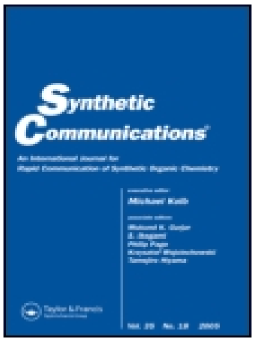

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Synthesis, Characterization, and Utility of Trialkyl(3-sulfopropyl)ammonium Betaines as New Phase Transfer Reagents

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ABSTRACT

Synthesis of water-soluble phase transfer reagents, trialkyl(3-sulfopropyl)ammonium betaines and its utility in various hydroxide-ion initiated reactions are described.

Phase Transfer Catalysis (PTC) is connected with conversions between chemical species situated in different phases (aqueous/organic).[1–3] Common cases are reaction between, on the hand, salts dissolved in water or present in solid phase, and on the other, substances, dissolved in organic media. The advantages of PTC method over conventional methods are increased rates of reaction, increased product

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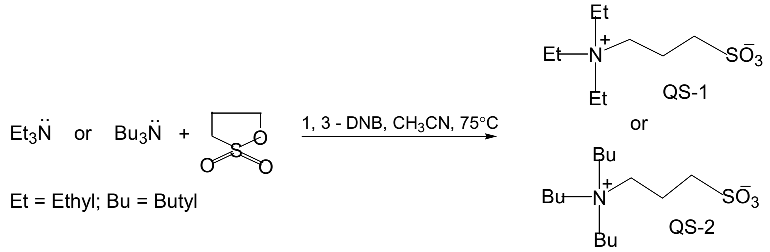
specificity, lower energy requirements, commercially available inexpensive catalysts, use of inexpensive non-toxic, recoverable solvents or use of liquid reactant as a solvent, use of inexpensive bases for anion generation, use of inexpensive oxidants, reduced cycle time and pollution prevention.

The nucleophilic ring opening of 1, 3-propanesultone by tertiary amines readily leads to sulfopropylbetaine type compounds. A brief literature survey[4–9] reveals that sulfobetaine monomers were considered as functional monomers and finds applicability as minor components for copolymers in various fields like synthetic textile fibres, hydrophilic and charged dispersing agents and protective colloids.

This communication deals with the synthesis of triethyl(3-sulfopropyl)ammonium betaine[**QS-1**] and tributyl(3-sulfopropyl)ammonium betaine [**QS-2**] and report its utility in hydroxide-ion initiated reactions as a new phase transfer reagent.

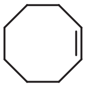
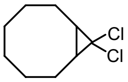
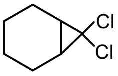
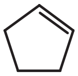
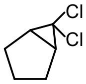
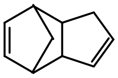
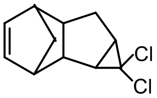
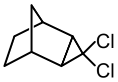
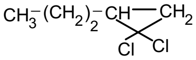
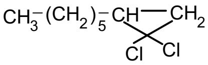
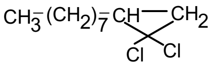
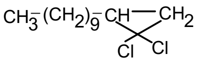
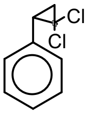
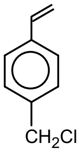
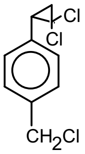
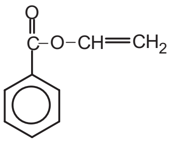
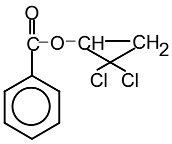
The synthesis of **QS-1** and **QS-2** as a new phase transfer reagents are described in Sch. 1. Quaternizations were performed at 75°C, using a stoichiometric ratio [propanesultone]/[amine] = 1.1 in the presence of an aprotic solvent, acetonitrile where the trialkyl(3-sulfopropyl)ammonium betaines are insoluble. Catalytic amount of 1,3-dinitrobenzene (**1,3-DNB**) is used as a free radical polymerization inhibitor in the present reaction.

In order to investigate the efficiency of the new phase transfer reagents under study, dichlorocarbene addition to different olefins have been chosen. The results shown in Table 1 establish the utility of trialkyl(3-sulfopropyl)ammonium betaines (**QS-1** and **QS-2**) for the dichlorocyclopropanation reactions. In the absence of the phase transfer reagent less than 1% conversion is detected (even after 3 h of reaction) by gas chromatography. Excellent yields of products were obtained in 2 h on using 1 mol% (based on the substrate amount) of the new catalyst



Scheme 1.

