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Methods of Preparation of Aromatic Anils

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Abstract

The aim of this study is to to prepare and identify and characterize the aromatic anils (Schiff's bases or benzylidene aniline) then used for kinetic study that is cooxidation in presence of oxalic acid by chromic acid in acetic acid medium.

Keywords: Aromatic Anils, Benzylidene aniline, Schiff's bases, Preparation.

1. Introduction

Primary aromatic amines, generally condense directly with benzaldehyde to form benzal derivatives or Anils otherwise known as Schiff's bases and these are formed either by simply mixing and shaking at ordinary temperature or by heating or by refluxing an aromatic aldehyde and an aromatic primary amine, in equimolar ratio, in absence or in presence of a suitable solvent. The simple anil formed between benzaldehyde and aniline is known as benzylidene aniline is represented by figure 1 (a).

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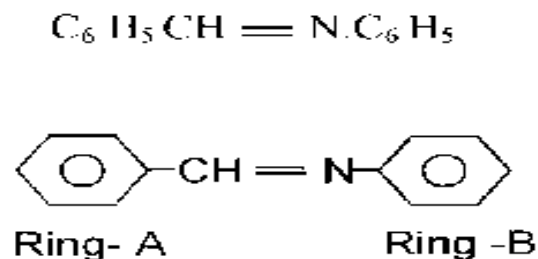


Figure 1 (a): benzylidene aniline

For easy reference, the benzaldehyde ring is termed as Ring-A and the aniline ring is termed as Ring -B. Detailed literature scanning reveal that these anils are very sluggish towards oxidizing agents, and only very few reports are available about their oxidation kinetics.

Aromatic anils otherwise called Schiff's bases, having two phenyl rings, one derived from benzaldehyde and another derived from aniline, so that we can have substituents in either of the two phenyl rings or in both and oxidising these substrates in order to understand the effect of these substituents with chromic acid in presence of oxalic acid the phenomenon being called cooxidation, in aqueous acetic acid medium, so that the researchers may have the satisfaction of contributing at least some, though not many, to the world of kinetics, hence the title investigation.

The aromatic anils prepared from:

- unsubstitutedbenzaldehyde and unsubstituted aniline,
- substituted benzaldehydes and unsubstituted aniline,
- unsubstitutedbenzaldehyde and substituted anilines, and
- substituted benzaldehydes and substituted anilines

To cut a long short, the aim of the researchers is: to prepare as many numbers of aromatic anils as possible, purify them, characterize them, and oxidise them, by Cr (VI) in presence of oxalic acid in aqueous acetic acid medium since the oxidation reaction was very sluggish towards Cr (VI).

A close observation of the simple aromatic anil which is formed by the condensation of an aromatic aldehyde and an aromatic primary amine (aniline) could lead to the preparation of number of anils as detailed in figure 1 (b).

Hence one could imagine the number of aromatic anils that could be prepared, how interesting it would be to study the oxidative cleavage of these aromatic anils by Cr (VI) in presence of oxalic acid in aqueous acetic acid

medium and how thrilling it would be to understand the effect of these substituents in presence of other substituents during oxidative cleavage.

For, convenient kinetic investigations, for logical arguments, for sensible discussions and to arrive at suitable mechanistic path way, the researchers have classified the aromatic anils in the following simple way so that discussions and arguments will be more logical (Table 1).

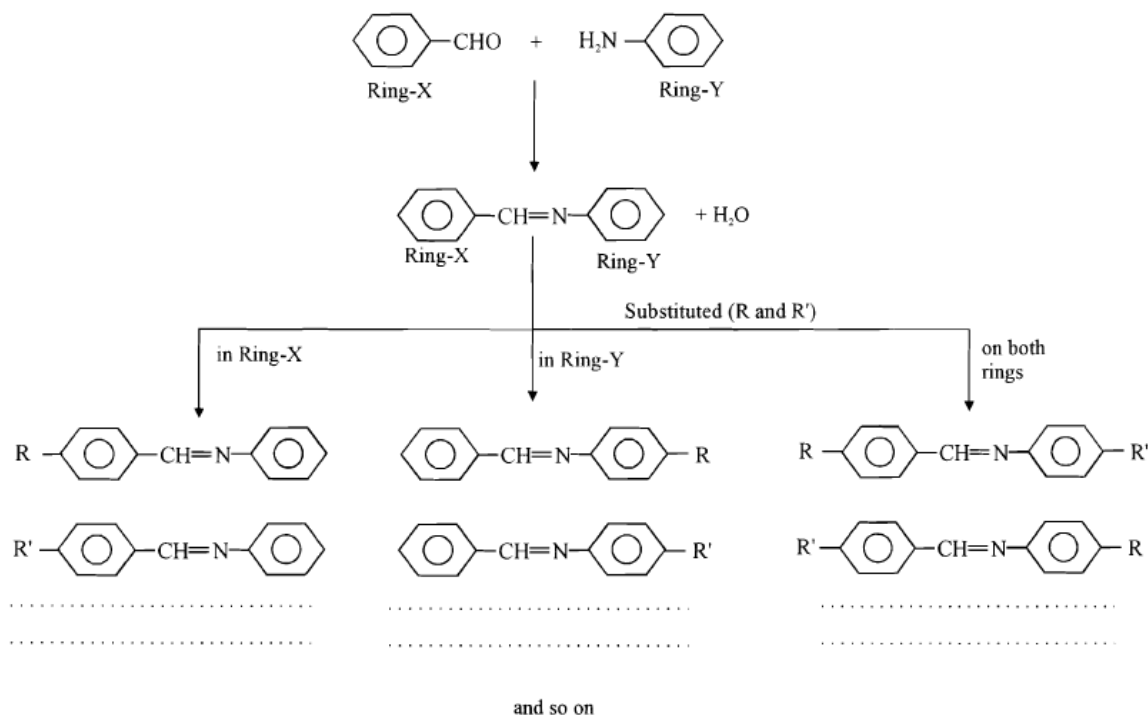
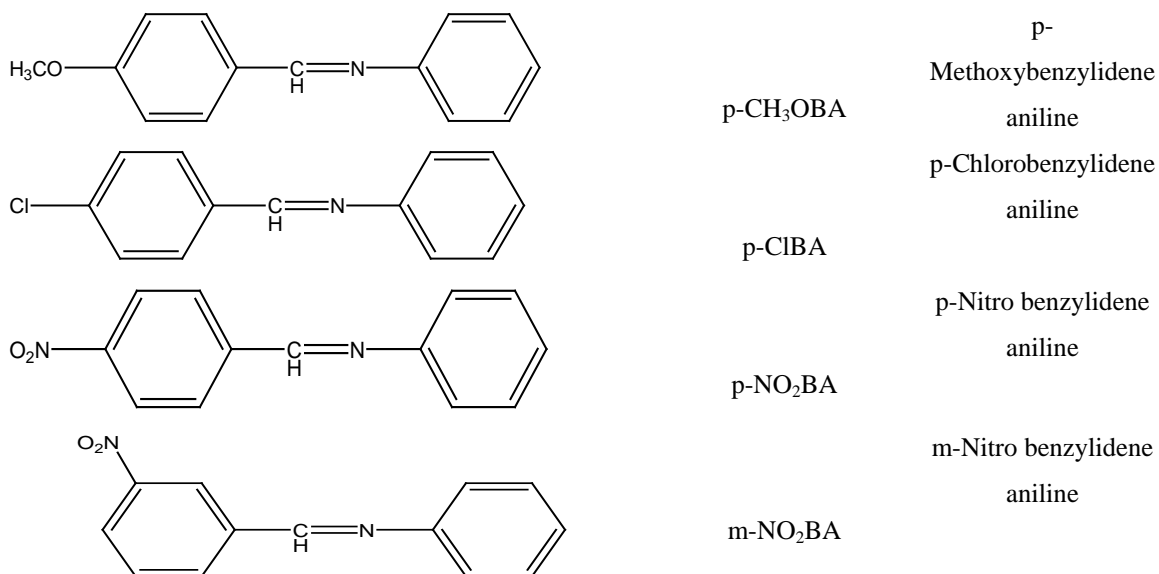


