
C H A P T E R - I I

INTRODUCTION, SYNTHESIS AND CHARACTERIZATION OF
6-METHYL-2-CHLORO QUINOLINE 3-CARBALDEHYDE
THIOSEMICARBAZONE

This chapter gives a detailed account of the use of 6-Methyl 2-Chloro quinoline 3-Carbaldehyde thiosemicarbazones. The method described is simple and involved in three stages.

EXPERIMENTAL :

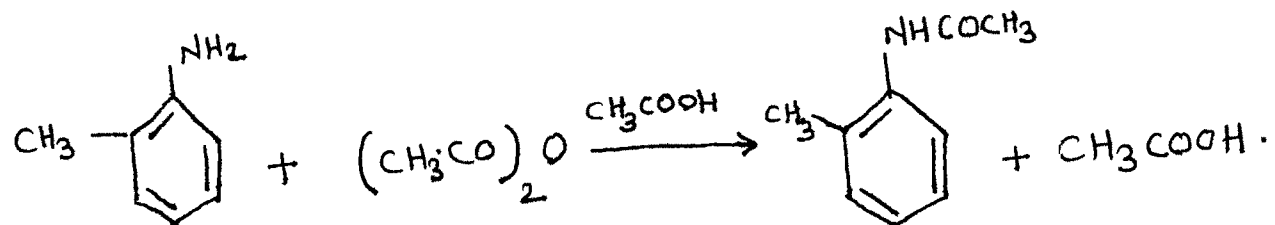
Synthesis of 6-Methyl 2-Chloro Quinoline 3-Carbaldehyde thiosemicarbazones (6-Me-QAT) has following stages.

1. Preparation of acetanilides.
2. Preparation of 6-Methyl 2-Chloro-quinoline-3-Carbaldehyde.
3. Conversion of aldehydes to thiosemicarbazones.

1. Preparation of acetanilides :

In 500 ml round bottomed flask, equipped with a reflux condenser, place 20.5 gm of Ortho-toulidine (20 ml, 0.22 mol) and 21.5 gm (20 ml, 0.21 mol) of acetic unhydride and 22 gms. (20 ml, 0.35 mol) of glacial acetic acid and 0.1 gm of zinc-dust¹, was taken. Boiled the mixture gently for 30 min. and then poured the hot liquid a thin stream into a 1-litre beaker containing 500 ml of cold water. Whilst stirring continually when cold (it is preferable cool in ice) filtered the crude product at the pump. Wash with little cold water, drain well and dry upon filter paper in air. The yield of acetanilide was 18 gm.

Reaction :

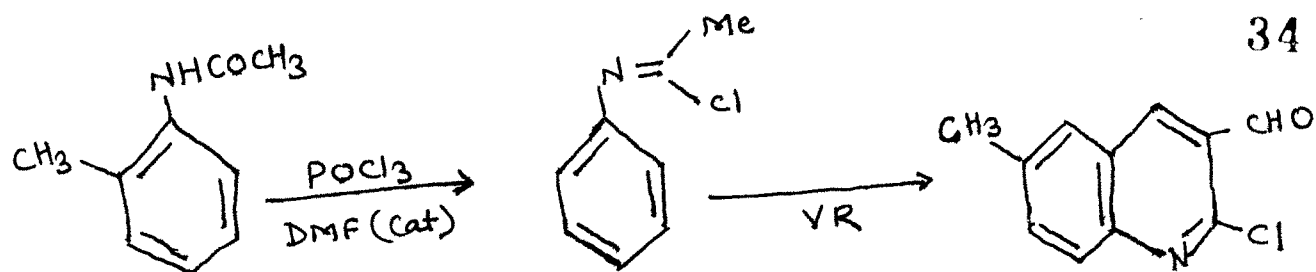


Stage No. 2 :

Synthesis of 6-Methyl 2-Chloro quinoline 3-Carbaldehyde:

The 6-Methyl 2-Chloro-quinoline 3-Carbaldehyde was prepared by Action of Vilsmeier's Reagent on Acetanilides². In a 100 ml flask equipped with drying tube was added dimethyl foramide (9.6 ml, 0.125 mol), the mixture was cooled in ice and phosphoryl chloride (32.2 ml, 0.35 mol) was added dropwise with stirring. This solution was added to Ortho-methyl acetanilide (0.05 mol) after five minutes. The solution was heated at 75°C under reflux for 16.5 hours. Then the reaction mixture was worked up as below.

