

Dichlorocarbene Addition of N-Vinylimidazole under Ultrasound Assisted a New Multi-Site Phase-Transfer Catalyst - A Kinetic Study

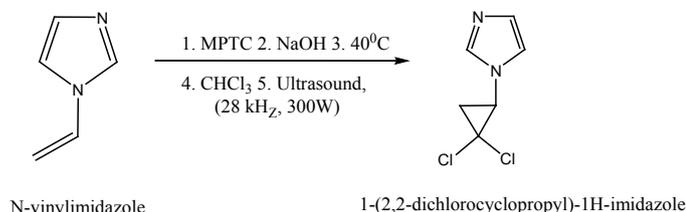
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Abstract

The kinetics for dichlorocyclopropanation of N-vinylimidazole with an excess of chloroform has been studied under multi-site phase-transfer catalyst and ultrasound irradiation conditions using aqueous sodium hydroxide as the base. The reaction was carried out at 40°C and a pseudo-first order rate is used to describe the reaction rate at high alkaline concentration (>30 wt.%). Kinetics of the reaction including the effects of the reaction conditions on the conversion of N-vinylimidazole was investigated. A rational explanation was made for a peculiar phenomenon that the conversion of N-vinylimidazole was increased and then decreased with an increase in the amount of sodium hydroxide and the kapp value increases with increasing other kinetic parameters that is the amount of multi-site phase-transfer catalyst, viz., N,N'-dihexyl-4,4'-bipyridinium dibromide, concentration of substrate, ultrasonication, stirring speed, temperature, etc.



Keywords: N-Vinylimidazole; Ultrasonic irradiation; Dichlorocyclopropanation; 1-(2,2-Dichlorocyclopropyl)-1H-Imidazole; MPTC.

Introduction

The reactions between mutually insoluble reactants can be effectively carried out by phase-transfer catalysis (PTC) which has been widely applied for the production of pharmaceuticals, agricultural chemicals, flavorants, dyes, perfumes, and environmental processes, etc. As the application of PTC grew, much effort was placed on the development of phase-transfer catalysts with higher catalytic efficiency. To this end, researchers have developed "multi-site" phase-transfer catalyst (MPTC). Recently, the catalytic behavior of multi-site phase-transfer catalysts have attracted much attention, due to the fact that multiple molecules of the aqueous reactant can be carried into the organic phase once a cycle, thus the catalytic efficiency is enhanced [1-5]. The application of ultrasound waves in chemistry was viewed as a merely convenient technique [6]. Many studies have been carried out and it is well documented that the advantages of ultrasound procedures are good yields, short reaction times and mild conditions [6-8]. No direct interaction is possible between ultrasound and matter, and so an indirect phenomenon, i.e., capitation must be facilitated to induce a reaction. Hence, ultrasound irradiation method [9-12] is now recognized as viable environmentally benign alternatives [9-15]. Although sonication methods have been initially applied to homogeneous reactions in a variety of solvents, this approach has now evolved into a useful technique in heterogeneous reactions [16-19].

In recent years, the application of ultrasound irradiation in organic synthesis has been broadly extended. It can increase the rate of reaction, yield and selectivity of desired product under very milder condition [6]. Hence, ultrasound technique has been considered as a convenient and environmentally benign technique [11,14]. Several studies have

been already reported, in which it is observed that the combination of Phase-transfer catalysis (PTC) with ultrasound is proved to be an effective technique for organic transformations compared to that at silence condition [20-25]. The Cannizarro reaction catalyzed by a PTC under ultrasonic condition showed that an ultrasonic wave of 20 kHz dramatically accelerated the rate of the reaction [26]. Wang et al. investigated the liquid-liquid multi-site phase-transfer catalyzed epoxidation and dichlorocyclopropanation of 1,7-octadiene and ethoxylation of p-chloronitrobenzene assisted by ultrasound energy, the reaction rates were greatly enhanced in all the reactions [27-29]. Ultrasound irradiation combined with liquid-liquid phase-transfer catalysis (LLPTC) has shown significant improvement in the reaction rate, but its application in LLPTC by dual-site phase-transfer catalyst was rarely reported. In general, the LLPTC system performed under ultrasound irradiation either in batch reactor or in continuous two phase flow reactor exhibited enhancement in overall reaction rate, compared to that of silence condition [30] due to mass transfer and effective mixing.

For the first time, we are evaluating the influence of ultrasound in association with a new multi-site phase-transfer catalyst viz.,

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N,N'-dihexyl-4,4'-bipyridinium dibromide (MPTC) on the synthesis of 1-(2,2-dichlorocyclopropyl)-1H-imidazole by dichlorocarbene addition of N-vinylimidazole as a limiting agent. We followed the kinetic study of dichlorocarbene addition of N-vinylimidazole using MPTC as catalyst under ultrasonic irradiation condition (28 kHz, 300W). Further, to the best of our knowledge, there is no literature reports regarding dichlorocyclopropanation of N-vinylimidazole with chloroform under MPTC – ultrasonication (denoted as “))))”).

Experimental

Chemicals

The reagents were used as received (SRL): N-vinylimidazole, chloroform, diethyl ether, sodium hydroxide, tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), tetrabutylammonium hydrogen sulphate (TBAHS), n-hexyl bromide, 4,4'-bipyridine (Aldrich) and other reagents for synthesis were guaranteed grade (GR) chemicals and were used as received without further purification.

Instrumentation

The FT-IR spectra were recorded on a Bruker-Tensor 27 FT-IR spectrophotometer. The ¹H NMR and ¹³C NMR spectra were recorded using Bruker 400 MHz and 100 MHz respectively using TMS as an internal standard. Gas chromatography was carried out using a GC-Varian 3700 model. Elemental analysis was performed on a Perkin-Elmer 240B elemental analyzer. The ultrasonic water bath, Equitron, Media Instrument Manufacturing Company, Chennai, India-600 004.

