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Synthesis of 1,4-bis (benzyloxy)Benzene Under Sonication and a Multi-Site Phase-Transfer Catalyst in Solid-Liquid Condition-Kinetic Aspects

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Abstract: ***The ultrasound assisted preparation of 1,4-bis(benzyloxy)benzene from the reaction of benzyl chloride (BC) and hydroquinone was carried out successfully using sodium hydroxide and catalyzed by a multi-site phase-transfer catalyst (MPTC) viz., 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2] octane dichloride in a solid–liquid reaction condition (SL-PTC). Water is only introduced in a trace quantity to the reaction system to avoid a serious hydration of sodium salt of hydroquinone in the reaction. The reaction is greatly enhanced in the solid–liquid system, catalyzed by multi-site quaternary ammonium salt (MPTC) and ultrasound irradiation (40 kHz, 300 W) in a batch reactor. The reaction mechanism is proposed and verified by examining the experimental evidence. A kinetic model is proposed in which a pseudo first-order rate law is sufficient to describe all the results.***

Keywords: Multi-site phase-transfer catalyst, ultrasound irradiation, solid-liquid reaction, 1,4-bis(benzyloxy)benzene, kinetics.

1. Introduction

Phase-transfer catalysis (PTC) is a powerful technique to promote the reaction between mutually immiscible reagents. PTC method was considered as a green chemistry procedure and it has been applied to over 600 industrial organic reaction processes [1], [2]. Generally PT Catalyst increases the reaction rates, product selectivity and yields and decreases the consumption of energy. Phase-transfer catalysts such as, quaternary ammonium, phosphonium salts, crown ethers, polyethylene glycols, and cryptands, have been used to carry out the reaction between the reactants, which exist in same or different phase(s) [3]-[8]. These catalysts were widely used in certain reactions viz. C-alkylation, O-alkylation, dichlorocarbene addition to double bonds, oxidation, reduction etc. Phase-transfer catalysis (PTC) can be divided into several categories, including liquid–liquid, solid–liquid, gas–liquid, liquid–liquid–solid, and liquid–liquid–liquid types. In which, the liquid-liquid phase-transfer catalysis is most commonly employed by PTC researchers.

The important considerations in the selection of the catalyst are economy of scale and efficiency of the phase transfer catalysts specifically on the industrial-scale preparation of organic substrates. In order to satisfy these needs, ‘‘multi-site’’ phase transfer catalysts (MPTCs) have been developed. The MPTCs offer the potential of providing greater PTC activity and, to effect a particular synthetic transformation under mild conditions. It is due to the presence of many active sites in the MPTC and generally it form many active intermediate (either two or more than two) and carry the active intermediate into the reaction medium per cycle in contrast to single site phase-transfer catalyst which transports only one active species per cycle.

The syntheses of MPTC derived from tertiary amines have been attracted much attention, and numerous efforts have been paid to develop the new multi-site phase-transfer catalysts for PTC catalytic methodology [9]-[14], which shows enormous catalytic activity over single-site PTC methodology. Very recently many reports in the literatures containing MPTC reveals that most of researchers are interested in the synthesis of MPTCs and explore their catalytic activity for various reactions. Many multi-site phase-transfer catalysts are reported for etherification [9], etherification [10], N-alkylation [11], dichlorocarbene addition [12], [13] and polymerization [14] reaction.

In general, ethers are one of the highest added-value chemicals that extensively used by various industries as the additives for petroleum chemicals and extractants [15]-[17]. Therefore, the potential value of the quaternary ammonium catalyst for Williamson synthesis of ethers and its versatility in the synthesis of all the ethers established after the development of phase-transfer catalysis [18],[19]

Ultrasound irradiation in a liquid medium can induce acoustic cavitation under specific experimental conditions. The mechanism of sonochemical effects was always of interest and centered on the idea that the collapse of acoustic cavitational bubbles would give rise to so-called ‘‘hotspots” of energy [20]-[22]. Ultrasonic irradiation in the liquid-liquid heterogeneous system can increase interfacial area coupled with local hot-spot generation, and has been resulted in the enhanced rate of the reaction [23], [24].

Ultrasonic irradiation combined with liquid-liquid PTC has enhance the formation of catalytic intermediate and thus, the rate of reaction is increased. In addition, MPTC combined with sonication reveals, the overall rate of the reaction effectively increased.

In this research contribution, we have focused on the synthesis of 1,4-bis(benzyloxy)benzene under solid-liquid condition in the presence of both multi-site phase-transfer catalyst (MPTC) and ultrasonic irradiation (40 kHz, 300 W) using sodium hydroxide as base.

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2. Experimental

2.1. Materials

All the reagents, including 1,4-diazabicyclo[2.2.2]octane, 1,4-dihydroxybenzene, benzyl chloride (BC), biphenyl, tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrahexylammonium bromide (THAB) and tetraoctylammonium bromide (TOAB), sodium hydroxide, n-hexane, toluene, chlorobenzene, anisole, diethyl ether and other reagents for synthesis were guaranteed grade (GR) chemicals and were used without further purification.