The reaction mixture was poured into ice water (300 ml) and stirred for 30 min. at 0-10°C. The product was filtered off and washed well with water (100 ml) dried (68% 6.5 gm). Then the product was recrystallised from ethyl acetate M.P. 113°C (reported M.P.113°C). Due to the lack of reactivity of 2-Chlorogroup³ it does not interfere with the derivative formed.

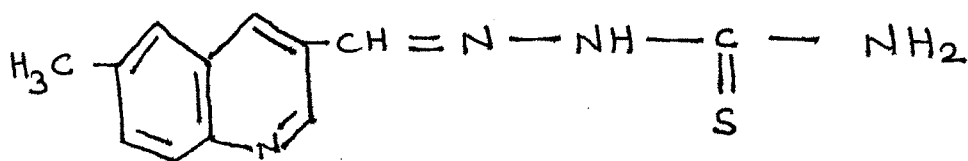


Stage No. 3 :

Synthesis of 6-Methyl-2-Chloro Quinoline-3-Carbaldehyde thiosemicarbazone.

The 6-Methyl 2-Chloro-quinoline-3-Carbaldehyde thiosemicarbazone (6-Me-QAT) was synthesised⁴ by refluxing equimolar quantities of 6-methyl-2-chloro quinoline-3-carbaldehyde and thiosemicarbazide in minimum amount of ethanol for 1 hour. White crystalline product was obtained, washed with distilled water, ether and finally with ethanol. It was recrystallised for ethanol. M.P. 225-226°C

Structure of 6-Me-QAT



Reagent solution :

0.055 gms of 6-Me-QAT was dissolved in DMF and water (1:1) and diluted to 100 ml with distilled water. The molarity of this solution 2.676×10^{-4} M. This solution was found to be stable for more than a week.

Other Reagents :

Reagent grade chemicals were used for preparing the solutions required for the study of various diverse ions. The common cations were used as either chlorides or nitrates and the anions used were either sodium or ammonium salts solutions.

Absorption Spectra of the Reagent :

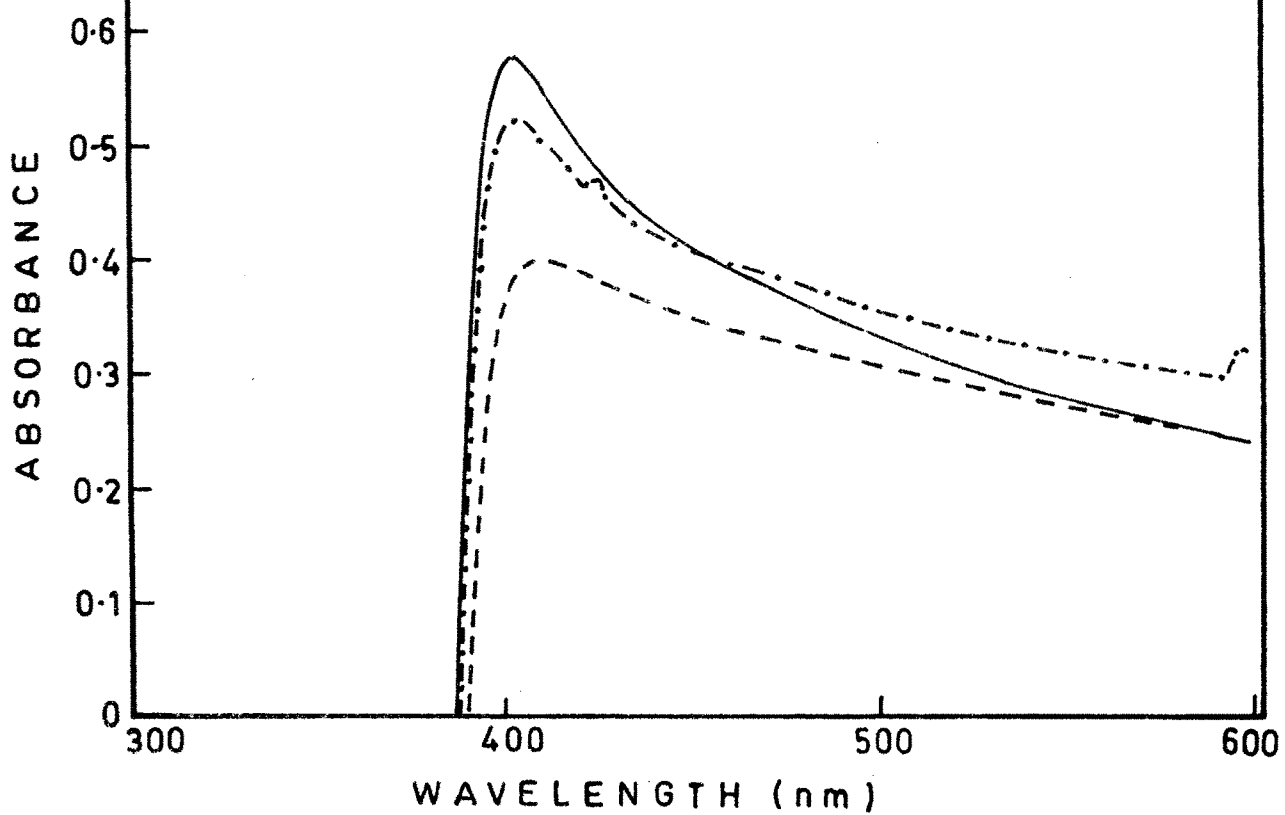
The absorption spectra of 6-methyl 2-Chloroquinoline-3-Carbaldehyde thiosemicarbazone in DMF + water (3:2) solution at pH 6, 5 and 8 are shown in the figure 2.1. The absorption band at 400 nm with molar extinction coefficients of 3.483×10^4 , 2.233×10^4 , 3.084×10^4 L Mole⁻¹ cm⁻¹ at pH 6, 5, 8 respectively. The UV spectrum of the reagent in DMF + water (3:2) medium shows that reagent has maximum absorption in the UV region and not in visible region.