Synthesis of multi-site phase-transfer catalyst

A mixture of 1.56 g (10 mmol) of 4,4'-bipyridine, 15 mL of n-hexylbromide, and 60 mL of ethanol was placed in a 250 mL three necked round bottomed Pyrex flask. The reaction was carried out at 60°C for 24 hours and was gently refluxed in the nitrogen atmosphere. The solvent was then completely removed under vacuum and onium salt, i.e., N, N'-dihexyl-4,4'-bipyridinium dibromide (MPTC) was washed with n-hexane (3 x 20 mL). The white solid MPTC was stored in CaCl₂ desiccators. m.p. 196°C; Yield: 90%; ¹H NMR (400 MHz, CDCl₃); δ. 0.82-0.85 (t, 6H-, CH₂-CH₃), 1.26-1.34 (m, 12H-CH₂-CH₃), 1.99-2.11 (m, 4H- N⁺-CH₂-CH₂), 4.63-4.67 (t, 4H- N⁺-CH₂), 8.52-8.59 (d, d 4H, pyCH), 8.95-9.15 (d, d 4H, N⁺-pyCH); ¹³C NMR (100 MHz, CDCl₃); δ 15.79 (ali-CH₃), 24.28, 27.46, 32.85, 33.06 (ali-CH₂), 64.21 (N⁺-CH₂), 124.64, 144.78, 147.28 (bipy-C); Elemental analysis Calc.: C, 54.33%; H, 7.05%; N, 5.76%; Found, C, 54.30%; H, 7.01%; N, 5.72%. (Scheme 1).

Kinetics of dichlorocarbene addition to N-vinylimidazole

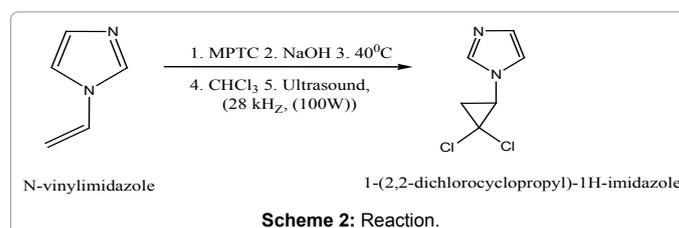
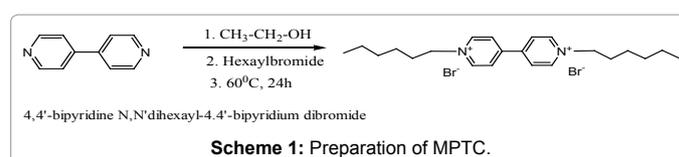
According to our experimental condition the mono-substituted product i.e., 1-(2,2-dichlorocyclopropyl)-1H-imidazole (Scheme 2) was produced from the reaction solution containing N-vinylimidazole. The kinetics of the reaction was performed in an ordinary 150 mL three-necked round bottom flask fitted with flat-bladed stirring paddle and a reflux condenser. The dichlorocarbene addition of N-vinylimidazole reaction was carried out by reverse addition method, i.e., by delayed addition of N-vinylimidazole. To the reaction flask, 30 mL of (30 wt%) aqueous NaOH, 0.72 mmol of respective phase-transfer catalyst and 25 mL chloroform (solvent) were added and stirred at 100 rpm for 5 min at 40°C to stabilize the catalyst. N-vinylimidazole (1.5 g, 15.95 mmol) in 10 mL chloroform preheated to 40°C was added to the reaction mixture at zero time. The reaction mixture was stirred at 200 rpm and

simultaneously the ultrasonic energy (28 kHz and 300 W) was passed through the reactor. Samples were collected from the organic layer of the mixture at regular intervals of time and each run consists of the six samples. The kinetics of the reaction was followed by estimating the amount of N-vinylimidazole disappeared using gas chromatograph. An aliquot of reaction mixture (1 μl) was injected into the column and the product was analyzed. The retention time for each compound was noted such as, chloroform (0.71 min) N-vinylimidazole (2.74 min), and 1-(2,2-dichlorocyclopropyl)-1H-imidazole (4.52 min). The pseudo-first order rate constants were calculated from the plots of -ln(1-X) versus time. The kinetic experiments were carried out in duplicate to confirm reproducibility of the results.

Results and Discussion

Nowadays, phase-transfer catalysis is a vital and very fascinating technique to conduct the reaction between immiscible reactants available in the heterogeneous system. In order to perform this immiscible substrate reaction more effectively, many researchers have devoted their attention to develop multi-site phase-transfer catalyst (more than one site) to replace the low active single-site phase-transfer catalyst (PTC). Particularly, dichlorocarbene addition to olefins using multi-site phase-transfer catalyst (MPTCs) aided by ultrasonic energy is an active area for current study. To strengthen further, a new dual-site phase-transfer catalyst viz., N,N'-dihexyl-4,4'-bipyridinium dibromide (MPTC) was prepared. To determine the catalytic activity of the newly synthesized MPTC, was employed for the catalysis of dichlorocarbene addition to N-vinylimidazole under identical pseudo-first order reaction conditions in association with ultrasonic irradiation (28 kHz, 300 W) and mechanical stirring 200 rpm. The pseudo-first order rate constant was determined by measuring the disappearance of N-vinylimidazole under regular intervals using gas chromatography.

Generally, the effect of ultrasonic energy for the promotion of dichlorocarbene addition to N-vinylimidazole was caused by the production of intense local conditions due to cavitations bubble dynamics, i.e., the nucleation, formation, disappearance and coalescence of vapors or gas bubbles in the ultrasonic field [31,32]. However, in phase-transfer catalyst reactions, rate enhancements are typically due to mechanical effects, mainly through an enhancement in mass transfer. In liquid-liquid bi-phase system, the presence of ultrasonic wave energy used to disrupt the interface by cavitation collapse near the liquid-liquid interface and impels jets of one liquid into other, forming fine emulsions and it leads to a dramatic enhancement in the interfacial contact area through which transfer of species can take place [33]. Therefore, the combination of quaternary onium ions (PTC) and ultrasound energy has proved to be a best and environmentally benign



catalytic method to conduct the organic addition reaction [34]. In view of the impact of ultrasonic energy, it is decided to conduct detailed kinetic study for dichlorocarbene addition to n-vinylimidazole using the superior new dual-site phase-transfer catalyst, viz., N,N'-dihexyl-4,4'-bipyridinium dibromide (MPTC) in association with ultrasonic wave energy and by varying the experimental parameters such as (substrate), (PTC), (NaOH), and temperature.

Ultrasonic energy

In the present work, we investigate the effect of ultrasound energy on the dichlorocyclopropanation of N-vinylimidazole. Ultrasound generate extremely fine emulsions provide enormous interfacial contact areas between immiscible liquid and thus the potential for greater reaction between the phase. This can be particularly beneficial in phase-transfer catalysis [35]. The combination of ultrasound irradiation with phase-transfer catalysis could give synergy effect in catalysis and the reaction rate could be greatly promoted [36,37].