2.2. Instrumentation

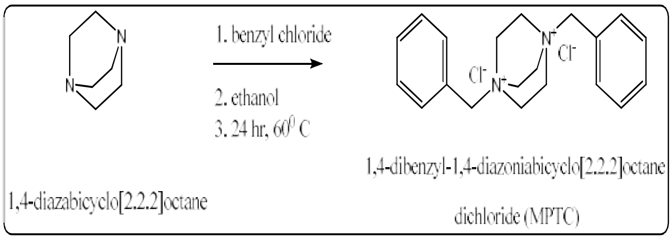
^{1}H NMR and ^{13}C spectra were recorded on a Bruker 300 MHz and 75 MHz respective using TMS as an internal standard. Gas chromatography was carried out using a GC-Varian 3700 model. Ultrasonic water bath, Equitron, Media Instrument Manufacturing Company, Chennai, India-600 004. The ultrasonic generator was a thermostatic bath equipped with dual frequencies (28/40 kHz) and electric power 300 W with 0.0126 W/mL of power density. Details of ultrasonic process equipment are well explained in our previous report [11].

3. Synthesis of multi-site phase-transfer catalyst (MPTC)

A mixture of 1,4-diazabicyclo[2.2.2]octane (DABCO, 5 g, 44.58 mmol), benzyl chloride (14.11 g, 111.43 mmol) and 80 mL of ethanol was placed in a 250 mL three necked round bottomed Pyrex flask. The reaction was carried out at 60°C for 30 hours and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and onium salt, i.e., 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride, (MPTC) was washed with n- hexane (4 x 25 mL). The colorless solid was stored in $CaCl_2$ desiccators. Yield: 92% (Scheme 1) [25].

1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride, (MPTC) :
^{1}H NMR (D_2O): 4.075 (s, 6H, **cyclic-H**), 5.055 (s, 2H, **benzyl-H**), 7.346-7.438 (m, 5H, **Ar-H**).
^{13}C NMR (D_2O): 65.13 (**cyclic –C**), 69.46 (**benzyl-C**), 124.92, 126.22, 130.86, 133.55 (**Ar-C**).
Elemental analysis: calculated: C-65.78, H-7.20, Cl-19.45, N-7.69; Found: C-65.75, H-7.17, Cl-19.41, N-7.67.

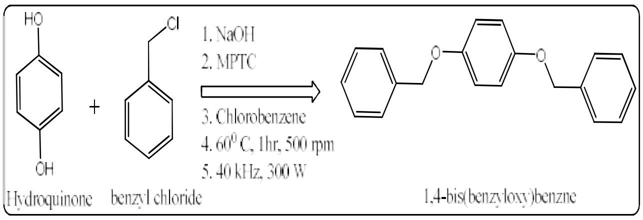
Scheme 1
Synthesis of MPTC



4. Synthesis of 1, 4-bis (benzyloxy) benzene

To the well powdered NaOH (8g) in trace amount of water, the 1,4-dihydroxybenzene (5g, 45.41mmol) was added under overhead stirring for few minutes to generate the 1,4-dihydroxybenzene anion. Then benzyl chloride (2.53g, 19.98mmol) and the newly synthesized MPTC (0.2 g) in chlorobenzene (30 mL) were added slowly. The reaction mixture was heated at 60^{o}C for 3 hours with vigorous stirring. The product formed was evidenced by Thin Layer Chromatography (TLC). The crude product was isolated by simple extraction with ethyl acetate (3 x 25 mL). The organic layer was collected and the solvent was evaporated under reduced pressure. The crude product was subjected to chromatography (SiO_2) employing hexane: ethyl acetate (9:1, v/v) as an eluent to obtain a pure monoderivative (1,4-bis(benzyloxy)benzene; Scheme 2) in the form of light yellowish liquid. The identity of the product was confirmed by ^{1}H NMR and ^{13}C NMR spectra of the product. ^{1}H NMR (300 MH$_Z$, $CDCl_3$): δ5.091 (s, 4H, Aliphatic-**H**), 7.173-7.194 (d, 4H, Ar-**H**), 7.198-7.391 (m, 10H, Ar-**H**) and ^{13}C NMR (75 MHz, $CDCl_3$): δ 70.71 (Aliphatic-**C**arbon**)**, 117.30, 127.16, 128.53, 129.14, 141.65, 150.05 (Ar-**C**arbon); Elemental analysis: Calculated: C, 82.76%; H, 6.29%;O, 11.06%; and Found: C, 82.73%; H, 6.25%; O, 11.02%.

Scheme 2
Synthesis of 1,4-bis(benzyloxy)benzene



5. Reaction Mechanism and Kinetic Model

Only a small amount of product was obtained when the reaction is carried out in a liquid–liquid two-phase condition, even in the presence of quaternary ammonium salt. It is due to serious hydration of sodium salt of 1,4-dihydroxybenzene. Therefore, small amount of water added to the reaction system in order to minimize the loss of reactant due to hydration. The reaction mechanisms of the solid–liquid phase-transfer catalysis can be classified as the non-soluble system (heterogeneous solubilization) and soluble system (homogeneous solubilization), which depend on the solubility of the inorganic salt of anion in the organic solvent. In this work, sodium salt of 1,4-dihydroxybenzene is sparingly soluble in organic solvent (chlorobenzene). First, sodium salt of 1,4-dihydroxybenzene dissolved in the organic solvent with the addition of quaternary ammonium salt. Phase-transfer catalyst (MPTC) Q^{2+} $(Cl^-)_2$ would react with Ph $(O^-Na^+)_2$ to form Q^{2+} (Ph $(O^-)_2$) in the solid–liquid interface. Then the formed Ph $(O^-Q^+)_2$ transfers from the solid–liquid interface to the bulk organic phase where it reacts with benzyl chloride(BC) and produce the desired product (1,4-bis(benzyloxy)benzene, Scheme 3) and The inorganic salt NaX precipitated as a solid form in the organic solution.

