Chapter IV

Model Studies Towards Fusicoccane diterpenes:

Construction of the 5,8,5-Fused Tricarbocyclic Ring System
IV.1. A B S T R A C T

A new stereocontrolled approach to cis,anti,cis-5,8,5- tricarbocyclic ring system from 5,5,5,5-fused tetraquinines is delineated. The basic concept in this approach is the recognition of a bicyclo[3.3.0]oct-1(5)-ene moiety as a masked cyclooctane-1,5-dione equivalent, Scheme IV.1. Thus, a C\textsubscript{14}^\textsuperscript{14}-tetraquinene \textsuperscript{14} emerged as the equivalent of a 5,8,5- fused system, Scheme IV.3 and was readily obtained from simple building blocks, cyclopentyl chloride and bicyclo[3.3.0]octan-2-carboxaldehyde \textsuperscript{19} employing Nazarov cyclisation as a key step, Scheme IV.7. Oxidation of \textsuperscript{14} with RuO\textsubscript{2}-NaIO\textsubscript{4} furnished the desired C\textsubscript{14}^\textsuperscript{14}-5,8,5-dione \textsuperscript{15} in excellent yield. The same strategy was further extended towards the enantioselective construction of the fusicoccane framework.

For this purpose, the chiron (-)-\textsuperscript{42}, readily obtained from R-(+)-limonene \textsuperscript{43}, Scheme IV.11 was coupled with 3-bromobicyclo[3.3.0]octane in the presence of lithium in a Barbier-type of reaction to furnish allylic alcohol \textsuperscript{46}, Scheme IV.13. Barium manganate oxidation of \textsuperscript{46} furnished the enone \textsuperscript{47} which was converted in to cross-conjugated dienone \textsuperscript{49} through bromination-dehydrobromination sequence. Nazarov cyclisation of \textsuperscript{49} afforded tetraquinane based enone \textsuperscript{51}. Thioacetalisation-reductive desulphurisation on \textsuperscript{51} furnished the C\textsubscript{18}-tetraquinene \textsuperscript{53}, Scheme IV.14. Oxidation with RuO\textsubscript{2}-NaIO\textsubscript{4} furnished the tricyclic C\textsubscript{18}-dione (+)-\textsuperscript{54} bearing the 5,8,5- skeleton present in fusicoccanes.
IV.2. OBJECTIVE AND BACKGROUND

The eight membered ring is the newest entrant into the diverse assemblage of carbocyclic rings present among isoprenoid natural products. In the recent past, the number of terpene carbon frameworks in which a cyclooctane ring is present as a part of condensed or bridged polycyclic system have proliferated rapidly. The cyclooctane bearing carbon frameworks have now been located among C₁₅-sesqui-, C₂₀-di- and C₂₅-sesterterpenes. Currently, nearly sixty natural products compose the structurally novel and complex family of cyclooctanoid natural products.

The eight membered ring bearing natural products are fairly widely distributed in Nature and have been encountered in terrestrial plants, marine organisms, pathogenic fungi and insects. These natural products are derived through interesting biosynthetic pathways and many of them exhibit promising biological active profile.

Among the more interesting carbocyclic variations that have surfaced in recent years embodying an eight membered ring are the uncommon 5,8- and 5,8,5-fused ring systems. Indeed, an eight membered ring shows an intriguing predilection towards partnering a five membered ring. Three sesquiterpenoids of marine origin, precapnelladiene 1, dactylol 2 and asteriscanolide 3 are examples of 5,8-fused cyclopentacyclooctane nucleus, Chart IV.1. The diterpenoids basmenone 4 from tobacco, cycloaraneosene 5 from a fungus and epoxydictymene 6 from a brown alga are based on the more intricate 5,8,5-assembly. Sesterterpenoids ophiobolins (eg. ophiobolin. H 7) and ceroplastols (eg. ceroplastic acid 8) also incorporates the 5,8,5 system.
The cyclooctanoid terpenes bearing 5,8- and 5,8,5-ring system pose considerable synthetic challenge due to the presence of uncommon assembly of carbocyclic rings, many stereogenic centres and complex functionalisation patterns. Synthetic quest for them presents a combination of unique synthetic problems. First of all, because of unfavourable entropic factors, commonly used method of ring formation are not conducive for the construction of cyclooctanes and new methodologies need to be developed for their creation. Secondly, cyclooctanes displayed
marked propensity towards transannular reaction and therefore synthetic manipulations on them have to be effected with marked/latent functionalities. Lastly, eight membered ring and its fused systems are conformationally flexible and therefore prediction and control of stereochemistry is rendered uncertain. This is a major problem in stereoselective synthesis as many of the cyclooctanoid natural products contain remote methyl group bearing stereogenic centres.

Largely, on account of the factors mentioned above, progress towards the total synthesis of cyclooctanoid natural products has been relatively slow. Dutta in 1976 was the first to describe an attempt towards the construction of the 5,8,5-ring system. This was followed by several other approaches for the realisation of 5,8- and 5,8,5-carbocyclic systems. However, it was in 1984 that the first synthesis of cyclooctanoid terpenes appeared in literature. Almost simultaneously, Mehta (precapnelladiene 1), Paquette (precapnelladiene 1) and Gadwood (dactylol 2) described the total synthesis of 5,8-fused bicyclic natural products. More recently, Wender has achieved the synthesis of the novel 5,8-fused natural product asteriscanolide 3.

In the meantime, synthetic efforts towards the construction of fused cyclooctanoid systems are continuing with much vigour. Up-to-date references to these studies have been provided. So far, only Takeshita's group has succeeded in the total synthesis of 5,8,5 - natural products. His efforts have culminated in the synthesis of cycloaraneosene 5 in 1986 and ceroplastic acid 8 in 1988. Our own efforts in the area, leading to the construction of 5,8,5-ring systems were completed in 1985 and reported in 1986.
For reasons delineated earlier the natural products based on 5,8,5-fused ring system appeared to us attractive and challenging targets of synthesis. To begin with our prime concern was to develop a general and flexible methodology for the construction of the basic 5,8,5-carbocyclic framework of well defined stereochemistry and substitution pattern. Efforts directed towards the successful realisation of this objective are described below.

IV.3. STRATEGY AND MODEL STUDIES

It was recognised, at the very outset that the main problem in constructing the 5,8,5-ring system resides in the formation of the eight membered ring and control of the stereochemistry on the flexible 5,8- and 5,8,5-ring systems. A solution therefore lay in designing a rigid substrate which is a cyclooctane equivalent and exhibits definite stereochemical preference in its reactivity. At the conceptual level, the bicyclo[3.3.0]octane ring system appeared to be an ideal and versatile cyclooctane equivalent. Oxidative or equivalent cleavage of the central bond in the bicyclic system (9 + 10 and 11 + 10) would furnish the functionalised cyclooctane ring, Scheme IV.1. More importantly, the

**SCHEME IV.1**

\[ \text{[O]} \quad 9 \quad [\text{[O]} \quad 10 \quad [\text{[O]} \quad 11 \]
spacial geometry of the cis-fused bicyclo[3.3.0]octane imparts its preferential reactivity on the exo-face (convex surface). Thus, in principle the requisite stereochemical features of the eight membered ring can be built into the bicyclic frame, Scheme IV.2.

