PART I

Preparation and Properties of Hydroxytriazenes

Abstract

In this part, preparation and qualitative reactions of several hydroxytriazenes are described.
Preparation and Properties of Hydroxytriazenes

In this part we have described the preparation and qualitative reactions of hydroxytriazenes listed below:

A. Phenylhydroxylamine Derivatives

\[ \text{C}_6\text{H}_5\cdot \text{N}=\text{OH} \]
\[ \text{N}=\text{N}_2\text{C}_6\text{H}_4\cdot \text{CH}_3(\text{p}) \]
\[ \text{II} \]
\[ \text{C}_6\text{H}_5\cdot \text{N}=\text{OH} \]
\[ \text{N}=\text{N}_2\text{C}_6\text{H}_4\cdot \text{COOH}(\text{o}) \]
\[ \text{IV} \]
\[ \text{C}_6\text{H}_5\cdot \text{N}=\text{OH} \]
\[ \text{N}=\text{N}_2\text{C}_6\text{H}_4\cdot \text{COCH}_3(\text{p}) \]
\[ \text{VI} \]
\[ \text{C}_6\text{H}_5\cdot \text{N}=\text{OH} \]
\[ \text{N}=\text{N}_2\text{C}_{10}\text{H}_7(2) \]
\[ \text{VIII} \]
\[ \text{C}_6\text{H}_5\cdot \text{N}=\text{OH} \]
\[ \text{N}=\text{N}_2\text{C}_6\text{H}_4\cdot \text{CH}_3(\text{p}) \]
\[ \text{X} \]
\[ \text{C}_6\text{H}_5\cdot \text{N}=\text{OH} \]
\[ \text{N}=\text{N}_2\text{C}_6\text{H}_4\cdot \text{SO}_3\text{H}(\text{o}) \]
\[ \text{XII} \]

B. Methylhydroxylamine Derivatives

\[ \text{CH}_3\cdot \text{N}=\text{OH} \]
\[ \text{N}=\text{N}_2\text{C}_6\text{H}_5 \]
\[ \text{XIII} \]
\[ \text{CH}_3\cdot \text{N}=\text{OH} \]
\[ \text{N}=\text{N}_2\text{C}_6\text{H}_4\cdot \text{CH}_3(\text{p}) \]
\[ \text{XIV} \]
Lamberger et al. (1,2,3,4), Gebhard and Thomson (6,7), and Elkins and Hunter (5) have described the preparation of hydroxytriazanes by reducing nitrobenzene or substituted nitrobenzenes with phenylhydrazine or substituted phenylhydrazines. Recently Seoani and Bhattacharyya (10,11,12) have prepared these compounds by reacting monosubstituted hydroxylamines with diazonium salt in acetate buffered solution at 0°C. The general mechanism of the reaction may be represented as follows:

\[
\begin{align*}
R_1N-NH + \text{N}^+\text{Cl}^- & \rightarrow R_1N-NH + \text{HCl} \\
& \quad (\text{where } R \text{ is an alkyl or phenyl radical and } R' \text{ is a phenyl radical or substituted phenyl radical.})
\end{align*}
\]

2. Phenylhydroxylamine Derivatives - 3-Hydroxy-1,3-diphenyltriazene has been reported as an excellent gravimetric reagent for copper and palladium (10,11). Apart from other good qualities, one remarkable advantage of this reagent is, that at low pH any excess of the reagent present in the reaction medium, on heating on a waterbath, during the usual processing of the complex, is completely hydrolysed into water soluble products which can easily be eliminated with water. This property imparts to this compound all the advantages of a water soluble reagent. The compounds listed above exhibit reactions similar to the parent triazene with different metallic ions. The main consideration in studying these compounds has been that any excess of the reagent in the acidic medium should...
be easily hydrolysed to water soluble products, to make the complex suitable for direct weighing. It was found that compounds II and V to XI do not give water soluble products on hydrolysis. Compounds III and IV and their complexes are not very stable. Thus these compounds (II to XI) possess no advantage over the parent compound. Compound XII is water soluble and gives water soluble complexes. But it possesses no advantage over 3-hydroxy-1-p-sulphonatophenyl-3-phenyltriazene reported earlier (12). However, compound I is superior to the parent compound in many respects and has been worked out in detail.

