KINETICS OF DICHLOROCYCLOPROPANATION USING 4-(DIMETHYLOCTYLAMMONIUM) PROPANSULTAN AND 1,4-BIS(TRIETHYLMETHYLAMMONIUM)BENZENE DIBROMIDE AS NEW PHASE TRANSFER CATALYSTS

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Abstract

The novel phase transfer catalysts S-8 [4-(dimethyloctylammonium) propansultan] and DB-X [1,4-bis(triethylmethylammonium)benzene dibromide] were synthesized and employed for high conversion synthesis of dichlorocyclopropane from various olefins.

Keywords: Phase transfer catalysis, dichlorocyclopropanation, conversion

INTRODUCTION

In recent years, the problems of two-phase reactions have been solved by the development of phase transfer catalysis (PTC) [1-3]. The advantages of the PTC method for synthesizing dichlorocyclopropane are increased reaction rate, increased conversion, low energy requirements; a commercially available and inexpensive catalyst, inexpensive, non-toxic and recoverable solvents, and inexpensive bases for anion generation. Searching for a more effective catalyst or multi-site catalysts to enhance the reaction or to elevate the conversion plays an important role in phase transfer catalysis [4-6]. Previously, sulfobetaine monomers were considered as functional monomers and were applied as minor components for copolymers in various fields, such as synthetic textile fibers.

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hydrophilic and charged dispersing agents, as well as protective colloids. In this work, S-8 [4-(dimethyloctylammonium) propansultan] and DB-X [1,4-bis(triethylmethylammonium)benzene dibromide] are employed for the first time as phase transfer catalysts to synthesize dichlorocyclopropane via dichlorocyclopropanation in an alkaline solution/organic solvent two-phase medium. The synthesis of S-8 and DB-X as new phase transfer catalysts is described in the following scheme.

\[
\begin{align*}
\text{H}_{2}C&\quad \text{O} \quad \text{O} \quad \text{H}_{2}C \\
&\quad \text{H}_{2}C&\quad \text{O} \quad \text{O} \quad \text{H}_{2}C \\
&\quad \text{H}_{2}C&\quad \text{O} \quad \text{O} \quad \text{H}_{2}C
\end{align*}
\]

\[
\text{C}_{2}H_{17}(\text{CH}_{3})_{3}\text{N} \quad \rightarrow \quad \text{C}_{2}H_{17}^{+} \quad \text{C}_{2}H_{5}\text{SO}_{3}^{-}
\]

**S-8**

\[
\begin{align*}
\text{BrH}_{2}C&\quad \text{Br} \quad \text{H}_{2}Br \quad 2\text{C}_{2}H_{5}\text{N} \\
&\quad \text{BrH}_{2}C&\quad \text{Br} \quad \text{H}_{2}Br
\end{align*}
\]

\[
\text{C}_{2}H_{5} \quad \text{C}_{2}H_{5} \quad \text{C}_{2}H_{5} \quad \text{C}_{2}H_{5}
\]

**DB-X**

Dichlorocyclopropane has been difficult to synthesize using conventional methods [7,8] until the technique of phase transfer catalysis was developed [9-13]. This work investigates the addition of dichlorocarbene to different olefins, including mono- and di-olefins, and the application of these two new phase transfer catalysts. The results of dichlorocyclopropanation are shown in Table 1. In the absence of a phase transfer catalyst, less than 1% conversion was detected even after 3 h of reaction. In contrast, high yields of products were obtained in 30 min after using 5 mol% (based on the substrate amount) of the new catalyst. Thus, the results reveal the remarkable efficiency of S-8 [4-(dimethyl-octylammonium) propansultan] and DB-X [1,4-Bis(triethylmethylammonium)benzene dibromide] as potential phase transfer catalysts.

**EXPERIMENTAL**

**General**

$^{1}$H NMR (400 MHz) was recorded on a BRUKER-AM-400 NMR spectrometer with TMS as an internal standard. The infrared spectra were measured on a Shimadzu FTIR-8700 spectrometer. Gas chromatography was carried out using Shimadzu GC-17 A instrument.