Infrared Spectra :

Infrared absorption spectra in the range 200 to 4000 cm⁻¹ were run on a Perkin Elmer IR Spectrophotometer using KBr Pallet technique. The characteristic absorption bands were observed as follows:

3125 cm⁻¹, NH stretch, 3280 cm⁻¹, NH₂ stretch 1650 cm⁻¹,
C = C; 1600 cm⁻¹ = C - N =; 1540 cm⁻¹, Pyridine ring;
750 cm⁻¹ = C = S.

FIG. 2-1 — ABSORPTION SPECTRA OF
6 Me - QAT IN DMF + H₂O (3:2) AT pH
(—) 6 , (- - - -) 5 , (- · - · - ·) 8 .



Preparation of buffer solutions :

The buffer solutions of pH 1 to 10 were prepared by the following procedure :

<u>pH</u>	<u>Composition of the mixture</u>
1	4.75 ml of N/5 HCl + 25 ml N/5 KCl and dilute to 100 ml.
2	5.3 ml N/5 HCl + 25 ml N/5 KCl, dilute to 100 ml.
3	20.55 ml of Na_2HPO_4 (N/5) + 79.45 ml of N/10 citric acid.
4	41.0 ml of 0.2 M CH_3COOH + 9 ml of 0.2 M CH_3COONa .
5	14.75 ml 0.2 M CH_3COOH + 35.26 ml CH_3COONa .
6	9 ml of 0.2 M CH_3COOH + 191.0 ml 0.2 M CH_3COONa .
7	12 ml 0.05 M borax + 188 ml solution containing 12.40 gm boric acid and 2.93 gm of NaCl in 1 litre.
8	19.071 gms Na_2BaO_7 dissolved in 500 ml distilled water.
9	19 gm $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ dissolved in 500 ml distilled water.
10	250 ml 0.1 M Boric acid + 219.5 ml 0.1 N NaOH diluted to 500 ml.



In addition to these buffer solutions standard buffer of pH-4 was prepared by dissolving 10.21 gm of potassium hydrogen phthalate in 1 litre.

Apparatus :

All the spectral measurements over the spectral region were done on a Carl Zeiss grating spectrophotometer and Hitachi 330→Spekol by using 10 mm matched pair of glass cuvettes. For measurement of pH values Elico Digital buffer (0.05 M) was used for the standardization of the pH meter.

REFERENCES

- 1 Text Book of Quantative Organic Chemistry,
A.I. Vogel.
- 2 Otto Meth - Cohn Bramha Narine and Brian Tarnawski,
The Ramage Laboratories, Department of Chemistry -
Journal of the Chemical Society - Perkin Transactions,
5 (1981) p. 1526.
- 3 Otto Meth - Cohn, Bramha Narine and Brain Tarnawski,
Roy, Hayes, Amitis Keyzad, Salah Rhoutai and Andrew
Robinson J.C.S. Perkin, I. 9, 2509 (1981).
- 4 A.I.Vogel Text Book of Quantitative Organic Chemistry.
