

Phase transfer catalyzed reaction of disodium salt of 1,3-dihydroxybenzene with propargyl bromide in solid-liquid biphasic condition

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Abstract

In the present work, the reaction between disodium salt of 1,3-dihydroxybenzene (in situ formation) and propargyl bromide was carried out in a solid-liquid biphasic phase transferring catalytic system at 50 °C. Higher selectivity of the bis-derivative (1,3-bis(prop-2-ynyl)benzene) was obtained under solid-liquid PTC condition. The conversion of propargyl bromide to more than 99% was achieved in the presence of tetra-n-butylammonium bromide (TBAB) as PTC catalyst. From the experimental evidence, no mono-derivative was observed. Experiments were conducted to increase the conversion of propargyl bromide such as, stirring speed, various PTCs, temperature, various solvents and amount of TBAB loading. All the experiments were conducted to obey pseudo-first order rate law. Apparent activation energy was also determined from the Arrhenius plot.

Keywords: Phase transfer catalyst; 1,3-dihydroxybenzene; 1,3-bis(prop-2-ynyl)benzene; solid-liquid reaction.

Introduction

The reaction of two or more reagents residing in two or more phases were difficult to conduct even when tedious conditions were employed. Due to the poor contact of the reactants, addition of catalyst, namely phase transfer catalyst, was carried the reaction efficiently as desired. Phase transfer catalysis has the several advantages over traditional conventional methods such as no need of expensive aprotic solvents, simpler work up, shorter reaction time and lower reaction temperatures [1-3]. Generally solid-liquid reaction improves the conversion

rate and selectivity of the desired product [4].

1,3-Bis(prop-2-ynyl)benzene is an important compound having vast synthetic applications. Most important of all is its use as triazole intermediate [5]. Synthetic methods of organic chemistry reveal alkyne groups to be the most reactive ones which increase the importance of the compound [6]. Low cost and high yield of the compound have attracted the attention of scientists to synthesize the compound as monomer for many polymeric compounds [7]. The reaction became much more important due to the presence of terminal alkyne which

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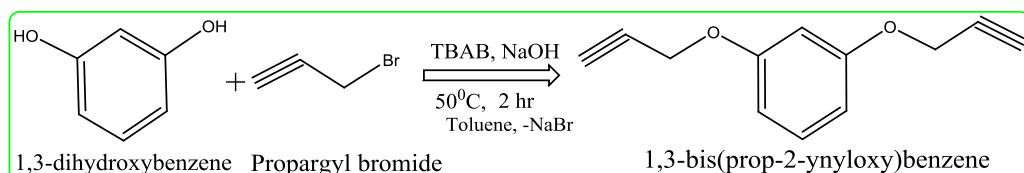
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helps in easy polymerization reactions under mild reaction condition, low temperature which is more favorable for linear and graft polymeric compounds [8].

Here, we report the reaction of disodium salt of 1,3-dihydroxybenzene

with propargyl bromide in solid-liquid phase transfer catalysis condition. The process to intensify the conversion of propargyl bromide and to improve the selectivity of production of bis-derivative is examined. The reaction scheme is represented here (Scheme 1).



Scheme 1. Synthesis of 1,3-bis(prop-2-ynyoxy)benzene

Experimental

Materials

1,3-Dihydroxybenzene, propargyl bromide, toluene and sodium hydroxide, and all of A.R. grade, were obtained from M/s E. Merck Ltd., Mumbai. The phase transfer catalysts used in this work were used as received from M/s Dishman Pharmaceuticals and Chemicals Ltd., Ahmedabad, India.

