

Green catalysis (Phase Transfer Catalysts, Chitosan)

Catalysis

Heterogeneous

- Distinct solid phase
- **Readily regenerated & recycled**
- **Readily separated**
- Rates not as fast
- Diffusion limited
- Sensitive to poisons
- Lower selectivity
- **Long service life**
- High energy process
- Poor mechanistic understanding

Vs

Homogeneous

- Same phase as reaction medium
- Expensive
- Difficult to separate
- **Very high rates**
- Not diffusion controlled
- **Robust to poisons**
- **High selectivity**
- Short service life
- **Mild conditions**
- Mechanisms well understood

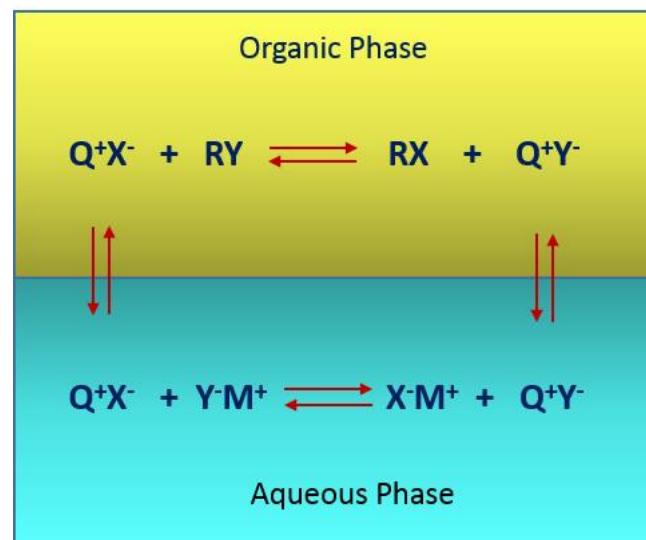
**Green
catalyst**



Phase-transfer catalysts

phase-transfer catalyst or **PTC** is a **catalyst** that facilitates the migration of a reactant from one **phase** into another phase where reaction occurs.

- Phase-transfer agents promote the solubility of ionic substances in nonpolar solvents. They transfer the ionic substance from an aqueous phase to a non-aqueous one.
- Phase-transfer agents increase the rates of reactions involving anions. The anion is relatively unsolvated and very reactive in nonpolar media compared to water or alcohols.



Mechanism

Phase-transfer catalysts

Phase-transfer catalysts are especially useful in green chemistry—by allowing the use of water, the need for organic solvents is reduced.

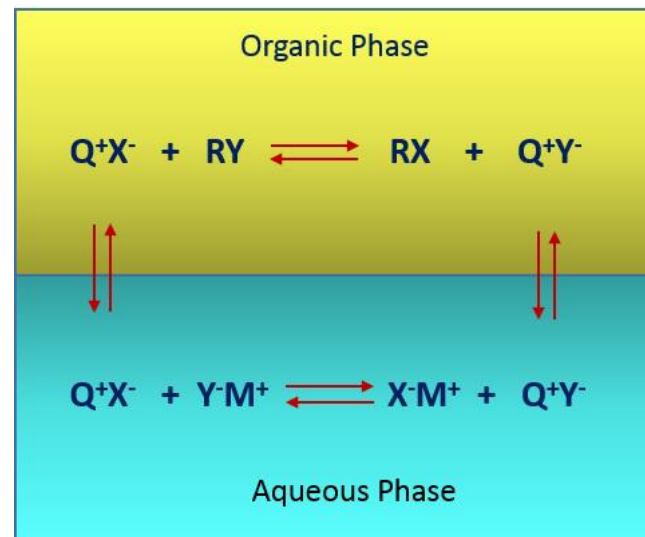
Advantages:

- faster reactions
- higher conversions or yields
- fewer byproducts
- eliminate the need for expensive or dangerous solvents to dissolve all the reactants in one phase,