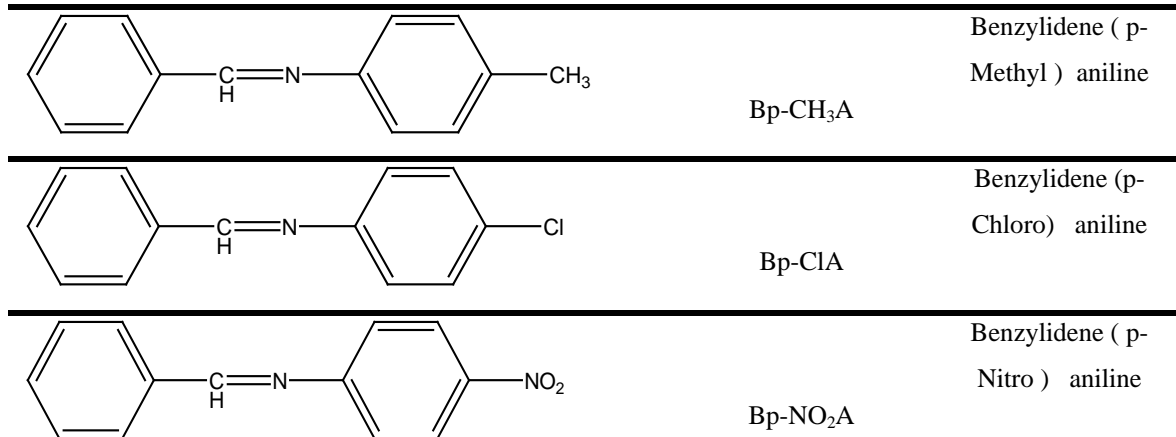
Figure 1 (b): preparation of number of aromatic anils

Table 1: aromatic anils classifications

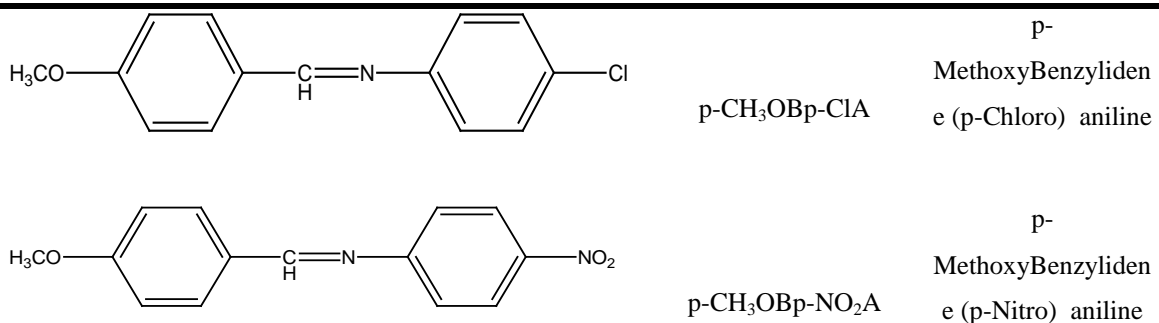
	Formulae	Abbreviations used	Name
1-	Aromatic Anil from unsubstituted benzaldehyde and unsubstituted aniline		
		BA	Benzylidene aniline
2-	Aromatic Anil from substituted benzaldehyde and unsubstituted aniline		
		p-CH ₃ BA	p-Methyl benzylidene aniline

