950, 1880, 1810, 1760 (CH arom. monosubstitued) ; 1650 (C=C) ; 1600, 1500.

^1H NMR (CCl_4) : s(6H) 0.87 : $C_{(8)}H_3$, $C_{(9)}H_3$; m(2H) 1-1.5: $C_{(1)}H$, $C_{(6)}H$; s(1H) 1.8 : CH_3 vinyl ; m(2H) 2.1-2.5 : $C_{(5)}H_2$; m(1H) 3.8 : $C_{(2)}H$; m(1H) 5.5 : C=C-H ; s(5H) 7.1 : Ph.

^{13}C NMR($CDCl_3$) : C_1 22.6 ; C_2 43 ; C_3 132.3 ; C_4 125.6 and 123.9 ; C_5 22.15 ; C_6 18.7 ; C_7 18.5 ; C_8 29.5 ; C_9 16.4 ; C_{10} 27.9 ; $C_{Ar(q)}$143.6 ; $C_{Ar(ortho)}$129.4 ; $C_{Ar(meta)}$128.7 ; $C_{Ar(para)}$125.6 and 123.9.

LR MS: 212 = M^+ ; 169=(M -43) ; 91 = tropylium ion.

7 oil (1.96g, 8.85 mmol) 60 % yield.

IR cm^{-1} : 2950-2860 (CH_3, CH_2) ; 1600 (C=C) ; 1260(S-CH_2).

^1H NMR (CCl_4) : m(9H) 0.7-1 with s(6H) 0.85 : $C_{(8)}H_3$, $C_{(9)}H_3$, $C_{(14)}H_3$; m(4H) 1.1-1.5 : $C_{(12)}H_2$ $C_{(13)}H_2$, s(3H) 2.0 : $C_{(10)}H_3$; m(2H) 2.6 : $C_{(11)}H_2$; m(4 lines)(2H) 5.43 : J_{AB}=10 Hz ; m(4 lines)(2H) 5.50 : J_{AB}=11Hz

^{13}C NMR ($CDCl_3$) : C(sp_2) 127.7, 133.5, 137.4, 133.1, 132.8, 127 ; 25.5 ; 25.5 ; 34.1 ; 21.7 ; 33.4 ; 32.2; 21.4 ; 13.4.

Mass (intensity): 222= M^+(12) ; 207= M -CH_3(100) ; 133 = M -SBu.

8 oil (1.05g, 11.2 mmol) 76 % yield.

IR cm^{-1} : 2940-2920 (CH_3, CH_2) ; 1600 (C=C) ; 1260 (S-CH_2).

^1H NMR (CCl_4) : s(6H) 0.90 : $C_{(8)}H_3$, $C_{(9)}H_3$; t(3H) 1.15 J=7Hz: $C_{(12)}H_3$; s(3H) 2.1 : $C_{(10)}H_3$; q (2H) 3.1 J = 7Hz: $C_{(11)}H_2$; m(4 lines) (2H) 5.5 J_{AB}= 10 Hz and m (4 lines)(2H) 5.6 J_{AB} = 11 Hz vinylic protons.

12 oil (1.76g, 7.4 mmol) 50 % yield. TLC: Rf= 0.5 (CH_2Cl_2/CH_3OH 98/2).

IR cm^{-1} : 3640, 3250 br.(OH) ,3030 (vinylic CH), 1610 1650(C=C), 1050 (C-O).

^1H NMR ($CDCl_3$) : s(6H) 1.0 : $C_{(8)}H_3$, $C_{(9)}H_3$; m(4H) 1.6-1.7: $C_{(12)}H_2$, $C_{(13)}H_2$; s(3H) 2.2: $C_{(10)}H_3$; m(1H) ≈ 2: (OH) ; t(2H) 2.8 J= 7Hz: $C_{(14)}H_2$; m(4H) 5.2- 6.2: vinylic H.

MS LR (intensity) : 238=M^+ (6.8) ; 223=M -CH_3 (7.4) ; 165=M -C_4H_9O (19.1) ; 133=165 -S (66.7) ; 105 =S$(CH_2)_4$OH (90.7) ; 91= tropylium ion (72.2) ; 73=$(CH_2)_4$OH (32.7).

13 oil (1.96g, 7.38 mmol) 50 % yield TLC: Rf= 0.5 (CH_2Cl_2/CH_3OH 98/2).

IR cm^{-1} : 3640, 3250 br.(OH) ,3030 (vinylic CH), 1610 1650(C=C), 1050 (C-O)

^1H NMR ($CDCl_3$) : s(6H) 1.0: $C_{(8)}H_3$, $C_{(9)}H_3$; m(8H) 1.2-1.8: $C_{(12)}H_2$, $C_{(13)}H_2$, $C_{(14)}H_2$, $C_{(15)}H_2$; s(3H) 2.16 : $C_{(10)}H_3$; t(2H) 2.8: $C_{(11)}H_2$; t(2H) 3.65 : $C_{(16)}H_2$; m(4H) 5.1-6.2 : vinylic H.

