

Preparation of 5-(*p*-Chlorophenylazo) Resacetophenone by Two Routes and Using its Oxime as Reagent for Qualitative and Quantitative Analysis of Some Bivalent Metals

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Resacetophenone was synthesised from resorcinol by Nencki's reaction and then coupled with diazonium salt of *p*-chloroaniline to obtain 5-(*p*-chlorophenylazo) resacetophenone. An alternate route was tried by changing the sequence of the reaction. Resorcinol was first coupled with diazonium salt of *p*-chloroaniline and then subjected to Nencki's reaction. The results of experiments, elemental analysis and IR spectral data suggested that the compounds obtained by both the methods were same. These also indicated that coupling before or after Nencki's reaction did not involve any structural change. Position of coupling was ascertained by the preparation of reductive derivative of the azo compound followed by conversion of —NH_2 group to —OH group.

Further, the compound was converted to its oxime with hydroxylamine hydrochloride. The oxime was coloured and had high molecular weight. It was consequently used as a chelating agent for qualitative and quantitative analysis of bivalent metals like Cu, Zn and Ni. On the basis of the quantitative data the structures of the complexes were assigned and probable use of the oxime as analytical reagent was suggested.

INTRODUCTION

A number of methods are available to prepare phenolic ketones^{1,2} like Friedel-Crafts reaction, Fries rearrangement, Hoesch reaction, etc. Various *o*-hydroxy-ketone derivatives are converted to their oximes³ and are used as chelating agents⁴. Oximes can thus be used as analytical reagents for estimation of metals⁵. It is widely known that phenols couple with diazonium salts to give coloured azo compounds⁶. Hence when diazo-coupled phenolic ketones are converted to their oximes they can be used for estimation of metals by forming coloured metal complexes. Nencki's reaction has been successfully used to prepare ketones from polyhydric phenols, particularly using dihydric phenols like resorcinol^{7,8}. In the present study resacetophenone was obtained by Nencki's reaction. Oximes of resacetophenone and its substituted derivatives have been studied as chelating agents for the estimation of bivalent metals^{9,10}. An attempt has been made to improve upon the efficiency of resacetophenone oxime as chelating agent by making it more sensitive in the following ways:

- (i) A chromophore has been added to the molecule to make it coloured so that completion of precipitation of bivalent metal could be more easily observed.
- (ii) By increasing the molecular weight of the oxime, which results in increase in the weight of the chelate, the experimental error could be minimised.

Work was, therefore, undertaken to couple resacetophenone with *p*-chlorobenzene diazonium chloride to obtain 5-(*p*-chlorophenylazo) resacetophenone. Gore *et al.*¹¹ reported that Fries reaction carried out on diacetyl-4-benzeneazo resorcinol showed no effect on azo group under the reaction conditions. This prompted to use an alternate route to prepare 5-(*p*-chlorophenylazo) resacetophenone. In this route resorcinol was first coupled with *p*-chlorobenzene diazonium chloride and then subjected to Nencki's reaction. That the azo group remained intact under the reaction conditions and the same compound was obtained by the alternate route was confirmed on the basis of preparation of derivatives and various experimental results. The structure suggested was based on elemental analysis, IR spectral data and conversion to a compound of known structure.

5-(*p*-Chlorophenylazo) resacetophenone was converted to 5-(*p*-chlorophenylazo) resacetophenone oxime by treating with hydroxylamine hydrochloride in pyridine. The structure suggested for the product was based on elemental analysis and IR spectral results.

Ethanol solution of this oxime was used to prepare metal chelates with CuSO₄, ZnSO₄ and NiSO₄ solutions for qualitative and quantitative analysis. It is well known that complexes which contain two six membered rings with two double bonds in each and metal atom at the centre are stable. The quantitative estimation data indicates the formation of stable chelates with the oxime reagent.

EXPERIMENTAL

All chemicals used were of LR grade and the melting points are uncorrected.

Resacetophenone (**II**) was prepared by adding resorcinol (**I**) to a hot mixture of powdered anhydrous ZnCl₂ and glacial acetic acid. Experimental conditions were same as that of Nencki's reaction adopted by Robinson *et al.*¹² The product obtained was found to have a melting point of 145°C.