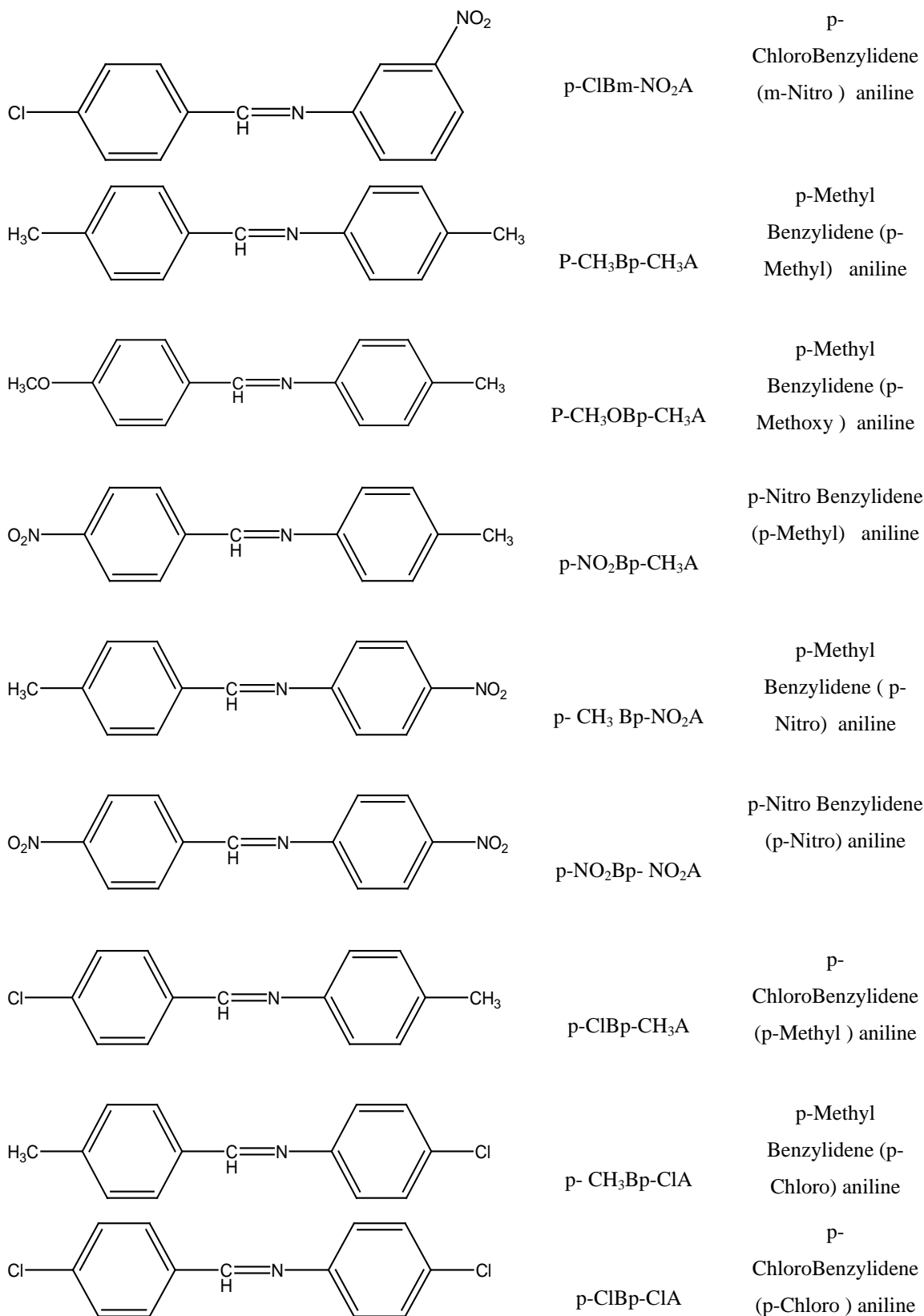


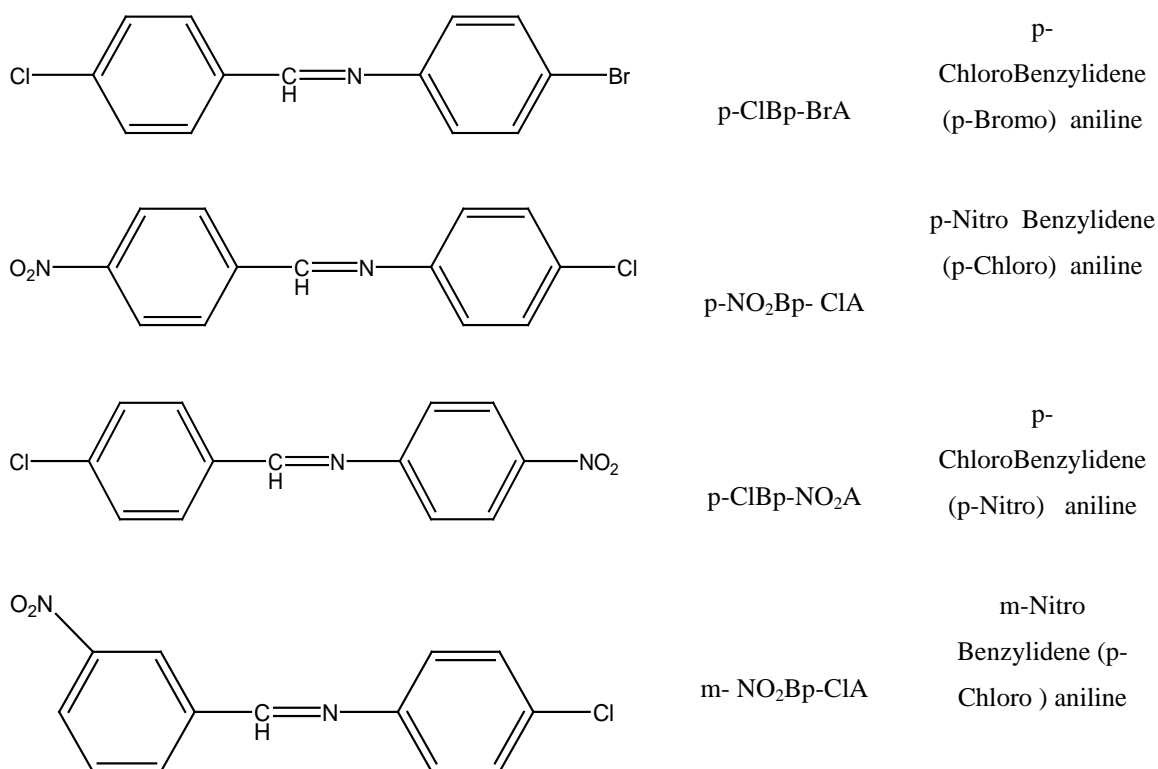
3- Aromatic Anil from unsubstituted benzaldehyde and substituted anilines



4- Aromatic Anil from substituted benzaldehyde and substituted anilines







2. Purification of Materials

2.1. Conductivity water

Conductivity water was used for all experiments. It was obtained by purifying water with a permutit ion exchanger and then distilling with alkaline permanganate from an all glass apparatus.

2.2. Alcohols

Ethanol and methanol were purified by the standard methods as described by Weissberger [1].

2.3. Benzaldehyde

50g (or 48 ml) of benzaldehyde was taken in a separating funnel. It was washed with 20 ml portions of 10% sodium bicarbonate solution until no more carbon dioxide was evolved and then washed with large amount of water. It was then dried with 5g of anhydrous magnesium sulphate or anhydrous calcium chloride. During the drying operation, 0.5g of hydroquinone or catechol was added. It was then distilled under reduced pressure. Large head and tail fractions were rejected. About 0.05g of hydroquinone or catechol was added. Boiling point of benzaldehyde is $179 \pm 1^\circ\text{C}$ [2].

2.4. Aniline

It was distilled in presence of zinc dust. The boiling point of aniline was $184 \pm 1^\circ\text{C}$. Further purification was carried out in presence of zinc dust [2].

The following chemicals are Merck reagents and used as such without further purification.