Method of Analysis

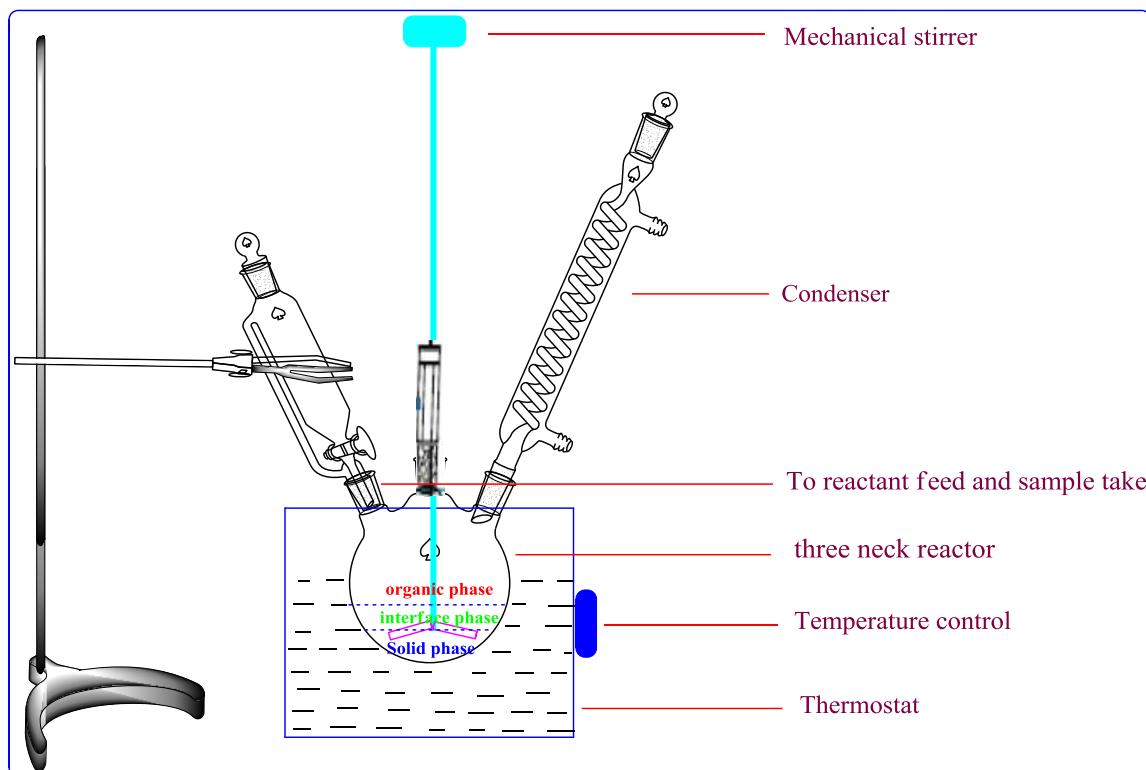
Experimental samples were taken at specific intervals of time and they were analyzed using GC technique. The kinetics was followed by estimating the amount of propargyl bromide (limiting reagent) that was disappeared and measured by a gas Chromatography (GC-Varian 3700 model). The analyzing conditions were as follows; Column, 30 m x 0.525 mm i.d. capillary column containing 100% poly(dimethyl siloxanen); injection temperature, 250 °C; FID detector (300 °C). Yields were determined from standard curve using biphenyl as an internal standard.

NMR Data: ^1H – NMR (δ ppm): 3.37 (C-H), 4.68 (CH₂), 6.38 to 7.39 Aromatic Protons. ^{13}C – NMR (δ ppm): 76.42 (C-H), 78.71 Propargyl Quaternary Carbon, 56.92 (CH₂), 159.61 Aromatic Quaternary Carbon,

100.42, 106.63, 130.74 (Aromatic C-H) Carbon values.

Kinetic procedure

The reaction was conducted on a 250 mL three-necked Pyrex round-bottom flask which permits agitating the solution, inserting the water condenser to recover organic reactant and also taking samples and feeding the reactants. This reaction vessel was supported at the centre of the water bath. The temperature was controlled at ± 2 °C by thermocouple using an electrically heated water bath. A suspension of 0.04 mol of disodium salt of 1,3-dihydroxybenzene was prepared in situ from 0.04 mol 1,3-dihydroxybenzene and 0.082mol sodium hydroxide by being heated in 20 mL toluene at 90 °C for 30 min . The total volume was made to 30mL by adding toluene. To start the reaction, 0.0015 mole of TBAB was introduced into the reactor. The reaction mixture was stirred at 1200 rpm and maintained at the desired temperature. The phase separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer at regular time intervals and analyzed by Gas chromatograph. The experimental set up was shown in scheme 2.



Scheme 2. Experimental set up for the solid-liquid PTC reaction

Results and discussion

The reactions were carried out pseudo-first order condition taking sodium hydroxide, 1,3-dihydroxybenzene as excess reagents and propargyl bromide as limiting reagent. The kapp values were obtained from the plot of $-\ln(1-X)$ versus time, where X is the concentration of reactant in the given time, t.

Effect of different phase-transfer catalysts and other catalysts

The conversion of propargyl bromide in the O-alkylation reaction between disodium salt of 1,3-dihydroxybenzene and propargyl bromide catalyzed by

various phase transfer catalysts are listed in Table 1. The controlled experiment is carried out with phase transfer catalyst which shows that there is no reaction without PTC. Tetra-n-butylammonium bromide (TBAB), benzyltriethylammonium chloride (BTEAC), tetra-n-butylammonium hydrogensulfate (TBAHS) were employed as phase transfer catalyst. In addition, with few phase transfer catalysts, triethyl ammine and potassium iodide were also used as catalysts, which has no activity on the O-alkylation reaction of phenol like compounds.

Table 1. The conversion of propargyl bromide under various PTCs and other catalysts (time 60, min.)