**SCHEME IV.2**

The strategic theme of our 5,8,5-approach emerged from the extension of Scheme IV.1. If 5,5-fused bicyclic system is equivalent to an eight membered ring, then a 5,5,5-fused system should be equivalent to a 5,8-ring system \( \text{12} \rightarrow \text{13} \) and 5,5,5,5-fused system should be equivalent of a 5,8,5-fused system \( \text{14} \rightarrow \text{15} \), Scheme IV.3. Since polyquinanes prefer the
stable cis, anti, cis-type ring fusion pattern and exhibit exo-selectivity, these stereochemical controls can be transcribed from them into the dicyclopenta[a,d]cyclooctane system during the unravelling oxidative step. Therefore, the design of tetraquinene \( \text{14} \) became our first objective and a new approach was envisaged towards this end.

Prior to the present work only few synthetic entries into the \( \text{C}_{14}\)-tetraquinane system had been recorded in the literature\(^{19}\) and none of these was particularly suitable for the synthesis of \( \text{14} \). Hence, a new reaction sequence for the construction of this linearly fused tetraquinene \( \text{14} \) was conceived based on the retrosynthetic analysis, in which a Nazarov cyclisation on \( \text{17} \) to give \( \text{16} \) was contemplated as the pivotal step. Efforts were immediately initiated to build the tetraquinene \( \text{14} \) as per the theme indicated in Scheme IV.4.

**SCHEME IV.4**

\[
\begin{align*}
\text{14} & \quad \text{16} & \quad \text{17} \\
\text{19} & \quad \text{20} & \quad \text{18}
\end{align*}
\]
The required bicyclo[3.3.0]octane-2-carboxaldehyde synthon was prepared as shown in Scheme IV.5. Cyclopentene was cyclopentannulated following the dichloroketene addition–diazomethane ring expansion–dechlorination methodology of Greene to furnish bicyclo[3.3.0]octan-3-one.

**SCHEME IV.5**

Reagents, Conditions & Yields:  

- a) CCl₃COCl, Zn–Cu, Ether, 12h;  
- b) CH₂N₂, MeOH, Ether, 5°C;  
- c) Zn, CH₃COOH, RT, 55% from 21;  
- d) Ph₃P⁺CH₂OCH₃Cl, Ether, Na-t-amyloxide, RT, 1h;  
- e) Cat. 35%, HClO₄, Ether, 82% from 24.

Reaction of the bicyclic ketone 24 with the ylide derived from methoxy methyl triphenyl phosphonium chloride and sodium-t-amyloxide gave the enol ether 25 which was directly hydrolysed with 35% perchloric acid to afford aldehyde 19 in 82% yield. Although at this state the aldehyde 19 was a mixture of both exo- and endo isomers, we proceeded further without recourse to any separation since in subsequent steps the C(3)-stereogenic
centre was going to be destroyed. The gross structure of 19 was fully commensurate with its IR and $^1$H-NMR data (vide experimental).

The two pieces 19 and 20 identified in Scheme IV.4 were now put together. Ultrasound promoted condensation of cyclopentyllithium 20 and aldehyde 19 furnished a mixture of epimeric alcohols 26 in 35% yield, Scheme IV.6. This alcoholic mixture 26 was directly subjected to PCC oxidation to afford the epimeric ketones 18 ($\nu_{\text{max}}$ 1700 cm$^{-1}$) in 85% yield. This epimeric mixture of ketones 18 was transformed into a single dienone

SCHEME IV.6

Reagents, conditions & yields: a) THF, rt, 10 min, 35%; b) PCC, DCM, 4 Å molecular sieves, RT, 2h, 85%; c) Br$_2$, CCl$_4$, 15h, RT, 91%; d) Li$_2$CO$_3$-LiBr, DMF, 80°C, 4h, 80%.
through a classical protocol. Addition of bromine to 18 resulted in the formation of α,α-dibrominated product 27 in 91% yield. The dibromide 27 was directly double dehydrobrominated in the presence of Li$_2$CO$_3$-LiBr in DMF to furnish the dienone 17 in 80% yield. The ν$_{\text{max}}$ 1610 cm$^{-1}$ in its IR spectrum, the presence of signals at δ 6.6 & 6.4 due to two β-olefinic protons of the enone moiety and the resonances at δ 190.6, 145.6, 144.7, 142.9, 141.6, in its $^{13}$C-NMR firmly confirmed the structure of this key product 17, Scheme IV.6.

The dienone 17 was now well set for a Nazarov cyclisation. Heating the dienone 17 in PPA at 100°C resulted in the expected cyclisation and a 4:1 mixture of tetraquinane-based enones 16 and 28 in a combined yield of 60% was realised, Scheme IV.7. The two enones were not separable by column chromatography or preparative tlc but some separation could be effected by MPLC. However, only the major isomer 16 was obtained pure and was characterised. The presence of $^{13}$C-resonances δ 207.3, 190.2, 147.6 in its $^{13}$C-NMR (Fig. IV.1) characteristic of a tetrasubstituted cyclopentenone moiety confirmed the structure of 16. Since these two enones were not readily separable, the mixture was carried through for the next deoxygenation step.

The enone mixture of 16 and 28 was converted into the corresponding thioacetals 29 & 30 (87%) and subjected to Na-Liq.NH$_3$ reduction to furnish a mixture of tetracyclic olefins 14 & 31, Scheme IV.7. As anticipated by us the two olefins were now readily separable on AgNO$_3$-SiO$_2$ gel and both of them were now fully characterised. The required C$_{14}$-tetraquinene hydrocarbon 14 of $C_2$-symmetry exhibited the expected 8-line $^{13}$C-NMR
Reagents, conditions & yields:  

- a) PPA, 100°C, 1h, 60%;  
- b) HSCH₂CH₂SH, PTS-C₆H₆, Δ, 0.5h, 87%;  
- c) Li.Liq.NH₃, Na, 74%;  
- d) RuO₂, NaIO₄, CCl₄-MeCN-H₂O, RT, 1h, 92%.