1. p-Chlorobenzaldehyde
2. p-Methyl benzaldehyde
3. p-Methoxybenzaldehyde
4. p-Nitro benzaldehyde
5. m-Nitro benzaldehyde
6. p-Chloro aniline
7. p-Methyl aniline
8. p-Nitro aniline
9. p-Bromo aniline

3. Preparations

The following aromatic anils (Table 1), were prepared by the standard methods [2,3]

3.1. Unsubstituted benzaldehyde and unsubstituted aniline

3.1.1. Benzylidene aniline

3.2. Substituted benzaldehyde and unsubstituted aniline

3.2.1. p-Methyl benzylidene aniline

3.2.2. p-Methoxybenzylidene aniline

3.2.3. p-Chlorobenzylidene aniline

3.2.4. p-Nitrobenzylidene aniline

3.2.5. m-Nitro benzylidene aniline

3.3. Unsubstituted benzaldehyde and substituted aniline

3.3.1 Benzylidene (p-Methyl) aniline

3.3.2 Benzylidene (p-Chloro) aniline

3.3.3 Benzylidene (p-Nitro) aniline

3.4. Substituted benzaldehyde and substituted aniline

3.4.1 p-Methyl Benzylidene (p-Methyl) aniline

3.4.2 p-MethoxyBenzylidene (p-Methyl) aniline

3.4.3 p-Nitro Benzylidene (p-Methyl) aniline

3.4.4 p-MethoxyBenzylidene (p-Nitro) aniline

3.4.5 p-Nitro Benzylidene (p-Nitro) aniline

3.4.6 p-ChloroBenzylidene (p-Methyl) aniline

3.4.7 p-Methyl Benzylidene (p-Chloro) aniline

3.4.8 p-ChloroBenzylidene (p-Chloro) aniline

3.4.9 p-ChloroBenzylidene (p-Bromo) aniline

3.4.10 p-Nitro Benzylidene (p-Chloro) aniline

3.4.11 p-ChloroBenzylidene (p-Nitro) aniline

3.4.12 m-Nitro Benzylidene (p-Chloro) aniline

3.4.13 p-ChloroBenzylidene (m-Nitro) aniline

3.4.14 p-MethoxyBenzylidene (p-Chloro) aniline

3.4.15 p-MethoxyBenzylidene (p-Nitro) aniline

The purity of these aromatic anils was checked by IR spectral studies and by comparing the physical constants with those found in the literature [2].

3.5 Preparation and characterization of Benzylidene aniline (BA)

0.1 mole of distilled dry benzaldehyde (10.6 g) was mixed with 0.1 mole of distilled dry aniline (9.3 g) in a round bottomed flask, closed with a ground glass stopper. Shaken vigorously for half an hour opening the stopper occasionally. It was cooled in ice bath and then filtered at the pump, washed several times with cold water, with dilute sodium bicarbonate solution and again with cold water. The sample was dried, yield was noted. The crude sample was recrystallised with dilute alcohol. The melting point was determined Table 2. The recrystallisation was repeated until to get theoretical melting point.

Table 2: Benzylidene aniline (BA)

Benzaldehyde	Aniline	Yield		Melting Point (°C)		Reference
		Theoretical	Experimental	Observed	Recorded	
0.1	0.1	0.1	0.088	54	54	1,2
mole	mole	mole	mole			

The IR spectra of the compound is given (Figure 2)

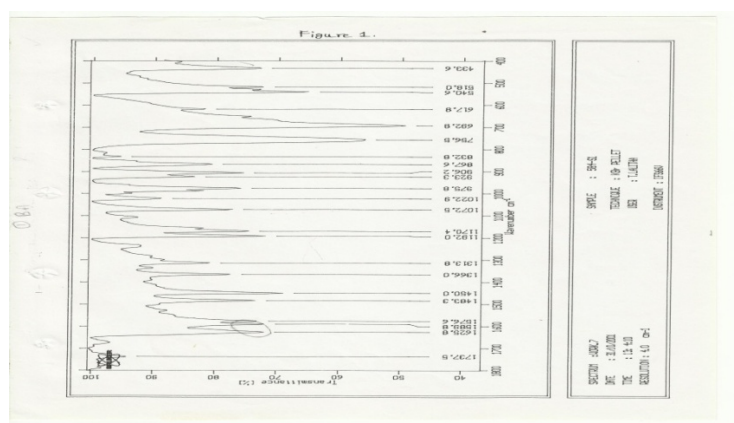


Figure 2: The IR spectra of the compound

3.6 Preparation and characterization of *p*-Methyl benzylidene aniline (*p*-CH₃BA)

0.1 mole of *p*-Methyl benzaldehyde (12 g) was dissolved in distilled and dry methanol. 0.1 mole of distilled dry aniline (9.3 g) was added in drops from a dropping funnel to *p*-Methyl benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium

bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 3..

Table 3: p-Methyl benzylidene aniline (p-CH₃BA)

p-MethyBenzald ehyde	Aniline	Yield		Melting Point (°C)		Reference
		Theoretical	Experimental	Observed	Recorded	
0.1	0.1	0.1	0.082	46	46	2
mole	mole	mol	mole			

The IR spectra of the compound is given (Figure 3)

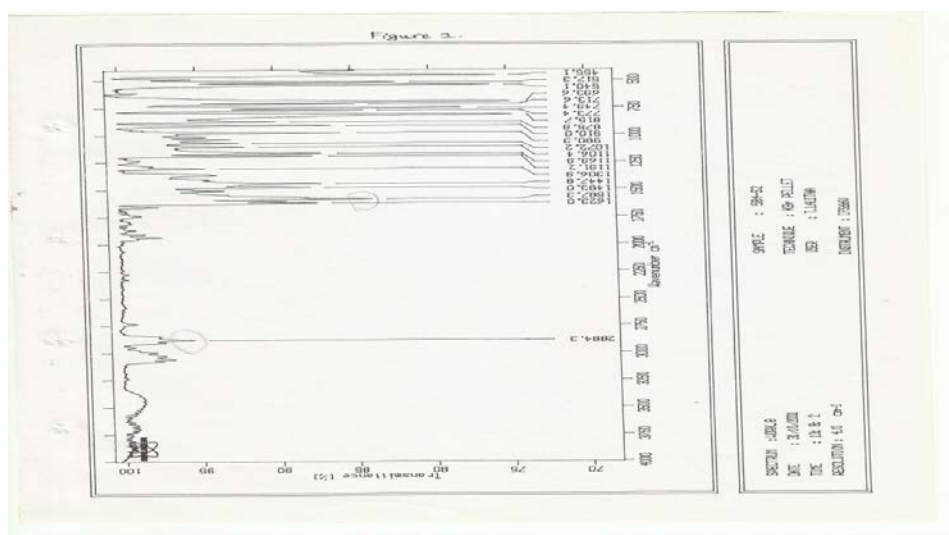


Figure 3: The IR spectra for the compound

3.7 Preparation and characterization of p-Methoxybenzylidene aniline (p-CH₃OBA)

0.1 mole of p-Methoxybenzaldehyde (13.6 g) was dissolved in distilled and dry methanol. 0.1 mole of distilled dry aniline (9.3 g) was added in drops from a dropping funnel to p-Methoxybenzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point Table 4.

