SYNTHESIS AND EVALUATION OF O, CARBOXY, O, CHLORO AND O, CYANO DERIVATIVES OF *N,N-DIETHYLBENZYLAMINE*

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ABSTRACT: *o, Carboxy, o, chloro and o,cyano derivatives of N,N-diethylbenzylamine were prepared. Physical properties like solubility, boiling/decomposition points*, relative density, refractive index, surface tension were determined. *Compounds are examined and analyzed on the basis of spectroscopic and analytical data.*

Key words: o, Carboxy-N, N-diethylbenzylamine, o, Chloro-N, N-diethylbenzylamine, derivatives of N, N-diethylbenzylamine

INTRODUCTION

A large variety of organic reagents are known which act as chelating agents. They show varying selectivity, specificity and stability constants [1-6]. Such reagents find many important applications in analytical chemistry [7-10]. Recent developments in theoretical chemistry, particularly those arising from the ligand field theory, have led to the deep understanding of factors responsible for the stability of metal complexes, the nature of their absorption spectra and other properties of interest to the chemists. Important groups of organic compounds to be considered with this reference are those which form complexes with metal ions usually by co-ordination through nitrogen or oxygen. Such organic compounds may provide a class of compounds that are potential agents for the identification and estimation of metals.

From the knowledge of the characteristics of the complexes formed with organic reagents and their stability and solubility data, it has become increasingly possible to design new organic reagents / chelating agents and to specify the scope and limitations of their use in analytical chemistry [11]. Recent studies on the chemistry of chelate forming molecules containing donor atoms like nitrogen, oxygen, etc. have been quite revealing [12]. The present work is related to N,N-dialkylbenzylamines and their derivatives. N,N-dialkyl-benzylamines are capable of co-ordination to metals through nitrogen.

The aromatic substitution reactions are not limited to azobenzene and benzylidene but are even more facile with N,N-dimethylbenzylamine [13,14]. N,N-dimethylbenzyl-amine and its derivatives containing $-NH_2$, -OH, etc., groups can act as effective chelating agents. These compounds are capable of forming five - or six-membered ring systems which would enhance the stabilities of the complexes formed with metals in favourable oxidation states.

MATERIALS AND METHODS

E. Merck, British Drug House and Riedel-de Haen chemicals were used without further purification. Solvents were of reagent quality and redistilled prior to use. N,N-diethylbenzylamine and their substituted derivatives were synthesized starting from N-bromosuccinimide (in CCl_4) and toluene or substituted toluene using benzoyl peroxide as catalyst followed by addition of dialkylamine in the presence of $NaHCO_3$ in distilled water under reflux.

The substituted benzylamines were separated and purified by column chromatography. Their purity was also checked by thin layer chromatography. Boiling /decomposition points were determined by Gallen Kamp M.P. apparatus. Refractive indices (by Abbe's refractometer), viscosity (using viscometer), surface tension (by Stalagmometer) and relative density were also determined for these new compounds as yet not reported in literature. λmax of these compounds were taken in ethanol (absolute) on Hitachi UV-visible spectrophotometer, model U-2000.

Preparations:

1.o-Carboxy-N,N-diethylbenzylamine: A one litre flask equipped with water condenser was charged with N-bromosuccinimide (88.5g, 0.5mol), o-toluic acid (68.07g, 0.5mol) and benzoyl peroxide (1.0g) (used as catalyst) in 250mL CCl_4. The mixture was refluxed for 6-8h until all the solid started floating on the liquid surface. The reaction mixture was filtered and diethylamine (52.2mL, 0.5mol) and $NaHCO_3$ (42.0g, 0.5mol) in distilled water (100mL) were added to the filtrate. The mixture was again refluxed for 4h. It was allowed to cool to room temperature and filtered. The filtrate was transferred to a separating funnel where two layers were formed. The organic layer was collected and passed through a column packed with silica gel No. 60 (70-230mesh ASTM). Ethanol-n-hexane (4:1) eluted an orange layer which on evaporation gave an orange red oily liquid. It was soluble in almost all organic solvents. (yield 40.0%, boiling point 120^{o}C, decomposition point 195^{o}C, relative density 1.045 gmL^{-1}, refractive index 1.646 at 23^{o}C, surface tension 37.2 dyn cm^{-1} at 23^{o}C) Fig. 1.

