



Research Article

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S-Alkylation of thiophenol under biphasic versus triphasic PTC condition using Tetrabutyl Ammonium Bromide as a Phase Transfer Catalyst

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ABSTRACT

Comparative study of S-Alkylation of thiophenol under Liquid-Liquid (L-L) biphasic versus Liquid-Liquid-Liquid (L-L-L) triphasic phase transfer catalysis (PTC) has been carried out. Various alkyl halides were used as an alkylating agent. Tetrabutyl ammonium bromide (TBAB) was used as Phase transfer catalyst. The rates of reaction were enhanced under the Liquid-Liquid-Liquid triphasic PTC as compared to the Liquid-Liquid biphasic PTC.

Keywords: Phase transfer catalysis, Tetrabutyl ammonium bromide, S-Alkylation, liquid-liquid, Liquid-Liquid-Liquid System.

INTRODUCTION

S-alkylation reactions for the synthesis of thioethers are very important from industry point of view. Thioethers are important in biology, notably in the amino acid methionine and the cofactor biotin. According to literature survey some of the catalysts used for the synthesis of thioethers are, Microwave assisted highly Efficient Solid state S-Alkylation [1], Cs_2CO_3 .TBAI [2], Cs_2CO_3 -CuI [3], methyl acetate on a sodium acetate- type fixed bed, and other alkylations by orthoesters or orthocarbonates on a potassium carbonate catalytic bed [4], fluoroalkylation of thiophenols by 1,2-dibromotetrafluoroethane activated by sulfur dioxide [5], Homogeneous catalytic fluoroalkylation of thiophenols, phenols and pyrrole by Freons $\text{BrCF}_2\text{CF}_2\text{Br}$ and $\text{CF}_2\text{ClCFCl}_2$ [6], Ionic Liquid-[pmIm]Br [7], Synthesis of various ethers is also reported by using various phase transfer catalysts under different conditions. One-pot, solid-phase synthesis of a thioether is also described by using Tetrabutyl ammonium iodide [8]. Various thioesters were obtained through an efficient phase-transfer catalysis method, by treating several thiophenols with different acyl chlorides, in a biphasic system composed of 10% aqueous NaOH and dichloromethane in the presence of tetrabutylammonium chloride [9], Gas-liquid phase-transfer synthesis of phenyl ethers and sulphides with carbonate as base and Carbowax as catalyst [10], S-alkylation of different substrates using different phase transfer catalysts is also reported [11].

A majority of PTC reactions are conducted under Liquid-Liquid conditions, wherein the organic phase is normally the reaction phase with associated transfer of aqueous phase reagent as an ion pair with phase transfer catalysts, such as quaternary ammonium and phosphonium salts, crown ethers, cryptands, polyethylene glycols etc. The high rate of reaction exhibited by Liquid-Liquid PTC reaction in comparison with conventional homogeneous reactions in hydroxylic solvents results from the presence of weakly solvated and highly reactive ion pair in organic media. A certain amount of water of hydration is co-extracted with the ion pair migrating from aqueous phase to the organic phase. This can sometimes interfere and fully suppress a reaction or lead it to byproduct formation. Liquid-Liquid PTC is also disadvantageous for systems, where the presence of water can lead to side reactions such as hydrolysis. Liquid-Liquid PTC involves heterogeneous reaction between two reagents located in an aqueous and an organic phase.

In liquid-liquid-liquid (L-L-L) PTC system, catalyst rich liquid phase is generated in between the aqueous and organic phase. If an aqueous phase is saturated by using appropriate salt and if the catalyst concentration exceeds certain quantity, third phase in L-L PTC system is generated. This catalyst rich middle phase does not allow the direct contact between the aqueous phase and organic phase therefore side reactions such as hydrolysis due to presence of water are totally suppressed. Catalyst rich middle phase is the main reaction phase for the phase transfer catalyst which catalyzes the reaction [12-14]. This phase can also be recovered and reused as it is immiscible with the aqueous phase.

In present work we have studied the S-alkylation of thiophenol under the influence of different halides by using tetra butyl ammonium bromide as a phase transfer catalyst under liquid-liquid and liquid-liquid-liquid phase transfer catalysis conditions.

Reaction scheme:

The generalized reaction is shown in **Fig. I**.