Table 4: p-Methoxybenzylidene aniline (p-CH₃OBA)

p-MethoxyBenzaldehyde	Aniline	Yield		Melting Point (°C)		Reference
		Theoretical	Experimental	Observed	Recorded	
0.1 mole	0.1 mole	0.1 mole	0.08 mole	56	56	2

3.8 Preparation and characterisation of p-Chlorobenzylidene aniline (P-CIBA)

0.1 mole of p-Chlorobenzaldehyde (14.04 g) was dissolved in distilled and dry methanol. 0.1 mole of distilled dry aniline (9.3 g) was added in drops from a dropping funnel to p-Chlorobenzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 5.

Table 5: p-Chlorobenzylidene aniline (p-CIBA)

p-ChloroBenzaldehyde	Aniline	Yield		Melting Point (°C)		Reference
		Theoretical	Experimental	Observed	Recorded	
0.1 mole	0.1 mole	0.1 mole	0.08 mole	65	66	2

3.9 Preparation and characterization of p-Nitro benzylidene aniline (p-NO₂BA)

0.1 mole of p-Nitro benzaldehyde (15.1 g) was dissolved in distilled and dry methanol. 0.1 mole of distilled dry aniline (9.3 g) was added in drops from a dropping funnel to p-Nitro benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium

bicarbonate solution, and with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 6.

Table 6: p-Nitro benzylidene aniline (p-NO₂BA)

p-Nitro Benzaldehyde	Aniline	Yield		Melting Point (°C)	
		Theoretical	Experimental	Observed	
0.1	0.1	0.1	0.078	93	
mole	mole	mole	mole		

3.10 Preparation and characterization of m-Nitro benzylidene aniline (m-NO₂BA)

0.1 mole (15.1g) of m-Nitro benzaldehyde, 0.1 mole (9.3 g) of pure and dry aniline and 20 ml of rectified spirit were taken in a round-bottomed flask fitted with a reflux condenser. The contents were refluxed in a water bath for about 20 minutes. Water was added and cooled. Oily layer separated out. It was induced to give crystals by scratching the sides of beaker with a glass rod. It was filtered and washed well with cold aqueous ethanol. It was recrystallised from aqueous methanol. Recrystallisation was repeated to get concordant melting point table 7.

Table 7: m-Nitrobenzylidene aniline (m-NO₂BA)

m-Nitro Benzaldehyde	Aniline	Yield		Melting Point (°C)		Reference
		Theoretical	Experimental	Observed	Recorded	
0.1	0.1	0.1	0.082	65	66	1
mole	mole	mole	mole			

3.11 Preparation and characterization of benzylidene (p-Methyl) aniline (Bp-CH₃A)

0.1 mole of benzaldehyde (10.6 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Methyl aniline (10.7 g) was added in drops from a dropping funnel to benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution and again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point. (Figure 4) table -8.

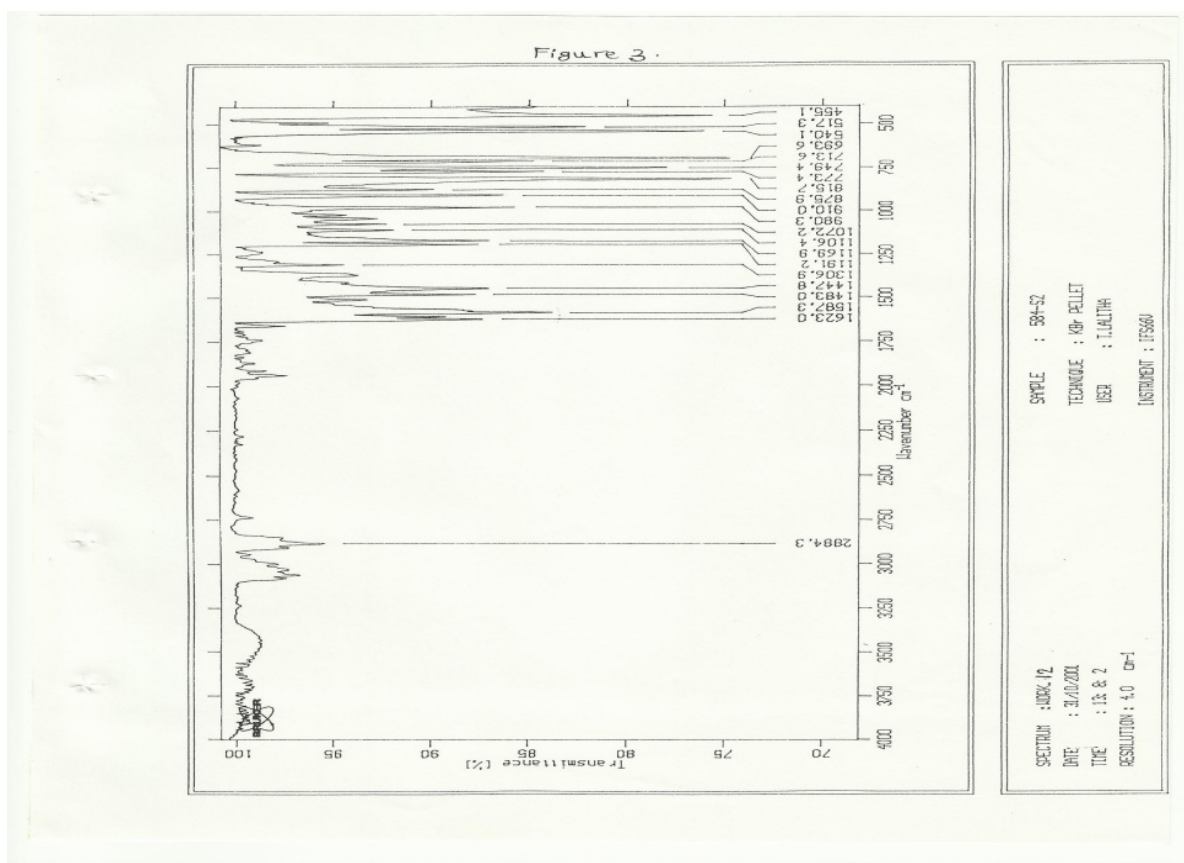


Figure 4: The IR spectrum of the compound

Table 8: Benzylidene p-Methyl aniline (Bp-CH₃A)

