

DIGITIZATION AND ETDs:

Initiatives at IGM Library, University of Hyderabad

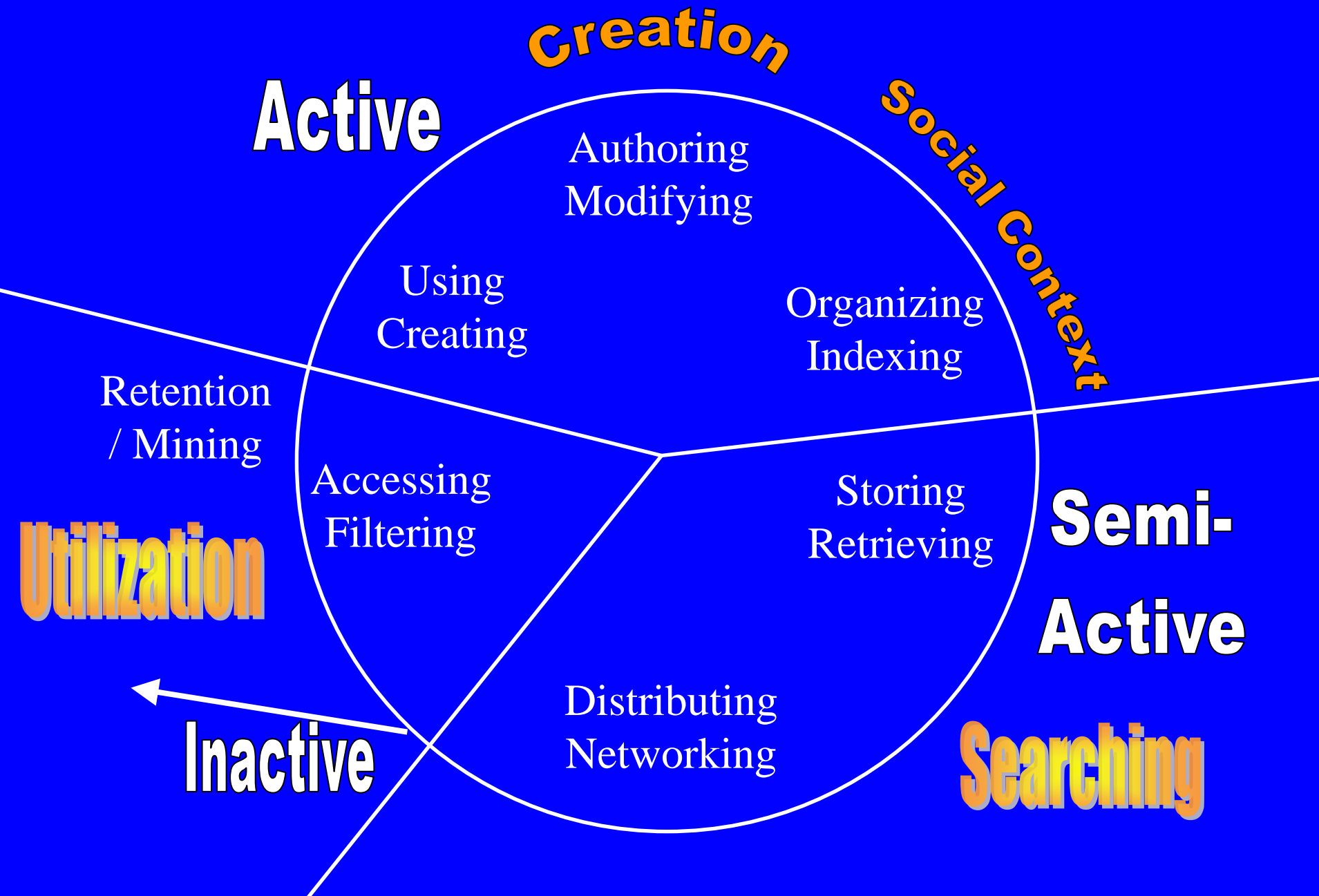
by

Dr. E. Rama Reddy
Librarian (Retd.),
IGM Library, UoH

Mail ID: enukondar@gmail.com
enukondar@yahoo.co.in

URL: www.uohyd.ernet.in

Information Life Cycle



Recorded Information

- Books & other documents
- Periodical publications
- Music, dance and other forms
- Paintings, Sculptures and fine arts
- Movies, video and audio
- Databases, software

If all of this is available on the Web

Selection of material for Digitization

- Digitization is expensive
- Materials need to be selected carefully
- Factors to be considered
 - Uniqueness of the materials
 - Demand for the materials
 - Physical condition of the materials
- Digitization policy is required to start digitization

Digitization policy

- Guidelines for access to materials
- Target audience or users
- Preservation of originals and digital files
- Ownership rights
- Commitment of support for digitization
- Selection criteria for choosing materials to digitize

Digitization of Thesis & Dissertations

- T & D are basis for graduate and doctoral education
- Represents focused and extensive study
- Involves intellectual labor over several years
- Guided by experts in the field
- Funded by scholarships and grants
- Resources are hidden in the libraries
- Digitization helps online access to many
- ETDs are gaining ground in the Universities slowly
- NDLTD is a global successful example
- Vidyanidhi and UGC efforts are in initial stages

NDLTD Goals

- Aiding universities to enhance graduate education, publishing and IPR efforts
- Helping improve the availability and content of theses and dissertations
- Educating ALL future scholars so they can publish electronically and effectively use digital libraries

Starting points of digitization

- Housing the digitization center
- Physical layout
- Personnel
- Training
- Courses and conferences
- Staff training

Digitization requirements

- Hardware
- Software
- Book Scanners
- OCR
- Digital camera

HARDWARE

- SERVER–Sun Microsystems 3500
 - 64 bit architecture
 - 2GB RAM
 - 400 GB HD stackable
 - SUN Solaris (OS)

DIGITAL SCANNER

- i2S Digibook 2000 Scanner (1)
- Zeutschel OS 5000 scanners (4)
- Window NT (Server)
 - Digital Camera
 - Scanning & Editing Software (Digibook 2000)
 - Book restorer software
 - 650mm x 850mm size

Book Scanner



- Zeuschel OS 5000 model
- The book scanner A2 for libraries and archives
- Product Advantages
 - 600 dpi resolution
 - 600 grey-scales
- fast scanning: approx. 2 sec. (A3, 200 dpi)
- automatic electronic image correction of the book curve (optional OS 5100TT)
- direct connection of a laser-printer for fast printing (optional)
- user friendly non reflecting cold top light

WEB SERVER

- Apache Web Server
- Documents shifted to this Server after OCR
- Linking Documents through Virtua/Visua (digital management software)

SCANNING & EDITING

- Max. size 650mm x 850mm
- Up to 600dpi resolution
- TIFF, TIFF4, JPEG (save format)
- 400 scans per hour (two pages)
- Geometrical correction
- Light & contrast, Crop, resize, binarization...
- Saving the images into JPG, TIFF, TIFF4

OCR (Optical Character Recognition)

- FineReader, Prime, Ominipage, etc.
- We are using FineReader
- Recognizes characters on binary images
- Saving
 - PDF
 - HTML
 - MS-WORD, EXCEL, PPT, ETC.

