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Synthesis and characterization of novel multi-site phase transfer catalyst and its catalytic efficiency for dichlorocarbene addition to citral

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Abstract

Novel soluble multi-site phase transfer catalyst was synthesized from low cost starting materials and its catalytic efficiency is assessed by observing the kinetics of dichlorocarbene addition to citral in the absence of solvents. This new synthesized phase transfer catalyst viz., 1,3,5-tris[4-{2,3-bis(triethylammoniummethylene chloride)}-phenoxymethyl]benzene possesses six active centers. This novel catalyst has higher activity than the commercially available single-site phase transfer catalysts. The dichlorocarbene addition to citral reaction was carried out at low temperature (40 °C) under pseudo-first order conditions by keeping low concentration of aqueous sodium hydroxide and excess of chloroform and the disappearance of citral were monitored by gas chromatography. The effect of various experimental parameters such as [substrate], [catalyst], [aqueous NaOH], stirring speed and temperature on the rate of the reaction has been studied, and based on the kinetic results obtained, a plausible mechanism is proposed.
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Keywords: Phase transfer catalyst; Dichlorocarbene; Citral; Multi-site; Interfacial mechanism; Dihalocyclopropane

1. Introduction

Phase transfer catalysis (PTC) is now recognized as a general and versatile technique applicable to a variety of organic reactions [1,2]. PTC was little more than a curiosity in the late 1960s when Makosza first published his biphase method for the generation of dichlorocarbene [3]. PTC method has a very broad scope of application. Chemically, the possibilities include the separation of compounds from an unreactive or unstable starting material and more generally the increase of yields or selectivities in a large number of syntheses. The "single-site" PTCs viz., quaternary phosphonium and ammonium salts, crown ethers, cryptands, etc., are immensely popular due to their availability and easy reaction work-up. The important considerations in the selection of the catalyst are economy of scale and efficiency of the PTC, specifically on the industrial-scale preparation of organic compounds. In order to cater to these needs, "multi-site" phase transfer catalysts (MPTC) have been developed. In general, MPTCs have more potential of offering greater PTC activity and to effect a particular synthetic transformation under mild reaction conditions. Idoux et al. [4] first reported the soluble and insoluble phosphonium ion containing MPTCs, which have only three active sites. Recently, Balakrishnan and Jeyachandran [5] also reported a quaternary ammonium ion containing two active sites. Benaglia et al. [6] have reported poly(ethylene glycol) supported quaternary ammonium catalyst recyclable in nature. The efficiency of the catalytic abilities of these MPTCs towards simple S_N2 reactions and some weak nucleophilic–electrophilic S_NAr reactions were reported. Wang and Hsieh [7] have reported the dihalocyclopropanation of 4-vinyl-1-cyclohexene in the presence of a novel soluble two-site PTC catalyst. Recently, dimeric [8–11], trimeric [12] and dendritic [13] chiral quaternary ammonium catalysts were synthesized from *o*-, *m*- or *p*-xylene dibromide, bis(bromomethyl)naphthalenes, 9,10-di(chloromethyl)anthracene, mesitylene tribromide

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and 3,5-dihydroxabenzylbromide, respectively. These CPTCs have been employed for C-alkylation of *N*-(diphenylmethylene)glycine *tert*-butyl ester to result in higher chemical yields and ee's.

Dihalocyclopropanation was previously a difficult reaction to conduct, and so the ease and economy of the new method attracted a broad interest in the organic chemical community. Dihalocyclopropanes are intermediate compounds for the synthesis of cyclopropane derivatives and other pharmaceutically valuable products [14]. Normally, halocarbene undergoes hydrolysis easily in the presence of water; hence, vigorous anhydrous conditions are required for its synthesis. These difficulties are eliminated when the synthesis of cyclopropane reactions are carried out in biphasic systems of concentrated sodium hydroxide in the presence of single-site PTCs and quaternary ammonium MPTCs that are more effective. There are numerous reports for the dichlorocarbene addition to various olefins using single-site PTCs [15–19].

By considering all the above-mentioned points, we have decided to synthesize a novel multi-site phase transfer catalyst containing the maximum number of possible active sites equaling six. For the first time, we have synthesized a new "1,3,5-tris[4-(2,3-bis(triethylammoniummethylene chloride)-phenoxymethyl)benzene" (TEAMCPB) as MPTC by a simple synthetic method using inexpensive starting materials. The product obtained at each step has been characterized by FT-IR, ^{1}H NMR, ^{13}C NMR and mass analysis. Furthermore, the amount of chloride ion present in the MPT catalyst was estimated by the Volhard method [20]. The efficiency of the TEAMCPB catalyst was elucidated by the addition of dichlorocarbene to citral under pseudo-first order condition. The kinetics of this reaction was studied and based on the obtained kinetic results a plausible mechanism has been proposed and also the catalytic efficiencies of the MPTC is compared with the commercially available single-site PTCs.