Benzaldehyde	p-Methyl Aniline	Yield		Melting Point (°C)		Reference
		Theoretical	Experimental	Observed	Recorded	
0.1	0.1	0.1	0.084	--	35	2,3
mole	mole	mole	mole			

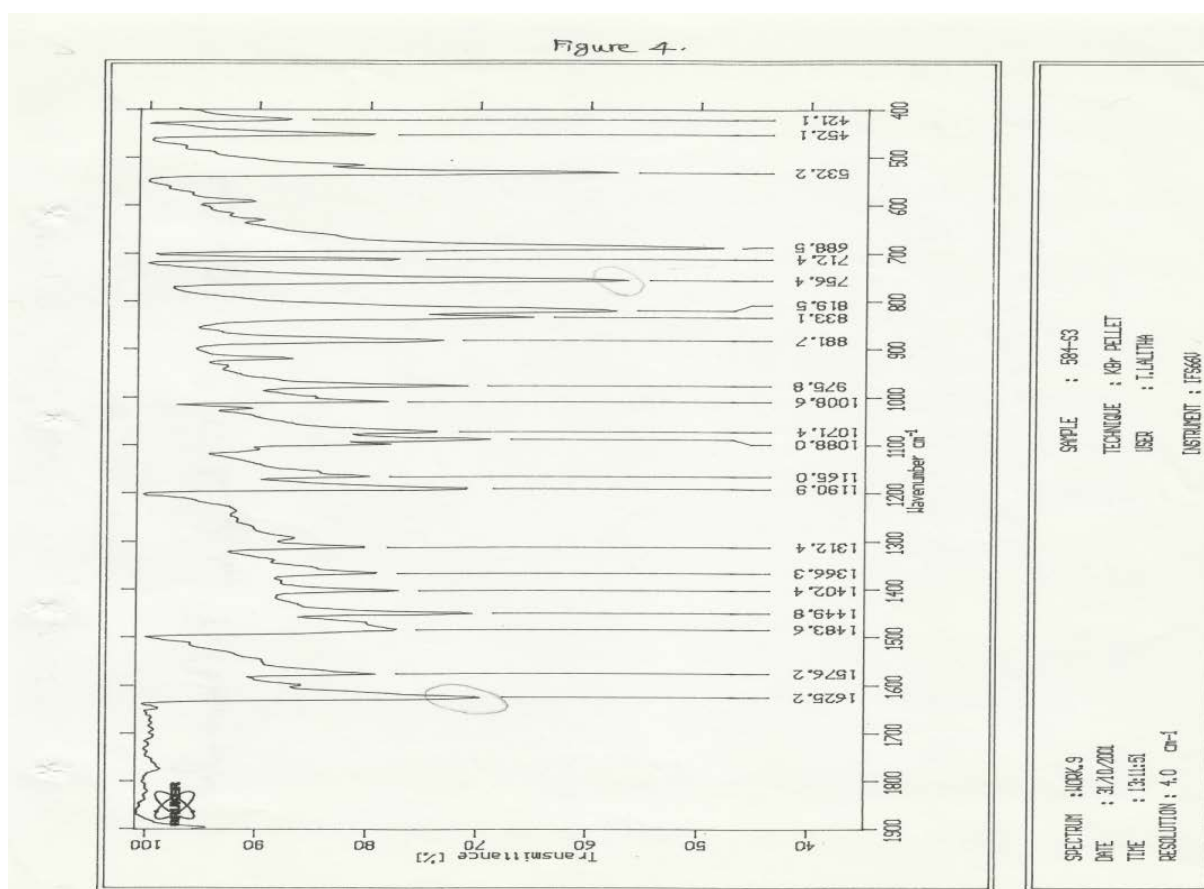
3.12 Preparation and characterisation of benzylidene (p-Chloro) aniline (Bp-CIA)

0.1 mole of benzaldehyde (10.6 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Chloro aniline (12.7 g) was added in drops from a dropping funnel to benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 9.

Table 9: Benzylidene (p-Chloro) aniline (Bp-Cl)

Benzaldehyde	p-Chloro Aniline	Yield		Melting Point (°C)		Reference
		Theoretical	Experimental	Observed	Recorded	
0.1	0.1	0.1	0.084	61	62	1
mole	mole	mole	mole			

The IR spectra of the compound is given (Figure -5).

**Figure 5:** The IR spectra of the compound

3.13 Preparation and characterisation of benzylidene (p-Nitro) aniline (Bp-NO₂A)

0.1 mole of benzaldehyde (10.6 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Nitro aniline (13.8 g) was added in drops from a dropping funnel to benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour,

cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table -10.

Table 10: Benzylidene (p-Nitro) aniline (Bp-NO₂A)

Benzaldehyde	p-Nitro Aniline	Yield		Melting Point (°C)		Reference
		Theoretical	Experimental	Observed	Recorded	
0.1	0.1	0.1	0.084	113	115	1,2
mole	mole	mole	mole			

3.14 Preparation and characterisation of p-Methyl benzylidene (p-Methyl) aniline (p-CH₃Bp-CH₃A)

0.1 mole of p-Methyl benzaldehyde (12 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Methyl aniline (10.7 g) dissolved in methanol was added in drops from a dropping funnel to p-Methyl benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 11.

Table 11: p-Methyl Benzylidene (p-Methyl) aniline (p-CH₃Bp-CH₃A)

p-Methyl Benzaldehyde	p- Methyl Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.09	92
mole	mole	mole	mole	

The IR spectra of the compound is given (Figure 6).