Compounds I (3,5), II(2), and X(7), are described in literature and the rest of the nine compounds are new ones.

B. Methylhydroxylamine Derivatives - These compounds possess common functional grouping - N(CH)N=N-, with the difference that the oxime group is attached to methyl group in place of phenyl group. This considerably reduces the acidic character of oxime group. The characteristic complex forming properties are retained but precipitating property is lessened. However, these compounds are fairly soluble in hot water as compared to the class A compounds, described above.

Because of the lengthy process involved in preparing crystalline methylhydroxylaminehydrochloride, we had to slightly modify the method for preparing compound XIII to XV. Solution of methylhydroxylamine was directly used for their preparation.

EXPERIMENTAL
Preparation of Phenylhydroxylamine - It was prepared as described by Vogel (13).
3-Hydroxy-1-p-tolyl-3-phenyltriazene (I) - Freshly prepared crystalline phenylhydroxylamine (84 g.) was dissolved in warm water (700 ml.) and the solution stirred mechanically with sufficient quantity of crushed ice to bring the temperature to 0°C. A solution of diazonium chloride prepared from p-toluidine (28 g.), hydrochloric acid (60 ml.), and 140 ml. of 10% sodium nitrite (14 g.) was then slowly added under mechanical stirring to this solution. Small portions of solution of sodium acetate (100 g. in 300 ml. of water) were occasionally added to the reaction mixture to prevent it from becoming too acidic. After the addition of diazonium salt was complete, the remaining portion of sodium acetate was added and the reaction mixture stirred for another five minutes; the temperature during the entire course of reaction being kept at about 0°C. The granular, light greenish yellow coloured precipitate of 3-hydroxy-1-p-tolyl-3-phenyltriazene was then filtered off under suction, washed thoroughly with water and crystallised twice from alcohol. It was obtained as greenish yellow coloured needles; yield 25 g., m.p. 125°C, literature 130°C (3), 131°C (5).

The difference of 5°C in the melting point cannot be explained. Similar differences in the melting points of the compounds reported in the literature have been pointed out by Sogami (9).

Analysis: Found: N, 16.311% 
C₁₆H₁₂N₃ requires: 16.302%.

Solubility-0.0030 g. per 100 g. of water at 32°C.

Other phenylhydroxylamine Derivatives - Compounds from IV to IX were prepared by following the above procedure, with only slight
modifications as required by the nature or the compound. The quantities of various reagents used were adjusted according to the requirement of the molar ratio. Details have not been included for the sake of brevity.

3-Hydroxy-1-p-bromophenyl-3-phenyltriazene (II) - After preparation, the compound was crystallised twice from 95% alcohol as deep green shining crystals; m.p. 150°C, literature 154.5°C (2).

Analysis: Found: N, 14.06%
C<sub>15</sub>H<sub>10</sub>N<sub>3</sub>Br requires: N, 14.38%

3-Hydroxy-p-hydroxyphenyl-3-phenyltriazene (III) - On adding p-hydroxybenzene diazonium chloride to phenyl hydroxylamine no compound separated out as it usually happens. It was also observed that the addition of sodium acetate gave a tarry product. Hence, the addition of this compound was considered unsuitable. At low pH formation of final product was fairly slow. Therefore, after mixing reactants at 0°C, the contents were filtered and the filtrate was kept at room temperature for about one hour when the compound separated out in a crystalline form. It was again crystallised from alcohol in the form of light-yellow shining needles; m.p. 114-115°C.

Analysis: Found: N, 18.03%
C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> requires: N, 18.34%

3-Hydroxy-1-O-carboxyphenyl-3-phenyltriazene (IV) - The compound, after preparation, was immediately filtered under suction. It was dissolved in minimum quantity of alcohol and filtered. The compound was precipitated from the filtrate by adding a small amount of water. It was again dissolved in minimum quantity of alcohol and kept in refrigerator over night when white needles crystallised;
m.p. 35°C.

