

## Oxidation of Amines: Part I Oxidation of Aromatic Primary Amines with Silver (I)

MUHAMMAD ZAFAR IQBAL AND IMRAN HAYAT  
*Institute of Chemistry, University of Punjab, Lahore (Pakistan)*

(Received 18th May 1982)

**Summary:** The oxidation of aromatic primary amines was studied in neutral, basic or acidic medium catalysed by silver(I). Various aromatic amines could be oxidised to corresponding azoderivatives. Electron withdrawing substituents were found to slow down the reaction and strong substituents did not allow the reaction to proceed. The presence of electron donating substituents such as  $-CH_3$  on aromatic amines enhanced the rate of reaction and higher yields of the products were obtained. The reactions were carried out at room temperature. Based on these observations, a mechanism for the oxidation of aromatic primary amines in presence of Ag(I) is proposed.

### Introduction

Oxidation of amines in presence of metal ions and oxides is known. Considerable selectivity with respect to functional groups and stereochemistry can be achieved by the choice of proper oxidant and under appropriate conditions. Permanganate<sup>1,3</sup> ion reacts with amines to give a variety of products i.e., amines such as N,N-dimethylbenzylamine can be readily oxidized<sup>4</sup> to benzaldehyde and benzylamines<sup>5</sup> are oxidized to N[ $\alpha$ -(benzylideneamino)-benzyl] benzamines,  $C_6H_5CH=NCH(C_6H_5)NHCOC_6H_5$  and N,N-(iminodibenzylidene)-bis [benzylamides],  $C_6H_5CONHCH(C_6H_5)NHCOC_6H_5$ . Tertiary amines can also be oxidized in presence of permanganate ions<sup>6,7,8</sup>. Primary aliphatic and aromatic amines<sup>9</sup> are converted to the corresponding aldehydes in presence of atleast fivefold molar excess of active manganese dioxide<sup>8,10</sup>. Primary aromatic amines are oxidized to corresponding azoderivatives when reacted with manganese(IV) oxide in petroleum ether. Secondary and tertiary amines are oxidized by manganese(IV) oxide to corresponding amides or aldehydes<sup>11</sup> and reaction is supposed to proceed through carbinolamine intermediate<sup>12</sup>. Oxidation of aniline to azobenzene with air in presence of Tl, Pb and Bi has also been reported<sup>13,14</sup>. Primary aliphatic amines are converted to nitriles by treating with twice the molar amount of lead tetracetate in refluxing benzene<sup>15,16</sup>. Ring substituted anilines in acetic acid<sup>17</sup> or benzene<sup>18</sup> react with lead tetraacetate to form symmetrically substituted azobenzenes.

Leonard<sup>19</sup> and co-workers have explored all possible oxidations of tertiary amines with mercuric acetate in

dilute aqueous acetic acid solutions. The initial step involves the removal of hydrogen from the  $\alpha$ -carbon atom to form an iminium salt.

Silver(II) is considered a powerful oxidant for primary and secondary amines<sup>20,21</sup>. Primary amines are best oxidized to imines and ultimately to aldehydes with  $Ag_2O_8$  whereas secondary amines react best with argentic picolinate<sup>22</sup>. Silver oxide is reported<sup>23</sup> to dehydrogenate 7-Chloro-1,3,4,5-tetrahydro-5-phenyl-2H-1, 4-benzodiazepin-2-one and is found superior to chromium trioxide and selenium dioxide. These and similar reactions prompted us to investigate the oxidation of primary amines in presence of silver(I).

### Experimental

Liquids were redistilled and solid chemicals recrystallised before use. Ultraviolet spectra were recorded on UV-Vis 220s Hitachi Spectrophotometer (180-900 nm). Melting points were taken on Gallenkamp melting point apparatus.

#### *Oxidation of Aniline with Ag(I)*

Aniline (0.9 ml, 0.93g, 10 mmol) was added to silver nitrate (1.69 g, 10 mmol) in 150ml of ethanol-water (2:1) and the reaction mixture stirred for 3.5h at room temperature. At the completion of the reaction (no greenish-black coloration with acidified  $K_2Cr_2O_7$  showing absence of aniline) silver mirror was formed. Solvent extraction with n-hexane gave an orange red solution,

and pure azobenzene (225mg, 24.7%) was obtained from it by column-chromatography using n-hexane as eluant. The purity of azobenzene was checked by thin layer chromatography (m.p. 71°C; UV: Lit<sup>24</sup>.  $\lambda_{\max}$  (C<sub>2</sub>H<sub>5</sub>OH) 318 nm; IR: 2900, 2800, 1910, 1850, 1740, 1550, 1450, 1420, 1340, 1260, 1180, 1110, 1040, 980, 890, 750, cm<sup>-1</sup>).