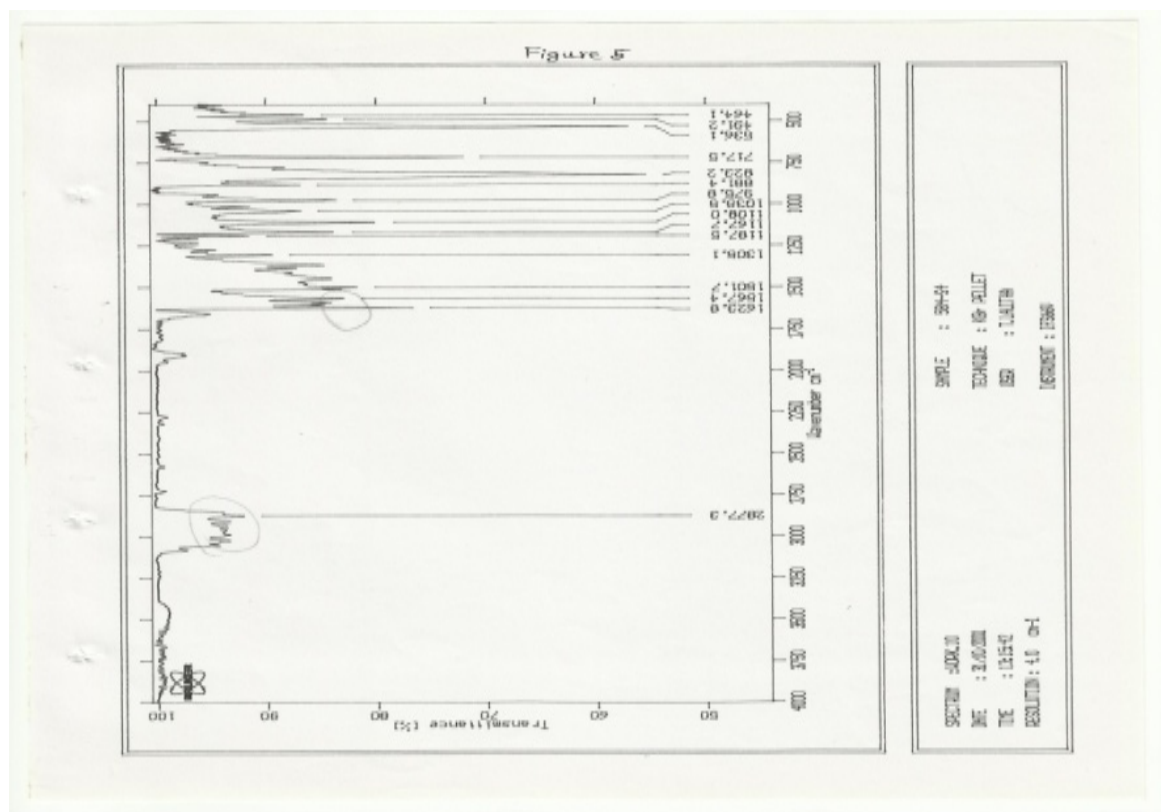


Figure 6: The IR spectra of the compound

3.15 Preparation and characterisation of p-Methoxybenzylidene (p-Methyl) aniline (P-CH₃OBp-CH₃A)

0.1 mole of p-Methoxybenzaldehyde (13.6 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Methyl aniline (10.7 g) dissolved in methanol was added in drops from a dropping funnel to p-Methoxybenzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 12.

Table 12: p-Methoxy benzylidene (p-Methyl) aniline (p-CH₃OB p-CH₃A)

p-MethoxyBenzaldehyde	p-Methyl Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1 mole	0.1 mole	0.1 mole	0.084 mole	90

3.16 Preparation and characterization of p-Nitro benzylidene (p-Methyl) aniline (P-NO₂Bp-CH₃A)

0.1 mole of p-Nitro benzaldehyde (15.1 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Methyl aniline (10.7 g) dissolved in methanol was added in drops from a dropping funnel to p-Nitro benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 13.

Table 13: p-Nitro benzylidene (p-Methyl) aniline (pNO₂ B p-CH₃A)

p-Nitro Benzaldehyde	p-Methyl Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.086	109
mole	mole	mole	mole	

3.17 Preparation and characterizations of p-Methyl benzylidene (p-Nitro) aniline (p-CH₃Bp-NO₂A)

0.1 mole (12.0g) of p-Methyl benzaldehyde, 0.1 mole (13.8 g) of pure p-Nitro aniline and 20 ml of rectified spirit were taken in a round-bottomed flask fitted with a reflux condenser. The contents were refluxed in a water bath for about 20 minutes. Water was added and cooled. Oily layer separated out. It was induced to give crystals by scratching the sides of beaker with a glass rod. It was filtered and washed well with cold aqueous ethanol. It was recrystallized from aqueous methanol. Recrystallisation was repeated to get concordant melting point table 14.

Table 14: p-Methyl benzylidene (p-Nitro) aniline (pCH₃- B p-NO₂A)

p-Methyl Benzaldehyde	p-Nitro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.076	112
mole	mole	mole	mole	

3.18 Preparation and characterization of p-Nitro benzylidene (p-Nitro) aniline (p-NO₂Bp-NO₂A)

0.1 mole (15.1g) of p-Nitro benzaldehyde, 0.1 mole (13.8 g) of pure p-Nitro aniline and 20 ml of rectified spirit were taken in a round-bottomed flask fitted with a reflux condenser. The contents were refluxed over a water bath for about 60 minutes. Water was added and cooled. Oily layer separated out. It was induced to give crystals by scratching the sides of beaker with a glass rod. It was filtered and washed well with cold aqueous ethanol. It was recrystallized from aqueous methanol. Recrystallisation was repeated to get concordant melting point table 15.

Table 15: p-Nitrobenzylidene (p-Nitro) aniline(p-NO₂Bp-NO₂A)

p-Nitro Benzaldehyde	p-Nitro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.088	137
mole	mole	mole	mole	

3.19 Preparation and characterization of p-Chlorobenzylidene (p-Methyl) aniline (p-ClBp-CH₃A)

0.1 mole of p-Chlorobenzaldehyde (14.04 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Methyl aniline (10.7 g) dissolved in methanol was added in drops from a dropping funnel to p-Chlorobenzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 16.

Table 16: p-Chloro benzylidene (p-Methyl) aniline (p-ClBp-CH₃A)

p- ChloroBenzalde hyde	p-Methyl Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.086	129
mole	mole	mole	mole	

3.20 Preparation and characterisation of p-Methyl benzylidene (p-Chloro) aniline (p-CH₃Bp-CIA)

0.1 mole of p-Methyl benzaldehyde (12 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Chloro aniline (12.7 g) dissolved in dry methanol was added in drops from a dropping funnel to p-Methyl benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 17.

Table 17: p-Methyl benzylidene (p-Chloro) aniline (p-CH₃Bp-CIA)

p-Methyl Benzaldehyde	p-Chloro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.088	110
mole	mole	mole	mole	

3.21 Preparation and characterization of p-Chlorobenzylidene (p-Chloro) aniline (p-C1Bp-CIA)

0.1 mole of p-Chlorobenzaldehyde (14.04 g) was dissolved in distilled and dry methanol. 0.1 mole of distilled dry p-Chloro aniline (12.74 g) dissolved in methanol was added in drops from a dropping funnel to p-Chlorobenzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 18.

