

CHAPTER - 1

I.1.1. Introduction

Acid catalyzed N-alkylation of benzylamine by alcohol has been carried out under pressure. Use of high pressure in organic synthesis is relatively a new concept gaining momentum rapidly. Matsumoto et al. in their recent reviews^{1,2} and Jurczak in his paper³ have elaborately discussed the recent developments of high pressure techniques in synthetic organic chemistry. High pressure played an important part in the development of industrial methods for the production of various useful materials such as synthetic diamond, ruby, borazone, etc. whereas the utility of high pressure in organic synthesis has not been widely explored in spite of its expected potentialities. In practice, the high pressure technique has gained the attention of organic chemists since the mid - 1970s when the pioneering studies of Dauben et al.^{4,5} testified to the advantage of high pressure application for an effective course of the Diels - Alder reaction. During the past decade this new direction of organic synthesis has greatly developed, arousing the interest of investigators. In the present investigation, a systematic study has been made to develop a pressure mediated process for synthesizing N-alkyl derivatives of benzylamine using alcohols as the alkylating

agents in presence of an acid catalyst. It can be noted in this context that acid catalyzed N-alkylation of benzylamine is not possible under atmospheric pressure. This has been established by the author in his laboratory.

N-alkyl derivatives of benzylamine (BA), particularly N,N-dimethylbenzylamine (DMBA), N,N-diethylbenzylamine (DEBA), N-methylbenzylamine (MBA), and N-ethylbenzylamine (EBA) have got innumerable applications in present day industries and research laboratories. DMBA has been used as a dehydrohalogenating agent, corrosion inhibitor and acid neutralizer^{6,7}. Use of DMBA as a cross-linking and polymerization catalyst in many hardenable epoxy resin compositions and polyurethane polymerization reactions has gained immense importance in recent years⁷⁻³². It has also been used as intermediate as well as catalyst in organic syntheses³³⁻³⁸. Amongst many other uses of DMBA, there are uses as binder in magnetic composition for flexible permanent magnet³⁹, catalyst in the preparation of magnetic toner⁴⁰, in coating compositions for inorganic particles⁴¹, in adhesive for chemical plating⁴² and in composition for electro-deposition on metal substrates to form high density film⁴³. DMBA in the form of quaternary ammonium salts (quats) also has innumerable uses such as in the manufacture of fabric softeners, organomodified clays, bactericidal and sanitizing agents, etc⁴⁴. The single largest market for benzyl-based quats is its use in the manufacture of fabric softener. The

second largest market is its use in the manufacture of organomodified clays. Organomodified clays are used to improve the lubricity and rheology of the drilling mud. Because of the rapid increase of well drilling, the use of the organoclays has grown rapidly. The third largest use of quats is in the bactericidal and sanitizer market. A wide variety of quat-solutions is used as sanitizing agents for cleansing eating utensils and food-processing equipments and as cleaning compounds in restaurants, dairies, and hospitals. They have advantages over phenols and chlorine-containing disinfectants in that they are non-irritating and odour-free and have relatively long-activity. Another significant use for quats is in hair treatment. Quaternaries have high affinity for proteinaceous substrates, and this property makes them useful for hair treatment and imparts antistatic effects, increases wetting, improves both wet and dry combing, and improves feel and lustre.

Uses of benzyl-based quats as catalysts in many industries and research laboratories are also worth mentioning. Trimethylbenzylammonium hydroxide, commercially known as Triton B, has been used for long as basic catalyst in many organic syntheses. But use of triethylbenzylammonium quats as phase transfer catalysts in past few years is of much more significance. The importance of DEBA and its quaternary salts, triethylbenzylammonium quats, can be easily

gauged from the huge literature published in recent years^{37,38,45-93}. The major use of triethylbenzylammonium quats has been as the phase transfer catalyst in varieties of chemical processes such as organic synthesis, polymerization reaction, polymer modification, rearrangement reaction, isomerization reaction, etc. It has also been used in epoxy resin composition⁷⁹⁻⁸³, zeolite preparation⁸⁹, analytical reagent⁸⁸. Triethylbenzylammonium hydroxide is a strong base catalyst used in basic hydrolysis⁸⁶ and pulp purification⁸⁷.