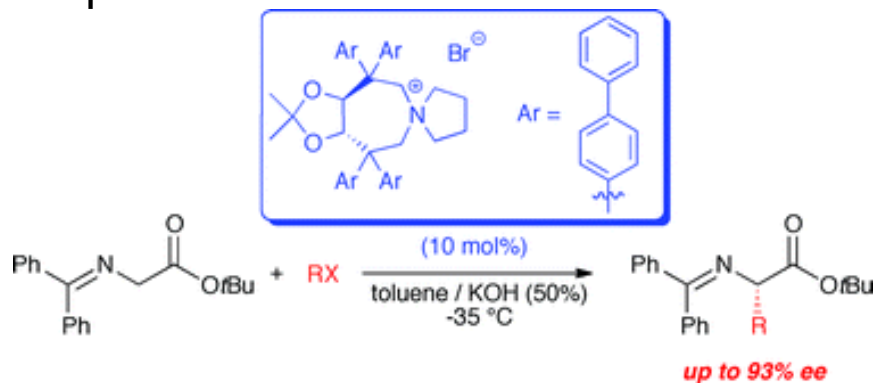
Phase-transfer catalysts

1. Quaternary ammonium salts

Example 1



Example 2

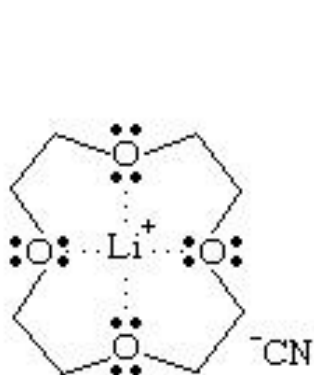


Ref: Waser et al. *Org. Biomol. Chem.*, **2012**, *10*, 251-254

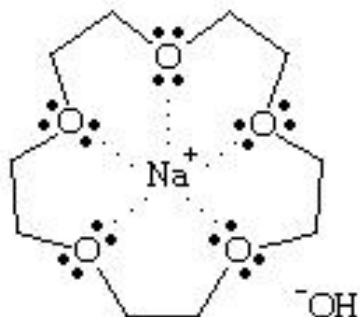
Phase-transfer catalysts

2. Crown ethers

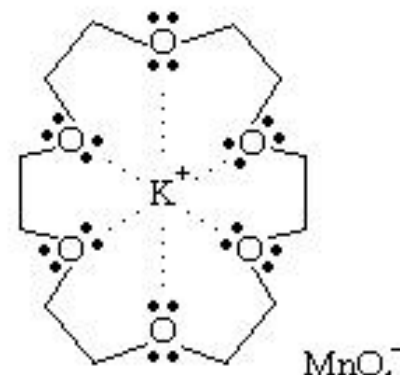
Crown ethers are specialized cyclic polyethers that surround specific metal ions to form crown-shaped cyclic complexes.