The ultrasound-assisted dual-site phase-transfer catalyst, viz., N,N'-dihexyl-4,4'-bipyridinium dibromide (MPTC) was carried out in a thermostatically batch reactor equipped with ultrasonic generator 28 kHz with output power of 300 W. The reaction rate also compared with 0 kHz and 40 kHz (300 W). The effect of the ultrasonic frequency on the rate k_{app} was represented in (Table 1). In our study at 50 min, in the presence of ultrasonic irradiation and 200 rpm the k_{app} of the reaction increased to almost 3.86 times and 2.04 times faster for 28 kHz (300 W) & 40 kHz (300 W) than without ultrasonic irradiation i.e., under silent condition (0 kHz). From these observations, it was inferred that the ultrasonic assisted multi-site phase-transfer catalyst significantly increased the k_{app} . The product yield decreased with increasing ultrasonic frequency (Table 1) in the order of k_{app} being 28 kHz (300 W) > 40 kHz (300 W) > 0 kHz. The reaction rate at 40°C with ultrasound (28 kHz, 300 W) was 3.86 larger than that at silent condition, showing the reaction rate effectively enhanced by ultrasound irradiation (Table 1) and (Scheme 3).

Effect of the agitation speed

The effect of agitation speed on the rate of dichlorocarbene addition to N-vinylimidazole using a dual-site phase-transfer catalyst viz., N,N'-dihexyl-4,4'-bipyridinium dibromide (MPTC), the reaction was studied by varying the agitation speed in the range of 100–1000 rpm along with ultrasonic irradiation 28 kHz (300 W). The other parameters such as (substrate), (MPTC), (NaOH) and temperature were kept constant. The pseudo first-order rate constants were evaluated from the plots of $-\ln(1-X)$ versus time (Figure 1). From the observed k_{app} , it is understood that the rate of the reaction increases on increasing the agitation speed, i.e., the rate constant was gradually increased from 100 to 200 rpm and then the rate constant of the reaction was not improved on increasing the stirring speed above 200 rpm. Similar trend of observation is already reported in effect of varying the stirring speed [38] and it was suggested that the reaction has followed interfacial mechanism. In the present study also, k_{app} is independent of the stirring speed at above 200 rpm, and this trend indicates that the reaction has proceeded through interfacial mechanism. In the general, biphasic phase-transfer catalysis reaction agitation speed is an vital role, but in the presence of ultrasound irradiation agitation effect is reduced due to ultrasound generate extremely fine emulsion from mixtures of immiscible liquids and provide enormous interfacial contact between the phase. Hence, in the presence of ultrasound energy the observed k_{app} values higher than the conventional method (Figure 1).

Effect of (substrate)

The effect of varying the concentration of N-vinylimidazole on the rate of dichlorocarbene addition was studied in the range of 10.63–31.91 mmol and keeping the other reagents as constant under the ultrasonic irradiation condition. From the pseudo-first order rate constants were evaluated (Table 2). The observed rate constants were increased on increasing the amount of substrate. This observation may be due to the presence of more number of active sites in the multi-site phase-transfer catalyst (MPTC) and higher concentration of substrate had cooperatively influenced the reaction and thus enhanced the more number of contacts between catalyst and substrate and hence reflected in enhanced k_{app} . Recently, Murugan et al. [39] have also reported the same dependency of rate constants for the dichlorocarbene addition to citral and α -pinene using multi-site phase-transfer catalyst.

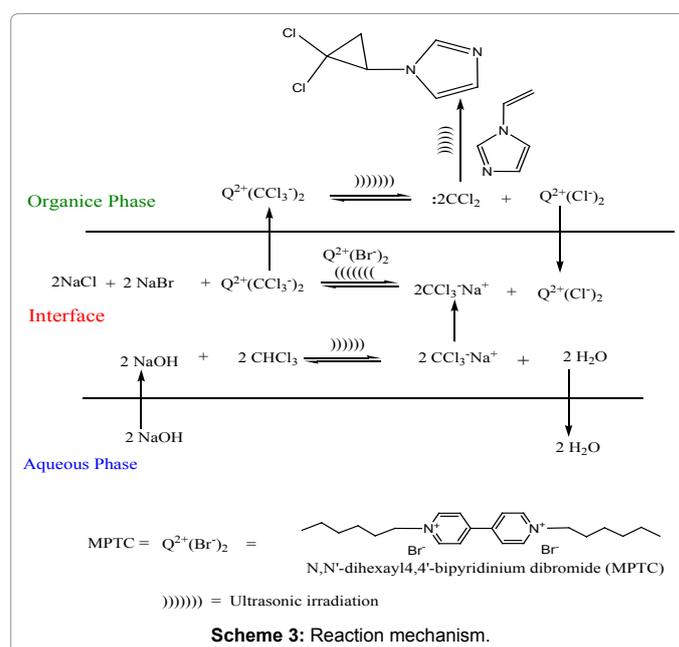
Effect of (MPTC)

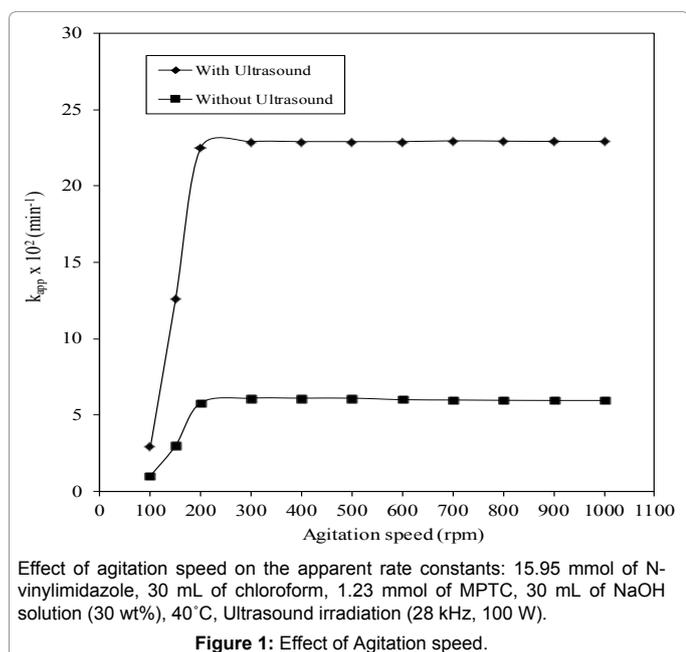
The effect of concentration of dual-site phase-transfer catalyst, viz., N,N'-dihexyl-4,4'-bipyridinium dibromide (MPTC) on the rate of the dichlorocarbene addition to N-vinylimidazole was studied in the range of 0.41–2.05 mmol and keeping the other experimental parameters as constant under the ultrasonic irradiation (28 kHz, 300W) condition. The pseudo-first order rate constants were evaluated from the plot of $-\ln(1-X)$ versus time. From the observed results, the rate constants are linearly dependent on the concentration of catalyst (Figure 2). The increased rate constants are attributed to increase in number of catalytic active site (N^+) which in turn enhances the more number of effective collisions between $Na^+CCl_3^-$ and MPTC in the interface. In other words, at higher concentration of MPTC, the generation of dichlorocarbene ($:CCl_2$) have been increased which in turn leads to increase in the