PTC	Structure	Catalyst loading (0.003 mol)	Conversion (%)
Controlled	\	\	0
KI	KI	0.003	0
Triethylamine		0.003	20
TBAB		0.003	98
BTEAC		0.003	97
TBAHS		0.003	94

Reaction condition: 0.04 mol of disodium salt of 1,3-dihydroxybenzene, 0.01 mol of propargyl bromide, 0.2 g of biphenyl, 50 mL of toluene, 0.0015 mol of catalysts, 50 °C, 1200 rpm, solvent toluene, time 60 min.

Effect of agitation speed on the conversion

To determine the effect of agitator speed on the above-mentioned reaction, the experiments were carried out at various range and Figure 1 shows the experimental results of the agitator speed effect on propargyl bromide conversion. Disodium salt of 1,3-dihydroxybenzene, which is in the solid phase, is added to the TBAB and toluene mixture; its dissolution is affected by the agitator speed because

of the enhanced mass transfer. Therefore, the increase in the active intermediate subsequently increases the reaction with propargyl bromide, which increases the conversion of propargyl bromide [9]. It can easily be observed from the figure that there is an increase in conversion from 78.21% to 98.09% as speed increases from 300 to 900 rpm, but beyond that the rise in conversion is very insignificant. Therefore, all further experiments were performed at 1200 rpm.

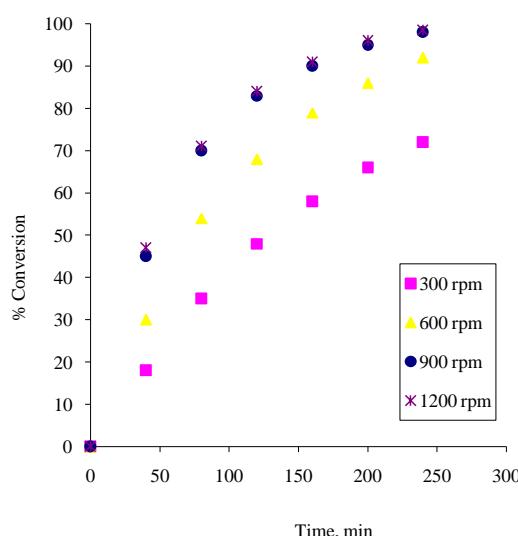


Figure 1. Effect of various stirring speeds on the conversion: 0.04 mol of disodium salt of 1,3-dihydroxybenzene, 0.01 mol of propargyl bromide, 0.2 g of biphenyl, 50 mL of toluene, 0.0015 mol of TBAB, 50 °C

Effect of reaction temperature

Generally, all the chemical reactions have influenced by temperature. But, PTC system requires mild condition thereby minimizing the side products formation. The effect of reaction temperature on the conversion was shown in Figure 2. It is clear that the reaction rate and conversion are both increased with increased temperature

[9-14]. The reason is the collision rate of reactants increased with increase in temperature. The activation energy (E_a) is 12.48 kcal/mol from the slope of the Arrhenius plot of $-\ln k_{app}$ versus $1/T$. The value of apparent activation energy shows that the solid-liquid reaction is under organic phase reaction control with agitation speed of 1200 rpm.

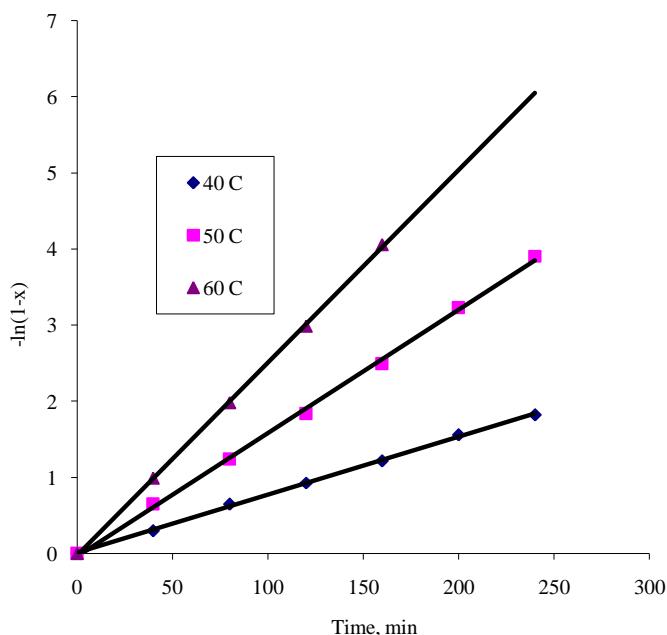


Figure 2. Effect of reaction temperatures on the conversion of propargyl bromide. 0.04mol of disodium salt of 1,3-dihydroxybenzene, 0.01 mol of propargyl bromide, 0.2 g of biphenyl, 50 mL of toluene, 0.0015 mol of TBAB, 1200 rpm.