Analysis: Found: N, 16.47%
C_{13}H_{14}N_3O_3 requires: N, 16.15%

3-Hydroxy-1-(3-hydroxy-4-carboxyphenyl)-3-phenyltriazene (V) - The compound was crystallised from alcohol as a yellowish crystalline substance; m.p. 178°C. It is soluble in sodium hydroxide solution.

Analysis: Found: N, 15.5%
C_{13}H_{11}N_3O_4 requires: N, 15.38%

3-Hydroxy-1-p-acetophenone-3-phenyltriazene (VI) - After preparation, the compound was twice crystallised from alcohol. It gave beautiful light yellow flakes; m.p. 154°C.

Analysis: Found: N, 16.23%
C_{14}H_{13}N_3O_2 requires: N, 16.47%

3-Hydroxy-1-p-anisidide-3-phenyltriazene (VII) - The compound was crystallised from alcohol. It gave light yellow flakes; m.p. 146.5°C.

Analysis: Found: N, 20.58%
C_{14}H_{14}N_3O_2 requires: N, 20.74%

Preparation of substituted phenylhydroxylamine: - The alcoholic solution of the corresponding nitro compound was reduced in the same way as described earlier. The solution was directly used for further reaction.

3-Hydroxy-1,3-p-ditolyltriazone (X) - After preparation, the compound was crystallised from alcohol; m.p. 131°C, literature 130.5°C (7).

Analysis: Found: N, 17.62%
C_{14}H_{16}N_3O requires: N, 17.42%

3-Hydroxy-1-phenyl-3-p-chlorophenyltriazene (XI) - This compound
was crystallised from alcohol as light yellow needles; m.p. 125°C.

Analysis: Found: N, 16.34%
C₁₂H₁₀N₃OCl requires: N, 16.94%

3-Hydroxy-1-p-sulphonatophenyl-3-p-tolyltriazene (XII) - The compound was crystallised from large volume of alcohol. It was actually the sodium salt of the sulphonic acid derivative having no sharp melting point. The crystals are light chocolate in colour.

Analysis: Found: N, 12.22%
(C₁₃H₁₂N₃O)SO₃Na.H₂O requires: N, 12.10%

Attempts to crystallise compounds VIII & IX in acetone, ether, alcohol, benzene and chloroform failed. However, the uncrystallised products gave same reaction with metallic ions as other reagents.

Preparation of methylhydroxylamine - It was prepared by the method given by Beckmann (8).

3-Hydroxy-1-phenyl-3-methyltriazene (XIII) - An aqueous solution of methylhydroxylamine, prepared by reducing 6.6 ml. of nitromethane with zinc dust in ammonium chloride medium was stirred mechanically with sufficient quantity of crushed ice to keep the temperature at 0°C. A solution of benzene diazonium chloride, prepared from 4.6 ml. of aniline, was then added slowly to the above solution under mechanical stirring. Small portions of a concentrated sodium acetate (20 g.) solution were added occasionally to prevent it from becoming too acidic and to maintain the pH at about 5.0. The compound was thrown out in the form of a white granular precipitate. It was filtered under suction, washed with ice-cold water and crystallised from warm water in the form of white needles; yield about 3 g., m.p. 69°C, literature 69-70°C (4), 72-73°C (5).
Solubility: 0.458 g. per 100 g. of water at 34°C. It is freely soluble in alcohol-water mixtures.

Analysis: Found: N, 27.60%
C₇H₇N₃O requires: N, 27.81%

3-Hydroxy-1-p-tolyl-3-methyltriazene (XIV) - After preparation the compound was crystallised from 75% alcohol; cream white needles; m.p. 110-111°C, literature 115-116°C (5).

Solubility: 0.0308 g. per 100 g. of water at 34°C and 0.0905 g. per 100 g. of water at 75°C. It is freely soluble in alcohol.

Analysis: Found: N, 25.62%
C₈H₁₁N₃O requires: N, 25.45%

3-Hydroxy-1-β-naphthyl-3-methyltriazene (XV) - It was crystallised from alcohol; light brown crystals; m.p. 140°-141°C, literature 143°-144°C (5).