Resacetophenone (15.5 g) was dissolved in 10% NaOH solution (85 mL) and cooled below 5°C. *p*-Chloroaniline (13 g) was diazotised with NaNO₂ solution (8 g in 40 mL water) in presence of 1 : 1 HCl (64 mL). Completion of diazotisation was checked with the help of starch iodide paper. The cold *p*-chlorobenzene diazonium chloride was then slowly added to the alkaline solution of resacetophenone with constant stirring. The temperature was maintained below 5°C. An orange coloured solid separated out. It was allowed to stand in ice bath for ½ h and then filtered, washed and purified from benzene and dried. The yield obtained was found to be about 78% and the melting point determined was 169°C. This compound was marked as **B1**. Elemental analysis and IR spectral analysis were recorded. It was represented as (**IV**) in the reaction scheme.

In the alternate route resorcinol (11 g) was first coupled with *p*-chlorobenzene diazonium chloride using similar procedure of diazotisation and coupling as mentioned above. The solid obtained (**III**) was purified from alcohol. Yield was around 77% and melting point detected was 195°C. This product was then subjected to Nencki's reaction with anhydrous ZnCl₂ and glacial acetic acid. The yield obtained was about 75%. It was marked as **B2**. The melting point was also found to be 169°C. Mixed melting point of **B1** and **B2** showed no depression.

Elemental analysis and IR spectral data were recorded. Further, both the compounds **B1** and **B2** were converted to their diacetyl derivatives with sodium acetate and acetic anhydride. Products obtained were purified from ethanol. Both the derivatives melted at 95°C and represented as (**V**) in the reaction scheme.

To ascertain the position of coupling the compound (**IV**) was first reduced with $\text{Na}_2\text{S}_2\text{O}_4$ to convert azo group to amino group and then amino group was converted to —OH group. For reduction the compound (**IV**) was dissolved in minimum amount of ethanol and refluxed in water bath for ½ h. Then 5% solution of $\text{Na}_2\text{S}_2\text{O}_4$ was added till the orange colour disappeared. The mixture was refluxed for another ½ h, then cooled to room temperature and filtered. The filtrate was concentrated in water bath till solid separated out. It was filtered and purified from ethanol to get yellow granules, which melted at 161°C. Elemental analysis was also carried out. The compound (**VI**), thus obtained, was tested for various functional groups like phenolic —OH, —NH₂, and —CO—CH₃. This compound (**VI**) was then diazotised with NaNO_2 in presence of HCl and refluxed with water for 1 h. Solid separated out on cooling was filtered, washed and purified from ethanol as bright yellow needles (**VII**). It decomposed at 230°C.

The oxime of compound (**IV**) was prepared with hydroxylamine hydrochloride in presence of pyridine and ethanol. The mixture was refluxed in water bath for 2 h. On pouring in ice, crystals of oxime separated out (**VIII**). It was purified from ethanol as shining reddish brown crystals. The melting point detected was 225°C. Elemental analysis and IR spectral analysis were recorded.

The above oxime was used as chelating agent.

Stock solutions of various metal ions were prepared by dissolving AR grade metal salts in distilled water. For qualitative studies, 0.2% ethanolic solution of the oxime was prepared and used for tests with CuSO_4 solution (pH 4.2), ZnSO_4 solution (pH 4.8) and NiSO_4 solution (pH 5.1). Different coloured precipitates of the chelates were obtained.

Estimation of Cu chelate: CuSO_4 solution (0.25%, 50 mL, pH 4.2) was prepared and warmed gently. To this warm solution oxime solution (0.2%, about 200 mL) in ethanol was added slowly with stirring. Greenish yellow precipitate of Cu chelate separated out. The precipitate was digested and filtered through sintered glass crucible. It was washed with water to make it free from SO_4^{2-} ions and excess of oxime. Then dried in an oven at $\approx 110^\circ\text{C}$. Cooled and weighed.