Spectrum (Fig.IV.2) with diagnostic resonances at 150.2, 142.7, 47.4, 45.4, 37.6, 35.9, 30.2, 26.1. On the other hand the other minor tetraquinene hydrocarbon 31 had 14-resonances in its ¹³C-NMR (Fig.IV.3), which confirmed its unsymmetrical structure. It is interesting to compare
the characteristic $^{13}$C-NMR chemical shifts of the bridgehead $sp^2$ carbon atoms in the polyquinanes displayed in Chart IV.2.$^{24}$

**CHART IV.2**

The required symmetrical tetraquinene 14 was oxidised with RuO$_2$-NaIO$_4$ according to the procedure of Sharpless$^{25}$ to furnish the crystalline 5,8,5-tricarbocyclic dione 15 in 92% yield. The $\nu_{\text{max}}$ 1680 cm$^{-1}$ and 8-line $^{13}$C-NMR spectrum (Fig. IV.4) with signals at $\delta$ 216.01, 211.8, 53.6, 45.0, 40.5, 33.9, 28.0, 24.0 were fully consonant with its structure. While the gross structure of 15 was fully secured, we had so far not addressed ourselves to the stereochemical question in 15 as well as its precursor tetraquinene 14. Although it is known that in polyquinanes the cis, anti, cis- stereochemistry is thermodynamically more stable, and it might have been generated during Nazarov cyclisation step, it needed to be established unambiguously.

The structure of 15 was secured through an interesting experiment. Dione 15 was readily and regioselectively transformed to the mono-1,3-
oxathiolane derivative 32 on treatment with 2-mercaptoethanol in the presence of PPTS. The $^{13}$C-NMR of 32 was devoid of any symmetry and exhibited a 16-line spectrum (Fig. IV.5) which showed that 32 has cis, anti, cis ring fusion with $C_2$-symmetry, Scheme IV.8. If the ring junction had been cis, syn, cis-33 then the resulting mono-1,3-oxathiolane 34 would have exhibited a 10-line spectrum due to $C_s$-symmetry. This result conclusively rules out cis, syn, cis-structure for 33 and establishes it and its tetraquinene precursor 14 as having cis, anti, cis-stereochemistry.

The isomeric olefin 31 was likewise oxidised with RuO$_2$-NaIO$_4$ to furnish the interesting ring system 35 in 92% yield, Scheme IV.9. Once again the presence of $\nu_{\text{max}}$ 1680 cm$^{-1}$ in its IR and resonances at $\delta$ 213.8 and 212.9 corresponding to two carbonyl groups in its $^{13}$C-NMR spectrum
confirmed the structure of the dione 35. The stereochemistry of the ring junction was assigned as cis, anti, cis on the basis of previous analogy.

**SCHEME IV.9**

```
31  \[\rightarrow\]  35
```

Reagents, Conditions & Yields: a) RuO₂, NaIO₄, CCl₄-MeCN-H₂O, 92%.

Having established a viable methodology for the construction of the 5,8,5- dione 15 employing a model tetraquinene 14, we ventured to amplify the scope of this theme for the construction of the carbocyclic framework of fusicoccane diterpenes.

**IV.4. SYNTHESIS: Towards the Enantioselective Construction of the Fusicoccane Framework**

Construction of the functionalised fusicoccane framework 36 following the 5,5,5,5 → 5,8,5 strategy demonstrated above required the generation of the appropriately substituted tetraquinene 37. The tetraquinene 37, in turn could be assembled through a pivotal Nazarov cyclisation as indicated in the retrosynthetic Scheme IV.10. Thus, 40 and 42 were indicated as two
starting synthons. An advantage of this theme was that employing a chiron an enantioselective approach to the tricyclic fusicoccane framework could be developed. We therefore decided to put in practice the retrosynthetic theme shown in Scheme IV.10. However, in order to avoid regeochemical problems, we decided to employ 3-bromobicyclo[3.3.0]octane instead of its methyl substituted derivative 40.

Of the two pieces, chiron ([\(\alpha\)]\(_D\)-7.9 ; c.1.0, CHCl\(_3\)) was readily prepared from R- (+)-limonene as shown in Scheme IV.11. Experimental details about its preparation have been described earlier in the first
Reagents, Conditions & Yields: a) i. m-CPBA, CHCl₃; ii. 1% H₂SO₄, THF-H₂O; iii. NaIO₄, THF-H₂O; iv. PtO₂, EtOAc, H₂, 20 psi; b) CH₃COOH, Piperidine, benzene.

chapter of this thesis. The other piece, the exo-3-bromobicyclo[3.3.0]octane 41 was prepared from bicyclo[3.3.0]octan-3-one 24 as shown in Scheme IV.12.

Reagents, Conditions & Yields: a) LAH, ether, RT, 1h, 80%; b) PBr₃, 0°C, 1h, quantitative.
Barbier-type reaction between chiral enal 42 and bromide 41 in the presence of lithium chips and under ultrasound irradiation led to the formation of diastereomeric mixture of allylic alcohols 46 in 40% yield, Scheme IV.13. Oxidation of this mixture of alcohols 46 was attempted with many oxidising agents like PCC, PDC, MnO₂ etc., but none of them gave the required enone 47. Only uncharacterisable complex mixtures were obtained in the reactions. However, this problem could be overcome by employing barium manganate as the oxidising agent which clearly gave the enone 47 (60:40) in 55% yield, as a mixture of diastereomers. Separation of stereoisomers was considered unnecessary at this stage. Carefully controlled mono-bromination α to the carbonyl group in 47 with 2,4,4,6-tetrabromocyclohexa-2,5-diene gave the bromo-enone 48 which was directly subjected to dehydrobromination with Li₂CO₃-LiBr in DMF to furnish dienones 49 & 50 (1:1) in 26% yield. The IR spectrum (ν max 1620 cm⁻¹) and the presence of ¹H-NMR resonances at δ 6.4 and δ 1.8 due to the β-proton and β-methyl groups of the two enone moieties confirmed its structure, Scheme IV.13.

The stage was now set for the Nazarov cyclisation step. However, the conditions employed earlier for the Nazarov-type cyclisation (PPA, 100°C) failed to effect the cyclisation in this case. Recourse to P₂O₅, methane sulphonic acid, BF₃-etherate, SnCl₄ etc. did not prove encouraging. After many trials, it was observed that PTS effected the desired cyclisation but in poor (20%) yield. Thus, exposure of 49 & 50 to PTS in refluxing toluene
SCHEME IV.13

Reagents, Conditions & Yields: a) Li, THF, 0-10°C, 1h, 40%; b) BaMnO₄, DCM, 15h, RT, 55%; c) 2,4,4,6-tetrabromocyclohexa-2,5-dienone, cat.HCl(gas), ether, RT, 12h; d) Li₂CO₃-LiBr. DMF, 80°C, 2h, 26% from 47.

provided the required tetracyclic enone 51, surprisingly as a single stereoisomer Scheme IV.14. This was a fortuitous outcome in same sense as it avoided the difficulty in separation but it did render the stereochemical assigned somewhat difficult. The structure of enone 51 was clearly indicated by its IR (νmax 1700, 1640 cm⁻¹), ¹H-NMR (δ 1.24 (3H, s), 0.97 (3H, d) and 0.88 (3H, d), Fig. IV.7) and ¹³C-NMR (Fig. IV.8) spectrum. However, delineation of its stereochemistry presented some difficulties. Since 51 is formed from 49 during thermodynamically controlled conditions, a more stable cis, anti, cis stereochemistry for the
Reagents, Conditions & Yields: a) PTS, toluene, 2h, 20%; b) HS-CH$_2$CH$_2$SH, PTS, C$_6$H$_6$, Δ; c) Li-Liq.NH$_3$, Na; d) RuO$_2$, NaI$_2$, CCl-MeCN-H$_2$O, 0.5, RT, 82%.