Reaction of Hydroxytriazenes with Metallic Ions

Qualitative reactions of the various reagents toward different metallic ions were studied by adopting conventional procedures using spot plate, microtest tube and hand centrifuge etc. pH was determined by using pH paper and also Beckman automatic pH meter, Model K-2. Completeness of precipitation was tested by applying spot test technique and using sensitive reagents like rubeanic acid in case of copper, dimethylglyoxime in case of nickel and palladium etc.

Details of the reactions of 3-hydroxy-1-p-tolyl-3-phenyltriazene and 3-hydroxy-1-p-tolyl-3-methyltriazene toward various elements are recorded in Table I. The reactions of other phenylhydroxylamine derivatives class A - are similar to those of
3-hydroxy-1-p-tolyl-3-phenyltriazene and the reactions of methylhydroxylane derivatives-class B resemble to those of 3-hydroxy-1-p-tolyl-3-methyltriazene.

Most of the complexes of 3-hydroxy-1-phenyl-3-methyltriazene are water soluble.

A characteristic property of the compounds belonging to class A is that they develop an intense yellow colour in alkaline medium. They also hydrolyse on heating in weakly acidic medium and the hydrolysed products give blue colour in alkaline medium, whereas compounds belonging to class B do not give the above reactions.

| Table 1: Comparative Study—Reactions of 3-hydroxy-1-p-tolyl-3-phenyltriazene and 3-hydroxy-1-p-tolyl-3-methyltriazene with various elements. |
|---------------------------------|---------------------------------|---------------------------------|
| Element                         | 3-Hydroxy-1-p-tolyl-3-phenyltriazene. | 3-Hydroxy-1-p-tolyl-3-methyltriazene. |
| Cu (II)                         | pH 2.0 to 7.0, Chocolate brown granular ppt., stable toward heat, N.R. | pH 3.8 to 7.0, reddish brown granular ppt., stable toward heat, N.R. |
| Hg (II)                         | pH 4.4 to 7.0, Bright yellow granular ppt., stable toward heat, N.R. | Below pH 5, N.R., above pH 6.5, yellowish brown ppt., N.R. |
| Fe (II)                         | pH 1.6 to 7.0, Yellowish brown granular ppt., stable toward heat, N.R. | pH 1 to 6, violet brown granular ppt., stable toward heat, N.R. |
| Mn (II)                         | Above pH 5.5, dirty brown ppt., unstable toward heat, N.R. | N.R. |
| Cd (II)                         | Above pH 6.0, light yellow fine ppt., N.R. | N.R. |
| Fe (II)                         | pH 4.9 to 7.0, Bluish black granular ppt., unstable toward heat, N.R. | N.R. |
Fe(III)  pH 4.5 to 7.0, bluish black granular ppt., unstable toward heat.  
Sn(II)  Above pH 6.5, yellow ppt., N.R.  
V(IV)  Only at low pH, grassy green ppt., fairly soluble in alcohol and unstable toward heat.  
Ni(IV)  pH 2 to 3.5, orange ppt., unstable toward heat.  
Ce(IV)  Below pH 2, light yellow colour.  
Au(III) Reduced to metallic state.  
Ag(I)  Ditto.  
Vanadate  Only at low pH, dark green ppt., fairly soluble in alcohol and unstable toward heat.  
Mo Turnbull  Only at low pH, unstable green solution, becomes turbid on keeping; unstable to heat.  
Molybdate Only at low pH, Deep orange ppt., unstable toward heat.  

Below pH 2, blue colour; above pH 4, violet blue ppt., N.R., masked by tartrate and fluoride. 
Below pH 2 brown ppt., and masked by fluoride. 
Below pH 2, Yellow ppt., changing to brown. N.R., masked by fluoride. 

Arsenic (III), bismuth (III), chromium (III), beryllium (II), thorium (IV), uranium (IV), platinum (IV), uranyl, tungstate, phosphate, alkali metals, and alkaline earth metals give no reaction with either of the reagents.
References

2. Ibid., Annalen, 420, 164.
3. Bamberger and Busdorf, Ber., 35, 3510; Bell XVI, 735, (1943).
7. Ibid., Bell XVI, 737 (1943).
11. Ibid., 28, 1616 (1956).
12. Ibid., 29, 397 (1957).