MS LR(intensity): 266=M^+ (8.6) ; 251=M -CH_3 (3.1) ; 165=M -$C_6H_{13}O$ (23,4) ; 133=165 -S (79.6) ; 91= tropylium ion (74.7).

14 oil (0.82g, 2.80 mmol) 19 % yield TLC: Rf= 0.65 (CH_2Cl_2/CH_3OH 98/2).

IR cm^{-1} : 3640, 3250 br.(OH) ,3030 (vinylic CH), 1610 1650(C=C), 1050 (C-O).

^1H NMR (CCl_4) : s(6H) 0.9 : $C_{(8)}H_3$, $C_{(9)}H_3$; m(15H) 1.15-2.2: $C_{(10)}H_2$, $C_{(11)}H_2$, $C_{(13)}H_2$, $C_{(17)}H_2$, $C_{(14)}H_3$; t(2H) 2.65 : $C_{(15)}H_2$; m(1H) ≈ 3.4: OH ; t(2H) 3.6 : $C_{(18)}H_2$; m(4H) 4.9-6.1: vinylic H.

Aldehydes Syntheses:

To a dichloromethane solution of oxalyl chloride (1.5 eq. vs alcohol) previously cooled to -60°C were added first DMSO (2 eq.), then alcohol and 20 minutes later Et_3N (5 eq.). After the end of the addition, mixture was allowed to warm up to room temperature. The medium was hydrolised with a saturated NH_4Cl solution, acidified with 2N HCl and extracted with dichloromethane. Organic layers were washed with a saturated $NaHCO_3$ solution and dried over Na_2SO_4. Solvents were evaporated under vacuum. Products isolated were in a good state of purity as checked by TLC. However every attempt to perform chromatography on silicagel or florisil led to substantial decomposition.

15 oil (1.08g, 4.59 mmol) 84 % yield; TLC: Rf=0.6 (CH_2Cl_2/CH_3OH 98/2).

IR cm^{-1} : 3000 (vinylic CH), 2750 (aldehydic H) ; 1700 (C=O), 1600 1635 (C=C).

^1H NMR ($CDCl_3$) : s(6H) 1.0 : $C_{(8)}H_3$, $C_{(9)}H_3$; m (2H) 1.4-1.9 $C_{(12)}H_2$; s(3H) 2.15 : $C_{(10)}H_3$; m(4H) 2.2-2.8: $C_{(12)}H_2$, $C_{(13)}H_2$; vinylic pattern with 5 lines, i.e. 2 systems: d(1H) 5.0 and d(1H)5.8 J≈ 10Hz, d(1H) 5.0 and d(1H) 5.9 J≈ 10Hz; s(1H) 9.6 : CHO.

16 oil (1.15g, 4.37 mmol) 80 % yield; TLC: Rf=0.6 (CH_2Cl_2/CH_3OH 98/2).

IR cm^{-1} : 2990 3030 (vinylic CH) 2700 (aldehydic H) ; 1715 (C=O) ; 1595 1635 (C=C).

^1H NMR ($CDCl_3$) : s(6H) 1.0 : $C_{(8)}H_3$, $C_{(9)}H_3$; m (13H) 1.2-2.9 with emerging s at 2.13: $C_{(10)}H_3$; vinylic pattern with 5 lines, i.e. 2 systems: d(1H) 5.10 and d(1H) 5.8 J≈ 10Hz, d(1H) 5.10 and d(1H) 6.0 J≈ 10Hz; s(1H) 9.6 : CHO.

17 oil (1.30g, 4.44 mmol) 81 % yield; TLC: Rf=0.7 (CH_2Cl_2/CH_3OH 98/2).

IR cm^{-1} : 3000 (vinylic CH) 2720 (CH aldehydic) ; 1720 (C=O) ; 1600 1635 (C=C).

^1H NMR (CCl_4) : s(6H) 1.0 : $C_{(8)}H_3$, $C_{(9)}H_3$ in a m(13H) 1.0-2.2 : $C_{(10)}H_2$, $C_{(11)}H_2$, $C_{(12)}H_2$, $C_{(13)}H_2$, $C_{(16)}H_2$,$C_{(14)}H_3$; m(4H) 2.2-2.9 : $C_{(15)}H_2$, $C_{(17)}H_2$; vinylic pattern with 5 lines, i.e. 2 systems: d(1H) 5.2 and d(1H) 5.9 J≈ 10Hz, d(1H) 5.2 and d(1H) 6.05 J≈ 10Hz; s(1H) 9.7 : (CHO).

Acids Syntheses:

A 2N $AgNO_3$ solution was added to a solution of NaOH 4N (3mL). Immediatly, formation of a brown precipited of Ag_2O occured. A dichloromethane solution of aldehyde (3.4 mL) was added to this mixture which was then warmed to 50°C. When a silver mirror was formed, the reaction was finished. The mixture was filtered, decanted. Organic layers were dried over Na_2SO_4 and solvents evaporated. Purification of the acid was performed on silicagel (eluent dichloromethane).