Polyquinane fusion appears reasonable. Stereochemistry to the C(6)-isopropyl group is based on the comparison of $^{13}$C-NMR chemical shifts between enone 51 and the enone 16 and model compounds$^{24}$ 55, 56 & 57 as shown in Chart IV.3. However, this stereochemical assignment should be regarded as only tentative.
The enone 51 was now prepared for the cyclooctane revelation protocol. Deoxygenation of 51 via thioacetalisation-desulphurisation sequence gave the labile olefin 53 which was directly subjected to RuO₂- NaIO₄ oxidation to furnish the crystalline (+)-dione 54 ([α]D + 15; c 0.1 CHCl₃) in 82% yield Scheme IV.14. The structure of dione 54 was fully secured through its IR (ν max 1680 cm⁻¹) and ¹H-NMR spectrum (Fig. IV.9) which exhibited methyl signals at δ 1.25 (3H, s), 1.0 (3H, d), 0.87 (3H, d). Thus, tricyclic C₁₈-dione 54 bearing the basic carbon skeleton of fusicoocanes and having desirable functionalisation in the eight membered ring became available from readily available building blocks.
IV.5. SUMMARY AND OUTLOOK

A short and general approach to functionalised cis, anti, cis 5,8,5-fused ring system 15 from the readily available bicyclo-[3.3.0]octan-3-one 24 has been developed via the novel tetraquinene hydrocarbon 14. A similar 5,5,5,5 → 5,8,5 methodology has been applied for the enantioselective construction of the fusicocccane carbon skeleton 54 employing the chiron (-)-42. The general protocol delineated here has built-in flexibility and can be readily adapted for the synthesis of ophiobolins and other 5,8,5-fused systems. The concept of using bicyclo[3.3.0]octene 9 as a cyclooctane dione equivalent can be extended to higher homologues and exploited for related complex syntheses. For example, homologue 58 of tetraquinene 14 can generate a 5,9,5-system 59 present in biologically important natural product jatropha trione 60.29
IV.6. EXPERIMENTAL

For a general write-up see the experimental section of the first chapter.

cis-Bicyclo[3.3.0]octan-8-one (24):^22

Into a 500 ml three necked RB flask fitted with a dry N\(_2\) inlet, an addition funnel and mercury seal was placed cyclopentene (10 g, 0.15 mol) in dry ether (250 ml). To this activated Zn-Cu couple (19.5 g, 0.3 mol) was added followed by trichloroacetyl chloride (17.7 ml, 0.18 mol) through an addition funnel over a period of 1 h. After the addition was over the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with water (100 ml) and the organic layer was separated. The aqueous layer was once again extracted with ether (100 ml x 3). The combined ethereal extract was washed, dried and concentrated to a crude bicyclic dichloroketone 22 (20 g) which was directly used for the next step.

To a solution of above crude bicyclic dichloroketone 22 (10 g, 60 mmol) in ether (100 ml) catalytic amount of methanol (1 ml) was added followed by an ethereal solution of diazomethane prepared by treating nitrosomethyl urea with KOH. The reaction mixture was kept at 5\(^\circ\)C for 1 h and excess diazomethane was destroyed with a few drops of acetic acid. Removal of the solvent furnished the crude ring expanded dichloroketone 23 (12 g) which was used as such for the next reaction.

Into a 100 ml RB flask the above crude bicyclic dichloroketone 23 (10 g, 57.0 mmol) was placed in acetic acid (50 ml) and cooled in an ice-bath.
To this zinc (4.0 g, 60.0 mmol) was added in small portions and the reaction mixture was stirred for 5 h. Then the reaction mixture was diluted with water (200 ml) and extracted with ether (250 ml x 3). The combined ethereal extract was washed with sat. NaHCO₃, water, dried and concentrated to crude product which was distilled at reduced pressure to afford the bicyclo[3.3.0]octan-3-one 24 (10 g) in 55% yield. The IR and ¹H-NMR data of 24 was found identical with the reported in the literature.

**IR**

: 1725 cm⁻¹

**¹H-NMR**

: 6.30 - 2.4 (4H, m), 2.0 - 1.0 (8H, m)

**cis-Bicyclo[3.3.0]octane-3-carboxaldehyde (19):**

Into a 50 ml three necked RB flask fitted with dry N₂ inlet, septum and mercury seal, methoxymethyltriphenyolphosphonium chloride (10.3 g, 17.0 mmol) was placed. The solid was suspended in of dry ether (10 ml) and freshly sublimed sodium t-amyloxide (1.87g, 17.0 mmol) in dry ether (5 ml) was added and the resulting dark red reaction mixture was stirred for 45 min at room temperature. To this the bicyclic ketone 24 (2.0 g, 15.6 mmol) in dry ether (5 ml) was added and the contents were stirred for 1 h. The reaction mixture was quenched by addition of water and extracted with ether (100 ml x 3). The combined ethereal extract was washed, dried and concentrated. The crude enol ether 25 thus obtained was used as such for the next step.

Into a 50 ml RB flask the above crude enol ether 25 was placed in ether (25 ml) and cooled in an ice-bath. To this 0.5 ml of 35%
perchloric acid was added and the reaction mixture was stirred for 6 h at room temperature. Then the reaction mixture was diluted with ether and quenched by careful addition of 5% NaHCO₃. The ethereal layer was separated and the aqueous layer was once again extracted with ether (50 ml x 3). The combined ethereal extract was washed, dried and concentrated to a crude product which was charged on a silica gel (20 g) column. Elution with pet ether resulted in the removal of triphenylphosphine derived impurities and further elution with 5% ethyl acetate - pet ether furnished the aldehyde 19 (1.81 g, mixture of epimers) in 82% yield. The IR and ¹H-NMR spectral values of 19 were found identical with the reported in the literature.²⁰

bp. : 110°/1.0 mm
IR : 2950, 2750, 1750, 1450, 1110 cm⁻¹
¹H-NMR : δ9.57 (2H, d, J = 4 Hz, O-C-H), 2.8 – 1.0 (m, 26H)

3-cis-Bicyclo[3.3.0]octan-1-cyclopentyl methanol (26):

