CHAPTER IV

INFRARED SPECTRA OF \( \pi \)-SUBSTITUTED TRICYCLENES
SUMMARY

Two infrared bands at 876 and 822 cm\(^{-1}\), respectively, are found to be characteristic of \(\pi\)-substituted tricyclenes. The previously reported frequency assignments for the cyclopropyl ring structure in the C-H stretching region near 3050 cm\(^{-1}\) have been confirmed for tricycle system also. The band at 858 cm\(^{-1}\) characteristic of nortricyclenes and some tricyclenes has been found to occur consistently in the tricyclene derivatives. It has been concluded from the present studies that the bands at 3050, 876, 858, and 822 cm\(^{-1}\) together form good evidence for detection of the \(\pi\)-substituted tricyclene ring system. Spectra of fifteen tricyclene derivatives have been studied and discussed in this chapter.
The α-santalene series constitutes a group of compounds containing the tricyclene skeleton in which the α-position has an aliphatic side-chain as substituent. Various interesting reactions which they undergo have already been discussed in the earlier chapters of this thesis. Studies on the infrared spectra of these compounds are described in this chapter. The relative paucity of adequate spectral data of substituted tricyclenes in literature and the availability of a good number of tricyclene derivatives at our disposal prompted us to examine their infrared spectra for some possible correlation. For the sake of comparison, some of the important findings of earlier workers regarding the spectral characteristics of cyclopropane ring, nortricyclene, and tricyclene systems are discussed below.

Several investigators have observed that the cyclopropyl ring structure in organic compounds can be identified from the characteristic absorption bands in specific infrared regions. Thus the bands in the region 3050, 1020 and 866 cm\(^{-1}\) have been attributed to this ring system.\(^{1-18}\) However, the reliability of some of these bands have been questioned by several workers.\(^{10,17,19,20}\)

In the case of nortricyclenes, two bands at 350-360 and 3050-3090 cm\(^{-1}\), respectively, were noted by Passivirta\(^{21}\) in the spectra of ten derivatives. He
reported the failure of the utility of the 1020 cm$^{-1}$ band in identification. Roberts and his co-workers$^{22}$ observed a strong band at 800-806 cm$^{-1}$ in four nortricyclenes substituted at the 7-position.

Schleyer and his co-workers$^{23}$ pointed out that the 854 cm$^{-1}$ band was associated with 1-substituted nortricyclenes and that there was no peak of significant intensity in any nortricyclene which did not possess this structural feature.
Hart and Martin\textsuperscript{24} examined 1-substituted nortricyclenes and found that the band at 784-788 cm\(^{-1}\) was remarkably constant and independent of the nature of the 1-substituent. But, this band varied widely in position (787-826 cm\(^{-1}\)) when the 1-substituent is maintained constant (methyl) and other groups were placed elsewhere (especially in the 3-position) on the nortricyclene ring system.\textsuperscript{23} The more intense band at 854 cm\(^{-1}\) was however, more varied in position (836-862 cm\(^{-1}\)) depending on the nature of the 1-substituent, but was relatively independent of other substituents.

In the tricyclene series, the infrared spectra have been measured in a few cases only. Herout and his co-workers\textsuperscript{25} examined the infrared spectra of \(\alpha\)-santalene, \(\alpha\)-santalol, and their corresponding dihydro derivatives, and observed that the bands at 1010-1020 cm\(^{-1}\) region, said to be characteristic of the cyclopropane ring were not reliable, because many oxygenated compounds also absorbed in this region. Corey\textsuperscript{26} reported a sharp absorption at 858 cm\(^{-1}\) which typified the tricyclene derivatives encountered in his work. No absorption at 1000-1020 cm\(^{-1}\) was observed. In some cases a band was observed at 3050 cm\(^{-1}\) which was attributed to the cyclopropane ring system. Hanack and Eggensperger\textsuperscript{27} observed two bands in the regions 3076-3100 cm\(^{-1}\) and 840-854 cm\(^{-1}\) in seven tricyclene derivatives substituted in the 1-position.
During the present investigations, the infrared spectra of fifteen compounds containing the tricyclene skeleton, in which the 8- or \( \tilde{\Pi} \)-position is substituted by various oxygenated and oxygen-free functional groups are examined. The compounds studied include hydrocarbons, acids, ester, alcohol, ketone and epoxide. Five characteristic regions are described in Table I and the absorption bands for possible correlation are discussed. It may be
mentioned that some of the compounds whose infrared spectra are described here, have not been prepared before. Among the compounds listed, \( \alpha \)-santalene and tricyclene were examined by Corey\textsuperscript{26} and found to absorb at 858 cm\(^{-1}\).