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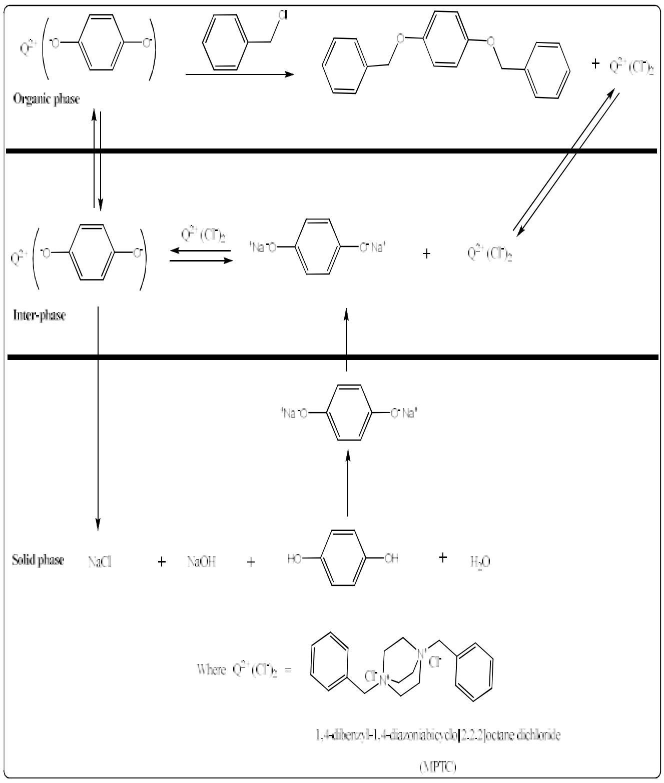
Scheme 3
Mechanism



5.1. Definition

The conversion (X) of benzyl chloride (BC) is defines as follows:

$X=1-\{[BC]_0/[BC]_{.o,i}\}$ 1

Where $[BC]_o$ and $[BC]_{o,i}$ represent the concentration of benzyl chloride at time (t) t=0 and t>0, respectively.

5.2 Rate expression

The rate expression for this reaction may be expressed as;

$-r_{BC} = k_{app} [BC]_o$ 2

Where k_{app} is the apparent reaction rate constant. This reaction is carried out in a batch reactor, so the diminution rate of BC with time (t) can we expressed as

$-d[BC]_0 / dt = -r_{BC} = k_{app} [BC]_{o,i}$ 3

On integrating the Eq. (3) yields:

$-\ln\{[BC]_0/[BC]_{.o,i}\} = -\ln(1-X) = k_{app}\, t$ 4

Using Eq. (4), we can get the k_{app} value experimentally by plotting –ln (1-X) against time, (t).

6. Results and Discussion

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 taking samples and feeding the reactants. This reaction vessel was supported at the centre of the sonicator. Known quantities of chlorobenzene (30 mL, solvent), sodium hydroxide (8g in 2mL water) and 0.2 g biphenyl (IS-internal standard) were introduced into the reactor. Then, 5g of 1,4-dihydroxybenzene (45.41mmol) and 2.53g of benzyl chloride (19.98mmol), 0.2g of the newly synthesized MPTC were introduced to the reactor to start the reaction. The reaction mixture was stirred at 500 rpm. The phase separation was almost immediate on arresting the stirring process. Samples were collected from the organic layer of the mixture at regular time intervals. A pinch of anhydrous $CaCl_2$ was placed in the sample vials to absorb any moisture present in the organic layer. The kinetics was followed by estimating the amount of benzyl chloride (limiting reagent) that 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, 250^0C; FID detector (300^0C). Yields were determined from standard curve using biphenyl as an internal standard.

6.1 Effects of Stirring Rate

To study the influence of agitation speed on the rate of benzyloxylation of 1,4-dihydroxybenzene, the speed of agitation was varied in the range of 0-500 rpm along with ultrasound irradiation (40 kHz, 300 W) using 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride (MPTC). In principle, the heterogeneous reaction is highly dependent to the agitation speed. As shown in Table-1, that the rate of the reaction increases linearly as the agitation speeds increased from 0 to 250 rpm. After increasing the speed of agitation there is no remarkable improvement in the reaction rate. This result suggested that the reaction is carried out in a solid–liquid phase under sonication. In fact, the reaction proceeds by accompanying with dissolving the Ph $(O^-Na^+)_2$ in chlorobenzene. The dissolving rate of Ph $(O^-Na^+)_2$ in chlorobenzene is highly influenced by the agitation speed. In general, a high concentration of Ph $(O^-Na^+)_2$ dissolving in organic solvent is obtained at a high agitation speed. Therefore, the conversion of benzyl chloride was increased with the increase in the agitation speed up to 250 rpm. For agitation speeds higher than 250 rpm, the conversion is influenced almost not at all by the agitation speed [11], [26]. This portrays that there is no mass-transfer resistant after 250 rpm and verifies that the reaction of Ph $(O^-Na^+)_2$ and benzyl chloride was carried out in a homogeneous solution, i.e. Ph $(O^-Na^+)_2$ first dissolves gradually in chlorobenzene and then reacts consecutively with benzyl chloride. The purpose of stirring is to provide a well mixing to dissolve Ph $(O^-Na^+)_2$ in the chlorobenzene in the presence of MPTC to form Q^{2+}(Ph $(O^-)_2$). Then, the dissolved Q^{2+}(Ph $(O^-)_2$) reacted with benzyl chloride to produce 1,4-bis(benzyloxy)benzene in the homogeneous solution. The k_{app} values indicate that the mechanical effects brought up by the use of low frequency ultrasounds are responsible of the enhancement of the kinetics by harsh mixing, enhancement of mass transfer and in solid-liquid systems, high erosion of the solid particles occurs and consequently the surface area is increased. The agitation speed was set at 500 rpm for further kinetic study. Some individual experiments are carried to find out the efficiency of sonication over conventional method. The results are,

(i) The reaction was carried out in conventional method; the observed k_{app} value is 7.1 x 10^{-3}, min^{-1}).