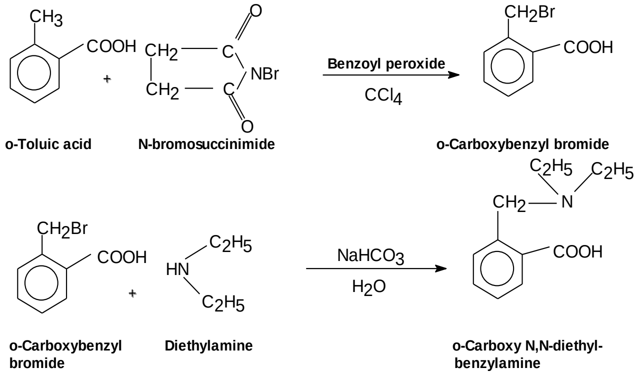

Fig. 1: Reaction Mechanism

2.o-Chloro-N,N-diethylbenzylamine: A one litre flask equipped with water condenser was charged with N-bromosuccinimide (88.5g, 0.5mol), o-chlorotoluene (58.6mL, 0.5mol) and benzoyl peroxide (1.0g) (used as catalyst) in 250mL CCl_4. The mixture was refluxed for 6-8h until all the solid started floating on the liquid surface. The reaction mixture was filtered and diethylamine (52.2mL, 0.5mol) and $NaHCO_3$ (42.0g, 0.5mol) in distilled water (100mL) were added to the filtrate. The mixture was again refluxed for 4h. It was allowed to cool to room temperature and filtered. The filtrate was transferred to a separating funnel where two layers were formed. The organic layer was collected and passed through a column packed with silica gel No. 60 (70-230mesh ASTM). n-Hexane eluted an orange layer which on evaporation gave an orange red oily liquid. It was soluble in almost all organic solvents. (yield 41.7%, boiling point 170°C, relative density 1.343 gmL^{-1}, refractive index 1.357 at 22°C, viscosity 29.73 $gcm^{-1}sec^{-1}$, surface tension 32.72 $dyn.cm^{-1}$ at 22°C) Fig. 2

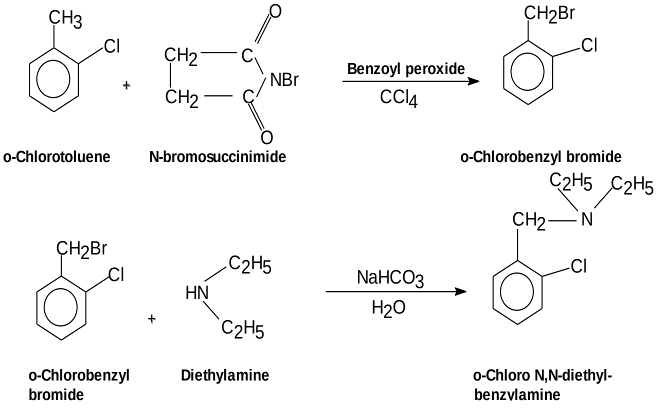

Fig. 2: Reaction mechanism

3. o-Cyano-N,N-diethylbenzylamine: A one litre flask equipped with water condenser was charged with N-bromosuccinimide (88.5g, 0.5mol), o-tolunitrile (59.2mL, 0.5mol) and benzoyl peroxide (1.0g) (used as catalyst) in 250mL CCl_4. The mixture was refluxed for 6-8h until all the solid started floating on the liquid surface. The reaction mixture was filtered and diethylamine (52.2mL, 0.5mol) and $NaHCO_3$ (42.0g, 0.5mol) in distilled water (100mL) were added to the filtrate. The mixture was again refluxed for 4h. It was allowed to cool to room temperature and filtered. The filtrate was transferred to a separating funnel where two layers were formed. The organic layer was collected and passed through a column packed with silica gel No. 60 (70-230mesh ASTM). n-Hexane: ether (4:1) eluted an orange layer which on evaporation gave a red oily liquid. It was soluble in almost all organic solvents. (yield 36.56%, λmax 251nm, boiling point 175°C, relative density 1.333 gmL^{-1}, refractive index 1.443 at 23°C, viscosity 31.01 $gcm^{-1}sec^{-1}$, surface tension 32.611 $dyn.cm^{-1}$ at 20°C) Fig. 3.