Effect of amount of TBAB loading

Figure 3 shows the effect of various tetra-n-butylammonium bromide loading on the etherification reaction between the disodium salt of 1,3-dihydroxybenzene and propargyl bromide in 50 °C [14]. When the loadings of TBAB are 0.0005, 0.001, 0.0015, 0.002 and 0.003 mole, the conversion of propargyl bromide gradually increased from 72% to

99.6%, with prolonging the reaction time to 4h. When the tetra-n-butylammonium bromide loading increased to 0.002 and 0.003 mole, conversion of propargyl bromide gradually increased to 98% in 160 min and 98.5% in 120 min, respectively. With prolonging the reaction time to 4 h, the conversion slightly increased to 98.8% and 99.6%, respectively.

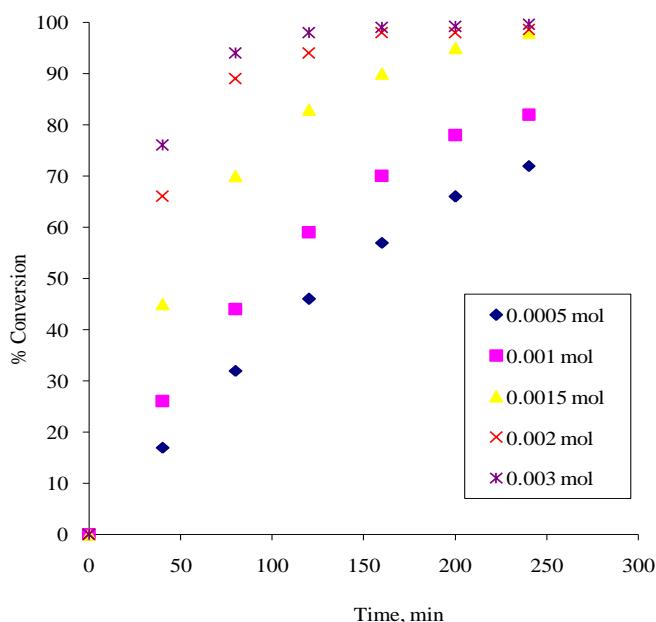


Figure 3. Effect of TBAB loading on the conversion of propargyl bromide: 0.04 mol of disodium salt of 1,3-dihydroxybenzene, 0.01 mol of propargyl bromide, 0.2 g of biphenyl, 50 mL of toluene, 50 °C, 1200 rpm.

Effect of organic solvent on the conversion

In this work, four solvents were applied to investigate the effect of their polarity and dielectric constant (ϵ) on the solid-liquid PTC reaction. From the Table 2, the reactivity of these solvents are acetophenone > o-dichlorobenzene >

chlorobenzene > toluene; It is clear from the results that the conversion increases with dielectric constant of the solvents. Toluene is chosen for all other experiments and the degradation of any organic solvent was not observed during or after the reaction.

Table 2. Effect of various organic solvents on the apparent rate constant

Solvents	Dielectric constant	Polarity	Kapp, min ⁻¹
Acetophenone	17.4	4.8	0.0254
o-dichlorobenzene	9.93	2.7	0.0236
Chlorobenzene	5.6	2.7	0.0204
Toluene	2.4	2.4	0.0163

Reaction condition: 0.04 mol of disodium salt of 1,3-dihydroxybenzene, 0.01 mol of propargyl bromide, 0.2 g of biphenyl, 50 mL of toluene, 0.0015 mol of TBAB, 50 °C, 1200 rpm.

Conclusion

In summary, the 1,3-bis(prop-2-ynyoxy)benzene was conveniently synthesized and investigated solid-liquid phase-transfer catalysis reaction

of 1,3-dihydroxybenzene and propargyl bromide in the presence of TBAB. Complete conversion of propargyl bromide could be obtained using moderate conditions. 100% selectivity

was observed in all the experiments. The factors affecting the conversion or reaction rate were studied. The results indicate that the solid-liquid interfacial mass transfer resistance is negligible at higher agitation speed above 900 rpm. Higher conversion was observed for tetra-n-butylammonium bromide among the other used catalyst. The conversion has linear relationship with increase in the temperatures and the reaction was well fitted into the pseudo-first order rate equation in these temperatures (40°C – 60°C). Which solvent has higher the dielectric constant shows higher reactivity regardless of polarity of solvent. Conversion of propargyl bromide is increased with increase in the tetra-n-butylammonium bromide loaded. Activation energy ($E_a = 12.48 \text{ kcal/mol}$) is calculated from the slope of the plot of Arrhenius plot.

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