0 kHz $k_{app} \times 10^2$ (min ⁻¹)	28 kHz, 300 W $k_{app} \times 10^2$ (min ⁻¹)	40 kHz, 300 W $k_{app} \times 10^2$ (min ⁻¹)
4.99	22.89	10.18

Effect of ultrasonic energy on the apparent rate constants: 15.95 mmol of N-vinylimidazole, 30 mL of chloroform, 1.23 mmol of MPTC, 30 mL of NaOH solution (30 wt%), 40°C, 200 rpm.

Table 1: Effect of ultrasonic energy.

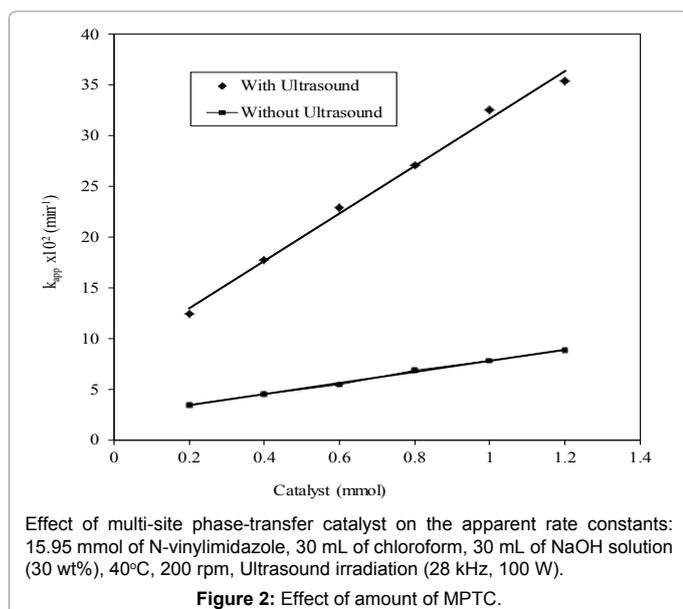




N-vinylimidazole (mmol)	10.63	15.95	21.27	26.59	31.91
With ultrasonic (28 kHz, 300W). $k_{app} \times 10^2$ (min ⁻¹)	12.89	22.98	28.22	31.42	37.28
Without ultrasonic (0 kHz). $k_{app} \times 10^2$ (min ⁻¹)	3.08	5.19	7.66	8.06	9.12

Effect of N-vinylimidazole on the apparent rate constants: 30 mL of chloroform, 1.23 mmol of MPTC, 30 mL of NaOH solution (30 wt%), 40°C, 200 rpm.

Table 2: Effect of substrate.



formation of complex, $Q^{2+}(CCl_3)_2$ MPTC in the organic phase. Further, not only higher rate of reactions were obtained due to the presence of more amount of phase-transfer catalysts but also intensification of the rate had occurred [40] and also there was a total suppression of side reactions leading to 100% selectivity of the product. The control experiments (without

stirring and 0 kHz) were also carried out for dichlorocarbene addition to N-vinylimidazole, there is no by product was find out even after 6 h of reaction. The linear dependence of the reaction rate constants on (MPTC) shows that the reaction is believed to proceed through the interfacial mechanism. The bilogarithmic plot of the reaction rate constant versus the concentration of the catalyst gave a straight line with a slope of 1.18. Similar report was observed by Starks [41] in the study of dichlorocarbene addition to cyclohexene using tridecylmethylammonium chloride as catalyst. Halpern et al. [42] have studied the dehydrobromination of phenethyl bromide using tetraoctylammonium bromide as a catalyst, zero order kinetics with respect to the catalyst amount was observed. The k_{app} value at 40°C with ultrasound (28 kHz, 300 W) was larger then that at silent condition, which indicates that the reaction rate effectively enhanced by ultrasonic irradiation.

Comparison of apparent rate constants with different phase-transfer catalysts

Quaternary ammonium salts are generally used as phase-transfer catalyst to promote reaction rate for immiscible reactions. In addition to ultrasound irradiation condition (28 kHz, 300 W) five different phase-transfer catalyst along with a new synthesized dual-site phase-transfer catalyst (MPTC) were used for dichlorocarbene addition to N-vinylimidazole. The four other single-site quaternary ammonium salts, such as tetrabutylammonium chloride (TBAC), tetrabutylammonium bromide (TBAB), tetrabutylammonium iodide (TBAI), and tetrabutylammonium hydrogensulphate (TBAHS) were investigated to test their relativities. The corresponding k_{app} values are depicted in (Table 3). The order of the reactivates in choosing the tetrabutylammonium cation group in this work is TBAHS>TBAC>TBAB>TBAI. Choosing a small size of the anionic ion in the halide groups of PTCs is favorable for a high reaction rate [40]. This phenomenon is more consistent with the interfacial reaction mechanism rather than the extraction reaction mechanism [43]. N,N' -dihexyl-4,4'-bipyridinium dibromide (MPTC) is more reactive then other quaternary salts, due to it is dual active site and lipophilic nature may be higher. The activity of the lipophilic cation (Q^+ for single site, Q^{2+} for double site) is determined mainly by two factors its extractability which depends on organophilicity of the catalyst and the anion pairs ($Q^+CCl_3^-$) for the single-site and $Q^{2+}(CCl_3^-)_2$ for dual-site catalyst. Further, the ultrasonic irradiation can enhance the rate for multi-site phase-transfer catalyst then single-site due to transfer of more ion pare to organic phase where the reaction take place pre cycle. Based on the above argument the order of the reactivities of these quaternary ammonium salts are in order MPTC>TBAHS>TBAC>TBAB>TBAI.

