



Comparative study of O-butylation of phenols under biphasic versus triphasic condition by using tetrabutyl ammonium hydrogen sulphate as Phase transfer catalyst

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ABSTRACT

Comparative study of O-butylation of phenols under Liquid-Liquid biphasic versus solid-liquid-liquid and Liquid-Liquid-Liquid triphasic phase transfer catalysis has been carried out. 1-Butyl bromide was used as an alkylating agent. Tetrabutyl ammonium hydrogen sulphate was used as Phase transfer catalyst. The rates of reaction were enhanced under the triphasic PTC as compared to the Liquid-Liquid PTC.

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Introduction

Aromatic ethers can be prepared by using various synthetic routes [1]. O-alkylation of phenols or phenoxide ions is carried out by using a suitable alkylating agent. Phenoxide are generated by reacting phenolic substance with a base such as sodium, sodium hydroxide, potassium hydroxide or sodium amide in benzene, toluene or dioxane as a solvent. Direct alkylation of phenols with diazomethane a hazardous reagent is widely applied [2]. Williamsons synthesis is most widely used for the preparation of symmetrical and asymmetrical ethers. Several new procedures for Williamson's synthesis using PTC under different condition were found to be most useful in terms of mildness of conditions, yield and convenience [3-7].

A large number of industrially important reactions involve the use of liquid-liquid PTC conditions. Main disadvantage of Liquid-liquid(L-L) PTC is that the catalyst remains distributed between the two liquid phases and it cannot be recovered easily. Presence of water leads to side reactions such as hydrolysis and oxidation in substituted aromatic compounds. These problems can be overcome by converting biphasic liquid-liquid PTC system into triphasic solid-liquid PTC and liquid-liquid-liquid (L-L-L)PTC condition. This not only reduces the side reactions but also intensifies the rate of the reaction and selectivity to the desired product is achieved.

Liquid-liquid PTC involves the heterogeneous reaction between the two reagent located in aqueous and organic phase. Solid liquid PTC reaction involves the reaction between anionic reagent in solid phase and reactant located in continuous organic phase. If trace quantity of water (omega phase) is added in solid -liquid PTC system it forms a thin film around the solid particle and it becomes solid reactant -omega aqueous omega phase-liquid organic phase i.e. triphase PTC system

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,

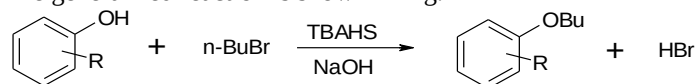
polyethylene glycols etc. The high rate of reaction exhibited by Liquid-Liquid PTC reaction in comparison with conventional homogeneous reactions in hydroxylic solvents results from the presence of weakly solvated and highly reactive ion pair in organic media. A certain amount of water of hydration is 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. Solid-liquid PTC system has several advantages over liquid-liquid PTC system [7-10]

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 [10-12]. This phase can also be recovered and reused as it is immiscible with the aqueous phase. Selective etherification of aromatic phenols catalyzed by tetrabutyl ammonium bromide as phase transfer catalyst using microwave irradiations and conventional heating has been reported by Yadav and et al. [13]

In the present work we have used tetrabutyl ammonium hydrogen sulphate which gives good yield for the selective O-butylation of various phenols

Reaction scheme:

The generalized reaction is shown in Fig. 1



Where R = -CH₃, -Cl, -OCH₃, -CHO,

Fig.1. Reaction scheme

Experimental:

Chemicals and catalyst: - Substituted phenols, Tetrabutyl ammonium hydrogen sulphate, n-butyl bromide were obtained from sd fine chemicals and all were of analytical grade.

Experimental set up:

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.

For Liquid-Liquid PTC the typical run were carried out by taking 0.01 mol phenols, 0.015 mol of NaOH in 15 cm³ water then 0.0045 mol of catalyst was added Organic phase contained 0.01 mol of n-BuBr in 15 cm³ of toluene. The reaction temperature was maintained at 90 °C and stirring speed 1200 rpm. The run was carried out for seven hours.

For liquid-liquid-liquid PTC the typical run were carried out by taking 0.01 mol phenols, 0.015 mol of NaOH in 15 cm³ water mixture was stirred for one hour at 90 °C at 1500 rpm speed. Aqueous phase was saturated with 0.051mol of NaCl. Then 0.0045 mol of catalyst was added which resulted into the formation of third phase after addition of 0.01 mol of n-BuBr in 15 cm³ of toluene. The reaction temperature was maintained at 90 °C and stirring speed 1200 rpm. The reaction was carried out for one hour.

Method of analysis:

Samples were withdrawn at the 0 minute and at the end of reaction 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 n-BuBr from the organic phase.

Results and discussion:

1-Bromobutane was used as an alkylating agent. The results obtained are presented in table-1.

From table-1 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 S-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.

O-butylated products were selectively formed in triphasic PTC system thereby giving 100 % selectivity to the desired product.

Separate experiment was performed for the reuse study of catalyst rich middle phase in L-L-L by taking 2-naphthol as an aromatic phenol and Tetrabutyl ammonium hydrogen sulphate as a phase transfer catalyst.

Conclusion:

Comparative study of O-butylation of aromatic phenols under biphasic versus triphasic PTC by using Tetrabutyl ammonium hydrogen sulphate as a PTC was done. Rates of the reaction were intensified in triphase PTC system as compared to biphasic PTC system, 100 % selectivities to the desired products was obtained and reaction time was also reduced.

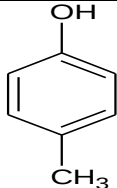
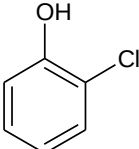
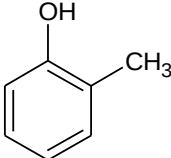
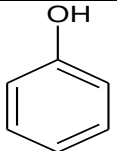
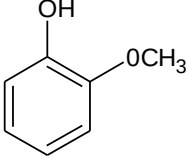
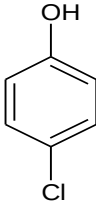
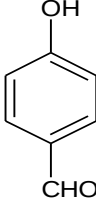
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Table-1. O-butylation of phenols under liquid-liquid biphasic versus solid-liquid-liquid and liquid-liquid-liquid phase transfer catalysis

No.	Substrate	Liquid-Liquid PTC (% conversion)	Solid-Liquid(ω)-Liquid PTC(% conversion)	Liquid-Liquid-Liquid PTC(% conversion)
1		70.35	95	99
2		34	96	98.76
3		74.26	92	98
4		11.67	84.71	95
5		65.21	89	90
6		31.23	71	89
7		11.36	47	82