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(ii) The reaction was carried out in conventional method (stirring only); the observed k_{app} value is 5.3 x 10^{-3}, min^{-1}).

(iii) In the presence of both ultrasonication (40 kHz, 300 W) and stirring (500 rpm), the observed k_{app} value is 24.63 x 10^{-3}, min^{-1}).

(iv) It is clear that, the rate constant for the combination of stirring and sonication is approximately 3.5 times higher than the rate constant obtained for the conventional one.

Table 1: Effect of stirring speed

Stirring speed (rpm)	k_{app} x 10^3, min^{-1} (40 KHz, 300 W)
0	5.30
50	8.52
100	12.18
150	16.40
200	20.23
500	24.65
300	24.80
350	25.05
400	25.15
450	25.35
500	25.41

Table 1: Effects of stirring speeds: 8g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride, 0.2g of MPTC, 30mL of chlorobenzene, 60^0 C; ultrasound condition (40 kHz, 300 W).

6.2 Effect of the amount of newly prepared MPTC

The influence of the amount of MPTC (viz., 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride) on the arylation of 1,4-dihydroxybenzene has been studied by varying amount of MPTC from 0.1g to 0.3g with respect to benzyl chloride (BC) under ultrasound irradiation (40 kHz, 300 W) keeping other experimental parameters as constant. As shown in Figure 1, the rate of conversion is increased with increasing in the amount of MPTC along with ultrasound irradiation (40 kHz, 300 W). The increase in the k_{app} value is attributed to the synergic effect of ultrasound might be enlarged [26]. The reaction rate or conversion is increased with increasing the usage of MPTC up to 0.2g and then there is no remarkable increase in conversion even increasing the catalyst amount. It revealed that more catalyst resulted in much faster initial reaction rate, leads to more inorganic salt produced and deposited on the particle surface, hence reducing the contact of the catalyst and the solid reactant, and hence the reaction rate was quickly diminished and terminated in the late reaction period (>40 min) with slight deviation to pseudo-first-order kinetics. Therefore, all the further experiments were done at 0.2g of catalyst concentration. The small amount of water (trace) can efficiently promote the solubilization of the solid reactant and thus enhance the formation of catalytic intermediate $[Q^{2+}(Ph(O^-)_2)]$.

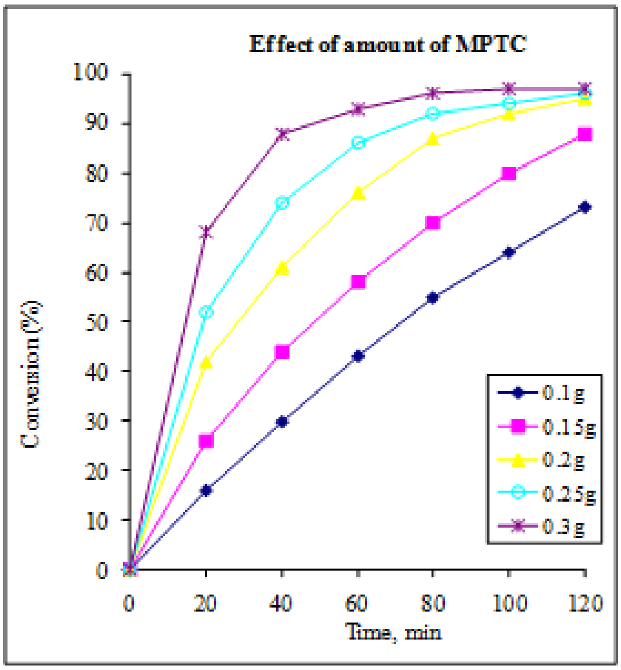

Figure 1: Effect of the amount of MPTC: 8g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride, 30mL of chlorobenzene, 500 rpm, 60^0 C; ultrasound condition (40 kHz, 300 W).

6.3 Effect of the concentration of benzyl chloride

To investigate the influence of benzyl chloride (BC) on the kinetics of synthesis of 1,4-bis(benzyloxy)benzene under ultrasonic irradiation condition (40 kHz, 300 W), the amount of benzyl chloride (BC) was varied from 2g to 3g. The results are shown in Table-2. The data clearly indicates that the k_{app} value increases with increasing the amount of benzyl chloride (BC). This observation due to presence of more number of active sites in the MPTC and higher concentration of substrate (BC) had co-operatively influence the reaction and thus enhance the more number of contacts between catalyst and substrate (BC), and hence it is reflected in enhanced K_{app} values. In addition ultrasound also enhance the rate of the reaction [26], [27], it may be due to reduces the surface area between the solid and organic phase, and hence more reactants collide to each other simultaneously we get higher k_{app} value.