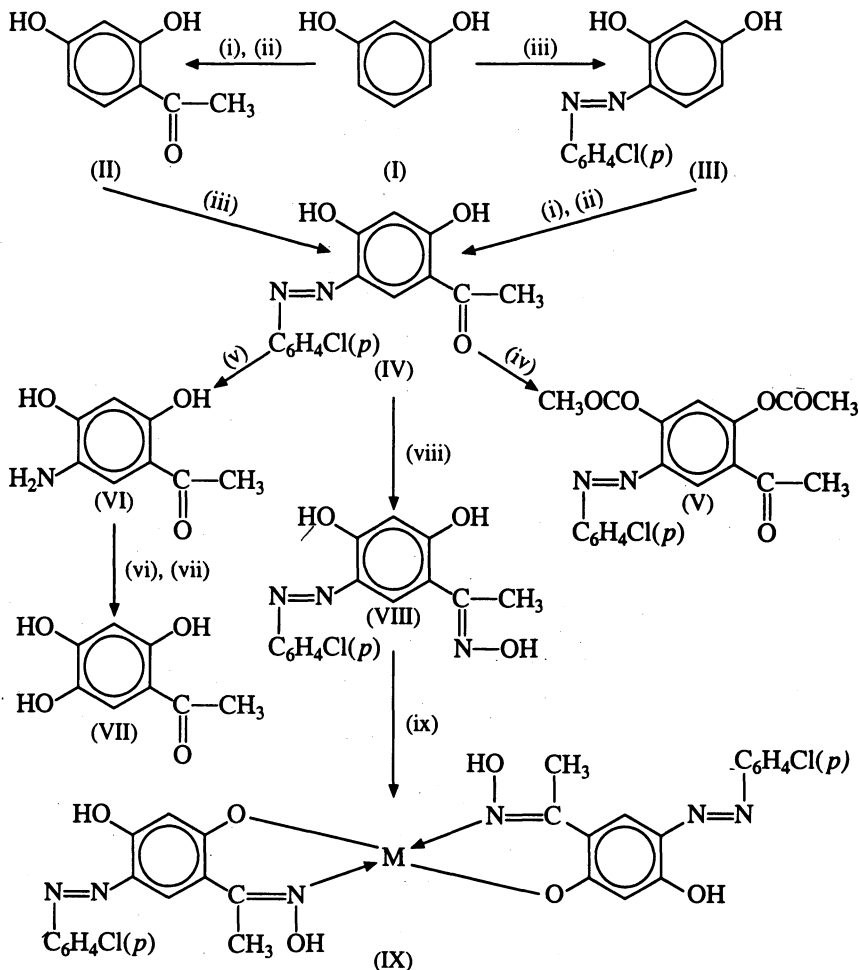
Similar procedure was followed with ZnSO_4 solution (0.25%, 50 mL, pH 4.8) and with NiSO_4 solution (0.25%, 50 mL, pH 5.1) to obtain the weights of Zn and Ni chelates.

Further attempt was made to establish the structure of chelate by decomposition method. Cu chelate (0.500 g) was decomposed with conc. HNO_3 (5 mL), the mixture was then treated with conc. H_2SO_4 (5 mL) and evaporated to dryness. It was diluted with water (about 20 mL) and Cu was estimated volumetrically by iodometric method using 20 mL of 10% KI; liberated iodine was titrated against $\text{Na}_2\text{S}_2\text{O}_3$ (0.05 N).

The oxime reagent was also used to estimate mixed chelate from an equal mixture of two salt solutions, CuSO_4 solution (0.25%, 25 mL) and ZnSO_4 solution (0.25%, 25 mL) of pH 4.4. The dry weight of the mixed chelate was determined.

The reagent could also be used to estimate Ni chelate from a mixture of Cu and Ni sulphate solution (0.25% of 50 mL each). Cu was first removed as CuS, and then weight of Ni chelate was determined. This estimation was compared with estimation of Ni in presence of Cu with known dimethylglyoxime reagent. Results obtained were used to compare the sensitivity of the oxime reagent.

Scheme for Reactions



M = Cu(II), Zn(II) or Ni(II)

- | | |
|--|---|
| (i) Anhydrous zinc chloride | (vi) Sodium nitrite and hydrochloric acid |
| (ii) Glacial acetic acid | (vii) Water |
| (iii) p -Chlorobenzenediazonium chloride | (viii) Hydroxylaminehydrochloride |
| (iv) Acetic anhydride | (ix) MSO_4 solution |
| (v) Sodium hydrosulphite | |

RESULTS AND DISCUSSION

Resacetophenone (II) on coupling with p -chlorobenzenediazonium chloride produced orange coloured azo compound with 78% yield. It melted at 169°C and

was marked as **B1**. The melting point of the compound **B2** obtained by alternate route was same as that of **B1**. Further, mixed melting point of the two compounds, **B1** and **B2**, did not show any depression. Diacetyl derivative prepared for both **B1** and **B2** also had same melting point of 95°C.