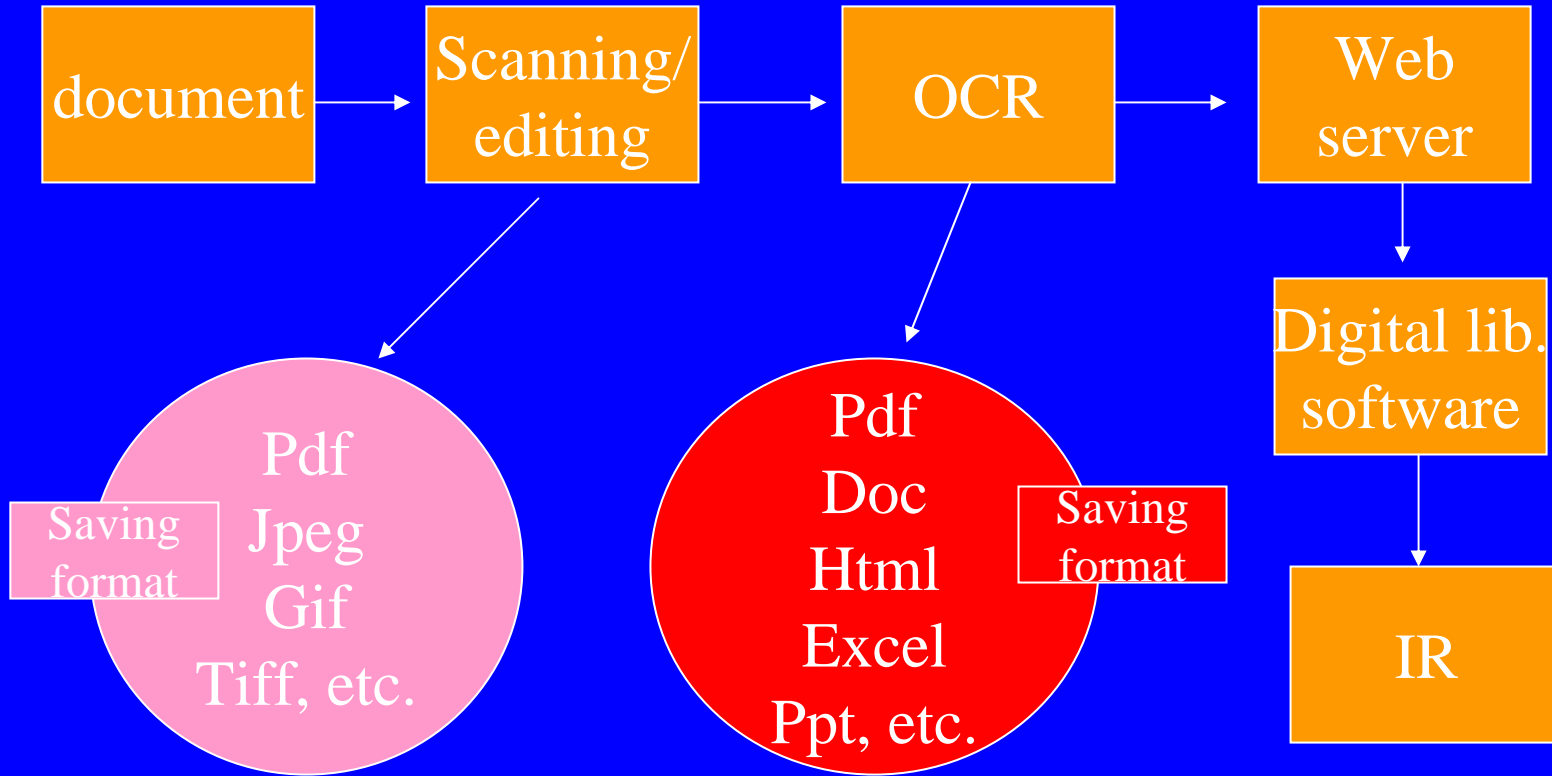
PDF (Portable Document Format)

- Why we prefer PDF?
 - Available on all platforms
 - Text, chart, graphics, picture, etc.
 - User friendly
 - Originality of the document
 - Word search
 - PDF viewer is freely available

LINKING THE DOCUMENT

- VISUA - Digital Library Software
 - Front end with C++, Pearls, etc.
 - Back end with Oracle
- Virtua – Library automation package
 - Supporting MARC-21
 - Tag-856 – Electronic resources

digitization process



PAGE SETTING

Configure Adjustments 120° Mode Automate Retouch Edit Help



Scan Format

Parameters

Name:

Width in mm :

Height in mm :

Resolution in dpi :

Number of pages :

Orientation :

Predefined Formats:

Format: Size:210*280
Format:00 Size:220*320
Format:1932 Size:210*320
Format:time Size:270*190

OK Delete Cancel Help

CAMERA SETTING, SCALING, VIEW, DPI, ETC.

The image shows a screenshot of the Digibook software interface. The main window is titled "- Digibook" and has a menu bar with "File", "Configure", "Adjustments", "120° Mode", "Automate", "Retouch", "Edit", and "Help". Below the menu bar is a toolbar with various icons for file operations and adjustments. The main workspace is a large white area with a red and a magenta border. A dialog box titled "Adjust Focus" is open in the center. The dialog box has two main sections: "Focus" and "Resolution (Camera Height)". The "Focus" section contains a vertical slider with a red line at the top, a value of "235", and an "Auto-Focus" button. The "Resolution (Camera Height)" section contains a vertical slider with values "0" at the top and "0 mm" at the bottom, and an "Auto-Justify" button. Below these sections is a "Sensitivity" section with two horizontal sliders: "Exposure time = 0.35 ms" and "Diaphragm =", each with an "Auto-Iris" button. At the bottom of the dialog box is a "Position" slider and "OK" and "Help" buttons. The status bar at the bottom of the window shows "C:\scan\nvr1", "Format: NNN 300x210, 375 dpi", "Page : 17", "JPEG 30", "CAPS NUM", and the system clock "12:44 PM".