When aniline (0.9 mls; 0.93g, 10 mmol) was added to silver(I) acetate (1.67g; 10.0 mmol) in 150 ml ethyl alcohol-water(2:1) and stirred for 3.5 hr at room temperature, silver mirror was formed. n-Hexane extracts and chromatography gave azobenzene (m.p. 71°C; UV: Lit.<sup>24</sup>  $\lambda_{\max}$  (C<sub>2</sub>H<sub>5</sub>OH) 319 nm, Obs. 318 nm).

#### *Oxidation of p-methyl aniline*

On adding p-methylaniline (1.07g, 10 mmol) to silver nitrate (1.69, 10 mmol) in 300ml ethanol-water (2:1) and stirring, silver mirror was immediately formed and reaction was complete within 30 minutes at room temperature. Solvent extraction with n-hexane and column chromatography gave 4,4-dimethylazobenzene (0.029, 21%) as orange red solid (m.p. 140°C; UV: Lit<sup>24</sup>  $\lambda_{\max}$  (C<sub>2</sub>H<sub>5</sub>OH), 326 nm; Obs. 326 nm); IR: 3200, 2850, 1560, 1440, 1350, 1360, 1180, 980, 740 cm<sup>-1</sup>).

#### *Oxidation of p-fluoroaniline*

p-Fluoroaniline (1.11g, 0.950 ml, 10.0 mmol) was added to 300 ml of ethyl alcohol-water (2:1) in which silver nitrate (1.69g, 10 mmol) was previously dissolved. The reaction mixture was stirred for 24 hr at room temperature when silver mirror was deposited. n-Hexane extracts gave 4,4-difluoroazobenzene (0.19g, 18%) as yellow solid (m.p. 101°C; UV:  $\lambda_{\max}$ . 230, 330, nm; IR: 4100, 3900, 3600, 3250, 2850, 2790, 2400, 2150, 1840, 1620, 1560, 1480, 1440, 1390, 1350, 1200, 1110, 1070, 990, 920, 740 cm<sup>-1</sup>).

#### *Oxidation of $\alpha$ -Naphthylamine*

Addition of  $\alpha$ -Naphthylamine (1.43g, 10 mmol) to silver nitrate (1.69g, 10 mmol) in 300 ml of ethanol-water (2:1) and stirring for 24 hours at room temperature, resulted in the formation of silver mirror. Solvent extraction with n-hexane and column chromatography

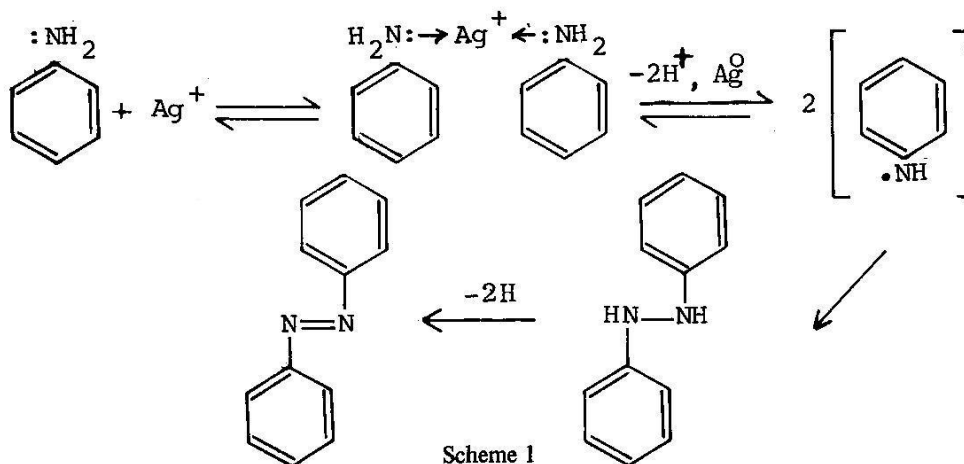
using n-hexane as eluent gave 1,1-azo-naphthalene (0.15g, 11%; UV: Lit<sup>24</sup>. 214, 266, 400 nm, Obs. 214, 265, 400 nm; IR: 4100, 2800, 2750, 2600, 2550, 1560, 1430, 1340, 1300, 1250, 1090, 1020, 850, 700 cm<sup>-1</sup>) and 1,4-naphthoquinone (0.16g, 10%; UV data: Lit<sup>24</sup> 255, 330 nm; Obs. 255, 330 nm; IR' 2825, 2750, 1700, 1480, 1350, 1300, 1250, 1100, 1020, 850, 700 cm<sup>-1</sup>).

#### **Results and discussion**

The soft and hard acid-base combination results in the formation of relatively unstable complex ions derived from an aromatic primary amine and Ag(I). The decomposition process involves oxidative elimination of nitrines which give hydrazobenzene and on further oxidation form azobenzene. Thus azobenzene (24.7%) was obtained from aniline in neutral medium but the yield was found to increase to 30% in basic medium (with NH<sub>4</sub>OH at pH9). It is interesting to note that in dimethyl sulphoxide solvent the yield of azobenzene was reduced to 7%. This is due probably to the entrapping of nitrines by DMSO. It was noticed that pH decreases from 7 to 6.5 indicating the release of H<sup>+</sup> and silver mirror is formed due to the reduction of Ag(I) to Ag(O). The proposed mechanism of the reaction is given in scheme I.

