Infrared Absorption Studies on Some New Potential Antimicrobial Diazotization Product of 4-aryl-Thiosemicarbazides

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ABSTRACT

The infrared absorption spectra of 4-aryl-3-thiosemicarbazides & 5-arylamino-1,2,3,4-thiatriazoles have been studied and structural assignments of importance to these systems made or suggested. Important conclusions drawn from the spectral data are: there is no suggestion of any thiol-thione tautomerism for the solid 4-aryl-3-thiosemicarbazides and that the thione structure predominates for these substances and that the diazotization products of the 4-arylthiosemicarbazides yield, 1,2,3,4-thiatriazole rather than the isomeric open chain thiocarbamylazides. The C=S, -N=C=S and cyclic -N=N=N- configurational assignments are discussed. Compounds 5-p-tolyl and 5-o-anisyl amino-1,2,3,4-thiatriazoles have shown antifungal activity against two fungi.

Key words: IR spectra and antifungal activity of 5-p-tolyl and 5-o-anisylamino 1,2,3,4-thiatriazoles.

INTRODUCTION

In a previous communication Lieber, Pillai and Hites reported that the reaction of 4-aryl-thiosemicarbazides\(^2-3\) (I) with nitrous acid as well as the reaction of aryl-isothiocynates (II) with hydrazoic acid leads to the identical 5-arylamino-1,2,3,4-thiatriazoles (III).

\[
\begin{align*}
\text{(I)} & : \quad \text{Ar-NH-C\text{-}}\text{NH-NH}_2 + \text{NHO}_2 \\
\text{(II)} & : \quad \text{Ar-NCS} + \text{H}_2\text{N} \\
\text{(III)} & : \quad \text{C-N=NH-Ar}
\end{align*}
\]
The 5-(substituted) amino-1,2,3,4-thiatriazoles (III), or treatment with base (NaOH) gives (II) and NH$_3$ as well as another produce also.

EXPERIMENTAL

IR Spectroscopic Studies

The IR spectra were recorded on a Perkin-Elmer single beam spectrometer, Model 12C. with sodium chloride prism. The position of the absorption maxima are listed in Table-1 & 2 with the intensities being indicated by the following symbols: s=strong, m=medium, w=weak; vw=very weak. The compounds studied were those reported upon in the previous communication. The spectra were taken in Nujol mulls & KBr. Disc.

RESULTS AND DISCUSSION

4-substituted thiosemicarbazides

All the important absorption bands of the 4-substituted thiosemicarbazides in the region 1640-780 cm$^{-1}$. Summarized in Table-1. No SH band was found in these compounds in the region 2600-2500 cm$^{-1}$, the range in which the SH stretching vibrations are most likely to appear. Thus clearly shows that there is no thiol-thione tautomerism in these compounds in the solid state.

A similar conclusion has been drown by Bogomolov & Co-workers. All the compounds studied showed N-H stretching models of vibrations. In general, the important infrared absorption frequencies of the 4-substituted thiosemicarbazides can be summarized in Table-1. The bonds due to hydrazino, -NHNH$_2$, Portion of the structure have been assigned on the basis of studies presented by Randall & Lieber. The 4-aryl-thiosemicarbazides show weak absorption at 1634 cm$^{-1}$. In addition to the absorption bands discussed above, bands due to other functional group and substituted aromatic rings were also observed.

5-(substituted) amino-1,2,3,4-thiatriazoles

The most significant observation arising out of this study of the infrared absorption spectra of a series of eight 5-arylamino-1,2,3,4-thiatriazoles, summarized in Table-2. In spectra there is absence...
of an absorption band in the region 2170-2080 cm
1, this rules out the presence of Azido group, supporting structure No. (III).

In addition to above other common absorbance are as below-

\[
\text{1260 cm}^{-1} : \text{cyclic } \text{-N-N=N- stretching vibrations.}
\]

\[
\text{1195, 1140, 1060 cm}^{-1} : \text{Aromatic C-H planar bending vibrations.}
\]

\[
\text{985, 955, 870 cm}^{-1} : \text{Aromatic C-H out of Plane bending vibrations.}
\]

\[
\text{800 cm}^{-1} : \text{C-Cl stretching vibrations.}
\]

### Table 2: 5-Arylamino-1,2,3,4-thiatriazoles

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Ar group</th>
<th>-NH (cm(^{-1}))</th>
<th>C=N (cm(^{-1}))</th>
<th>Aromatic C=C (cm(^{-1}))</th>
<th>N=N (cm(^{-1}))</th>
<th>C-S (cm(^{-1}))</th>
<th>N-C-S (cm(^{-1}))</th>
<th>Aromatic C-H</th>
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<tbody>
<tr>
<td>1</td>
<td>Phenyl</td>
<td>3380</td>
<td>1595</td>
<td>1600, 1495</td>
<td>1375, 1495</td>
<td>1460</td>
<td>3130</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>o-Anisyl</td>
<td>3350</td>
<td>1575</td>
<td>1608, 1585</td>
<td>1370, 1490</td>
<td>1460</td>
<td>3100</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>p-Tolyl</td>
<td>3340</td>
<td>1540</td>
<td>1600, 1490</td>
<td>1370, 1490</td>
<td>1465</td>
<td>3040</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1-Pyridyl</td>
<td>3270</td>
<td>1570</td>
<td>1610, 1480</td>
<td>1370, 1490</td>
<td>1450</td>
<td>3040</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>p-Hydroxyphenyl</td>
<td>3380</td>
<td>1585, 1580</td>
<td>1605, 1485</td>
<td>1370, 1480</td>
<td>1455</td>
<td>3040</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>p-Chlorophenyl</td>
<td>3290</td>
<td>1535</td>
<td>1600, 1495</td>
<td>1380, 1480</td>
<td>1455</td>
<td>3040</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3: Antifungal screening of 5-arylamino-1,2,3,4-thiatriazoles

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Aryl Group</th>
<th>Aspergillus Niger (ppm)</th>
<th>Fusarium oxyporium (ppm)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>1000 100 10</td>
<td>1000 100 10</td>
</tr>
<tr>
<td>1</td>
<td>Phenyl</td>
<td>65 36 15</td>
<td>65 32 14</td>
</tr>
<tr>
<td>2</td>
<td>p-Tolyl</td>
<td>82 59 36</td>
<td>81 58 36</td>
</tr>
<tr>
<td>3</td>
<td>1-Pyridyl</td>
<td>68 40 30</td>
<td>67 40 30</td>
</tr>
<tr>
<td>4</td>
<td>Cyclohexyl</td>
<td>57 55 36</td>
<td>59 56 35</td>
</tr>
<tr>
<td>5</td>
<td>o-Anisyl</td>
<td>84 50 38</td>
<td>86 50 36</td>
</tr>
<tr>
<td></td>
<td>Dithane M-45</td>
<td>100 81 68</td>
<td>100 80 68</td>
</tr>
</tbody>
</table>
Antifungal Activity

Test fungi Aspergillus niger and Fusarium oxyporium were obtained from the IARI, New Delhi and maintained on Agar compounds (1 to 5) were screened invitro by Agar Plate Technique at different concentration (1000, 100 & 10 ppm), Dithane M-45, a commercial fungicide was also tested under similar condition for comparison.

Results of fungicidal activity were summarized in Table-3. It is evident from the data the most active were 5-p-tolyl and 5-o-anisyl amino –1,2,3,4-thiatriazoles.

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REFERENCES