From the detailed examination of the infrared spectra of compounds belonging to the tricyclene series listed in Table I (p. 220), it was found that four prominent and well-defined bands near 3050, 876, 854, and 832 cm\(^{-1}\), respectively, are quite characteristic of these compounds. Excepting the 854 cm\(^{-1}\) band, none of the other two bands has so far been reported in literature as characteristic of tricyclenes. It is suggested that these four bands together could be employed for the identification of the tricyclene ring system.
<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Details of Spectrum</th>
<th>Name of Compound</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>150/A</td>
<td>Tricyclene</td>
<td>H</td>
</tr>
<tr>
<td>II</td>
<td>14/A</td>
<td>(\alpha)-Santalene</td>
<td>(-\text{CH}_2\cdot\text{CH}=(\text{CH}_3)_2)</td>
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<td>III</td>
<td>70/A</td>
<td>Dihydro (\alpha)-santalene</td>
<td>(-(\text{CH}_2)_2\cdot\text{CH}(\text{CH}_3)_2)</td>
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<tr>
<td>IV</td>
<td></td>
<td>(\alpha)-Santalol</td>
<td>(-\text{CH}_2\cdot\text{CH}=(\text{CH}_3))</td>
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<tr>
<td>V</td>
<td></td>
<td>Dihydro (\alpha)-santalol</td>
<td>(-(\text{CH}_2)_2\cdot\text{CH}(\text{CH}_3))</td>
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<tr>
<td>VI</td>
<td>66/A</td>
<td>Tricycloekasantalol</td>
<td>(-\text{CH}_2\cdot\text{CH}_2\text{OH})</td>
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<tr>
<td>VII</td>
<td>65/A</td>
<td>Tricycloekasantalic acid</td>
<td>(-\text{CH}_2\cdot\text{COOH})</td>
</tr>
<tr>
<td>VIII</td>
<td></td>
<td>Methyl ester of tricycloekasantalic acid</td>
<td>(-\text{CH}_2\cdot\text{COOCH}_3)</td>
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<tr>
<td>IX</td>
<td>157/A</td>
<td>2-Isopropenyl 3[(\bar{\mu})]-tricyclyl propanol</td>
<td>(-\text{CH}_2\cdot\text{CH}=(\text{CH}_3)\cdot\text{CH}_3)</td>
</tr>
<tr>
<td>X</td>
<td></td>
<td>2-Isopropyl 3[-(\bar{\mu})]-tricyclyl propanol</td>
<td>(-\text{CH}_2\cdot\text{CH}.\text{CH}(\text{CH}_3)_2)</td>
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<td>XI</td>
<td>157/B</td>
<td>2-homo-(\bar{\mu})-tricyclyl, 3-keto butanol</td>
<td>(-\text{CH}_2\cdot\text{CH}-\text{COCH}_3)</td>
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<tr>
<td>XII</td>
<td></td>
<td>Teresantalol</td>
<td>(-\text{OH})</td>
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<tr>
<td>XIII</td>
<td></td>
<td>Semicarbazone of (\alpha)-santalal</td>
<td>(-\text{CH}_2\cdot\text{CH}=(\text{CH}_3)\cdot\text{CH}_2\cdot\text{N}.\text{NHCONH}_2)</td>
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<td>XIV</td>
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<td>(\alpha)-Santalene epoxide</td>
<td>(-\text{CH}_2\cdot\text{CH}-\text{C}-(\text{CH}_3)\cdot\text{CH}_3)</td>
</tr>
<tr>
<td>XV</td>
<td></td>
<td>Teresantalic acid</td>
<td>(-\text{OH})</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

