Abstract

In this part preparation and qualitative reactions of $N$-acylated phenyl and methyl hydroxylamines have been described.
Preparation and Properties of N-Acylated Phenyl and Methyl Hydroxylamines

Shome (4) has reported the use of N-benzoylphenylhydroxylamine as a gravimetric reagent for iron (III), aluminium (III), and titanium (IV). Earlier (3) he gave a list of compounds belonging to cupferron in which the nitroso group is replaced by R (where R is CHO, COCH₃, COC₆H₅, CONH₂, CONHCS₆H₅, CSNH₂, CSNHCS₆H₅, CSNHCH₂CH:CH₂). Since then nothing has been reported. Feigl (2) has also indicated the possibility of interesting results from these compounds.

In view of the above observations, study of acylated phenyl and methyl hydroxylamines as analytical reagents was undertaken. The following compounds were prepared:

\[
\begin{align*}
\text{I} & : \text{C₆H₅.N} - \text{OH} \\
\text{II} & : \text{CH₃.N} - \text{OH} \\
\text{III} & : \text{CH₃.N} - \text{OH}
\end{align*}
\]

EXPERIMENTAL

Preparation of N-Acetylphenylhydroxylamine (I) - Bamberger and Destras (1) have reported the preparation of N-acetylphenylhydroxylamine by the action of acetic anhydride on phenylhydroxylamine. We have prepared it by the action of acetyl chloride on phenylhydroxylamine in benzene. The reaction may be written as under:

\[
\text{C₆H₅.N-OH} + \text{Cl CO.CH₃} \rightarrow \text{C₆H₅.N-CH₃} + \text{HCl.}
\]

The reaction was done in the presence of little water and
small amounts of sodium bicarbonate were occasionally added to keep the medium slightly alkaline.

10.9 g. of phenylhydroxylamine was taken in a 250-ml. flask and dissolved in 50 ml. of benzene. 5 ml. of water and 1g. of sodium bicarbonate were introduced into it. Acetyl chloride solution (8 g.) dissolved in 10 ml. benzene was gradually added. After each addition the mixture was vigorously shaken till effervescence ceased. Water layer was kept alkaline to litmus by the gradual addition of sodium bicarbonate. In all about 10 g. of sodium bicarbonate were required. Near the completion of the reaction, addition of acetyl chloride changed the colour of the reaction mixture from yellow to pink but on shaking, it again changed to yellow. At this stage, before adding more acetyl chloride, a drop of reaction mixture was tested with Tollen's reagent. Negative test indicated the completion of the reaction. It took about two and a half hours in all. Benzene layer was separated. The solvent was evaporated off on a water bath. The product solidified on cooling. It was crystallised from hot water and also from benzene petroleum ether mixture. In both the cases white shining needles were obtained; yield about 10 g., m.p. 66.8°C, literature m.p. 67-67.5°C (1).

It is soluble in alcohol, benzene, ether, hot water and caustic soda solution and insoluble in petroleum ether. Its solubility in water at 33.5°C is 4.7 g. per 100 g. of water. The compound is highly stable in the solid state but its solution is decomposed if not stored properly in well stoppered bottles.

Analysis: Found N, 8.90%
C₉H₈NO₂ requires N, 9.271%
Preparation of N-Benzoylmethylhydroxylamine (II) - A well cooled aqueous solution of methylhydroxylamine prepared by reducing 15 ml. of nitromethane with zinc dust in ammonium chloride medium was stirred mechanically and 32 g. of benzoyl chloride was added drop by drop. 25 g. of sodium bicarbonate were added in small quantities at a time to keep the reaction mixture distinctly alkaline. The addition of benzoyl chloride was stopped when a test drop of reaction mixture gave a negative test with Tollens's reagent. Stirring was continued for another half an hour. It was filtered under suction and the filtrate was heated to dryness on a water bath. The compound was extracted from the residue with methyl alcohol. Small quantities of ether were added to the extract to throw out inorganic matter. It was filtered and filtrate was concentrated on water bath. Very light yellow coloured needles separated out on strong cooling, yield 8 g.

Analysis: Found N, 8.15%

C_H_NO requires N, 8.09%

It is actually the sodium salt of N-benzoylmethylhydroxylamine and has no sharp melting point. It is highly soluble in water (40.5 g per 100 g of water at 17°C), and alcohol and sparingly soluble in ether, chloroform, and benzene.

Reactions of N-Acetylphenylhydroxylamine and N-Benzoylmethylhydroxylamine

Reactions of N-acetylphenylhydroxylamine and N-benzoylmethylhydroxylamine with various metallic ions were studied by adopting conventional procedures. Apparatus and solutions were the same as described earlier in Part I of Section A.
The results are recorded in Table I.

<table>
<thead>
<tr>
<th>Element</th>
<th>N-Acetylphenylhydroxylamine</th>
<th>M-Benzoylmethylhydroxylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)</td>
<td>Below pH 1.2, purple colour, unstable; pH 1.5 to 3.2, orange colour; pH 3.8 to 10.0, yellow colour. Reaction not masked by tartrate, phosphate and cyanide.</td>
<td>Below pH 1.0, purple blue colour, unstable; between pH 1.2 to 3.0, reddish-brown colour; between pH 4 to 8, orange colour; between pH 8 to 10, yellow colour. Reaction not masked by tartrate, phosphate and cyanide.</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>Below pH 2.0, no reaction; pH 4 to 8, orange colour; above pH 9.0, light yellow colour.</td>
<td>Below pH 2.5, no reaction; pH 3 to 8, orange colour; above pH 9.0, yellow colour.</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>Below pH 2.5, deep yellow colour with slight turbidity. Reaction not masked by tartrate and cyanide.</td>
<td>Below pH 2.5, deep yellow colour. Reaction not masked by tartrate and cyanide.</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>Above pH 5.0, slight yellow colour.</td>
<td>pH 4 to 6, light yellowish brown colour.</td>
</tr>
<tr>
<td>Au(III)</td>
<td>Reduced.</td>
<td>Reduced.</td>
</tr>
<tr>
<td>Ag(I)</td>
<td>No reaction.</td>
<td>Reduced.</td>
</tr>
<tr>
<td>Tungstate</td>
<td>Below pH 2, yellow ppt., not quantitative. Reaction masked by tartrate and fluoride.</td>
<td>pH about 2, white ppt., not quantitative. Reaction masked by tartrate and fluoride.</td>
</tr>
<tr>
<td>Molybdate</td>
<td>Below pH 2, yellowish white ppt., not quantitative.</td>
<td>About pH 2, white ppt., not quantitative.</td>
</tr>
</tbody>
</table>

These reagents do not give any colour reaction with cobalt(II), nickel(II), palladium(II), manganese(II), zinc(II),
mercury(II), chromium(III), bismuth(III), antimony(III),
aluminium(III), thorium(IV), platinum(IV), uranium(IV), cerium(IV),
uranyl, zirconyl, alkali metals, and alkaline earth metals on
spot plate testing.

N-Acetethylhydroxylamine (III) - The preparation of this
compound is not simple and the yield is also very poor. Moreover
it does not possess any advantage over N-benzoylmethylhydroxylamine,
hence details have not been given.

References

1 Bamberger and Destraz, Ber., 35, 1883.
2 Feigl, F., "Chemistry of Specific, Selective, Sensitive,
4 Ibid., Analyst, 75, 27(1950).