Adjust Focus

Focus

Resolution (Camera Height)

235

0

0 mm

Auto-Justify

Sensitivity

Exposure time = 0.35 ms

Diaphragm =

Auto-Iris

Position

OK Help

C:\scan\nvr1 Format: NNN 300x210, 375 dpi Page : 17 JPEG 30 CAPS NUM 12:44 PM

Restoration

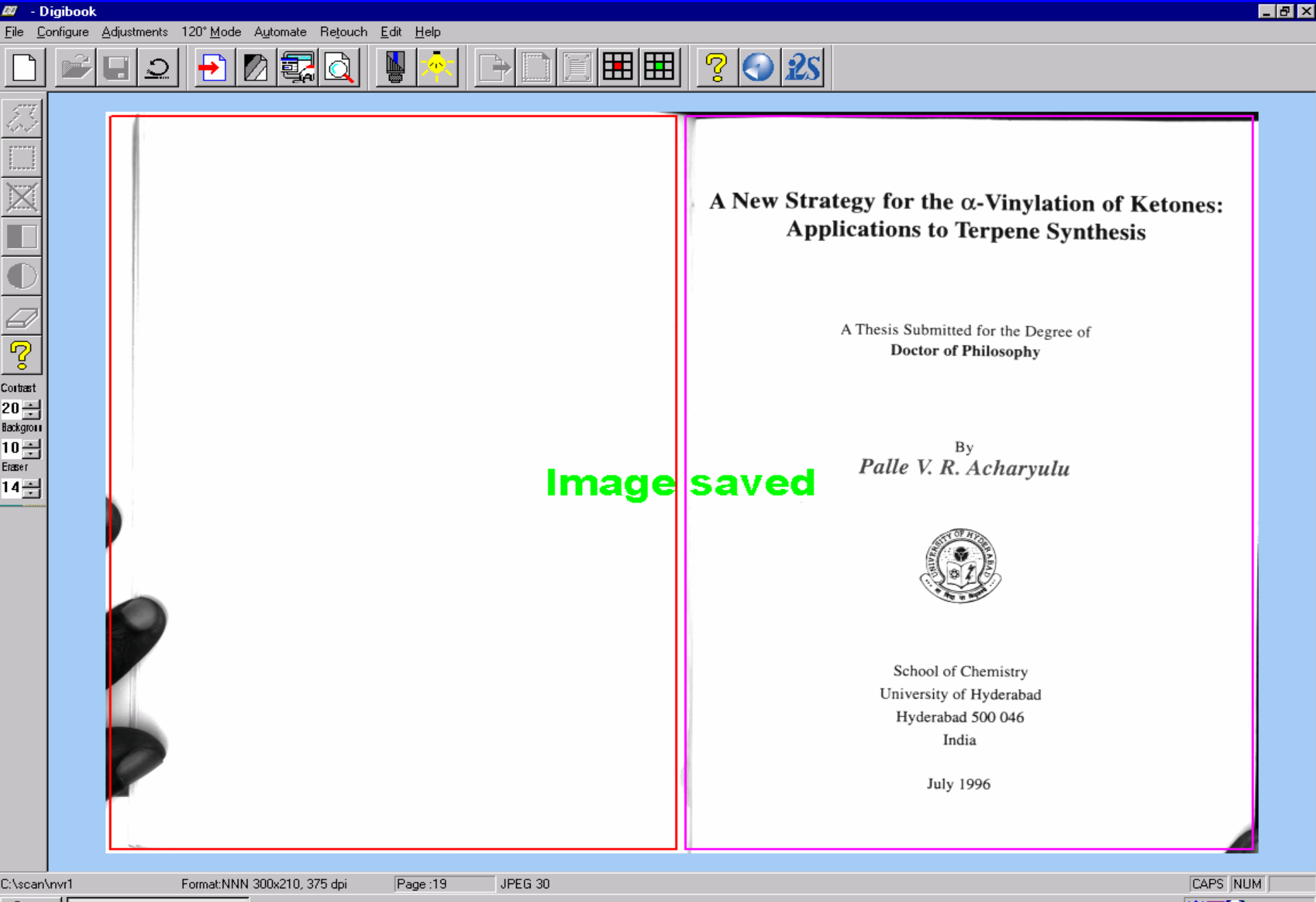


- [-] Processings
 - Lighting correction
 - Resize
 - Deskew
 - Crop
 - Minimal rectangle
 - Despeckle
 - Filter
 - Negative
 - Adjustment of histogram
 - Colorimetric curves
 - Light and contrast
 - Areas detection
 - Geometrical correction**
 - Page edge detection
 - Curvature correction
 - Binarization
 - Transformation
 - Color Conversion
 - Hue, Saturation, Lightness
 - ICC Profile
 - Photoshop(R) script



**EDITING
TOOLS**

SCANNING THE DOCUMENT



SCAN TWO PAGE VIEW

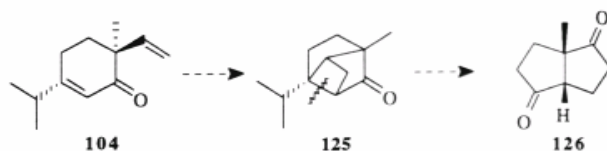
Digibook

File Configure Adjustments 120* Mode Automate Retouch Edit Help



to convert it to a diquinane derivative like **126** through an intramolecular [2+2]-photocycloaddition-fragmentation strategy. Scheme 41.

Scheme 41

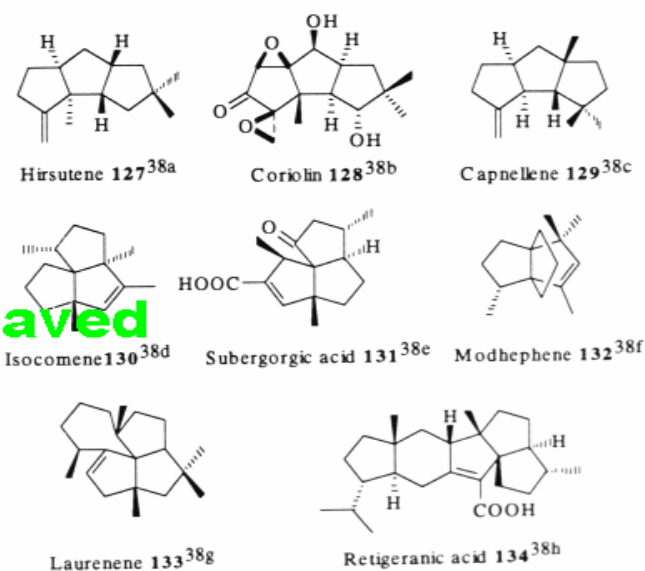


The *cis*-diquinane frame-work, with a quaternary carbon centre, is an important structural moiety present in a variety of polyquinane based natural product skeleta. Some representative examples of the natural products containing this structural moiety are delineated in Chart 4.^{38a-h} These molecules constitute challenging targets for the synthesis because of the dense functionalisation and unusual carbocyclic frame-work.

Synthetic strategies towards these molecules require a simple and rapid assembly of the *cis*-diquinane moiety endowed with a quaternary carbon centre. Although several strategies for the construction of these moieties were reported in the literature, the enantioselective approaches are limited. The following is an account of a novel enantioselective approach for the easy and rapid access of the *cis*-diquinane moiety from readily available chiral (+)-limonene **106** and (+)-2-carene **111**.