The elemental analysis data of **B1** and **B2** were as follows:

Compound **B1**: C = 57.60, H = 3.82 and N = 9.69%.

Compound **B2**: C = 57.55, H = 3.79 and N = 9.72%

The IR spectra of both **B1** and **B2** were found to be identical (peak observed at around 1640 cm⁻¹ can be accounted for >C=O group and around 1550 cm⁻¹ for —N=N group).

The above data indicates that the compounds **B1** and **B2** are same as suggested in structure (IV). It can, therefore, be concluded that coupling carried out after or before Nencki's reaction did not involve any structural change.

While deciding the position of coupling the product was subjected to reduction with sodium hydrosulphite which gave the amino compound (VI) having melting point 161°C. It gave tests for free phenolic —OH groups and —NH₂ groups. The elemental data for the compound of molecular formula C₈H₉O₃N were found to be: C = 57.48, H = 5.39 and N = 8.38 against the expected values of C = 57.52, H = 5.45% and N = 8.4%.

This compound (VI) on diazotisation followed by replacement of diazo group by —OH gave (VII), a known compound identical with that of 2,4,5-trihydroxy acetophenone¹³. This indicated the presence of —NH₂ group in 5 position in compound (VI) which in turn confirms the presence of diazo group in compound (IV) in position 5. Hence, the suggested structure of compound (IV) is 5-(*p*-chlorophenylazo) resacetophenone.

Compound (VIII) obtained from (IV) by oximation reaction gave shining reddish brown crystals of melting point 225°C. Elemental analysis results, for molecular formula C₁₄H₁₂O₃N₃Cl were found as C = 54.81, H = 3.98, N = 13.80%. Expected C = 54.99, H = 3.92, N = 13.74% and IR spectral data (peak around 1600 cm⁻¹ accounted for >C=N stretching around 3300 cm⁻¹ for —O—H stretching frequency) confirms the suggested structure.

This oxime (VIII) was used as reagent for qualitative and quantitative analysis of bivalent metals like Cu, Zn and Ni. The analysis results were shown as:

Metal chelates	Colour of chelates	Gravimetric results (weight of chelates)		
		Wt. obtained	Wt. expected	Error
Cu chelate	Greenish yellow	0.342 g	0.337 g	+0.005 g
Zn chelate	Brown	0.309 g	0.312 g	-0.003 g
Ni chelate	Faint orange	0.287 g	0.292 g	-0.005 g

The amount of chelate obtained indicates that two moles of oxime reagent react with 1 mole of metal sulphate.

Further, attempt was made to establish the structure of chelate by estimation of copper from a known weight of copper chelate. Volumetric estimation of copper resulted in the following analysis:

Wt. of copper obtained = 0.487 g; Wt. of copper expected = 0.482 g

These data confirmed the structure (IX) of chelate as shown in the reaction scheme. Chelates having such structures are known to be stable.

Estimation of mixture of Cu and Zn chelates from a mixture of equal amount of two salt solutions (pH 4.4) gave results as:

Wt. of chelate obtained = 0.329 g; Expected wt. = 0.324 g

Error = +0.005 gm

It can, therefore, be inferred that there is no hindrance of one cation over another in the formation of the chelate. The experimental results to compare the sensitivity of the reagent for estimation of Ni from a mixture of Cu and Ni salts against the established DMG reagent was found to be comparable as shown below:

Wt. of Ni chelate obtained (expected) = 0.285 g (0.292 g). Error = -0.007 g

Wt. of Ni dmg obtained (expected) = 0.252 (0.257 g). Error = -0.005 g.

Thus the reagent is useful in estimation of one metal cation in the presence of another with little modification.

The results shown above make it clear that the oxime reagent may prove to be a competitive one as quantitative analytical reagent.

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