18 oil (0.5g, 1.9 mmol) 56% yield; TLC: Rf=0.35 (CH_2Cl_2/CH_3OH 98/2).

IR cm^{-1} : 3600-2400 (acidic OH); 1700 (C=O); 1650 (shoulder) 1595: (C-C); 1230 (C-O).

^1H NMR ($CDCl_3$) : s(6H) 1.0 : $C_{(8)}H_3$, $C_{(9)}H_3$; m(2H) 1.4-1.9 : $C_{(12)}H_2$; s(3H) 2.05 : $C_{(10)}H_3$; m(4H) 2.2-2.9 : $C_{(11)}H_2$, $C_{(13)}H_2$; vinylic pattern with 5 lines, i.e. 2 systems: d(1H) 5.15 and d(1H) 5.9 J≈ 10Hz, d(1H) 5.15 and d(1H) 6.05 J≈ 10Hz; br s(1H) 12 : COOH.

MW 252.37 $C_{14}H_{20}O_2S$: Calc. C%:66.63 H%:7.99; found: C%:66.49 H%:7.81

19 oil (0.27g, 0.95 mmol) 28% yield ; TLC: Rf=0.35 (CH_2Cl_2/CH_3OH 98/2).

IR cm^{-1} : 3600-2400 (OH acid) ; 1700 (C=O); 1640 1600 (C=C); 1255 (C-O).

^1H NMR ($CDCl_3$) : s(6H) 1.1 : $C_{(8)}H_3$, $C_{(9)}H_3$; m(6H) 1.2-2.0 : $C_{(12)}H_2$, $C_{(13)}H_2$, $C_{(14)}H_2$; s(3H) 2.2 :

$C_{(10)}H_3$; m(4H) 2.1-3.0 : $C_{(11)}H_2$, $C_{(15)}H_2$; vinylic pattern with 5 lines, i.e. 2 systems: d(1H) 5.1 and d(1H) 5.85 J≈ 10Hz, d(1H) 5.1 and d(1H) 6.05 J≈ 10Hz; br s(1H) 12 : COOH.

MW= 280.43, $C_{16}H_{24}O_2S$: Calc. C%: 68.53 H%: 8.63; Found: C%: 67.87 H%: 8.26.

20 oil (0.28g, 0.92 mmol) 27% yield.

IR cm^{-1} : 3600-2700 (OH acid) ; 1700 (C=O); 1635 1595 (C=C); 1235 (C-O).

^1H NMR (CCl_4) : s 1.05 : $C_{(8)}H_3$, $C_{(9)}H_3$ in a m(13H) 1.0-2.2 : $C_{(10)}H_2$, $C_{(11)}H_2$, $C_{(12)}H_2$, $C_{(13)}H_2$, $C_{(16)}H_2$, $C_{(14)}H_3$; m(4H) 2.2-3.15 : $C_{(15)}H_2$, $C_{(17)}H_2$; vinylic pattern with 5 lines, i.e. 2 systems: d(1H) 5.2 and d(1H) 5.9 J≈ 10Hz, d(1H) 5.2 and d(1H) 6.1 J≈ 10Hz; br s(1H) 9.5: COOH.

MW= 308.48 $C_{18}H_{28}O_2S$: Calc. C%: 70.09 H%: 9.15; Found: C%: 69.91 H%: 9.13.

Synthesis of bis-cycloheptatrienyldisulfide 9.

A solution of Δ_3 Carene adduct 5 (14.75 mmol) in THF (40 mL) was cooled to 0°C. Potassium tertiobutylate was added slowly to the mixture. When addition was finished, the temperature was allowed to warm up to 0°C. Then the medium was hydrolised with a NH_4Cl solution and extracted with diethylether. Organic layers were washed with water, then dried over Na_2SO_4 and solvents were evaporated. The product was obtained as a brown oil. Chromatography on silicagel (eluent: hexane) yielded a slightly yellow oil.

9 oil (2.43g, 7.4 mmol) 50 % yield. Rf= 0.86 (CH_2Cl_2/CH_3OH 9/1).

IR cm^{-1} : 3000 (CH) ; 2960-2870 (CH_3) ; 1670 1600 (C=C).

^1H NMR : s(6H) 0.96 : $C_{(8)}H_3$, $C_{(9)}H_3$; s(3H) 2,15 : $C_{(10)}H_3$; two vinylic systems each with two protons, d(1H) 5.23 d(1H) 5.89 J= 10.25 Hz, d(1H) 5.25 d(1H) 6.25 J= 10.5 Hz.

MS LR (intensity) 330=M^+(6.5) ; 165= M-165(100); 133=165 -S.

UV c=1 $x10^{-3}$ mol l^{-1} (EtOH) λmax= 274 nm, logε= 2.89.

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