51

Chart 4



Intramolecular [2+2]-photocycloaddition in the enone **104**, effected through irradiation from a 450W Hanovia medium pressure lamp through a pyrex filter, afforded the tricyclic ketone **125** in 87% yield, Scheme 42. The IR spectrum of the product **125** exhibited a strong absorption at 1759 cm⁻¹

52

C:\scan\nvr1

Format:NNN 300x210, 375 dpi

Page :243

JPEG 30

CAPS NUM

Start - Digibook

1:25 PM

EDITING -1

Book Restorer - chem * (0001 / 217)

Book Edit Insert Tools View ?

Styles

- Standard page
- Standard image block
- Section 1
- Section 3
- Section 4
- Section 5

- 0001
 - TH2217_0019.JPG
- 0002
 - TH2217_0021.JPG
- 0003
 - TH2217_0023.JPG
- 0004
 - TH2217_0025.JPG
 - TH2217_0027.JPG
 - TH2217_0029.JPG
 - TH2217_0031.JPG
- 0005
 - TH2217_0032.JPG
- 0006
 - TH2217_0033.JPG
- 0007
 - TH2217_0035.JPG
- 0008
 - TH2217_0037.JPG
- 0009
 - TH2217_0038.JPG
- 0010
 - TH2217_0039.JPG
- 0011
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 - TH2217_0041.JPG
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- 0014
 - TH2217_0043.JPG
- 0015
 - TH2217_0044.JPG
- 0016
 - TH2217_0045.JPG
- 0017
- 0018
- 0019
- 0020

0001

0002


0003

0004

A New Strategy for the α -Vinylolation of Ketones:
Applications to Terpene Synthesis

A Thesis Submitted for the Degree of
Doctor of Philosophy

By
Palle V. R. Acharyulu



School of Chemistry
University of Hyderabad
Hyderabad 500 046
India

July 1996

Selection = 1 page(s) 98%

Click on the explorer icon to select an element


EDIT – CROP & EARSE FINGER

The screenshot displays the 'Book Restorer - chem * (0001 / 217)' application window. The main workspace shows a scanned page of a thesis. The page content includes:

**A New Strategy for the α -Vinylaton of Ketones:
Applications to Terpene Synthesis**

A Thesis Submitted for the Degree of
Doctor of Philosophy

By
Palle V. R. Acharyulu



School of Chemistry
University of Hyderabad
Hyderabad 500 046
India

July 1996

The 'Minimal rectangle' dialog box is open, showing the following settings:

- Minimal rectangle search: []
- Crop margin in mm: 5
- Sensibility: 2 %
- Crop
- Erase fingers

The software interface includes a menu bar (Book, Edit, Insert, Tools, View), a toolbar, a left sidebar with 'Styles' and 'Processings' panels, and a right sidebar with various tool icons. The status bar at the bottom indicates 'Selection = 1 page(s)' and '100%' zoom.

EDIT - PERFECT PAGE

Book Restorer - chem * (0001 / 217)

Book Edit Insert Tools View ?

Styles

- Standard page
- Standard image block
- Section 1
- Section 3


Restoration

- Processings
 - Lighting correction
 - Resize
 - Deskew
 - Crop
 - Minimal rectangle
 - Despeckle
 - Filter
 - Negative
 - Adjustment of histogram
 - Colorimetric curves
 - Light and contrast
 - Areas detection
 - Geometrical correction
 - Page edge detection
 - Curvature correction
 - Binarization
 - Transformation
 - Color Conversion
 - Hue, Saturation, Lightness
 - ICC Profile
 - Photoshop(R) script
 - OCR
 - Scripts

A New Strategy for the α -Vinylolation of Ketones:
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Doctor of Philosophy

By
Palle V. R. Acharyulu



School of Chemistry
University of Hyderabad
Hyderabad 500 046
India

July 1996

Selection = 1 page(s) 203.4 mm 50.6 mm 139%

Start Book Restorer - chem... 3:03 PM

EDIT- APPLYING GEOMETRICAL CORRECTION

Book Restorer - chem * (0040 / 215)

Book Edit Insert Tools View ?

Restoration

- Processings
 - Lighting correction
 - Resize
 - Deskew
 - Crop
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 - Filter
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 - Scripts

0018

0019

0036

0037

0038

0039

The next key operation in this sequence was to set up the cyclopropylcarbinyl-homallylic rearrangement in the activated "push-pull" cyclopropyl carbinol derivatives. For this purpose, the ester moiety in **81a,b-85a,b** was reduced using Dibal-II at low temperatures, to furnish the corresponding cyclopropyl carbinols **86-90**, respectively, as diastereomeric mixtures. The spectral data of the mixtures enabled their gross characterization.

Having obtained the required cyclopropyl carbinols **86-90** the objective now was to carry-out a fragmentation sequence to access the desired α -vinyl ketones by activating the hydroxyl group. To execute this protocol, the carbinols **86-90** were reacted with methanesulphonyl chloride in pyridine, to obtain the corresponding "push-pull" mesylates. Not surprisingly, the mesylates were not isolated but instead we directly obtained the α -vinyl ketones **91-95**. However, the α -vinyl ketones **62** were found to be contam-

Scheme 24

61

96

62

R=H, Me, Ph

R₁=Me

29

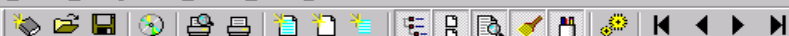
Selection = 1 page(s) 100%

Start Book Restorer - chem 3:31 PM

EDIT - AFTER APPLYING GEMOETRICAL CORRECTION

Book Restorer - chem * (0040 / 215)

Book Edit Insert Tools View ?



- TH2217_0043.JPG *
- 0018
- TH2217_0044.JPG *
- 0019
- TH2217_0045.JPG *

Restoration



- Processings
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- Binarization
- Transformation
- Color Conversion
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- ICC Profile
- Photoshop(R) script
- OCR
- Scripts

0037

0038

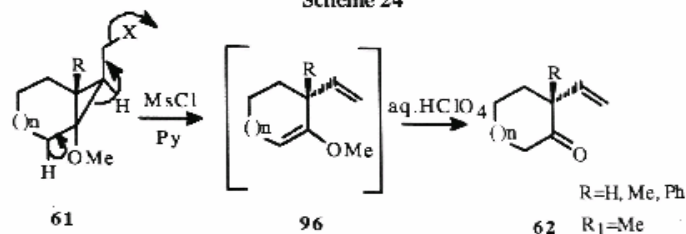
0039

0040

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Scheme 24



29

Selection = 1 page(s)

139%

EDIT - ANGLE DEGREE CORRECTION

Book Restorer - chem * (0095 / 214)

Book Edit Insert Tools View ?

TH2217_0100.JPG *
0073
TH2217_0101.JPG *
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TH2217_0102.JPG *

Restoration

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 - Colorimetric curves
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 - Curvature correction
 - Binarization
 - Transformation
 - Color Conversion
 - Hue, Saturation, Lightness
 - ICC Profile
 - Photoshop(R) script
 - OCR
 - Scripts

0091

0092

0093

0094

100.0

200.0

100.0

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Elemental analysis

Optical rotation

Chromatography

General

^{13}C NMR assignment differing by only 2-3 ppm can, in some cases, be interchanged.