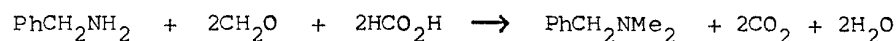
The major uses of N-methylbenzylamine and N-ethylbenzylamine are as intermediates in organic syntheses of industrial and medicinal importance as well as of academic interest⁹⁴⁻¹⁰⁵. Their use in resin composition^{106,107}, polymerization reaction¹⁰⁸, as indicator in Co (II) estimation¹⁰⁹, in the manufacture of hair dyes¹¹⁰ are worth-mentioning.

N-alkylation of amines has been a subject of wide interest amongst researchers. Lots of research papers have already been published on this subject. Following is a short review covering some of the N-alkylation methods important and relevant for benzylamine.

(i) N-Methylation of Amines by Formaldehyde in Formic Acid Solution (Clarke et al., 1933)¹¹¹ :

N-methylation of benzylamine and some other simple aliphatic amines have been reported by Clarke et al. as early as in 1933. They carried out the process by warming

the amine in formic acid solution with formaldehyde, and got tertiary amine over 80%. In this method, one molecular proportion (or slightly more) of formaldehyde has been reportedly found sufficient for each methyl group introduced. It is therefore mainly the formic acid which supplies the hydrogen involved in the reduction.

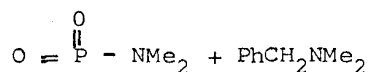
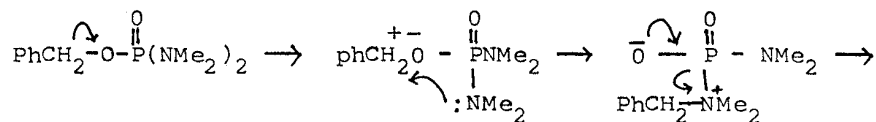
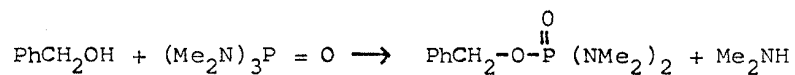


- (ii) N-Alkylbenzylamine by Electrolytic Reductive Amination of Benzaldehyde [Young and Robinson, 1933]¹¹² :

Young and Robinson synthesized N-ethylbenzylamine by electrolytic reduction of a mixture of anhydrous EtNH₂ and PhCHO in MeOH. A modest 70% yield had been reported. Similarly N-methylbenzylamine had been prepared either from benzaldehyde and methylamine or benzylamine and formaldehyde.

- (iii) Conversion of Benzyl Alcohol into N,N-Dimethylbenzylamine by Hexamethylphosphoric Triamide [Monson and Priest, 1971]¹¹³ :

Benzyl alcohol can be made to react with hexamethylphosphoric triamide [(Me₂N)₃PO] at reflux to afford N,N-dimethylbenzylamine in modest yield (71%).



(iv) The Formic Acid-Formaldehyde Methylation of Benzylamine [Pine and Sanchez, 1971]¹¹⁴ :

The formic acid-formaldehyde methylation of benzylamine favours the formation of tertiary amine over secondary amine even when less than stoichiometric amounts of formaldehyde are used. When benzylamine in 3 molar equivalent of formic acid (88%) is allowed to react with 0.5 - 4.0 molar equivalent of formaldehyde at 80°C for 24 h, the major basic product is N, N-dimethylbenzylamine. In addition, benzaldehyde, N-benzylformamide, N-benzyl-N-methylformamide and N-methyldibenzylamine are formed as by-products. Reported conversions of benzylamine to N, N-dimethylbenzylamine and N-methylbenzylamine are respectively 75% and 0.1% .