The infrared spectra were recorded generally using a Perkin-Elmer Infracord, Model 137B spectrophotometer equipped with sodium chloride optics. In some cases a Grubb Parsons double beam infrared spectrometer was also employed. A standard polystyrene film was used for wave-length calibrations. The spectra of solid compounds were taken as nujol mulls and of liquid samples as liquid films. The shoulder at 3050 cm\(^{-1}\) region was sharp and characteristic in the spectra taken on the Infracord spectrophotometer, but not well resolved in the spectra taken in the Grubb Parsons spectrometer.

RESULTS AND DISCUSSION

Ring deformation region (1010-1020 cm\(^{-1}\))

Except for the three hydrocarbons (I, II, III), all other compounds described in Table I are oxygenated compounds, such as alcohols, acids and esters. The alcohols show intense absorption at about 1040 cm\(^{-1}\) and thus mask the band at 1010-1020 cm\(^{-1}\). Similar is the case with acids and esters where the bands due to cyclopropane are not prominent. Hence, for detection of cyclopropane ring in oxygenated compounds, this region is not reliable. In the case of hydrocarbons such as tricyclene, \(\alpha\)-santalene, and dihydro \(\alpha\)-santalene, there are weak bands at 1010-1020 cm\(^{-1}\), but these are
not prominent enough to be assigned to the cyclopropane ring system. Hence, this absorption is found to be undependable for identification of tricyclene ring system.

**C-H Stretching region (\(\sim 3050 \text{ cm}^{-1}\))**

As seen in Table I, a sharp band or shoulder was observed at about 3050 cm\(^{-1}\) in all the compounds examined and this may be taken as an evidence for the C-H stretching of the hydrogen atoms attached to cyclopropane ring system. For the exact location of the C-H vibrational absorption bands, it would be necessary to have better resolution in this region, but in the present work, the sodium chloride optics employed gave sufficient indication of a sharp band or shoulder near 3050 cm\(^{-1}\) in the case of the tricyclene derivatives studied, thus confirming the usefulness of this band for the identification of the tricyclene system. The absorption bands generally lie in the range 3050-3100 cm\(^{-1}\).

The only interfering group in this region is the carbon-carbon double bond; the C-H stretching adjacent to \(\text{C} = \text{C}\) bond will be seen as a shoulder at about 3010-3040 or 3075-3095 cm\(^{-1}\). Therefore, in unsaturated compounds such as \(\alpha\)-santalene (II), \(\alpha\)-santalol (IV), Prins alcohol from \(\alpha\)-santalene (IX), and \(\alpha\)-santalal semicarbazone (XIII), this band may not be reliable as an evidence for the presence of a cyclopropane ring. But
in the rest of the saturated compounds listed in Table I, a sharp shoulder was observed in this region, which can be attributed to the tricyclene system. Thus, in addition to the three characteristic bands in the region 820-880 cm\(^{-1}\), the band at 3050 cm\(^{-1}\) provides a confirmatory evidence for the tricyclene derivatives.

Hence, contrary to Allen's findings,\(^1\) the band at \(\sim3050\) cm\(^{-1}\) appears to be useful for the diagnosis of cyclopropane ring system in case of saturated compounds of the tricyclene series, including hydrocarbons and oxygenated derivatives.