Elemental analyses were performed on a Perkin-Elmer 240C-CHN analyzer.

Optical rotations were measured on AUTOPOL IITM polarimeter and JASCO DIP 370 digital polarimeter.

Analytical thin-layer chromatographies (tlc) were performed on (10 x 5 cm) glass plates coated (250 μm) with Acme's Silica gel G or GF₂₅₄ (containing 13% of calcium sulphate as binder). Visualization of the spots on tlc plates was achieved either by exposure to iodine vapour or UV light or by spraying sulfuric acid and heating the plates at 120°C. Column chromatography was performed using Acme's silica gel (100-200 mesh) and the amount of silica gel used is approximately in the ratio of 1.25 and the column was usually eluted with ethyl acetate-hexane, unless mentioned otherwise.

All reactions were monitored by employing the technique, using appropriate solvent systems for development. Moisture-sensitive reactions were carried out by using standard syringe septum.

83

text help.

Selection = 1 page(s) 100%

Start Book Restorer - chem... 4:41 PM

EDIT - AFTER APPLYING ANGLE DEGREE CORRECTION

The screenshot displays the 'Book Restorer' software interface. The main window shows a document page with a table of contents on the left and a text block on the right. The table of contents lists sections 0092 through 0095. The text block on the right contains the following content:

Elemental analysis
Elemental analyses were performed on a Perkin-Elmer 240C-CHN analyzer.

Optical rotation
Optical rotations were measured on AUTOPOL IITM polarimeter and JASCO DIP 370 digital polarimeter.

Chromatography
Analytical thin-layer chromatographies (tlc) were performed on (10 x 5 cm) glass plates coated (250 m μ) with Acme's Silica gel G or GF₂₅₄ (containing 13% of calcium sulphate as binder). Visualization of the spots on tlc plates was achieved either by exposure to iodine vapour or UV light or by spraying sulfuric acid and heating the plates at 120°C. Column chromatography was performed using Acme's silica gel (100-200 mesh) and the amount of silica gel used is approximately in the ratio of 1:25 and the column was usually eluted with ethyl acetate-hexane, unless mentioned otherwise.

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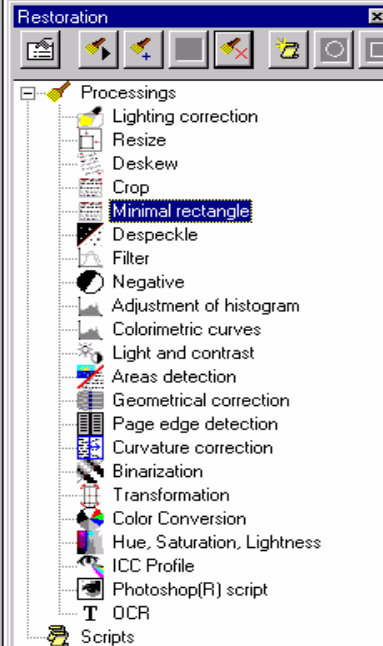
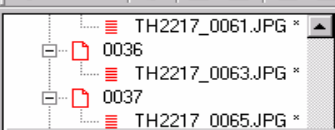
83

The software interface includes a 'Restoration' menu on the left with options such as 'Geometrical correction', 'Page edge detection', and 'Curvature correction'. The top menu bar includes 'Book', 'Edit', 'Insert', and 'Tools'. The bottom status bar shows 'Selection = 1 page(s)', '20.3 mm', '35.5 mm', and '139%'.

GEOMETRIACAL CORRECTION

Book Restorer - chem * (0058 / 215)

Book Edit Insert Tools View ?



present among pheromones, antibiotics, cytotoxins and antitumor agents. Consequently, there has been a great deal of interest in the synthesis of germacrane-based sesquiterpene natural products and many new and ingenious methodologies have been developed.³⁶

The ready availability and the strategic disposition of both the isopropyl and methyl groups in the α -vinyl ketone **64**, turned our attention towards the synthesis of deoxycurdione **66**, a germacrane type sesquiterpenoid. Our approach towards the synthesis of germacrane ring system through an oxy-Cope pathway is delineated through the retrosynthetic route shown in Scheme 37.

Scheme 37

As per this protocol, nucleophilic addition of isopropenyl lithium to the ketone (+)-**64**, was expected to deliver the 1,2-divinylcyclohexanol **65a,b**. An oxy-Cope rearrangement was expected to lead the germacrane skeleton.



AFTER GEOMETRICAL CORRECTION

Book Restorer - chem * (0058 / 215)

Book Edit Insert Tools View ?

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0036
TH2217_0063.JPG *
0037
TH2217_0065.JPG *

Restoration

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 - Page edge detection
 - Curvature correction
 - Binarization
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 - OCR
 - Scripts

0055

0056

0057

0058

present among pheromones, antibiotics, cytotoxins and antitumor agents. Consequently, there has been a great deal of interest in the synthesis of germacrane-based sesquiterpene natural products and many new and ingenious methodologies have been developed.³⁶

The ready availability and the strategic disposition of both the isopropyl and methyl groups in the α -vinyl ketone **64**, turned our attention towards the synthesis of deoxycurdione **66**, a germacrane type sesquiterpenoid. Our approach towards the synthesis of germacrane ring system through an oxy-Cope pathway is delineated through the retrosynthetic route shown in Scheme 37.

Scheme 37

CC(C)C1=CC=C(C)C(=O)C1 (**66**) \rightarrow CC(C)C1=CC=C(C)C(O)C1 (**65 a,b**) \rightarrow CC(C)C1=CC=C(C)C(=O)C1 (**64**)

As per this protocol, nucleophilic addition of isopropenyl lithium to the ketone (+)-**64**, was expected to deliver the 1,2-divinylcyclohexanol **65a,b**. An oxy-Cope rearrangement was expected to lead the germacrane skeleton.

47

Selection = 1 page(s) 139%

3:59 PM

OCR - APPLYING ON THE EDITED PAGES

Default - ABBYY FineReader 6.0 Corporate Edition - [11 - Text]

File Edit View Batch Image Process Tools Window Help

English Times New Roman 4 B I U

Open&Read Open Image Read Check Spelling Save

9

10

11

12

Check Spelling

Not in dictionary

Spectroscopically and the data was found in good agreement with their formulations. While the ester 157 (Fig. 37 & 38) shows a 16 line ¹³C NMR spectrum with carbonyl carbon resonances at 214.9 and 175.4 corresponding to the ketone and ester groups, the hydroxy lactone 163 (Fig. 39 & 40) exhibited the lactone carbonyl and the acetal attached carbon at 178.5 and 107.1, respectively, confirming the assigned structure.