Effect of the amount of inorganic salt

In this study, sodium bromide was produced as a byproduct from the reaction. Therefore, the addition of NaBr naturally affects the equilibrium of each component between the two phases. The results are showing Table 4. The addition of NaBr enhances the reaction as a result of a salting out effect in the aqueous phase and also the formed dichlorocarbene is more favorable to staying in the organic phase. Meanwhile, hydrolysis of dichlorocarbene in the aqueous phase is minimized. For Comparison, the two apparent rate constants obtained from the phase-transfer catalytic reaction [43] in the presence and absence of ultrasonic irradiation are also shown in (Table 4). It is obvious that the ultrasonic irradiation enhances the reaction.

Effect of temperature

The effect of varying the temperature on the rate of dichlorocarbene addition to N-vinylimidazole was carried out in the temperature

range of 303–323 K and keeping the other experimental parameters as constant under the ultrasonic irradiation condition (28 kHz, 300 W). The pseudo-first order rate constants were evaluated from the plot of $-\ln(1-X)$ versus time. The observed values indicate that the reaction rate constants were increased on increasing the temperature in association with ultrasonic energy [40,43]. The energy of activation is calculated from Arrhenius plot (Figure 3), $E_a=15.76$ kcal mol⁻¹. The other thermodynamic parameters such as entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) for dichlorocarbene addition to N-vinylimidazole were determined from Eyring's equation and the obtained values are 14.7 eu, 15.1 kcal.mol⁻¹ and 16.9 kcal mol⁻¹ respectively. The activation energy (E_a) reported by Chiellini et al. [44] for ethylation of phenylacetonitrile was 20 kcal mol⁻¹ and for this an interfacial mechanism was proposed. Tomi and Ford [45] observed a higher E_a value for the polystyrene bound benzyltriethylammonium ion catalyzed reaction, which was controlled by intrinsic reactivity under triphase reactions. Murugan et al. [39] reported the higher E_a value for the dichlorocarbene addition to α -pinene was 15.3 kcal mol⁻¹ and proposed an interfacial mechanism. Therefore, this study also gives higher E_a value (i.e., 15.76 kcal. mol⁻¹), and hence, it is suggested that dichlorocarbene addition to N-vinylimidazole should be proceed through an interfacial mechanism.

Effect of NaOH concentration

The reaction rates were measured in the range of 4.41M-20.45M (15-45 g NaOH). The k_{app} values of dichlorocyclopropanation strongly depend on the concentration of sodium hydroxide [46]. The k_{app} constants were found to increase with an increase in sodium hydroxide concentration (Figure 4). This may be attributed to the fact that hydroxide ions are less solvated by water molecules and thereby the activity of the hydroxide ion increases [47]. It is interesting to note that the conversion decreased conspicuously after adding 30 g of sodium hydroxide. It is because the solution was saturated by the addition of 30 g of sodium hydroxide and 7.89 mmol of N-vinylimidazole to 30 mL of water, leading to the salting out of N-vinylimidazole as a black gel. Under this circumstance, the dichlorocyclopropanation system would be changing from a liquid–liquid PTC to a liquid–solid (NaOH) PTC. The change would decrease the reaction rate sharply. As shown in (Figure 4), the conversion is first increased with an increase in the amount of NaOH up to 30 g and then decreased with any further increase in the amount of NaOH.

Mechanism

Generally, in dichlorocarbene addition reaction has been performed in two steps. In the beginning, concentrated sodium hydroxide was treated with chloroform which abstracts a proton and then an intermediate species $CCl_3^-Na^+$ was generated. Further, it was catalyzed by MPTC and followed by the addition of electrophile $:CCl_2$ (dichlorocarbene). In the phase transfer catalyzed reaction, the two important classes of mechanisms are believed to be operative, viz., Stark's extraction mechanism [48] in which the hydroxide ion might be extracted from the aqueous reservoir into the organic phase with the help of quaternary onium cations. In the case of Makosza's interfacial mechanism [49], the abstraction of proton from the organic substrate by the hydroxide ion occurs at inter-face and the resulting organic anion is ferried from the interface into the bulk organic phase by the phase-transfer catalyst for subsequent reaction. In view of these backgrounds, in our study also it is concluded that the dependence of kinetic data on the (PTC), (NaOH), temperature and higher E_a value and these observation has strongly proved that the reaction may be preceded through an interfacial mechanism. In the interfacial mechanism, the

hydroxide anion first reacted with the chloroform in the organic phase without the help of quaternary onium cations to produce $CCl_3^-Na^+$. Then the anion of MPTC catalyst was exchanged by $CCl_3^-Na^+$ to form an active intermediate of $Q^{2+}(CCl_3)_2$ which can react with the double bond containing N-vinylimidazole to form dichlorocyclopropanated product, viz., 1-(2,2-dichlorocyclopropyl)-1H-imidazole (Scheme 3). In the presence ultrasonic energy 28 kHz, (300W) the formation of the product increased due to increasing the formation of dichlorocarbene ($:CCl_2$).

Conclusion

In this study, a new multi-site phase-transfer catalyst, viz., N,N'-dihexyl-4,4'-bipyridinium dibromide (MPTC) was synthesized and successfully used to carried out a dichlorocarbene addition to N-vinylimidazole under organic/aqueous bi-phase medium. The reaction is dramatically enhanced by adding a small amount of MPTC along with ultrasonic energy 28 kHz (300W). At a low alkaline concentration, the conversion is low due to less formation of dichlorocarbene. A rational explanation was made for a peculiar

PTC	MPTC	TBAHS	TBAC	TBAB	TBAI
With ultrasonic (28 kHz, 300 W). $k_{app} \times 10^2$ (min ⁻¹)	22.98	15.87	12.54	10.56	09.52
Without ultrasonic (0 kHz). $k_{app} \times 10^2$ (min ⁻¹)	5.90	3.91t	3.39	2.78	2.69