Into a 50 ml three necked RB flask, fitted with dry N₂ inlet, pressure equalising addition funnel and mercury seal, freshly cut lithium pieces (140 mg, 20.0 mmol) were placed and dry THF (5 ml) was introduced. To this mixture chlorocyclopentane (2.1 g, 15 mmol) in dry THF (5 ml) was slowly added through addition funnel and the reaction was subjected to ultrasound by placing the RB flask in ultrasound generator containing water, where it gives maximum agitation. After all the lithium metal had reacted a solution of the aldehyde (1.5 g, 10.5 mmol) in dry THF (5 ml) was slowly added to it and the reaction mixture was sonicated for further 10 min. The reaction mixture was quenched by addition of saturated NH₄Cl solution (50
ml) and extracted with ether (100 ml x 3). The combined organic extract was washed, dried and concentrated to a crude product (1.5 g) which was filtered through a silica gel (10 g) column to furnish the alcohol 26 (760 mg, epimeric mixture) in 35% yield.

bp. : 160°C/0.1 mm
IR : 3400, 2950, 1450, 1060, 1010 cm⁻¹
¹H-NMR : δ3.30 (2H, t, J = 7Hz, -CH-OH), 2.4 - 0.8 (44H, series of m)
Analysis : C₁₄H₂₄O Calcd: C, 80.71; H, 11.61
Found: C, 80.42; H, 11.60

3-cis-Bicyclo[3.3.0]octan-1-cyclopentyl ketone (18):

To a suspension of pyridinium chlorochromate (1.0 g, 7.0 mmol) in dry dichloromethane (10 ml) containing activated molecular sieves (4 Å, 1. g) was added the alcohol (760 mg, 3.65 mmol) at ice-bath temperature. The contents were stirred for 2 h and diluted with dry ether (50 ml). Then the contents were filtered through a florisil pad and repeatedly washed with dry ether. Removal of the solvent gave the crude product which was filtered through a silica gel (5 g) column by eluting with 10% ethyl acetate - pet ether to furnish the ketone 18 (640 mg) in 85% yield as an epimeric mixture.

bp. : 140°C/0.1 mm
IR : 2950, 1700, 1450, 1100 cm⁻¹
¹H-NMR : δ3.2 - 2.8 (4H, m), 2.7 - 2.3 (4H, m), 2.2 - 1.0 (36H, m)
Analysis : C₁₄H₂₂O Calcd: C, 81.50; H, 10.75
Found: C, 81.47; H, 10.73
1,1'-Dibromo-3-cis-bicyclo[3.3.0]octan-1'-cyclopentyl ketone (27):

In to a 25 ml three necked RB flask fitted with a dry N₂ inlet, pressure equalising addition funnel and mercury seal, ketone 18 (600 mg, 2.9 mmol) was placed in dry carbontetrachloride (5 ml). Bromine (1.0 g, 6.2 mmol) solution in dry carbontetrachloride (5 ml) was added slowly through addition funnel and stirred for 15 h at room temperature. The reaction mixture was quenched by addition of saturated NaHCO₃ and extracted with dichloromethane (25 ml x 3). The combined organic extract was washed, dried and concentrated. The crude product thus obtained was filtered through a silica gel (15 g) column to furnish the dibromoketone 27 (960 mg) in 91% yield. The pure product was recrystallised from pet ether.

mp. : 53°C

IR : 2950, 1700, 1450, 1220, 940 cm⁻¹

¹H-NMR : δ3.0 - 2.2 (8H, series of m), 2.1 - 1.4 (12H, series of m)

Analysis : C₁₄H₂₀Br₂O

Calcd: C, 46.17 ; H, 5.53

Found: C, 46.34 ; H, 5.58

3-cis-Bicyclo[3.3.0]octan-1'-cyclopentyl-2,1'-dienone (17):

Into a 25 ml three necked flask fitted with a dry N₂ inlet, septum and mercury seal, LiBr (865 mg, 10 mmol), Li₂CO₃ (740 mg, 10 mmol) were placed. The solid mixture was suspended in dry dimethylformamide (5 ml) and dibromoketone 27 (1.0 g, 2.75 mmol) in dry dimethylformamide (5 ml) was added. The reaction mixture was heated at 80°C for 4 h with stirring. Then the reaction mixture was poured into ice-cold water (50 ml) and extracted with ether (50 ml x 3). The combined ethereal extract was
washed, dried and concentrated to a crude product which was filtered through a small silica gel (5 g) column. Elution with 10% ethyl acetate - pet ether furnished the dienone \( J_7 \) (385 mg) in 80% yield.

**bp.** : 140°C/0.1 mm

**IR** : 3050, 2950, 1440, 1370 cm\(^{-1}\)

**\(^1\)H-NMR** : \( \delta \) 6.6 (1H, br s, \(-\text{CH}=-C=\)), 6.4 (1H, br s, \(-\text{CH}=-C=\)), 3.7 - 3.1 (1H, m), 3.0 - 1.4 (15H, series of m)

**\(^{13}\)C-NMR** : \( \delta \) 190.6, 145.0, 144.7, 142.9, 141.6, 51.4, 39.6, 39.3, 35.0, 33.5, 31.5, 25.1, 22.3

**Analysis** : C\(_{14}\)H\(_{18}\)O  
Calcd: C, 83.12 ; H, 8.97  
Found: C, 83.02 ; H, 8.99

**cis,anti,cis-Tetra cyclo[6.6.0.0\(^{2\prime},6\prime,10\prime,14\prime\}]tetradec-1(8)-en-7-one (16) and cis,anti,cis-tetracyclo[6.6.0.0\(^{2\prime},6\prime,10\prime,14\prime\}]tetradec-2(6)-en-7-one (28):**

Into a 25 ml three necked RB flask fitted with a dry N\(_2\) inlet, septum and mercury seal, polyphosphoric acid (5 ml) was placed and heated to 100°C. Then the dienone \( J_7 \) (300 mg, 1.5 mmol) was added and heating was continued with vigorous stirring at 100°C for 1 h. The reaction mixture was brought to room temperature, and poured into ice and extracted with ether (50 ml x 3). The combined ethereal extract was washed, dried and concentrated to give a crude product which was filtered through a silica gel (5 g) column. Elution with 5% ethyl acetate - pet ether furnished the tetracyclic enones 16 and 28 (120 mg) in 60% yield (regio isomeric mixture of enones in approximately 4:1 ratio from which only major isomer 16 could be separated in small amounts using MPLC and characterised).