Ignore Ignore All Add... Replace Replace All

Dictionary language: English

Undo Options... Close

Trimethylsilyl iodide mediated ring opening of the α -allyl- β -methoxy cyclopropyl ester 162 furnished the α -alkyl- γ -oxo-cyclopropylester 157 and the corresponding hydroxy lactone 163 in 63% and 22% yields respectively. Scheme 62. Both the products obtained were characterised analytically and spectroscopically and the data was found to be in good agreement with their formulations. While the ester 157 (Fig. 37 & 38) shows a 16 line ¹³C NMR spectrum with carbonyl carbon resonances at 214.9 and 175.4 corresponding to the ketone and ester groups, the hydroxy lactone 163 (Fig. 39 & 40) exhibited the lactone carbonyl and the acetal attached carbon at 178.5 and 107.1, respectively, confirming the assigned structure.

Scheme 63

157 164 163

Reagents, conditions and yields: (a) O_2 , PdCl₂, CuCl, DMF, H₂O, R.T., 6 h, 70% (b) PTS, C₆H₆, Δ , 2 h, 45%.

As could be envisaged from the Scheme 60 the α -allyl- γ -oxo-ester

Scheme 62. Both the products obtained were characterised analytically and spectroscopically and the data was found to be in good agreement with their formulations. While the ester 157 (Fig. 37 & 38) shows a 16 line ¹³C NMR

English (United States)

Start Default - ABBYY Fine... 11:06 AM

BLOCKING TEXT, PICTURE, SPELLING CORRECTION

Check Spelling

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Not in dictionary

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tions. While the ester 157 (Fig. 37 & 38)
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Suggestions:

Ala	DTLA
Dal	Dalai
Daly	Dana
lala	de la

Dictionary language: English

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Times New Roman 4 B I U

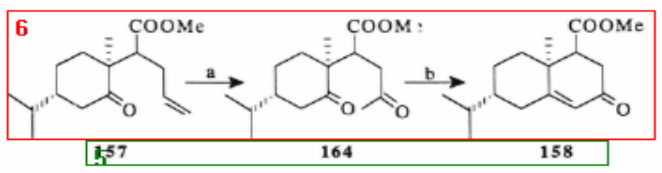
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the α -allyl- β -methoxy
propylester 157 and
% yields respectively.
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s a 16 line ^{13}C NMR
5 214.9 and 175.4
oxy lactone 163 (Fig.
l attached carbon at δ

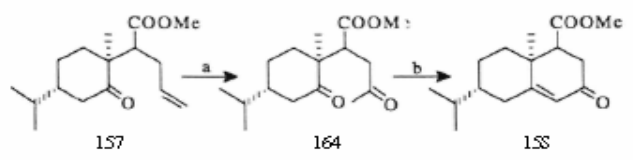
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the corresponding hydroxy lactone 163 in 63% and 22% yields respectively.
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Scheme 63



Scheme 63



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Scheme 62. Both the products obtained were characterised analytically and
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formulations. While the ester 157 (Fig. 37 & 38) shows a 16 line ^{13}C NMR

BLOCKING TEXT, PICTURE, CHECK SPELLING

The screenshot displays the ABBYY FineReader 6.0 Corporate Edition interface. The main window shows a document titled "A New Strategy for the α -Vinylolation of Ketones: Applications to Terpene Synthesis". A "Check Spelling" dialog box is open, highlighting the word "Terpene" as "Not in dictionary". The dialog box provides a list of suggestions: Terrene, Serene, Teepee, and Terence, along with buttons for "Resume", "Ignore All", "Add...", "Replace", and "Replace All". The document text is partially obscured by the dialog box. The status bar at the bottom indicates the language is "English (United States)".

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Teepee	Tepee
Terence	Terata

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Degree of Philosophy

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A Thesis Submitted for the Degree of Doctor of Philosophy

By Palle V. R. Acharyulu

School of Chemistry University of Hyderabad Hyderabad 500 046 India

July 1996

Applications to Terpene Synthesis

English (United States)

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1 A New Strategy for the α -Vinylolation of Ketones:
Applications to Terpene Synthesis

2 A Thesis Submitted for the Degree of
Doctor of Philosophy

3 By
Palle V. R. Acharyulu



4 School of Chemistry
University of Hyderabad
Hyderabad 500 046
India

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AFTER OCR

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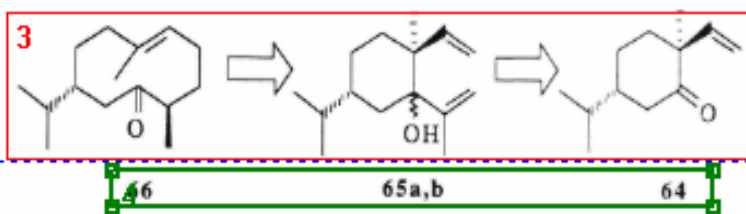
July 1996

BEFORE OCR

present among pheromones, antibiotics, cytotoxins and antitumor agents. Consequently, there has been a great deal of interest in the synthesis of germacrane-based sesquiterpene natural products and many new and ingenious methodologies have been developed.³⁶

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Scheme 37



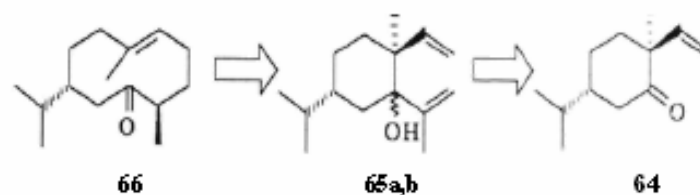
5 As per this protocol, nucleophilic addition of isopropenyl lithium to the ketone (+)-**64**, was expected to deliver the 1,2-divinylcyclohexanol **65a,b**. An oxy-Cope rearrangement was expected to lead the germacrane skeleton.

AFTER OCR (21kb)

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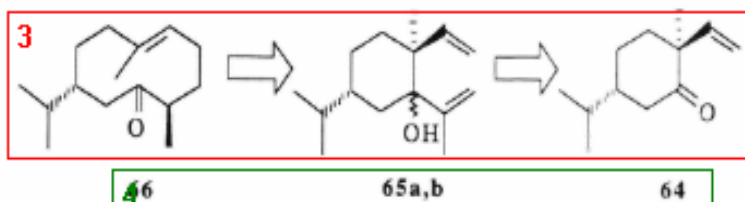
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BEFORE OCR

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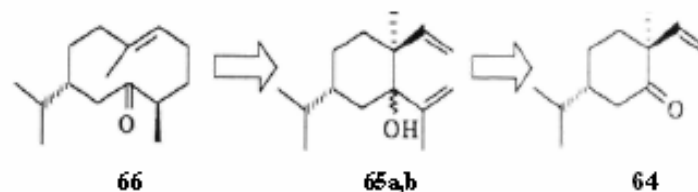
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AFTER OCR