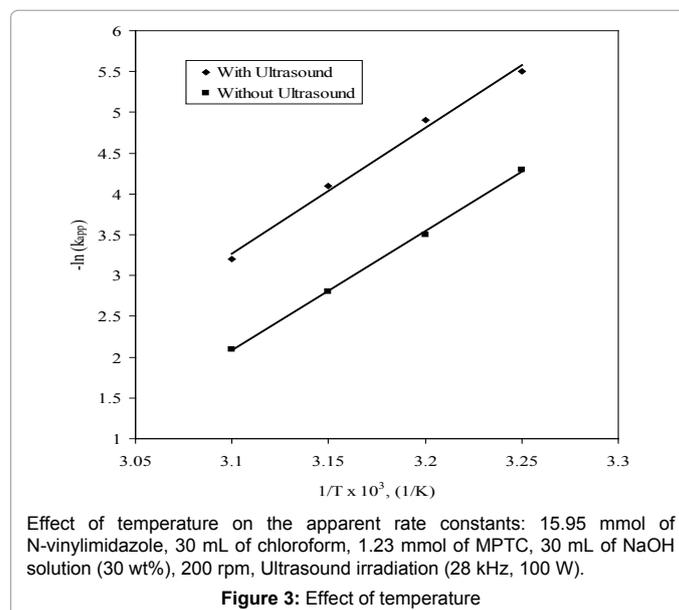
Effect of phase-transfer catalysts on the apparent rate constants: 15.95 mmol of N-vinylimidazole, 30 mL of chloroform, 30 mL of NaOH solution (30 wt.%), 40°C, 200 rpm.

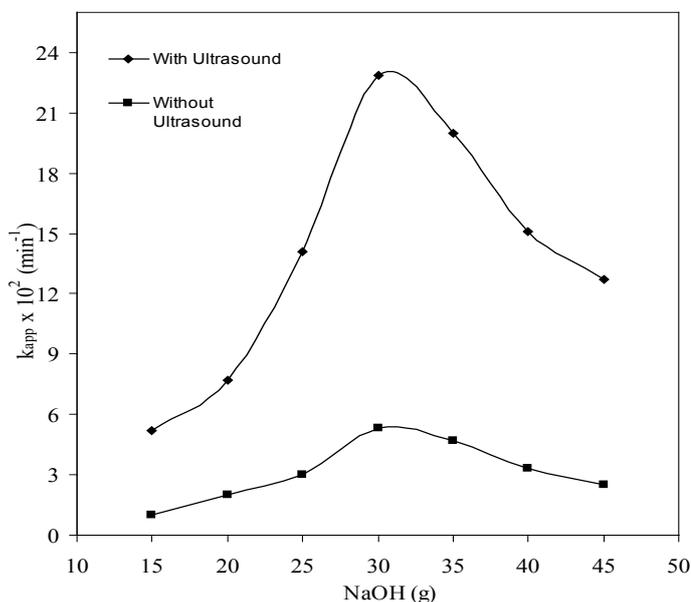
Table 3: Effect of various phase-transfer catalysts.

With ultrasonic (28 kHz, 300W).						
$k_{app} \times 10^2$ (min ⁻¹)	22.98	24.6	26.9	29.51	33.68	36.11
Without ultrasonic (0 kHz).						
$k_{app} \times 10^2$ (min ⁻¹)	5.58	6.31	7.08	7.64	8.46	9.06

Effect of Inorganic salt on the apparent rate constants: 15.95 mmol of N-vinylimidazole, 30 mL of chloroform, 1.23 mmol of MPTC, 30 mL of NaOH solution (30 wt.%), 40°C, 200 rpm.

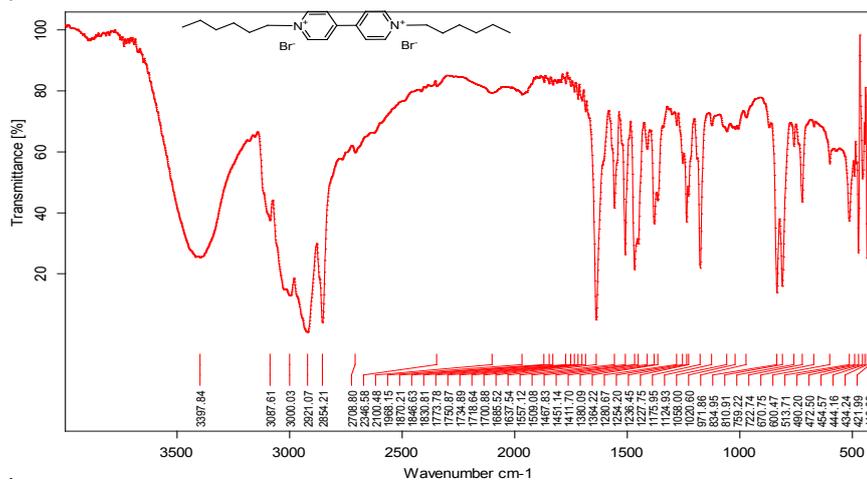
Table 4: Effect of inorganic salt.





Effect of sodium hydroxide on the apparent rate constants: 15.95 mmol of N-vinylimidazole, 30 mL of chloroform, 1.23 mmol of MPTC, 40°C, 200 rpm, Ultrasound irradiation (28 kHz, 100 W).