Table 18: p-Chloro benzylidene (p-Chloro) aniline (p-C1Bp-CIA)

p-Chloro Benzaldehyde	p-Chloro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.084	110
mole	mole	mole	mole	

3.22 Preparation and characterization of *p*-Chlorobenzylidene (*p*-Bromo) aniline (*p*-C1Bp-Br)

0.1 mole of *p*-Chlorobenzaldehyde (14.04 g) was dissolved in distilled and dry methanol. 0.1 mole of *p*-Bromo aniline (17.2 g) dissolved in methanol was added in drops from a dropping funnel to *p*-Chlorobenzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 19.

Table 19: *p*-Chloro benzylidene (*p*-Bromo) aniline (*p*-C1B p-BrA)

p-ChloroBenzaldehyde	p-Bromo Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.084	61
mole	mole	mole	mole	

3.23 Preparation and characterization of *p*-Nitro benzylidene (*p*-Chloro) aniline (*p*-NO₂Bp-ClA)

0.1 mole of *p*-Nitro benzaldehyde (15.1 g) was dissolved in distilled and dry methanol. 0.1 mole of *p*-Chloro aniline (12.74 g) was also dissolved in methanol and added in drops from a dropping funnel to *p*-Nitro benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 20.

Table 20: *p*-Nitro benzylidene (*p*-Chloro) aniline(*p*-NO₂Bp-Cl A)

p-Nitro Benzaldehyde	p-Chloro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.087	127
mole	mole	mole	mole	

3.24 Preparation and characterization of *p*-Chlorobenzylidene (*p*-Nitro) aniline (*p*-CIBp-NO₂A)

0.1 mole (14.04 g) of *p*-Chlorobenzaldehyde, 0.1 mole (13.8 g) of *p*-Nitro aniline and 20 ml of rectified spirit were taken in a round-bottomed flask fitted with a reflux condenser. The contents were refluxed over a water bath for about 20 minutes. Water was added and cooled. Oily layer separated out. It was induced to give crystals by scratching the sides of beaker with a glass rod. It was filtered and washed well with cold aqueous ethanol. It was recrystallized from aqueous methanol. Recrystallisation was repeated to get concordant melting point table 21.

Table 21: *p*-Chloro benzylidene (*p*-Nitro) aniline (*p*-CIB p-NO₂A)

p-ChloroBenzald ehyde	p-Nitro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.087	132
mole	mole	mole	mole	

3.25 Preparation and characterization of *m*-Nitro benzylidene (*p*-Chloro) aniline (*m*-NO₂Bp-CIA)

0.1 mole of *m*-Nitro benzaldehyde (15.1 g) was dissolved in distilled and dry methanol. 0.1 mole of *p*-Chloro aniline (12.74 g) dissolved in methanol was added in drops from a dropping funnel to *m*-Nitro benzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallised from dilute methanol. Recrystallisation was repeated until to get concordant melting point table 22.

Table 22: *m*-Nitro benzylidene (*p*-Chloro) aniline (*m*-NO₂Bp-CI A)

p-Nitro Benzaldehyde	p-Chloro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.08	90
mole	mole	mole	mole	

3.26 Preparation and characterization of p-Chlorobenzylidene (m-Nitro) aniline (p-CIBm-NO₂A)

0.1 mole (14.5 g) of p-Chlorobenzaldehyde, 0.1 mole (13.6 g) of pure m-Nitro aniline and 20 ml of rectified spirit were taken in a round-bottomed flask fitted with a reflux condenser. The contents were refluxed over a water bath for about 60 minutes. Water was added and cooled. Oily layer separated out. It was induced to give crystals by scratching the sides of beaker with a glass rod. It was filtered and washed well with cold aqueous ethanol. It was recrystallized from aqueous methanol. Recrystallization was repeated to get concordant melting point table 23.

Table 23: p-Chloro benzylidene (m-Nitro) aniline (p-CIBm-NO₂A)

p-ChloroBenzaldehyde	m-Nitro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.08	123
mole	mole	mole	mole	

3.27 Preparation and characterization of p-Methoxybenzylidene (p-Chloro) aniline (p-CH₃OBp-ClA)

0.1 mole of p-Methoxybenzaldehyde (13.6 g) was dissolved in distilled and dry methanol. 0.1 mole of p-Chloro aniline (12.74 g) dissolved in methanol was added in drops from a dropping funnel to p-Methoxybenzaldehyde with vigorous shaking. After the addition, the mixture was heated with a low flame initially and then to boiling. Heating was continued for half an hour, cooled in ice bath followed by stirring with the glass rod. The contents were kept aside for half an hour. The contents were filtered. The precipitate was washed several times with water, with dilute sodium bicarbonate solution, again with cold water, dried and yield was noted. Recrystallized from dilute methanol. Recrystallization was repeated until to get concordant melting point table 24.

Table 24: p-Methoxy benzylidene (p-Chloro) aniline (p-CH₃OBp-ClA)

p-MethoxyBenzaldehyde	p-Chloro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1	0.1	0.1	0.08	95
mole	mole	mole	mole	

3.28 Preparation and characterization of p-Methoxybenzylidene (p-Nitro) aniline (p-CH₃OBp-NO₂A)

0.1 mole (13.6g) of p-Methoxybenzaldehyde, 0.1 mole (13.8 g) of p-Nitro aniline and 20 ml of rectified spirit were taken in a round-bottomed flask fitted with a reflux condenser. The contents were refluxed over a water bath for about 20 minutes. Water was added and cooled. Oily layer separated out. It was induced to give crystals by scratching the sides of beaker with a glass rod. It was filtered and washed well with cold aqueous ethanol. It was recrystallized from aqueous methanol. Recrystallization was repeated to get concordant melting point table 25.

Table 25: p-Methoxy benzylidene (p-Nitro) aniline (P-CH₃OB-p-NO₂A)

p-MethoxyBenz aldehyde	p-Nitro Aniline	Yield		Melting Point (°C)
		Theoretical	Experimental	Observed
0.1 mole	0.1 mole	0.1 mole	0.084 mole	100

4. Conclusions

In this study we prepare, identify, and characterize the aromatic anils (Schiff's bases or benzylidene aniline) then we used them for kinetic study, the cooxidation was done in presence of oxalic acid by chromic acid in acetic acid medium.

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