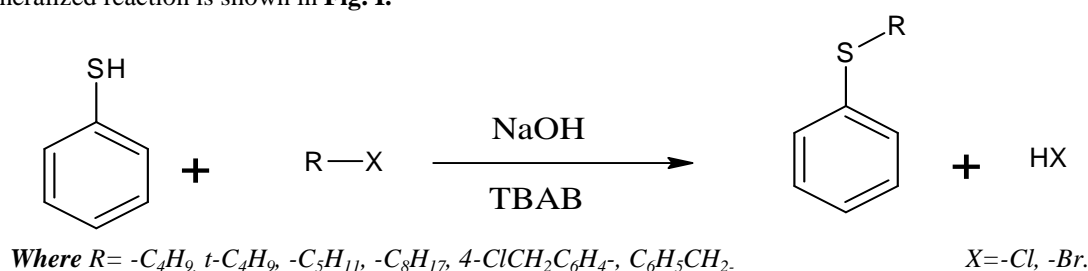


Fig. I: Reaction scheme

EXPERIMENTAL SECTION

The Phase transfer catalyst Tetrabutyl Ammonium Bromide, Thiophenol and toluene of AR grade were obtained from M/s. s.d. Fine Chem. Pvt. Ltd., Mumbai, India. All other chemicals were analytical reagents obtained from M/s. s.d. Fine Chem. Pvt. Ltd. Mumbai.

Experimental Setup and reaction procedures:

a. Liquid-Liquid (L-L) PTC: The reactions were studied in 5 cm i.d. reactor of 100 cm³ capacity which was equipped with six blade turbine impeller and reflux condenser. The reactor was kept in isothermal oil bath at desired temperature. The typical run were carried out by taking 0.01 mol thiophenol, 0.015 mol of NaOH in 15 cm³ water it was stirred at 100 °C for one hour to convert the thiophenol into sodium thiophenoxide then 0.00045 mol of TBAB catalyst was added. Organic phase contained 0.01 mol of alkyl halide in 15 cm³ of toluene. A zero sample was withdrawn from the organic phase. The reaction temperature was maintained at 90 °C and stirring speed 1200 rpm, the run was carried out for seven hours.

b. Liquid-Liquid-Liquid (L-L-L) PTC: The reactions were studied in 5 cm i.d. reactor of 100 cm³ capacity which was equipped with six blade turbine impeller and reflux condenser. The reactor was kept in isothermal oil bath at desired temperature. The typical run were carried out by taking 0.01 mol thiophenol, 0.015 mol of NaOH in 15 cm³ water mixture was stirred for one hour at 100 °C at 1200 rpm speed to ensure the formation of sodium thiophenoxide, aqueous phase was saturated with 0.051 mol of NaCl. Then 0.0045 mol of Tetrabutyl ammonium bromide was added as phase transfer catalyst which resulted in the formation of third phase. To this 15 cm³ of toluene was added with 0.01 mol of alkyl halide. The reaction temperature was maintained at 90 °C and stirring speed 1200 rpm. A zero sample was withdrawn from the organic phase before stirring. The run was carried out for one hour. Same procedure was repeated for all the alkyl halides used in the reaction.

Method of analysis:

Samples were withdrawn at the 0 minute and after seven hours in Liquid-Liquid PTC reactions and after one hour in triphasic Liquid-Liquid-Liquid PTC system and analyzed by Gas chromatography (**Chemito model**) by using 5 m stainless steel column packed with SE-30 as a liquid stationary phase. The conversion was based upon disappearance of alkyl halides from the organic phase.

RESULTS AND DISCUSSION

Different alkyl halides were studied for the reaction with thiophenol under Liquid-Liquid Phase PTC and Liquid-Liquid-Liquid phase PTC condition. Results are summarized in **table-I**.

From table-I, it is clear that the rates of the reaction were increase under the triphasic PTC condition as compared to biphasic PTC condition. Percentage conversion in case of L-L PTC is low, when this biphasic system was converted to triphasic L-L-L PTC, percentage conversions were suddenly increased. Drastic increase in the rate of reaction was observed when catalyst rich middle phase was used as the main reaction phase in L-L-L PTC system

Table-I: S-Alkylation of thiophenol under biphasic versus triphasic PTC condition using Tetrabutyl Ammonium Bromide as a Phase Transfer Catalyst.

Entry	Substrate	Liquid-Liquid PTC (% conversion) 7 Hrs.	Liquid-liquid-Liquid PTC (% conversion) 1-Hr.
1.	n-BuBr	77.2	98.2
2.	t-BuCl	38.4	89
3.	C ₅ H ₁₁ Br	90.5	94.3
4.	C ₈ H ₁₇ Br	70.0	96.0
5.	4-Cl-C ₆ H ₄ CH ₂ Cl	75.40	94.3
6.	C ₆ H ₅ CH ₂ Cl	66.0	98.5

CONCLUSION

Liquid –Liquid PTC can be elegantly modified to convert it into Liquid-Liquid-Liquid PTC to enhance the rate of reaction and selectivity, thereby improving the profitability and environmental benefits. The novelties of phase transfer catalyzed S-alkylation of thiophenol were studied under L-L-L PTC with TBAB as the catalyst with reference to L-L PTC. The concentration of catalyst influences the formation of third liquid phase (catalyst rich middle phase) and distribution of catalyst. It was observed that third liquid phase was the main reaction phase Effect of various alkyl halides was studied. The reaction rates were intensified in the L-L-L PTC versus L-L PTC and 100 % selectivity to the product was obtained.

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