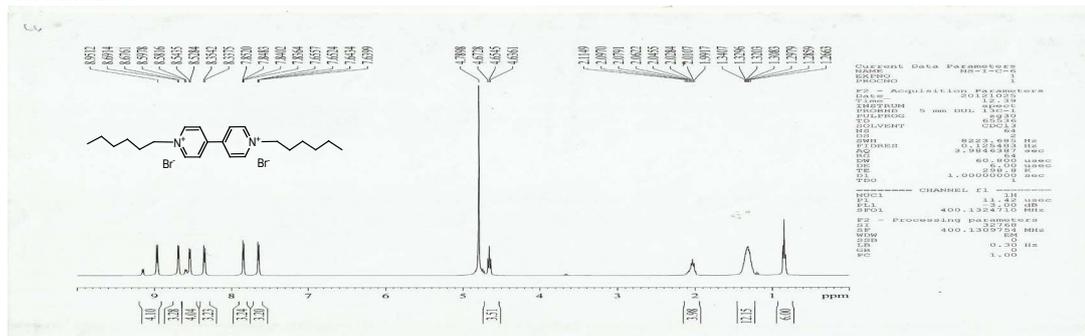
IR MPTC

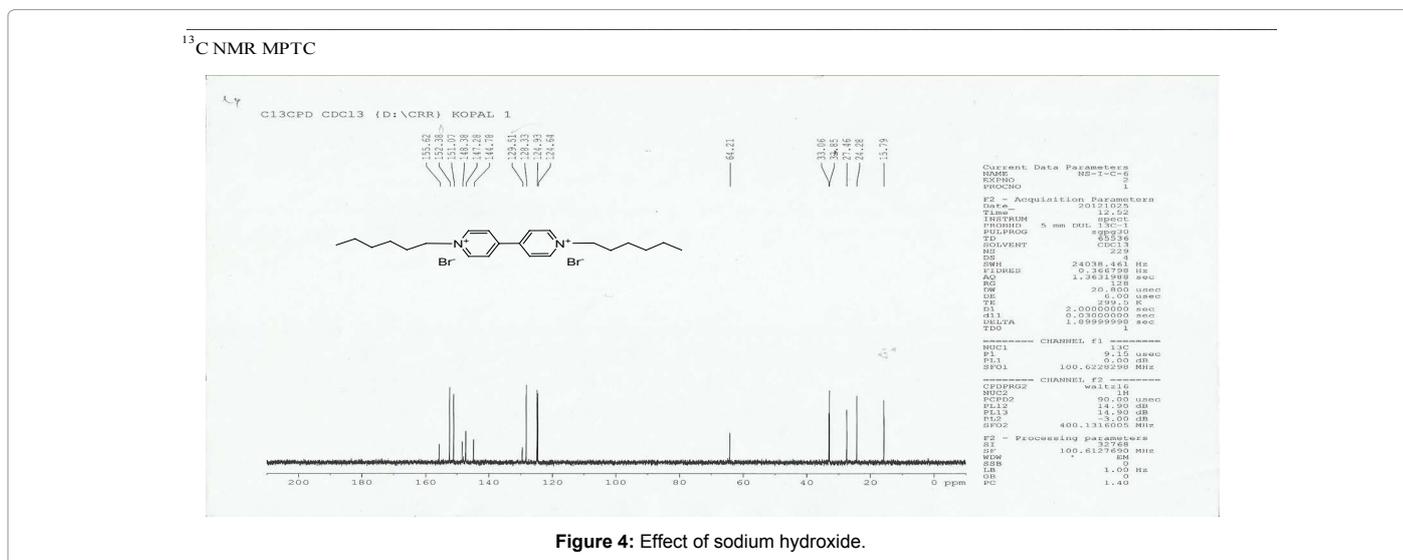


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¹H NMR MPTC





phenomenon that the conversion of N-vinylimidazole was increased and then decreased with an increase in the amount of sodium hydroxide and the k_{app} value increases with increasing other kinetic parameters that is the amount of multi-site phase-transfer catalyst, viz., N,N'-dihexyl-4,4'-bipyridinium dibromide, concentration of substrate, ultrasonication, stirring speed, temperature, etc. Due to salting out effect the addition of inorganic salt enhances the rate. The proposed interfacial mechanism is well used to explain the reaction behavior.

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References

- Starks CM, Liotta CL, Halpern M (1994) Phase-Transfer Catalysis: Fundamental, Applications, and Industrial Perspectives. New York: Chapman & Hall p: 237.
- Wang DH, Weng HS (1995) Solvent and salt effects on the formation of third liquid phase and the reaction mechanisms in the phase transfer catalysis system - Reaction between N-butyl bromide and sodium phenolate Chem Eng Sci 50: 3477-86.
- Yadav GD, Reddy CA (1999) Kinetics of the n-Butoxylation of p-Chloronitrobenzene. Ind Eng Chem Res 38: 2245-53.
- Yadav GD, Motirale BG (2010) Selective oxidation of methyl mandelate to methyl phenyl glyoxylate using liquid-liquid-liquid phase transfer catalysis. Chem Eng J 156: 328-36.
- Baj S, Siewniak A (2010) Tri-liquid system in the synthesis of dialkyl peroxides using tetraalkylammonium salts as phase-transfer catalysts Appl Catal A: Gen 385: 208-13.
- Mason TJ, Luche JL (1997) Chemistry under Extreme or Non-Classical Conditions. In: Eldick RV, Hubbard CD (eds) Wiley, New York p: 317.
- Gaplovsky A, Gaplovsky M, Toma S, Luche JL (2000) Ultrasound Effects on the Photopinacolization of Benzophenone J Org Chem 65: 8444-47.
- Namboodiri VV, Varma RS (2002) Solvent-free sonochemical preparation of ionic Liquids. Org Lett 4: 316-63.
- Price GJ (1993) Current Trends in Sonochemistry. Royal Society of Chemistry Cambridge.
- Luzzio FA, Moore WJ (1993) Ultrasound in oxochromium(VI)-mediated transformations. Ultrasound-mediated preparation and applications of chromyl chloride. J Org Chem 58: 512-15.
- Luche JL (1997) A few questions on the sonochemistry of solutions. Ultrasonics Sonochem 4: 211-15.
- Psillakis E, Mantzavinos D, Kalogerakis N (2004) Development of a hollow fibre liquid phase microextraction method to monitor the sonochemical degradation of explosives in water. Anal Chim Acta 501: 3-10.
- Flint EB, Suslick KS (1991) The Temperature of Cavitation. Science 231: 1397-99.
- Thomson LH, Doraiswamy LK (1999) Sonochemistry: Science and Engineering. Ind Eng Chem Res 38: 1215-49.
- Rajagopal R, Jarikote V, Srinivasan KV (2002) Ultrasound promoted Suzuki cross-coupling reactions in ionic liquid at ambient conditions. Chem Commun 616-17.
- Yang HM, Huang YS (2011) Green benzylation of sodium salicylate by phase transfer catalysis with third-liquid phase-transfer catalysis. J Taiwan Inst Chem Eng 42: 265-70.
- Loupy A, Luche JL, Sasson Y, Neumann R (1997) Handbook of Phase Transfer Catalysis. London: Blackie Academic and Professional p.369-404.
- Yang HM, Chen YG (2012) Ultrasound assisted third-liquid phase-transfer catalysis esterification of potassium 4-methoxyphenylacetate by dual-site phase-transfer catalyst. J Taiwan Inst Chem Eng 43: 897-03.
- Adewuyi YG (2001) Sonochemistry: Environmental Science and Engineering Applications. Ind Eng Chem Res 40: 4681-15.
- Loupy A, Luche JL (1997) Hand Book of Phase Transfer Catalysis. In: Sasson Y, Neumann R (eds) London: Blackie Academic and Professional p: 369.
- Yang HM, Peng GY (2010) Ultrasound-assisted third-liquid phase-transfer catalyzed esterification of sodium salicylate in a continuous two-phase-flow reactor Ultrason Sonochem 17: 239-45.
- Yang HM, Chiu CC (2011) Ultrasound-assisted phase-transfer catalysis: Benzylation of sodium 4-acetylphenoxide by dual-site phase-transfer catalyst in a tri-liquid system. Ultrason Sonochem 18: 363-69.
- Hua Q, Dabin L, Chunxu L (2011) Ultrasonically-promoted synthesis of mandelic acid by phase transfer catalysis in an ionic liquid Ultrason Sonochem 18: 1035-37.
- Dandia A, Singh R, Bhaskaran S (2011) Facile stereoselective synthesis of spiro [indole-oxiranes] by combination of phase transfer catalyst and ultrasound irradiation and their bioassay. Ultrason Sonochem 18: 1113-17.
- Wang ML, Vivekanand PA (2011) Sonocatalyzed synthesis of 2-phenylvaleronitrile under controlled reaction conditions – A kinetic study. Ultrason Sonochem 18: 1241-48.