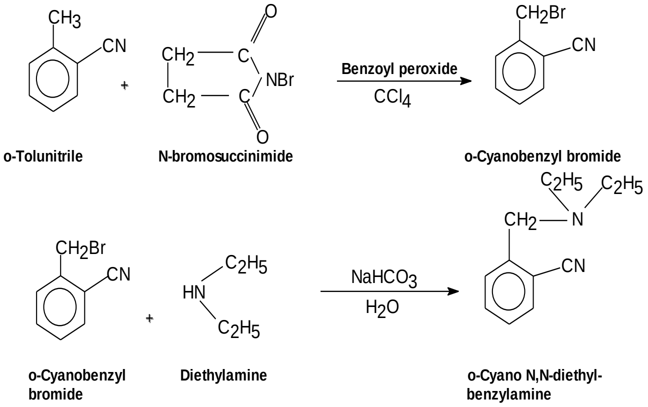

Fig 3: Reaction mechanism

RESULTS AND DISCUSSION

Substituted derivatives of N,N-diethylbenzylamines were synthesized by an indirect brominating method. The compounds were separated and purified by column chromatography. The purity of these ligands was also checked by T.L.C. Physical parameters such as m.p. / b.p./ dec.p., λmax, refractive indices, viscosity, surface tension, relative density etc. were also determined.

IR spectra of o-carboxy-N,N-diethylbenzylamine indicates O-H stretching vibrations at $3350cm^{-1}$. Ar-H stretching frequency was observed at $3050cm^{-1}$. The absorption bands appeared at 2950 and $2900cm^{-1}$ are assigned to C-H stretching vibrations for methyl and methylene groups. The C $=$ O stretching frequency was indicated at $1700cm^{-1}$. The aromatic C $=$ C was observed at 1600 and 1620 cm^{-1}. The O-H bending vibrations are seen at $1415cm^{-1}$. C-H in-plane bending also occur around $1285\text{-}1065cm^{-1}$ and out of plane bending around $900\text{-}735cm^{-1}$.

IR spectrum of o-chloro-N,N-diethylbenzylamine indicates Ar-H frequency at $3010cm^{-1}$. The bands appeared at 2960 and 2875 are attributed to C-H stretching vibration for methyl and methylene groups. The aromatic C $=$ C was indicated at $1600cm^{-1}$. C-N bond of the type $-CH_2\text{-}N(C_2H_5)_2$ was observed at $1330cm^{-1}$. The absorption band appeared in the range $1160\text{-}1020cm^{-1}$ may be assigned to in-plane bending of C-H and between 860 $-700cm^{-1}$ due to out of plane bending.

IR spectra of o-cyano-N,N-diethylbenzylamine shows aromatic C-H stretching frequency around 3065 cm^{-1}.The absorption bands indicated at 2900, 2875 and $2800cm^{-1}$ are assigned to C-H stretching vibrations for methyl and methylene groups. Characteristics frequency of C $\equiv$ N bond was found at 2240 cm^{-1}.

Table-1
Infrared absorption spectra

No.	Empirical Formula	IR Absorption bands (cm^{-1}) and Intensity
1	**$C_{12}H_{17}NO_2$**	**3350broad, 3050w, 2950m, 2900w, 1700s, 1620w, 1600m, 1500m, 1485w, 1445w, 1395m, 1305m, 1285m, 1230w, 1100m, 1065m, 985w, 900m, 850w, 795m, 735m, 660m.**
2	**$C_{11}H_{16}NCl$**	**3010w, 2960m, 2875m, 1600s, 1570s, 1470s, 1330m, 1160w, 1100m, 1060s, 1020m, 950m, 860m, 790s, 700m, 610m.**
3	**$C_{12}H_{16}N_2$**	**3065w, 2900m, 2875s, 2800s, 2240s, 1605m, 1580w, 1495m, 1440s, 1355s, 1230m, 1180m, 1120m, 1040m, 980w, 950w, 875m, 860m, 750s, 700s, 640m.**

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