Table 1. Dichlorocarbene addition to different olefins using QS-1 and QS-2.

			% Conversion[a]	
Entry	Substrate	Product	QS-1	QS-2
1			85	88
2			90	92
3			89	90
4			93	90
5			70	72
6	CH_3-$(CH_2)_2$–CH=CH_2		93	90
7	CH_3-$(CH_2)_5$–CH=CH_2		89	91
8	CH_3-$(CH_2)_7$–CH=CH_2		86	90
9	CH_3-$(CH_2)_9$–CH=CH_2		85	87
10			98	96
11			90	88
12			75	79

[a] % conversion by gas chromatography.

thus revealing the remarkable efficiency of trialkyl(3-sulfopropyl)ammonium betaines as potential phase transfer reagents.

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 PERKIN-ELMER model 983 IR Spectrometer. Gas Chromatography was carried out using Shimadzu SC-14B instrument.

Synthesis of Triethyl(3-sulfopropyl)ammonium Betaine [QS-1] and Tributyl(3-sulfopropyl)ammonium Betaine [QS-2]

The reagents, QS-1 and QS-2 were prepared according to the literature procedure described elsewhere.[4,9] 1, 3-Propanesultone (1.2 g, 0.001 mol) was dissolved in dry acetonitrile (20 mL) and transferred into a 150 mL two-necked flask. The solution was deaerated and 1.3 mL (0.001 mol) triethylamine (for QS-1) or 2.4 mL (0.001 mol) tributylamine (for QS-2) was added to the solution. 0.001 g (0.0006 mol) of 1, 3- dinitrobenzene was added to the reaction mixture, which is used as a free radical polymerization inhibitor in the process. The reaction stirred under gentle refluxing condition at 75°C for 7 h under nitrogen atmosphere. To the cold reaction mixture 20 mL diethyl ether was added and a precipitate was collected (90% yield) and filtered repeatedly washed with ether (3 times). The white, solid QS-1 or QS-2 (highly hygroscopic) was stored in a $CaCl_2$ desiccator. **QS-1**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.68$ (t, 2H, -CH_2), 3.54 (t, 2H, CH_2), 3.12 (t, 2H, -CH_2), 2.82 (q, 2H, -CH_2), 2.15 (q, 2H, -CH_2), 1.65(q, 2H, -CH_2), 1.26–1.13 (m, 6H, -CH_3), 0.82 (t, 3H, -CH_3). ν_{max}/cm^{-1}: 2926, 2208, 1649, 1486, 1378, 980, 803. **QS-2**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.26$ (t, 2H, -CH_2), 3.67 (t, 2H, -CH_2), 3.41–3.17 (m, 8H, -CH_2), 2.85 (t, 2H, -CH_2), 2.19 (t, 2H, -CH_2), 1.68 (t, 2H, -CH_2), 1.30–1.28 (m, 12H, -CH_2, CH_3), 0.86–0.82 (t, 3H, -CH_3). ν_{max}/cm^{-1}: 2924, 2080, 1644, 1207, 1042, 980, 805.

General Procedure for the Dichlorocarbene Addition to Olefins Using the New Phase Transfer Reagents, QS-1 and QS-2

The 150 mL three-necked round bottomed flask was charged with 20 mL (40% w/w) NaOH, 1 mol% of the phase transfer reagent (based on the substrate amount) [QS-1 or QS-2] and chloroform (20 mL). The ingredients were conditioned for 10 min in the thermostat maintained at 45°C. Olefin (0.5 mL) was added to the reaction mixture and stirred for 2 h at 500 rpm. The sample from the organic layer was withdrawn by a hypodermic syringe and analyzed by Gas Chromatography (Shimadzu GC 14B with flame ionization detector using 100% methylpolysiloxane, dbl capillary column, 15 m ×0.525 mm and nitrogen as carrier gas. To the cold reaction mixture, ether (20 mL) was added and the ethereal layer was washed repeatedly with water and dried over anhydrous magnesium sulfate. The compound was purified using silica gel column chromatography. The spectral data matched with the spectra of the authentic samples.[10]

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