Table 2: Effect of amount of benzyl chloride

Benzyl chloride (BC), g	k_{app} x 10^3, min^{-1} (40 kHz, 300 W)
2	17.43
2.25	21.52
2.50	24.65
2.75	29.30
3	32.78

Table 2: Effect of amount of benzyl chloride (BC): 8g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 0.2g of MPTC, 30mL of chlorobenzene, 500 rpm, 60^0 C; ultrasound condition (40 kHz, 300 W).

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6.4 Effect of temperature

For the temperature effect, the temperature was varied from 313 K to 353 K (Figure 2) keeping other similar operating conditions on the reaction of 1,4-dihydroxybenzene with benzyl chloride. The kinetic profile of the reaction is obtained by plotting -ln (1-X) versus time. It is obvious that the reactivity is increased with an increase in the temperature along with ultrasonic effect [28]. The reason is that the number of reactant molecules which possess higher activation energy at a higher temperature and thus the ultrasonic wave easily passes through the reactor [29], [30]. The other point is that the collision of the reactants at higher temperature is also increased. Hence, the apparent rate constant is increased at higher temperature. Arrhenius plots were made in Figure 5 of $–\ln k_{app}$ against 1/T to get activation energy o f 46.96 $kJ.mol^{-1}$. This high activation energy demonstrates that this ultrasound assisted Solid-Liquid reaction with multi-site phase-transfer catalyst (MPTC) was controlled and the mass-transfer resistance between phases was unimportant under ultrasonic irradiation. Hence, we proposed an interfacial mechanism for our present study [27], [31], [32].

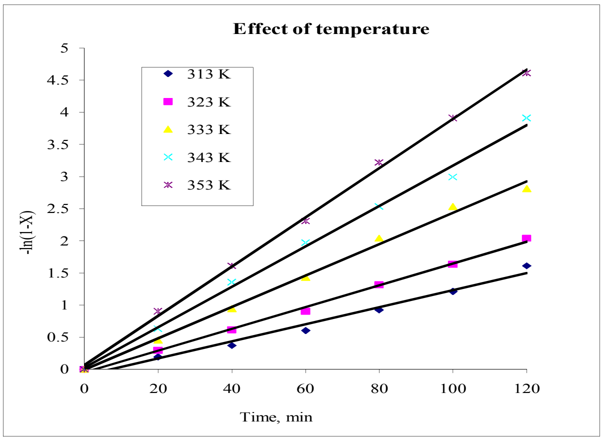


Figure 2: Effect of temperature: 8g of NaOH in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride, 0.2g of MPTC, 30mL of chlorobenzene, 500 rpm, and ultrasound condition (40 kHz, 300 W).

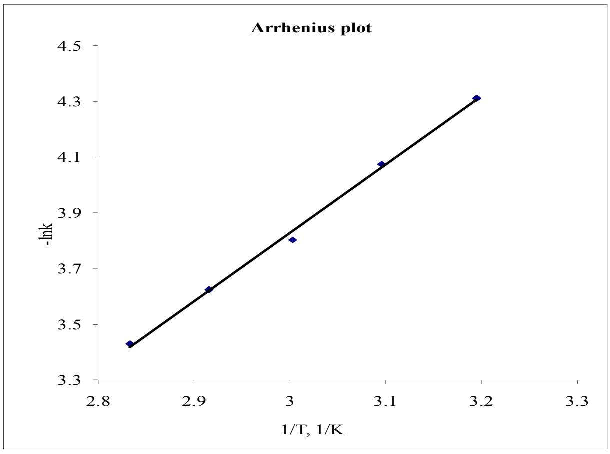


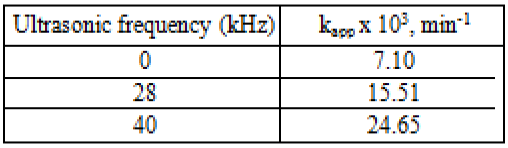
Figure 5: Arrhenius plot; 8g of NaOH in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride, 0.2g of MPTC, 30mL of chlorobenzene, 60^0 C, 500 rpm, ultrasound condition (40 kHz, 300 W).

6.5 Effect of variation of ultrasonic frequencies

Ultrasonic irradiation is defined as acoustic waves which are produced from low frequency high power ultrasound (20 kHz -100 MHz) [33], [34]. They create cavities which are the formation, growth and implosive collapse irradiated with sound [34]. The low ultrasonic frequency induces high powerful liquid-jet due to the higher time for bubble growth and in solid-liquid system, ultrasonic frequency affects the surface morphology of the particulate phase from the impact of liquid-jet and hot-spot generated by ultrasonic wave [35]. It has been reported that a combination of PTC and ultrasound is often better than either of the two techniques alone [36]. Many reported PTC works revealed that multi-site phase-transfer catalyst (MPTC) combined with ultrasound shows the highest potential to increase the rate of the reaction or conversion [35], [37].

To study the effect of ultrasound frequency, two different ultrasonic frequencies (28 kHz, 40 kHz) is used having the same output power of 300 W. The reaction is also carried out without ultrasound (conventional method). The mass-transfer resistant plays an important role in interfacial reaction although the use of ultrasound increases the mixing of the two phases [37]. The kinetic profile of the reaction is obtained by plotting –ln (1-X) against time. In our experimental condition at 30 minutes, without ultrasonic irradiation (silent condition) the k_{app} values is 7.10 $x10^{-3}$, min^{-1} but in the presence of ultrasonic condition the k_{app} values are 15.51 x 10^{-3}, min^{-1} and 24.65 x 10^{-3}, min^{-1} for 28 kHz (300 W) and 40 kHz (300 W), respectively (Table-3). Hence, the overall k_{app} was increased by increasing the ultrasonic frequency in the order of 0 kHz (conventional method) <28 kHz (300 W) <40 kHz (300 W) for our system (Table 3) .Similar trend was observed by Entezari et al [38], [39].