$\text{LiCN} \cdot 12\text{-crown-4}$



$\text{NaOH} \cdot 15\text{-crown-5}$

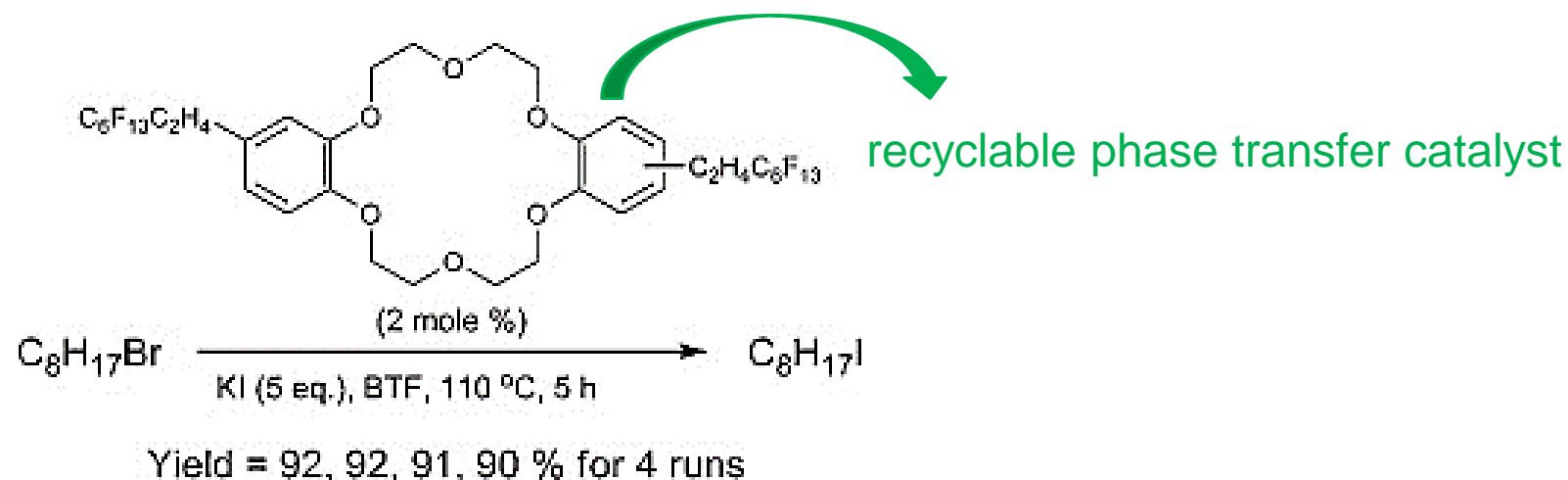


$\text{KMnO}_4 \cdot 18\text{-crown-6}$

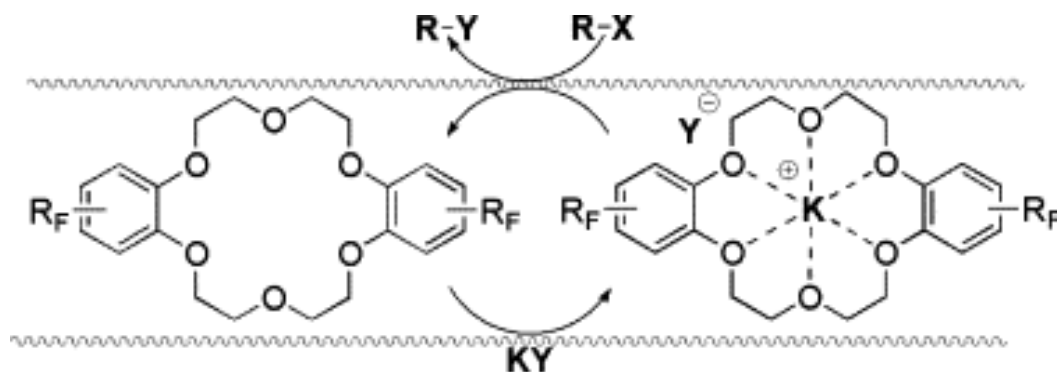
Crown ether as Catalyst

Example 1

Aliphatic and aromatic nucleophilic substitution reaction



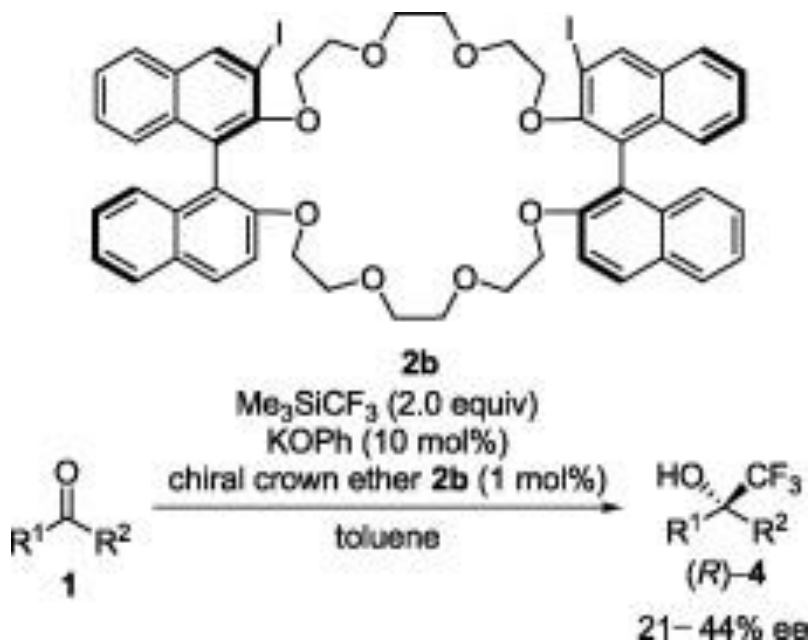
Mechanism



Crown ether as Catalyst

Example 2

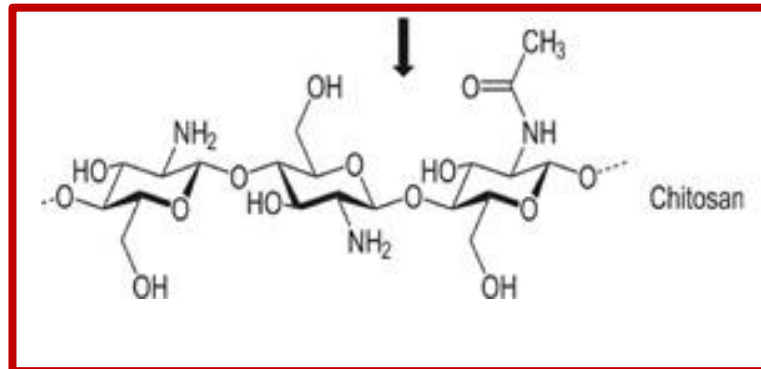
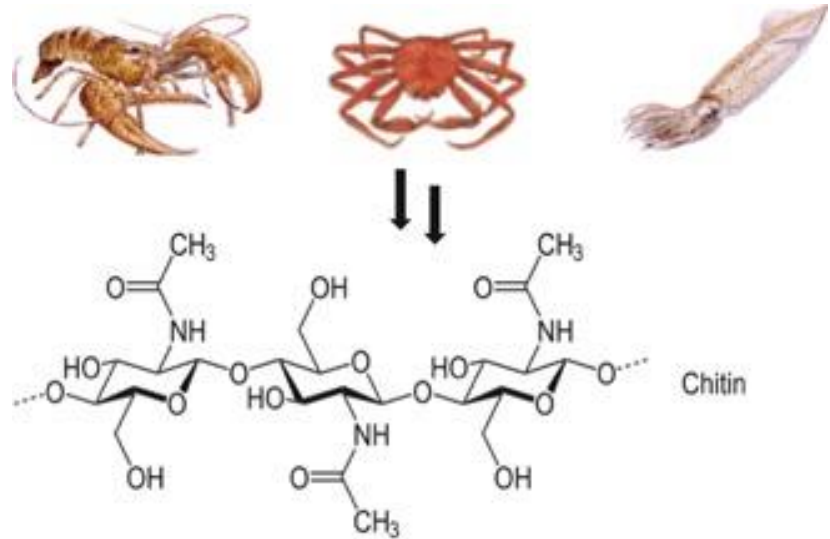
Crown ether as asymmetric catalyst in enantioselective trifluoromethylation of aldehydes and ketones