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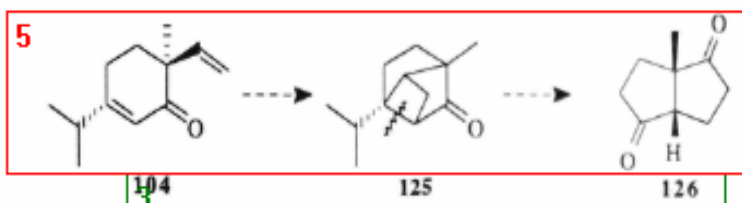
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BEFORE OCR (size 993kb)

AFTER OCR (size 21kb)

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2 Scheme 41

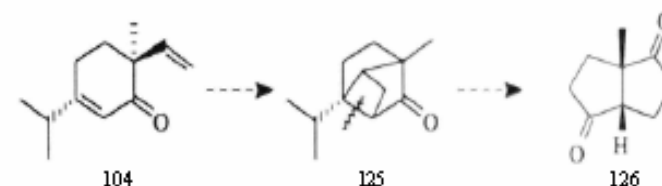


4 The *cis*-diquinane frame-work, with a quaternary carbon centre, is an important structural moiety present in a variety of polyquinane based natural product skeleta. Some representative examples of the natural products containing this structural moiety are delineated in Chart 4.^{38a-b} These molecules constitute challenging targets for the synthesis because of the dense functionalisation and unusual carbocyclic frame-work.

Synthetic strategies towards these molecules require a simple and rapid assembly of the *cis*-diquinane moiety endowed with a quaternary carbon centre. Although several strategies for the construction of these moieties were reported in the literature, the enantioselective approaches are limited. The following is an account of a novel enantioselective approach for the easy and rapid access of the *cis*-diquinane moiety from readily available chiroirs R- (+)-limonene 106 and (+)-2-carene 111.

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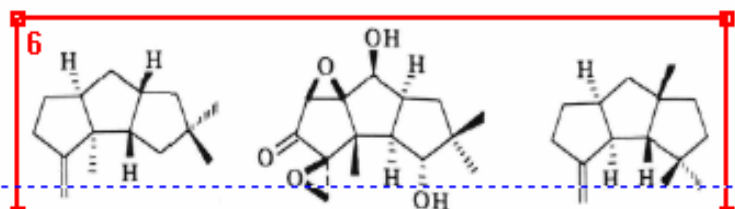
Scheme 41



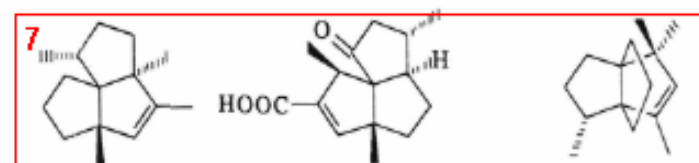
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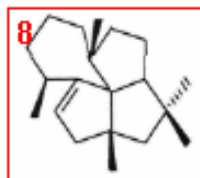
Chart 4



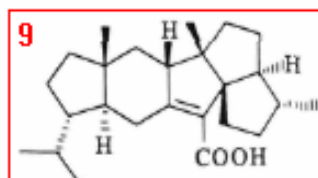
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Isocomene 130^{38d} Subergorgic acid 131^{38e} Modhephene 132^{38f}



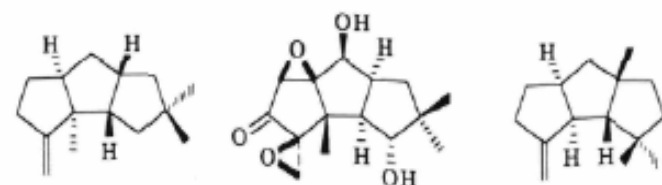
Laurenene 133^{38g}



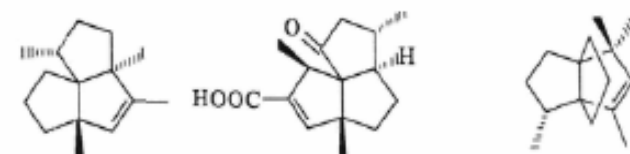
Retigeranic acid 134^{38h}

5 Intramolecular [2+2]-photocycloaddition in the enone 104, effected through irradiation from a 450W Hanovia medium pressure lamp through a pyrex filter, afforded the tricyclic ketone 125 in 87% yield, Scheme 42. The IR spectrum of the product 125 exhibited a strong absorption at 1759 cm⁻¹

Chart 4



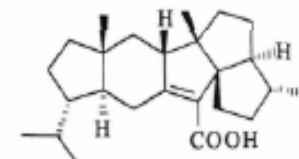
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Laurenene 133^{38g}



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**A New Strategy for the α -Vinylolation of Ketones:
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A Thesis Submitted for the Degree of
Doctor of Philosophy

By
Palle V. R. Acharyulu



School of chemistry
University of Hyderabad
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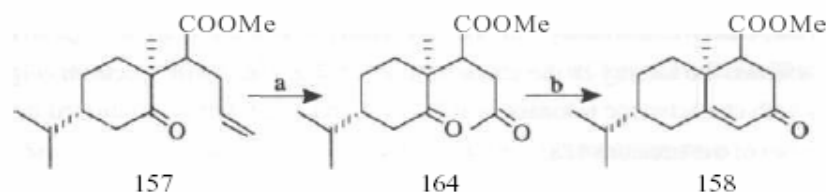
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Trimethylsilyl iodide mediated ring opening of the α -allyl- β -methoxy cyclopropyl ester 162 furnished the α -alkyl- γ -oxo-cyclopropylester 157 and the corresponding hydroxy lactone 163 in 63% and 22% yields respectively, Scheme 62. Both the products obtained were characterised analytically and spectroscopically and the data was found to be in good agreement with their formulations. While the ester 157 (Fig. 37 & 38) shows a 16 line ^{13}C NMR spectrum with carbonyl carbon resonances at δ 214.9 and 175.4 corresponding to the ketone and ester groups, the hydroxy lactone 163 (Fig. 39 & 40) exhibited the lactone carbonyl and the acetal attached carbon at δ 178.5 and 107.1, respectively, confirming the assigned structure.

Scheme 63



Reagents, conditions and yields: (a) O_2 , PdCl_2 , CuCl , DMF , H_2O , R.T., 6 h, 70% (b) PTS , C_6H_6 , Δ , 2D, 45%.