This mechanism is analogous to that proposed by Pausacker and Scroggie<sup>17</sup> for the oxidation of amines in presence of lead tetra-acetate.

In presence of electron donating groups such as -CH<sub>3</sub> at para position with respect to -NH<sub>2</sub> in aniline i.e. p-methyl-aniline, the reaction becomes faster and was complete within ½ hr which is 1/8th the normal time required by aniline at room temperature. Introducing fluoro-group at para-position to -NH<sub>2</sub> group slows down the reaction due to greater inductive effect induced by more electronegative fluorine atom causing even less electron pair donating ability of -NH<sub>2</sub> group to silver(I). In presence of -NO<sub>2</sub> group on aniline the reaction rate is reduced to the extent that no appreciable amounts of azobenzene could be obtained because -NO<sub>2</sub> group is expected to withdraw the charge density. Bond between -NH<sub>2</sub> and Ag(I) is weakened to the extent that coupling reaction does not take place resulting in absence of azobenzene even after 48 hours. Silver (I) carbonate, silver(I) chlorate and silver(I) lactate were unable to oxidize aniline to azobenzene.



When  $\alpha$ -naphthylamine was oxidised with Ag(I), naphthaquinone and 1,1-azonaphthalene were produced. Oxidation of  $\alpha$ -naphthylamine to naphthaquinone in presence of lead tetracetate has already been reported<sup>14</sup>. Due to the greater involvement of amine nitrogen in resonance of aromatic system less electron charge density is available for coordinate bond formation and hence slowing down the reaction.

#### References

1. N. Kornblum, R.J. Clutter and W.J. Jones, *J. Am. Chem. Soc.*, **78**, 4003 (1956).
2. N. Kornblum and W. J. Jones, *Org. Syn.*, **43**, 87 (1963).
3. M. Wei and R. Stewart, *J. Am. Chem. Soc.*, **88**, 1974 (1966).
4. J.B. Lee and T.G. Clarke, *Tetrahedron Letters*, 415 (1967).
5. H. Shechter., S.S. Rawalay and M. Jubis, *J. Am. Chem. Soc.*, **86**, 1701 (1964).
6. W.V. Farrar, *J. Chem. Soc.*, 3255 (1954).
7. R.C. Cookson and M.E. Trevett, *J. Chem. Soc.*, 2689 (1956).
8. S.W. Pelletier and W.A. Jacobs, *J. Am. Chem. Soc.*, **76**, 4496 (1954) and references therein.
9. R.J. Highet and W.C. Wildman, *J. Am. Chem. Soc.*, **77**, 4399 (1955).
10. M.Z. Barakat, M.F. Abdel-Wahab, and M.M. El-Sadr, *J. Chem. Soc.*, 4685 (1956).
11. H.B. Henbest and A. Thomas, *J. Chem. Soc.*, 3032 (1957).
12. H.B. Henbest and M.J. W. Stratford, *Chem. Ind. (London)*, 1170 (1961).
13. O.W. Brown and W.C. Frishe, *J. Phys. and Colloid Chem.*, **51**, 1394-1400 (1947).
14. K.H. Pausacker and J.G. Scroggie, *J. Chem. Soc.*, 4003 (1954).
15. M.L. Mihailovic and Andreejevic, *Tetrahedron Letters*, 461 (1965).
16. A. Stojilkovic, V. Andrejevic and M.L. Mihailovic, *Tetrahedron*, **23**, 721 (1967).
17. K.H. Pausacker and J.G. Scroggie, *J. Chem. Soc.*, 4003 (1954).
18. E. Baer and A.L. Tosoni, *J. Am. Chem. Soc.*, **78**, 2857 (1956).
19. N.J. Leonard and W.K. Musker, *J. Am. Chem. Soc.*, **81**, 5631 (1959).
20. R.G.R. Bacon and W.J. W. Hanna, *J. Chem. Soc.*, 4962 (1965).
21. R.G.R. Bacon and D. Stewart, *J. Chem. Soc.*, 1384 (1966).
22. R.G.R. Bacon, W.J.W. Hanna and D. Stewart, *J. Chem. Soc.*, 1388 (1966).
23. R.I. Fryer, G.R. Archer, B. Brust, W. Zally and L.H. Sternback, *J. Org. Chem.*, **30**, 1308 (1965).
24. Robert C. Weast (Editor), *Hand Book of Chemistry and Physics* published by CRC Press, 18901 Cranwood Parkway-Cleveland, Ohio, 44128, U.S.A. 55th Ed. 1974-75.