Table 3: Effect of ultrasonic frequency



Ultrasonic frequency (kHz)	k_{app} x 10^3, min^{-1}
0	7.10
28	15.51
40	24.65

Table 3:Influence of ultrasonic frequencies: 8g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride,0.2g of MPTC, 30mL of chlorobenzene, 500 rpm, 60^0 C;

6.6 Effect of organic solvents

The influence of various organic solvents on the rate of arylation of 1,4-dihydroxybenzene was followed under otherwise standard reaction conditions. The four different solvents are used to find out the k_{app} value. The polarity of organic solvent affects the dissolution of solid reactant anion in organic solvent. With adding 2 mL of water, the more polar solvent induced the higher activity of phase-transfer catalyst, because a higher content of (Ph $(O^-Q^+)_2$) was acquired. From the plot of –ln (1-X) against time, the k_{app} values are obtained. From the Table-4, chlorobenzene possesses a higher k_{app} value among the five organic solvents.

Table 4: Effect of organic solvents

Solvent	Dielectric constant (ε ª)	$K_{app} \times 10^3$, min^{-1}
Chlorobenzene	5.6	24.65
Anisole	4.3	20.85
Toluene	2.4	18.41
Hexane	2.2	8.5

Table 4: Influence of organic solvents: 8g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride, 0.2g of MPTC, 30mL of chlorobenzene, 500 rpm, 60^0 C; ultrasound condition (40 kHz, 300 W).

6.7 Effect of volume of chlorobenzene

In a homogeneous reaction, the reaction follows the intrinsic kinetic law. The conversion or the reaction rate is directly proportional to the concentration of the reactants in 120 min of reaction. A dilute concentration of the reactant is obtained using a large amount of organic solvent. The conversion of benzyl chloride is increased with the decrease in the volume of chlorobenzene. Figure 3 shows the dependence of the % conversion on the volume of chlorobenzene. The k_{app} value is inversely proportional to the volume of chlorobenzene, as expected.

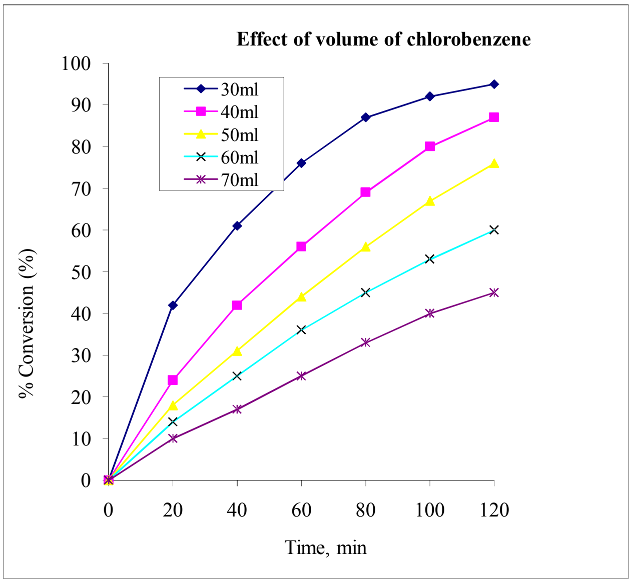


Figure 3: Effect of volume of chlorobenzene: 8g of NaOH in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride, 0.2g of MPTC, 60^0 C, 500 rpm, ultrasound condition (40 kHz, 300 W).

6.8 Effect of MPTC and single-site phase-transfer catalysts

Quaternary ammonium salts are generally used as phase-transfer catalysts to promote reaction rate. Several phase-transfer catalysts were employed in addition with MPTC to evaluate their efficacy in the reaction of benzyl chloride with 1,4-dihydroxybenzene at 60^0 C and 500 rpm under ultrasonic condition (40 kHz, 300 W). These five phase-transfer catalysts were tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrahexylammonium bromide (THAB) and tetraoctylammonium bromide (TOAB). Table 1 depicts the apparent rate constants for these five catalysts. Among these, MPTC shows higher reactivity due to it posses dual-active sites and it coordinated with the anion $(Ph(O^- Na^+)_2$ and form the active intermediate $Q^{2+}((Ph(O^-)_2)$ in the interface, which is more organophilic in nature therefore it is frequently transferred to the bulk organic phase where the intrinsic reaction take place [23], [24]. The above said process is continued up to limiting reagent disappeared. Therefore, the conversion is as fast as compared with other single site PTC's [11]. In general, a more oleophilic cation is more effective to transfer anions into the organic phase. Therefore, the order of catalytic reactivity are MPTC > TOAB > THAB > TBAB > TBAC. In addition, the role of counter anion is also important. Comparing the results for TBAB, TBAC and TBAI, the order of the reactivity of these anions is $I^- > Br^- > Cl^-$. Since softer and more oleophilic anions are more effective than harder and less oleophilic anions, the order of catalytic reactivity is TBAI > TBAB> TBAC. In general, the iodide of a quaternary cation is a co-catalyst, forming benzyl iodide in situ and rapidly which is more reactive than the benzyl chloride.