26. Entezari MH, Shamel AA (2000) Phase-transfer catalysis and ultrasonic waves I. Cannizzaro reaction *Ultrason Sonochem* 7: 169-72.
27. Wang ML, Rajendran V (2007) Ultrasound assisted phase-transfer catalytic epoxidation of 1,7-octadiene – A kinetic study. *Ultrason Sonochem* 14: 46-54.
28. Wang ML, Rajendran V (2007) Kinetics for dichlorocyclopropanation of 1,7-octadiene under the influence of Ultrasound assisted phase-transfer catalysis conditions. *J Mol Catal A Chem* 273: 5-13.
29. Wang ML, Rajendran V (2007) Ethoxylation of *p*-chloronitrobenzene using phase-transfer catalysts by ultrasound irradiation – A kinetic study. *Ultrason Sonochem* 14: 368-74.
30. Yang HM, Chen CH (2009) Catalytic esterification of sodium salicylate in third-liquid phase under ultrasound-assisted tri-liquid phase-transfer catalysis. *J Mol Catal A Chem* 312: 107-13.
31. Lindley J, Mason TJ (1987) Sonochemistry, Part 2-Synthetic Applications. *Chem Soc Rev* 16: 275-11.
32. Mason TJ (1997) Ultrasound in Synthetic Organic Chemistry. *Chem Soc Rev* 26: 443-51.
33. Gogate PR, Tatak PA, Kanthale PM, Pandit AB (2002) Mapping of Sonochemical reactors: Review, analysis and experimental verifications. *AIChE J* 48: 1542-60
34. Davidson RS, Safdar A, Spencer JD, Robinson B (1987) Applications of ultrasound to organic chemistry. *Ultrasonics* 25: 35-39.
35. Ambulgekar GV, Bhanage BM, Samant SD (2005) Low temperature recyclable catalyst for Heck reactions using ultrasound *Tetrahedron Lett* 46: 2483-85.
36. Li JT, Li XL (2007) An efficient and practical synthesis of methylene dioximes by combination of ultrasound and phase transfer catalyst. *Ultrason Sonochem* 14: 677-79.
37. Nandurkar NS, Bhanushali MJ, Jagtap SR, Bhanage BM (2007) Ultrasound promoted regioselective nitration of phenols using dilute nitric acid in the presence of phase-transfer catalyst. *Ultrason Sonochem* 14: 41-45.
38. Wang ML, Lee ZF (2006) Kinetic study of synthesizing Bisphenol. A diallyl ether in a phase transfer catalytic reaction *Bull. Chem Soc Jpn* 79: 80-87.
39. Murugan E, Gopinath P (2008) Catalytic activity of novel soluble multi-site phase transfer catalyst in dichlorocarbene addition to α -pinene. *J Mol Catal A Chem* 294: 68-73.
40. Entezari MH, Kruus P (1996) Effect of frequency on sonochemical reactions II. Temperature and intensity effects *Ultrason Sonochem* 3: 19-24.
41. Starks CM, Owens RM (1973) Phase-transfer catalysis. II. Kinetic details of cyanide displacement on 1-halooctanes. *J Am Chem Soc* 95: 3613-17.
42. Halpern M, Sasson Y, Rabinovitz M (1984) Hydroxide-ion initiated reactions under phase-transfer catalysis conditions. 6. Dehydrobromination of (2-bromoethyl) benzene via slow hydroxide-ion extraction. *J Org Chem* 49: 2011-12.
43. Yang MH, Lin DW (2001) Third-liquid phase-transfer catalyzed esterification of sodium benzoate with novel dual-site phase-transfer catalyst under ultrasonic irradiation. *Catal Commun* 14: 101-106.
44. Chiellini E, Solaro R, Antone SD (1980) Heterogeneous ethylation of henylacetonitrile. *J Org Chem* 45: 4179-83.
45. Tomoi M, Ford WT (1981) Mechanisms of Polymer-Supported Catalysis. 2. Reaction of Benzyl Bromide with Aqueous Sodium Cyanide Catalyzed by Polystyrene-Bound Onium Ions. *J Am Chem Soc* 103: 3828-32.
46. Halpern M, Sasson Y, Willner L, Rabinovitz M (1981) Hydroxide ion initiated reactions under phase transfer catalysis conditions II. The roles of water and quat. *Tetrahedron Lett* 22: 1719-22.
47. Landini D, Maia A, Podda G (1982) Nonhydrated anion transfer from the aqueous to the organic phase: enhancement of nucleophilic reactivity in phase-transfer catalysis. *J Org Chem* 47: 2264-68.
48. Starks CM, Owens RM (1973) Phase-transfer catalysis. II. Kinetic details of cyanide displacement on 1-halooctanes. *J Am Chem Soc* 95: 3613-17.
49. Makosza M, Bialecka E (1977) Reactions of organic anionx. LXXIII. Alkylation of phenylacetonitrile at the interface with aqueous sodium hydroxide. *Tetrahedron Lett* 18: 183-86.