**bp.** : 140°C/0.1 mm
IR : 2950, 1690, 1640, 1450, 1390 cm⁻¹

¹H-NMR : δ 3.4 - 2.9 (3H, m), 2.8 - 1.0 (15H, series of m)

¹³C-NMR (fig. IV.1) : δ 207.2, 190.2, 147.6, 57.2, 47.2, 46.7, 41.3, 35.4, 32.0, 29.8, 29.4, 27.7, 26.2, 24.3

Analysis : C₁₄H₁₈O Calcd: C, 83.12 ; H, 8.97
Found: C, 83.15 ; H, 8.93


Into a 50 ml RB flask fitted with a reflux condenser tetracyclic enone mixture 16 and 28 (200 mg, 1.5 mmol) was placed in dry benzene (25 ml). To this ethane dithiol (0.5 ml) and PTS (15 mg) were added and the contents were refluxed for 30 min. Then reaction mixture was diluted with benzene (50 ml) and washed with saturated NaHCO₃ solution. The crude product obtained was charged on a silica gel (3 g) column. Elution with pet ether resulted in the removal of ethane dithiol impurities and further elution with 5% ethyl acetate - pet ether furnished the mixture of thioacetals 29 and 30 (200 mg, mixture of regio isomers) in 87% yield.

IR : 2950, 1450, 1270 cm⁻¹

¹H-NMR : δ 3.25 (8H, s, -S-CH₂-CH₂-S-), 3.3-1.2 (36H, series of m)


Into a two necked 100 ml RB flask, fitted with a guard tube and septum, was taken freshly distilled liq.NH₃ (50 ml). To this was added freshly cut
sodium metal (115 mg, 5 mmol) piece by piece. The resulting blue solution was stirred for 5 min and thioacetal (200 mg, 0.72 mmol) in dry ether (5 ml) was added slowly to it. The reaction mixture was quenched with saturated \( \text{NH}_4\text{Cl} \) solution after all the ammonia had evaporated. The reaction mixture was diluted with water (25 ml) and the aqueous layer was extracted with \( n \)-pentane (50 ml x 3). The combined pentane extract was washed, dried and concentrated to a crude product which showed two components on silver nitrate impregnated TLC plate. The crude product was chromatographed on a silver nitrate impregnated silica gel (20 g) column. Elution with pentane furnished the symmetric tetraquinene hydrocarbon 14 (80 mg).

bp. : \( 130^\circ \text{C}/0.1 \text{ mm} \)
IR : 2950, 1440 cm\(^{-1}\)
\(^1\)H-NMR : 63.1 - 2.6 (4H, m), 2.5 - 2.2 (2H, m), 1.9 - 1.2 (14H, m)
\(^{13}\)C-NMR : 6150.2, 142.7, 47.4, 45.4, 37.6, 35.9, 30.2, 26.1
(fig. IV.2)
Mass : \( \text{C}_{14}\text{H}_{20} \quad \text{M/e} \quad \text{Calcd: } 188.1564 \)
Found: 188.1584

Further elution with 10% benzene - pentane furnished unsymmetric tetraquinene hydrocarbon 31 (20 mg) in a combined yield of 74% (4:1).

bp. : \( 130^\circ \text{C}/0.1 \text{ mm} \)
IR : 2950, 1450, 1000 cm\(^{-1}\)
\(^1\)H-NMR : 63.2 - 2.9 (1H, m), 2.6 - 1.2 (19H, series of m)
\(^{13}\)C-NMR : 6148.3, 142.4, 55.1, 48.1, 47.0, 44.5, 40.7, 35.7, 33.9, 32.1, 29.1, 27.9, 27.4, 25.8
(fig. IV.3)
Mass : \( \text{C}_{14}\text{H}_{20} \quad \text{M/e} \quad \text{Calcd: } 188.1564 \)
Found: 188.1586
Into a 25 ml RB flask the symmetric tetraquinene hydrocarbon \( I_4 \) (80 mg, 0.42 mmol) was taken in a mixture of carbontetrachloride, acetonitrile and water (each 2 ml). To this mixture were added sodium metaperiodate (213 mg, 1.0 mmol) and ruthenium dioxide (3 mg). After being stirred for 30 min, the reaction was diluted and extracted with dichloromethane (25 ml x 3). The combined organic extract was washed and dried. The crude product obtained after removal of the solvent was filtered through a small silica gel (5 gm) column with 10% ethyl acetate - pet ether to furnish the dione 15 (85 mg) in 92% yield. The dione was recrystallised from pet ether - dichloromethane mixture.

**mp.** : 66°C

**IR** : 2950, 1690, 1440, 1250, 1180 cm\(^{-1}\)

**\(^{1}\)H-NMR** : 63.05 (2H, t, J = 8Hz), 2.6 - 1.4 (18H, series of m)

**\(^{13}\)C-NMR** : 5216.1, 211.8, 53.6, 45.0, 40.5, 33.9, 28.0, 24.0

**Analysis** : \( C_{14}H_{20}O_{2} \)

Calcd: C, 76.32 ; H, 9.15

Found: C, 76.40 ; H, 9.17

9,9-(Ethylene oxathio)-cis,anti,cis-Tricyclo[6.9.0.0\(^3\)\(^7\)]tetradec-2-one (32):

A solution of diketone 15 (75 mg, 0.34 mmol), 2-mercapto ethanol (0.2 ml) and PPTS (25 mg) in dry benzene (20 ml) was refluxed with a Dean-Stark water separator for 3 h. The reaction mixture was diluted with benzene (25 ml), washed with aqueous NaHCO\(_3\) and water, then dried. The crude product obtained after removal of the solvent was charged of a silica gel (10 g) column. Elution with 5% ethyl acetate - pet ether removed sulfur impuri-
ties. Further elution with 10% ethyl acetate - pet ether furnished the
1,3-oxathioacetal ketone 32 (72 mg) in 72% yield, which was recrystallised
form hexane.

mp. : 91°C
IR : 2950, 1680, 1440, 1200, 1100, 1060, 840 cm⁻¹
¹H-NMR : 6.4 - 4.0 (2H, m, -O-CH₂CH₂-S-), 3.2 - 2.9 (4H, m, -O-
CH₂CH₂-S), 2.6 - 1.2 (18H, series of m)
¹³C-NMR : 6218.7, 98.5, 70.2, 53.4, 52.1, 43.2, 42.2, 41.6, 39.9,
( fig. IV.5) 35.5, 35.2, 33.1, 29.1, 28.6, 24.0, 23.8
Analysis : C₁₆H₂₄O₂S  Calcd: C, 68.52; H, 8.62
Found: C, 68.56; H, 8.59
cis,anti,cis-Tricyclo[6.6.0.0²,6]tetradeca-10,14-dione (35):

Into a 25 ml RB flask the unsymmetric tetraquinene hydrocarbon 31 (20
mg, 0.1 mmol) was placed in a mixture of carbontetrachloride, acetonitrile
and water (each 1 ml). To this mixture were added sodium metaperiodate
(110 mg, 0.5 mmol) and ruthenium dioxide (3 mg). After being stirred for
30 min the reaction mixture was diluted and extracted with dichloromethane
(25 ml x 3). The combined organic extract was washed and dried. The crude
product obtained after removal of solvent was filtered through a small
silica gel (5 g) column with 10% ethyl acetate - pet ether to furnish the
dione 35 (21 mg) in 90% yield, which was recrystallised from hexane -
dichloromethane mixture.