Table 5: Effect of MPTC and phase-transfer catalysts

PTC (g)	$k_{app} \times 10^3$, min^{-1} (40 kHz, 300 W)
MPTC	24.65
TOAB	21.22
THAB	19.42
TBAI	17.61
TBAB	16.16
Aliquat 336	12.53
TBAC	11.62

Table 5: Effect of various PTC's: 8g of NaOH, in 2mL H_2O, 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride, 30mL of chlorobenzene, 500 rpm, 60^0 C; ultrasound condition (40 kHz, 300 W).

6.9 Effect of various sodium hydroxide concentrations

In general, in PTC catalyzed reactions, base has the subtle influence in the rate of the reaction. The formation of 1,4-dihydroxybenzene anion depends on the amount of the sodium hydroxide in addition with water. Kinetic experiments were carried out, by employing 4 to 16g of NaOH (keeping 2mL water constant) under otherwise similar reaction conditions. The good conversion rate was obtained under 8g NaOH in 2 mL water. The kinetic profile of the reaction is obtained by K_{app} against amount of NaOH. The k_{app} values tremendously increased with increasing in basicity of OH^- ion (Figure 4). It suggest that the hydroxide ions which are less solvated by water molecules and there by the k_{app} value increases [40], [41].

In solid–liquid system, the addition of small amount of water can be useful in forming the catalytic intermediate for conducting intrinsic reactions. To study the effect of volume

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of water, the volume of water is varied as 1 mL, 2mL, 3mL and 8mL keeping 8g NaOH as constant. When the volume of water increases the conversion rate decreased and the system converted to the liquid-liquid system when the 8 mL water added to the 8g base. The increase in the reaction rate with small amount of water was mainly due to effectively involve in the production of $Q^{2+}(Ph(O^-)_2)$ without the hydration in the inter-phase, thus enhancing the intrinsic reaction rate. When more water was added, the effective concentration of $Q^{2+}(Ph(O^-)_2)$ in the inter-phase would be decreased and the reaction rate was reduced [42].

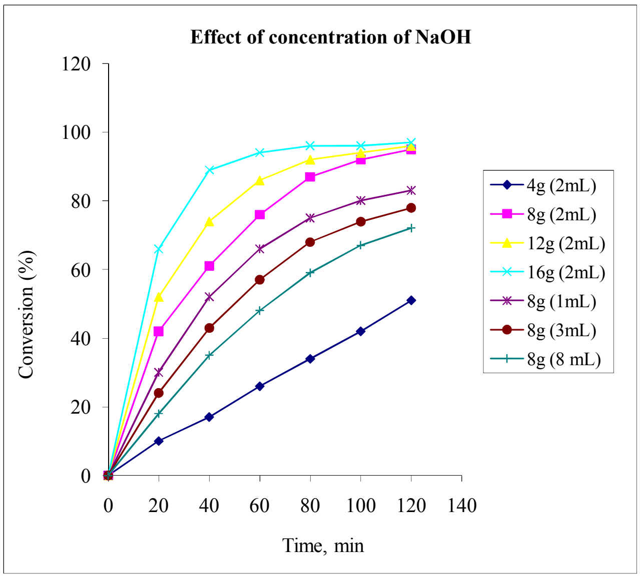

Figure 4: Effect of NaOH concentrations: 0.2g of biphenyl (internal standard), 45.41mmol of 1,4-dihydroxybenzene, 19.98mmol of benzyl chloride, 0.2g of MPTC, 30mL of chlorobenzene, 60^0 C, 500 rpm, ultrasound condition (40 kHz, 300 W).

7. Conclusion

From this research contribution, the results are as follows
(i) The ether 1,4-bis(benzyloxy)benzene was successfully synthesized as single spot from the reaction of 1,4-dihydroxybenzene and benzyl chloride under ultrasonic-MPTC condition.
(ii) The synthesized MPTC's catalytic activity was well explored with many PTC for the etherification reaction.
(iii) The reaction mechanism and the apparent rate constants were obtained from the experimental results, the apparent rate constants are found to be directly dependent on each kinetic variables, viz., concentration of MPTC, concentration of NaOH, ultrasonic frequencies, stirring speed and temperature.
(iv) However it decreases with increase in the volume of water and volume of chlorobenzene.
(v) Combination of MPTC and Sonication shows higher potential than individual one.
(vi) Activation energy was calculated from the Arrhenius plot.

8. Acknowledgments

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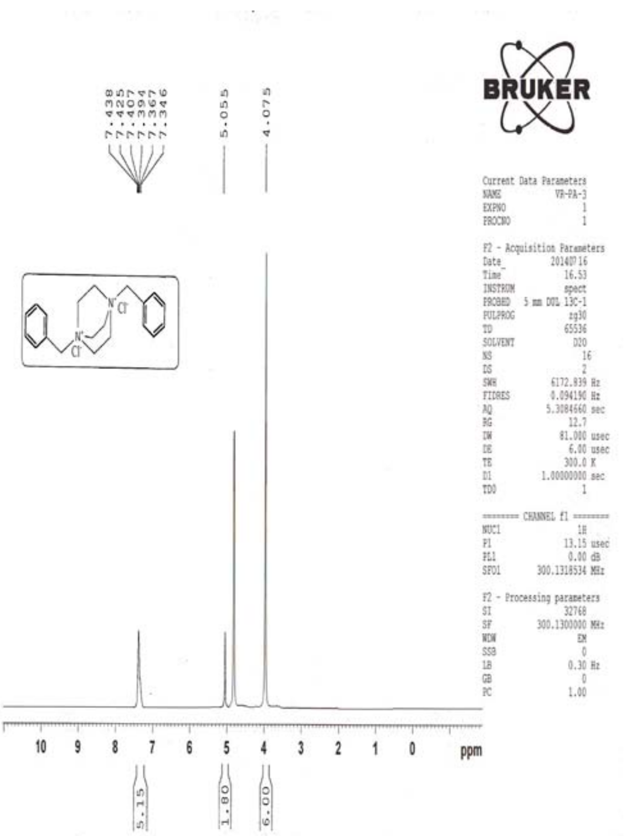
Supporting information