As could be envisaged from the Scheme 60 the α -allyl- γ -oxo-ester 157, was subjected to Wacker-type oxidation following the Tsuji conditions to

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260			\a Hyderabad: \b University of Hyderabad, \c 1996.
300			\a 191p.
502			\a Thesis (Ph.D.)--Dept. of Chemistry, University of Hyderabad, Hyderabad, 1996.
650		0	\a a-vinylation, ketones
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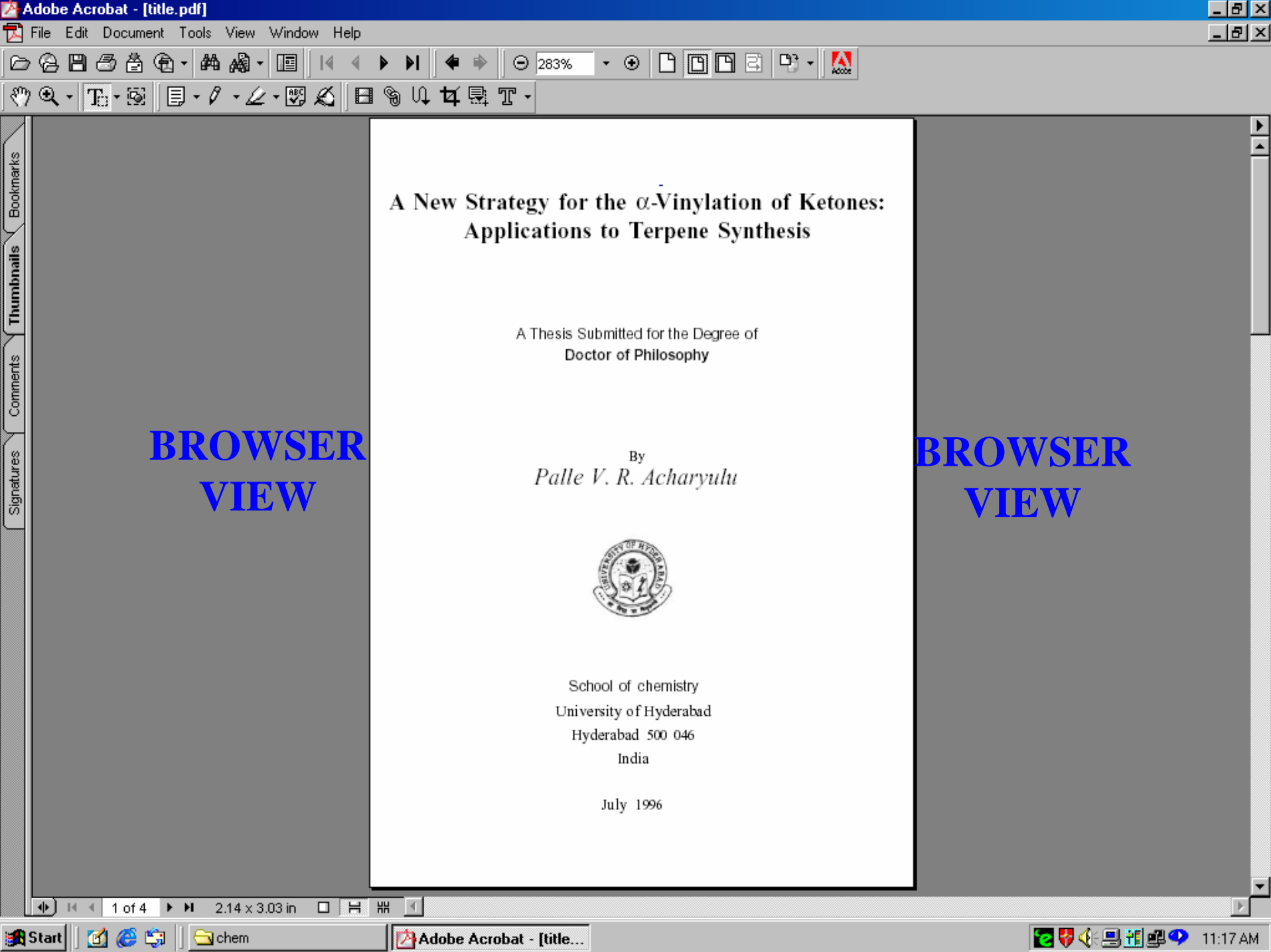
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A New Strategy for the α -Vinylation of Ketones: Applications to Terpene Synthesis

A Thesis Submitted for the Degree of
Doctor of Philosophy

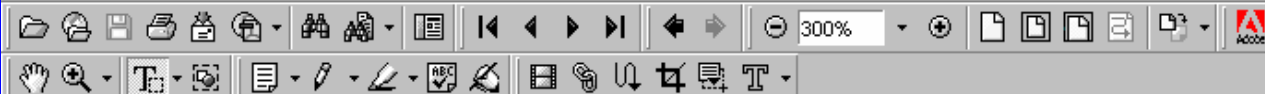
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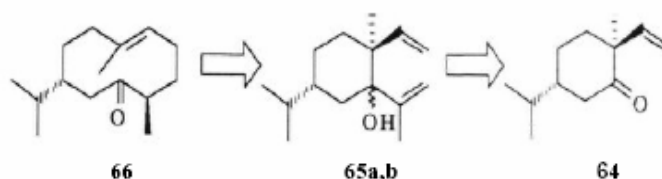
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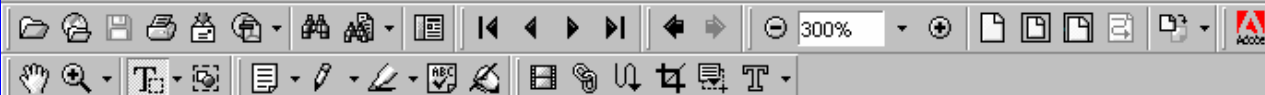
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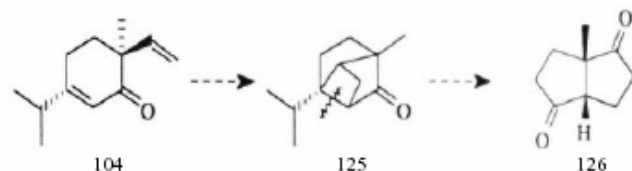
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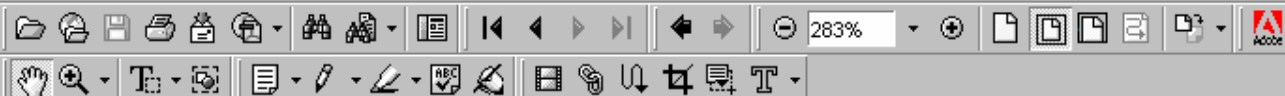


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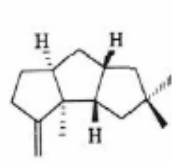
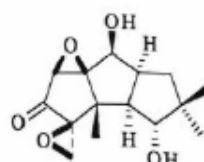
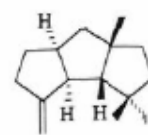
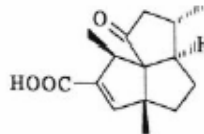
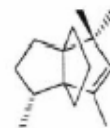
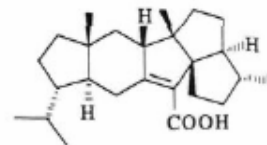
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Chart 4

Hirsutene 127^{38a}Coriolin 128^{38b}capnellene 129^{38c}Isocomenol 130^{38d}Subergorgic acid 131^{38e}Modhephene 132^{38f}Laurenene 133^{38g}Retigeranic acid 134^{38h}

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