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# Triphenylselenonium Salts as Effective Phase-Transfer Catalysts

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**Synopsis.** Triphenylselenonium salts work as highly efficient phase-transfer catalysts for nucleophilic substitution reaction of octyl bromide and addition reaction of dichlorocarbene to olefins.

Quaternary onium salts such as ammonium salts and phosphonium salts have been extensively used as phase-transfer catalysts.[1-3] Recently we have found that sulfonium salts having bulky and hydrophobic groups also work as phase-transfer catalysts.[4-7] Among them, triphenylsulfonium salts displayed the catalytic activity even under strongly alkaline conditions, and the activity was higher than that of commercial phase-transfer catalysts such as benzyltriethylammonium chloride and octadecyltrimethylammonium chloride. In this paper we wish to report the catalytic activity of triphenylselenonium salts.

## Results and Discussion

The catalytic activity was tested in the substitution reaction of octyl bromide with several nucleophilic reagents under liquid–liquid two-phase conditions. The results are summarized in Table 1.

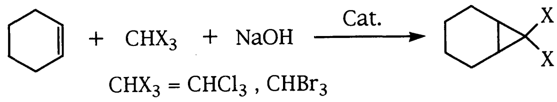
$$n\text{-}C_8H_{17}Br + MX \xrightarrow[CHCl_3/H_2O]{Cat.} n\text{-}C_8H_{17}X + MBr \qquad (1)$$

MX: KSCN, NaSCN, LiSCN, KI, NaOPh

The reaction of octyl bromide with potassium thiocyanate in chloroform-water system at 60 °C proceeded smoothly in the presence of triphenylselenonium bromide to afford octyl thiocyanate quantitatively. No substitution product was obtained in the absence of the catalyst. All triphenylselenonium salts used here displayed the catalytic activity irrespective of counter ions, and the activity was higher than that of benzyltriethylammonium chloride and tetraphenylphosphonium bromide, and comparable to that of triphenylsulfonium bromide.

The catalyst triphenylselenonium bromide also worked as an effective catalyst for substitution reaction with other nucleophilic reagents such as sodium thiocyanate, lithium thiocyanate, sodium phenoxide, and potassium iodide. It should be noted that the substitution of phenoxide under strongly alkaline conditions proceeded in the presence of triphenylselenonium bromide.

The effectiveness of these selenonium salts under alkaline conditions was further demonstrated in the addition of dichlorocarbene to an olefinic double bond. When the reaction was carried out using cyclohexene, chloroform, and sodium hydroxide in the presence of triphenylselenonium chloride, dichloronorcarane was obtained in 70% yield (Table 2).



(2)

Other selenonium salts also displayed the catalytic activity. The addition of dibromocarbene was also achieved in the same manner by using bromoform instead of chloroform. These addition reactions could be applied to other olefins such as 2-methyl-2-butene and styrene to afford the corresponding cyclopropanes.

Table 1. Substitution Reaction of Octyl Bromide with Nucleophilic Reagents Catalyzed by Triphenylselenonium Salts Under Phase Transfer Conditions[a)]

| Reagent | Cat. | $\frac{[\text{Cat.}]}{[n\text{-}C_8H_{17}Br]}$ | Time / h | Yield / % |
|---|---|---|---|---|
| KSCN | $Ph_3Se^+Cl^-$ | 0.1 | 4 | 99 |
| KSCN | $Ph_3Se^+Br^-$ | 0.1 | 4 | 99 |
| KSCN | $Ph_3Se^+I^-$ | 0.1 | 4 | 95 |
| KSCN | $Ph_3Se^+BF_4^-$ | 0.1 | 4 | 89 |
| KSCN | $Ph_3Se^+Br^-$ | 0.05 | 4 | 92 |
| KSCN | BTEAC[b)] | 0.05 | 4 | 8 |
| KSCN | $Ph_4P^+Br^-$ | 0.05 | 4 | 13 |
| KSCN | $Ph_3S^+Br^-$ | 0.05 | 4 | 87 |
| NaSCN | $Ph_3Se^+Br^-$ | 0.05 | 4 | 85 |
| LiSCN | $Ph_3Se^+Br^-$ | 0.05 | 4 | 54 |
| KI | $Ph_3Se^+Br^-$ | 0.1 | 24 | 84 |
| NaOPh | $Ph_3Se^+Br^-$ | 0.1 | 24 | 78 |