mp. : 129°C
IR : 2950, 1680, 1450, 1260 cm⁻¹
¹H-NMR : 63.0 - 2.0 (11H, series of m), 1.9 - 1.1 (9H, m)
C-NMR (fig. IV.6):  δ 213.8, 212.9, 62.2, 45.2, 43.5 (2C), 42.7, 41.7, 40.0 (2C),
                   33.9, 33.5, 26.1, 23.9

Analysis:  C_{14}H_{20}O_2
Calcd:  C, 76.32 ; H, 9.15
Found:  C, 76.30 ; H, 9.14

3-endo-Hydroxy-cis-bicyclo[3.3.0]octane (45):

Into a 100 ml RB flask ketone 24 (5 g, 40.3 mmol) was placed in dry ether (60 ml) and cooled in ice bath. To this lithium aluminium hydride (1.5 g, excess) was added. The reaction mixture was stirred at room temperature for 30 min and then excess lithium aluminium hydride was destroyed by careful addition of ethyl acetate followed by saturated Na$_2$SO$_4$ solution. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (100 ml x 3). The combined organic extract was washed, dried and concentrated. The crude product thus obtained was distilled at reduced pressure to furnish endo alcohol 45 (4.5 g) in 90 % yield.

IR:  3450, 2950, 1100 cm$^{-1}$

$^1$H-NMR:  δ 3.97 (1H, m, CH-OH), 3.0 - 1.0 (13H, series of m)

exo-3-Bromo-cis-bicyclo[3.3.0]octane (41):

Into a 50 ml two necked RB flask fitted with a pressure equalising addition funnel and mercury seal, bicyclic alcohol 45 (5 g, 40 mmol) was placed and cooled in ice-bath. To this phosphorous tribromide (5.4 g, 20 mmol) was added drop wise and the reaction mixture was stirred for 1h. Then the reaction mixture was poured into ice cold water and extracted with
ether (50 ml x 3). The combined ethereal extract was washed with saturated NaHCO₃, water and dried. The crude product obtained after removal of the solvent was distilled at reduced pressure to furnish bromide 4₁ (6.0 g) in 80% yield. The IR and ¹H-NMR spectral values of 4₁ were found identical with the reported in the literature.²⁶

bp. : 110°C/0.1 mm
IR : 2950, 1200, 910 cm⁻¹
¹H-NMR : δ 4.5 (1H, m, -CHBr), 2.9–2.6 (2H, m), 2.4–1.1 (10H, series of m)

55-Isopropyl-2-methyl cyclopent-1-ene-1-carboxaldehyde (42):

Enantiomerically pure enal 4₂ was prepared from R-(-)-limonene according to the procedure described in the experimental section of the chapter I.

3'-cis-Bicyclo[3.3.0]octa-2-methyl-5-isopropyl-1-ene-1-cyclopentyl methanol (46):

Into a 50 ml three necked RB flask, fitted with dry N₂ inlet, a rubber septum and mercury seal, freshly cut lithium pieces (140 mg, 20.0 mmol) were placed and dry THF (10 ml) was introduced. To this mixture bromide 4₁ (4.6 g, 25 mmol) and enal 4₂ (1.5 g, 10.0 mmol) in dry THF (5 ml) were added. Then the reaction mixture was subjected to ultrasound by placing the RB flask in an ultrasound generator containing water, where it gives maximum agitation for 1 h. Occasionally crushed ice was added to the water present in the sonicator to maintain the temperature constantly at 15–20°C.
The reaction mixture was quenched with saturated NH₄Cl solution and then extracted with ether (50 ml x 3). The combined ethereal extract was washed and dried. The crude material obtained after removal of the solvent was chromatographed on a silica gel (25 g) column. Elution with 5% ethyl acetate - pet ether removed the unreacted bromide impurities and further elution with 10% ethyl acetate - pet ether furnished the allylic alcohol 46 (1.0 g) in 40% yield as a diastereomeric mixture.

bp. : 160°C/ 0.1 mm
IR : 3450, 2950, 1440, 1000 cm⁻¹
¹H-NMR : δ 4.2 (2H, br d, J = 12 Hz, -CH-OH), 3.8 - 1.2 (40H, series of m), 1.63 (6H, br s, -C==C-CH₃), 0.92 (6H, d, J = 7Hz, -CH-CH₃), 0.75 (6H, d, J = 7Hz, -CH-CH₃)
Analysis : C₁₈H₃₀O Calcd: C, 82.38 ; H, 11.52
Found: C, 82.30 ; H, 11.55

3'-cis-Bicyclo[3.3.0]octa-2S-isopropyl-1-en-1-cyclopentyl ketone (47):

Into a 100 ml RB flask allylic alcohol 46 (1.0 g, 3.8 mmol) in 50 ml of dry dichloromethane was placed. To this freshly prepared dry barium manganate²⁷ was added and the reaction mixture was stirred vigorously for 15h. Then the reaction mixture was filtered through a buchner funnel and the solid remained was washed repeatedly with dichloromethane (50 ml). The filtrate was concentrated to give a crude product which was filtered through a small silica gel (10 g) column with 10% ethyl acetate - pet ether to furnish enone 47 (540 mg) in 55% yield as diastereomeric mixture.

bp. : 150°C/0.1 mm
IR : 2950, 1660, 1450, 1360, 1150 cm⁻¹

H-NMR : 63.2 - 2.9 (2H, m), 2.6 - 2.0 (6H, m), 1.95 (6H, br s, -C=C-CH₃), 1.8 - 1.0 (30H, m), 0.95 (6H, d, J = 7Hz, -CH-CH₃), 0.75 (6H, d, J = 7Hz, -CH-CH₃)

Analysis : C₁₈H₂₈O Calcd: C, 83.02 ; H, 10.84
Found: C, 83.15 ; H, 10.90

3-cis-Bicyclo[3.3.0]octa-2-methyl-5S-isopropyl-1,2-dien-1-cyclopentyl ketone (49) and (50):

Into a 50 ml three necked flask fitted with a dry N₂ inlet, septum and mercury seal, was placed 2,4,4,6-tetrabromocyclohexa-2,5-dienone (1.23 g, 3.0 mmol) in dry ether (20 ml). To this suspension enone 47 (500 mg, 1.9 mmol) in dry ether (10 ml) was added and catalytic amount of HBr gas was bubbled through the reaction mixture to initiate the reaction. Then the reaction mixture was stirred for 12 h at room temperature, quenched with aqueous NaHCO₃ solution and extracted with ether (25 ml x 3). The combined extract was washed, dried and concentrated to give an oily crude bromo-enone 48 which was directly used for further reaction.