2. Experimental section

2.1. Synthesis of 1,3,5-tribromomesitylene (*2*)

Mesitylene (10 ml, 72.0 mmol), 2.5 equivalent of *N*-bromosuccinamide (44.8 g, 252 mmol) and catalytic amount of benzoyl peroxide (8.75 g, 36.0 mmol) and CCl_4 (100 ml) were taken in a 150 ml RB flask. The reaction mixture was refluxed for 6 h at 70 °C. After completion reaction time, the formation of imide was removed by filtration and the solvent was eliminated from the filtrate by distillation to give the pale yellow solid of 1,3,5-tribromomesitylene. Yield is 96%.

FT-IR (KBr) cm^{-1}: 584 (C–Br), 1618 (C=C); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.34 (s, 6H, methylene), 6.78 (s, 3H, aromatic); *m*/*e* [M^+] 353.45 (100%), 261.9 (22%), 169.25 (18%), 77.67 (36%).

2.2. Preparation of 1,3,5-tris[4-(2,3-dimethyl-phenoxymethyl)]benzene (*3*)

1,3,5-Tribromomesitylene **2** (5 g, 14.0 mmol), 3,5-dimethylphenol (5.13 g, 42.0 mmol), methanol (50 ml) and NaOH (0.5 g, 42.0 mmol) were taken in a 150 ml round bottom flask. The reaction mixture was refluxed in an oil bath at 70 °C for 12 h. Then the solvent was removed from the reaction mixture by vacuum distillation. The crude product of 1,3,5-tris[4-(2,3-dimethylphenoxymethyl)]benzene **3**. The crude product of **3** was purified silica gel column chromatography using benzene:ethyl acetate (80:20, v/v). The yield is 92%, mp 134–135 °C.

FT-IR: KBr (cm^{-1}): 1218 (C–O), 1623 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.3 (s, 18H, methyl), 5.23 (s, 6H, phenoxy methylene), 6.38 (s, 6H, phenoxy aromatic), 6.44 (s, 3H, phenoxy aromatic), 7.07 (s, 3H, mesityl aromatic); ^{13}C NMR (75 MHz): 21.4, 78.5, 111.7, 122.4, 125.6, 138.7, 142.2, 164.3; *m*/*e* EI-S [M^+] = 480.34.

2.3. Synthesis of 1,3,5-tris[4-(2,3-bis-chloromethyl) phenoxymethyl]benzene (*4*)

1,3,5-Tris[4-(2,3-dimethylphenoxymethyl)]benzene **3** (3.50 g, 7.28 mmol), *N*-chlorosuccinamide (7.12 g, 47.3 mmol), benzoyl peroxide (8.13 g, 33.5 mmol) and CCl_4 (60 ml) were taken in a 150 ml round bottom flask. The reaction mixture was refluxed for 6 h at 70 °C. After completion of reaction time, the formation of imide from the reaction mixture was removed by filtration and the filtrate containing CCl_4 solvent was eliminated by vacuum distillation. The yellow coloured chlorinated compound **4** was obtained in 87% yield, mp 47–148 °C.

FT-IR (KBr pellet) (cm^{-1}): 722 (C–Cl), 1027 (C–O), 1620 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.34 (s, 12H, methylene), 5.27 (s, 6H, phenoxy methylene), 6.57 (s, 6H, phenoxy aromatic), 6.68 (s, 3H, phenoxy aromatic), 7.33 (s, 3H, mesitylene aromatic); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 54.4, 72.2, 110.3, 121.1, 124.0, 138.4, 145.2, 162.7; *m*/*e* EI-MS [M^+] 680.24.

2.4. 1,3,5-Tris[4-{2,3-bis(triethylammoniummethylene chloride)}- phenoxymethyl]benzene(TEAMCPB)(*5*)

1,3,5-Tris[4-(2,3-bis-chloromethyl)phenoxymethyl]benzene **4** (2.50 g, 3.63 mmol) was quaternised in an inert atmosphere (N_2) with excess of triethylamine (25 ml) in the presence of acetonitrile (50 ml) for 12 h at 70 °C. Then the solvent was removed from the reaction mixture by vacuum distillation and the crude product of quaternised compound **5** was washed with *n*-hexane (3 × 10 ml). Further it was purified by silica gel column chromatography using benzene:methanol (70:30, v/v) as an eluent. The obtained yield is 86%. (Scheme 1).

FT-IR (KBr pellet) (cm^{-1}): 1015 (C–O), 1020 (C–N), 1110 (N^+CH_2), 1620 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$)

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