Chitosan

Hard outer skeleton of crustaceans such as shellfish, including crab, lobster, and shrimp contain **chitin** shells.

Treating the chitin with an alkaline substance, such as sodium hydroxide provide **Chitosan**.

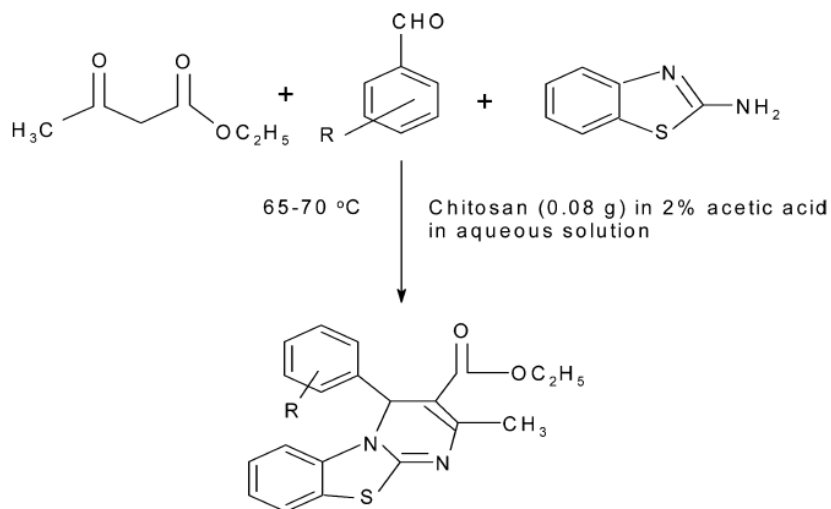


Chitosan as catalyst

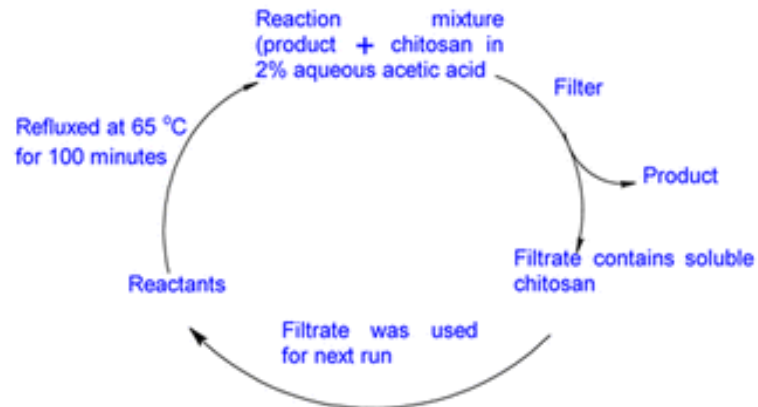
Chitosan has been used as an efficient biodegradable and reusable green catalyst for multicomponent reaction.

The chitosan catalyst can be reused 10 times in fresh reaction.

Scheme 1. Preparation of 4*H*-Pyrimido [2,1-*b*]benzothiazole Derivatives



Reusability of catalyst



Properties of our catalyst

- *Biodegradable
- *Reusable
- *High Yielding
- *Biocompatible
- *Very Active
- *Non toxic
- *Inexpensive

Ref: Sahu et al. *Ind. Eng. Chem. Res.* **2014**, 53, 6, 2085–2091

Chitosan nanoparticle as catalyst

Chitosan nanoparticles efficiently used for the Hantzsch reaction under metal and solvent free conditions.

Advantages:

simple procedure
green condition
excellent yields
short reaction time.



Scheme 2 Hantzsch reaction of carbonyl compounds and ammonium acetate catalyzed by chitosan NPs.

Thank you