**870-878 cm\(^{-1}\) region**

The data in Table I show that significant absorptions appear consistently in the 870-878 cm\(^{-1}\) region with the majority centered near 875 cm\(^{-1}\). A sharp band at 876 cm\(^{-1}\) appears to be characteristic of \(\bar{\pi}\)-substituted tricyclenes. The only possible interfering group in this region is the exocyclic methylene bond (\(\bar{\pi}C=CH_2\)); the out-of-plane deformation of the attached hydrogen atoms in the carbon-carbon double bond appears at about 830 cm\(^{-1}\). Even in the presence of a \(\bar{\pi}C=CH_2\) group in an aliphatic chain, the band characteristic of \(\bar{\pi}\)-substituted tricyclene shows itself prominently as in the case of the alcohol (IX).

A deviation is observed in the case of teresan-talic acid (XV) which absorbs on the higher frequency
side in this region. This acid contains a methyl group and a carboxyl group as substituents at C(7). Probably the absence of \(-\text{CH}_2\) grouping in the C(7) substituent \((-\text{COOH})\) might have caused the disappearance of the band at 876 cm\(^{-1}\). As similar compounds of this type were not available, further study of the significance of this deviation was not pursued.

820-860 cm\(^{-1}\) region

The sharp band at 854 cm\(^{-1}\) and the somewhat less intense band at about 822 cm\(^{-1}\) are characteristic of all the hydrocarbons and the oxygenated compounds of the \(\text{H}\)-substituted tricyclene series encountered in the present work. The slight shift from the value reported by Corey\(^{26}\) (858 cm\(^{-1}\) in carbon tetrachloride solution) may be due to the fact that our spectral studies were carried out with liquid films. The shape of the curve in the region 800-880 cm\(^{-1}\) is almost the same in all \(\text{H}\)-substituted cases and is characteristic of the tricyclene system as in Fig. I (p. 225).

An interfering group which absorbs in the neighbourhood is the trisubstituted double bond \(R_1R_2C=CHR\) at 790-840 cm\(^{-1}\), but the interference is only with the band at 822 cm\(^{-1}\) and not with that at 854 cm\(^{-1}\).

Earlier findings of Passivirta,\(^{21}\) Hart and Martin,\(^{24}\) and Schleyer and his co-workers\(^{23}\) that the band at 854 cm\(^{-1}\)
Infrared spectra:

A. Dihydro \(\alpha\)-santalene(III) (liquid cell, 0.05 mm.)
B. Tricycloekeasantalic acid (VII), (In Nujol).
C. Keto-alcohol (XI) (liquid film).
is very characteristic of nortricyclene system may be recalled here. Schleyer showed that the band remains constant at 854 cm⁻¹ when the 1-substituent remains constant (methyl) and that its position is relatively independent of groups elsewhere on the nortricyclene system.

The results obtained in the present investigations may be interpreted in the light of the above findings as follows. The band at 854 cm⁻¹ arises from the nortricyclene skeleton. This band remains constant at 854 cm⁻¹ in all the compounds examined in the present work quite in agreement with Schleyer's observation. Schleyer's observations may be extended on the basis of the present results as follows:

(i) When the substituents, methyl and -CH₂-X (where X is H or any functional group) are introduced at the C(7) position of the nortricyclene skeleton, the band at 854 cm⁻¹ remains unaltered, and in addition two peaks appear at 8966, 876 and 822 cm⁻¹, respectively.

(ii) When one substituent is methyl and the other a carboxyl group at C(7) as in terosantalic acid, the absorption at 822 cm⁻¹ becomes intense and that at 876 cm⁻¹ either disappears or shifts to the higher frequency side.
The occurrence of the band at 822 cm$^{-1}$ in the spectra of the $\mathrm{I}$-substituted tricyclenes may be explained as due to the shift of the previously reported band (800-806 cm$^{-1}$),$^{22}$ (784-788)$^{23,24}$ to higher frequency side on account of the presence of two substituents at C(7) of the nortricyclene skeleton. Thus, the band at 822 cm$^{-1}$ may be useful for identification of the position of substituents in the nortricyclene system.

\[
\begin{array}{c}
\text{COOH} \\
\text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

XV
REFERENCES