^{1}H NMR spectra of 1,4-dibenzyl-1,4-diazoniabicyclo[2.2.2]octane dichloride (MPTC)



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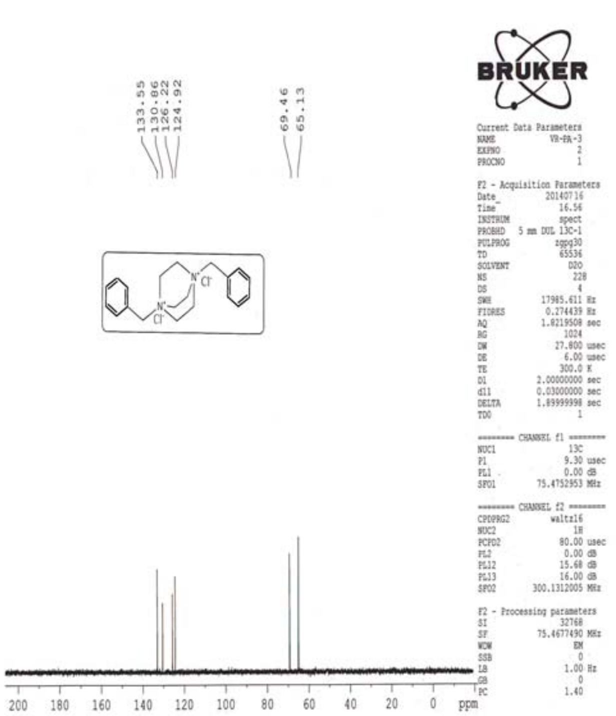

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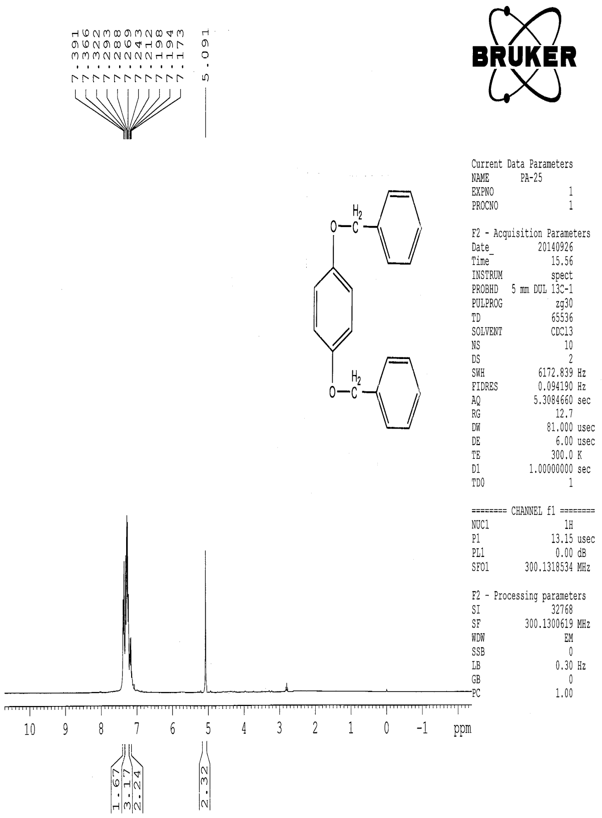

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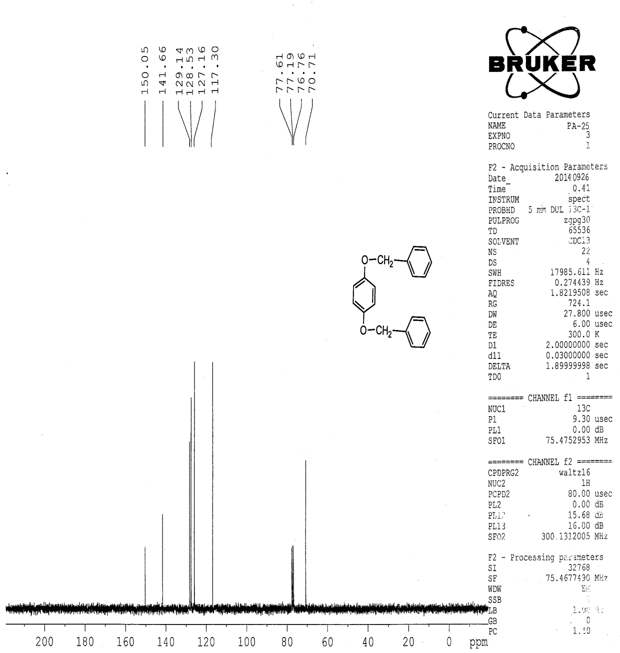

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PL13                 16.00 dB
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