a) Reaction conditions: Temp=60 °C, $[n\text{-}C_8H_{17}Br]$=1.65 M (in $CHCl_3$), 1 ml; [KSCN, NaSCN, LiSCN]=8.0 M (in $H_2O$), 3 ml; [KI]=4.0 M (in $H_2O$), 3 ml; [NaOPh]=2.0 M (in $H_2O$), 3 ml, (1 M=1 mol dm$^{-3}$). b) Benzyltriethylammonium chloride.

Table 2. Addition Reaction of Dihalocarbenes to Olefins Catalyzed by Triphenylselenonium Salts[a]

| Olefin | Haloform | Cat. | Yield of substituted cyclopropane (%) |
|---|---|---|---|
| Cyclohexene | $CHCl_3$ | $Ph_3Se^+Cl^-$ | 70 |
| Cyclohexene | $CHCl_3$ | $Ph_3Se^+Br^-$ | 66 |
| Cyclohexene | $CHCl_3$ | $Ph_3Se^+I^-$ | 71 |
| Cyclohexene | $CHCl_3$ | $Ph_3Se^+BF_4^-$ | 63 |
| 2-Methyl-2-butene | $CHCl_3$ | $Ph_3Se^+Br^-$ | 63 |
| Styrene | $CHCl_3$ | $Ph_3Se^+Br^-$ | 78 |
| Cyclohexene | $CHBr_3$ | $Ph_3Se^+Br^-$ | 34 |
| 2-Methyl-2-butene | $CHBr_3$ | $Ph_3Se^+Br^-$ | 71 |
| Styrene | $CHBr_3$ | $Ph_3Se^+Br^-$ | 47 |

a) Reaction conditions: Temp=25° C, Time=15 min, Haloform=10 ml, Olefin=15 mmol, NaOH=2 g, Cat.=0.15 mmol.

## Experimental

**Materials.** Triphenylselenonium chloride,[8)] triphenylselenonium bromide,[9)] triphenylselenonium iodide,[8)] and triphenylselenonium tetrafluoroborate[8)] were prepared by literature procedure. Octyl bromide, cyclohexene, 2-methyl-2-butene, styrene, and solvents were purified by distillation after appropriate drying. Other reagents were obtained commercially and were used without further purification.

**General Procedure for Substitution Reaction of Octyl Bromide with Nucleophilic Reagents.** A typical procedure is decribed for the reaction of octyl bromide with potassium thiocyanate. To a glass tube containing triphenylselenonium bromide (64.4 mg, 0.165 mmol) was added a solution of potassium thiocyanate (2.33 g, 24 mmol) dissolved in distilled water (3 ml) followed by a solution of octyl bromide (319 mg, 1.65 mmol) in chloroform (1 ml). An internal standard (cyclohexylbenzene) was added to the reaction mixture and the tube was heated at 60 °C for 4 h. Analysis of the organic phase by GLC (Carbowax 20 M on Celite 545) indicated 99% yield of octyl thiocyanate.

**General Procedure for Addition Reaction of Dihalocarbenes.** A typical procedure is described for the addition reaction of dichlorocarbene to cyclohexene. To a stirring mixture of cyclohexene (1.23 g, 15 mmol), chloroform (10 ml), and powdered sodium hydroxide (2 g, 50 mmol) was slowly added triphenylselenonium chloride (51.9 mg, 0.15 mmol) at room temperature, and allowed to react for further 15 min. The mixture was acidified with 10% sulfuric acid, extracted with ether, and dried. After evaporation of the solvent, the residue was analyzed by GLC (Silicone SE-30 on Celite 545). The yield of product dichloronorcarane was 70%.

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