Into a 25 ml three necked RB flask fitted with a dry N₂ inlet, septum and mercury seal LiBr (430 mg, 5 mmol), Li₂CO₃ (370 mg, 5 mmol) were placed. This solid mixture was suspended in 5 ml of dry dimethylformamide and the above crude bromo-enone 48 in dry dimethylformamide (5 ml) was added. The reaction mixture was heated at 80°C for 2 h. Then the reaction mixture was poured into ice cold water (10 ml) and extracted with ether (25 ml x 3). The combined ethereal extract was washed, dried and concentrated. The crude product thus obtained was charged on a silica gel (10 g) column.
Elution with 10% ethyl acetate - pet ether removed less polar impurities and further elution with 15% ethyl acetate - pet ether furnished the dienones 49 and 50 (130 mg) in 26% yield as a diastereomeric mixture.

bp. : 150°C/0.1 mm
IR : 2950, 1620, 1440, 1360 cm⁻¹
¹HNMR : δ 6.35 (2H, br s, −C=CH), 3.2 − 1.8 (12H, series of m), 1.75 (6H, br s, −C=C−CH₃), 1.7 − 1.2 (20H, series of m), 0.88 (6H, d, J = 7Hz, −CH−CH₃), 0.75 (6H, d, J = 7Hz, −CH−CH₃)

Analysis : C₁₈H₂₆O Calcd: C, 83.66 ; H, 10.14
Found: C, 83.69 ; H, 10.17

2-Methyl-5-isopropyl-cis,anti,cis-tetracyclo[6.6.0.0^2.6,0^10,14]tetradec-1(8)-en-7-one (51):

Into a 25 ml RB flask dienoned 49 and 50 (150 mg, 0.58 mmol) in dry toluene (10 ml) were placed. To this mixture catalytic amount of PTS (5 mg) was added and the reaction mixture was refluxed for 2 h. Then the reaction mixture was diluted with benzene (50 ml) and washed with saturated NaHCO₃, water and dried. The crude product obtained after removal of the solvent was filtered through a small silica gel (5 g) column. Elution with 5% ethyl acetate- pet ether furnished a single tetracyclic enone 51 (30 mg) in 20% yield.

[α]D : +25.5 (c 0.5, CHCl₃)
bp. : 150°C/0.1 mm
IR : 2950, 1700, 1640, 1020 cm⁻¹
Into a 25 ml RB flask fitted with a reflux condenser, tetracyclic enone 51 (100 mg, 0.39 mmol) was placed in dry benzene (10 ml). To this was added ethane dithiol (0.5 ml) and p-toluenesulfonic acid (15 mg) and the reaction mixture was refluxed for 30 min. The reaction mixture was diluted with benzene (25 ml) washed with saturated NaHCO$_3$ solution and dried. The benzene extract was concentrated to give the crude product which was charged on a silica gel (15 g) column. Elution with 5% ethyl acetate - pet ether removed the ethane dithiol derived impurities. Further elution with 10% ethyl acetate - pet ether furnished the thioacetal 52 (110 mg) in 90% yield.

IR : 2950, 1460, 1370, 1020 cm$^{-1}$

$^1$H-NMR : 63.2 - 3.0 (4H, m, -S-CH$_2$-CH$_2$-S-), 3.0 - 1.3 (17H, series of m), 1.08 (3H, s, -C-CH$_3$), 0.95 (3H, d, J = 7Hz, -CH-CH$_3$), 0.85 (3H, d, J = 7Hz, -CH-CH$_3$)

Analysis : C$_{18}$H$_{26}$O

Calcd: C, 83.66 ; H, 10.14

Found: C, 83.64 ; H, 10.11
3-methyl-6S-isopropyl-cis,anti,cis-tricyclo[9.3.0.0^3,7]tetradeca-2,9-dione (54):

Into a two necked 100 ml RB flask, fitted with a guard tube and septum, was taken freshly distilled liq. NH₃ (50 ml). To this was added freshly cut sodium metal (60 mg, 2.7 mmol) piece by piece. The resulting blue solution was stirred for 5 min and the thioacetal 52 (100 mg, 0.3 mmol) in dry ether (2 ml) was added slowly to it. After stirring for 1 h, the reaction mixture was quenched by careful addition of NH₄Cl. After all the ammonia had evaporated, the reaction mixture was diluted with water (25 ml) and extracted with pentane (50 ml x 3). The combined pentane extract was washed, dried and concentrated to a crude tetracyclic hydrocarbon 53 which was directly used for further reaction.

Into a 25 ml RB flask, the above crude hydrocarbon 53 was taken in a mixture of carbon tetrachloride, acetonitrile and water (each 2 ml). To this mixture were added sodium metaperiodate (213 mg, 1.0 mmol) and ruthenium dioxide (3 mg). After being stirred for 30 min the reaction mixture was diluted and extracted with dichloromethane (25 ml x 3). The combined organic extract was washed and dried. The crude product obtained after removal of the solvent was filtered through a small silica gel (5 g) column to furnish the dione 54 (50 mg) in 82% yield, which was recrystallised from hexane - dichloromethane mixture.

\[ [\alpha]_D \] : +15 (c 0.3, CHCl₃)

mp. : 61°C

IR : 2950, 1690, 1450, 1020 cm⁻¹
$^1$H-NMR: 6.34 - 3.2 (1H, m), 2.6 - 1.3 (16H, series of m), 1.25 (3H, s, -C-CH$_3$), 1.0 (3H, d, J = 7Hz, -CH-CH$_3$), 0.87 (3H, d, J = 7Hz, -CH-CH$_3$)

$^{13}$C-NMR: 158.59, 55.89, 53.19, 49.02, 48.55, 46.55, 43.7, 34.5, 34.4, 32.9, 30.7, 26.6, 25.1, 24.4, 22.1, 19.6

Analysis: $C_{18}H_{28}O_2$  
Calcd: C, 78.21; H, 10.21  
Found: C, 78.27; H, 10.31
IV.7. SPECTRA

Fig. IV.1 $^{13}$C-NMR spectrum (25 MHz) of 16
Fig. IV.2 $^{13}$C-NMR spectrum (25 MHz) of $14$

Fig. IV.3 $^{13}$C-NMR spectrum (25 MHz) of $31$
Fig. IV.4 $^{13}$C-NMR spectrum (25 MHz) of 15

Fig. IV.5 $^{13}$C-NMR spectrum (25 MHz) of 32
Fig. IV.6 $^{13}$C-NMR spectrum (25 MHz) of 35
Fig. IV.7 $^1$H-NMR spectrum (100 MHz) of 51

Fig. IV.8 $^{13}$C-NMR spectrum (25 MHz) of 51
Fig. IV.9 $^1$H-NMR spectrum (100 MHz) of 54
VI.8. REFERENCES


