

## LINEAR UNSUBSTITUTED POLYETHYLENE GLYCOLS AS PHASE TRANSFER CATALYSTS

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Phase transfer catalysis (PTC) by agents such as 18-crown-6 ether is well-known<sup>1</sup>. Recently, it has been shown<sup>2</sup> that carbowax, i.e. linear polyethylene glycol (PEG), can complex with alkali ions (notably  $K^+$ ) and transfer the complexed salt into organic phases, with an efficiency comparable to that of 18-crown-6. There is also a report of the use of oligoethylene glycol ethers as phase transfer catalysts in nucleophilic substitutions<sup>3</sup>. These have prompted us to explore the use of unsubstituted linear PEG as an inexpensive phase transfer catalyst. Indeed, we find that PEG can be successfully used as a PTC for a variety of organic reactions. The table below illustrates the versatility of PEG as a PTC. The reactions are conveniently performed, and we illustrate a typical procedure, for the O-alkylation of  $\beta$ -naphthol, a reaction considered troublesome by classical methods<sup>4</sup>. To a solution of  $\beta$ -naphthol (10mM) in 6 g neat PEG-400 (15mM) were added benzyl chloride (20mM), KOH pellets (20mM) and 1 ml water, and stirred at room temp. for 1 hr. Routine work-up and silica gel chromatography led to the isolation of  $\beta$ -naphthyl benzyl ether in 83% yield.

PEG is also able to generate 'purple benzene' by solubilizing solid  $KMnO_4$  into benzene. In an adaptation of the Sam-Simmons procedure<sup>5</sup>, using PEG, benzyl alcohol could be oxidized to benzoic acid, isolable in over 85% yields. Though no complications in the reaction or product isolation arise, PEG is permanganate labile, a problem that could perhaps be obviated by using its diether as the PTC. The advantages of PEG over crown-ether are its cost and that it does not require the ball-mill step. The electronic spectrum of the PEG-purple benzene is identical with that reported<sup>5</sup>, and we infer that the features of the reaction in both cases are similar.

REACTION	CONDITIONS	YIELD WITH PEG AS PTC	REMARKS
1. $\text{PhCH}_2\text{Cl} + \text{KSCN}$ (50 mM) (75 mM) → $\text{PhCH}_2\text{SCN}$	PEG-1500 (20 mM), $\text{CHCl}_3$ solvent, 200ml, 2 hr reflux	85% after isolation and recrystallization.	With oligoethylene glycol dimethyl ether. 90%, estd. by NMR (ref. 3). With $\text{Bu}_4\text{NCl}$ as PTC, n-BuBr gave 70% yield (ref. 6).
2. $\text{PhCH}_2\text{OH} + \text{KOCl}$ (10 mM) (40 mM) → $\text{PhCHO}$	PEG-6000 (16 mM), solvent EtOAc, 30ml, 30 min. room temp.	60% isolated as its 2,4- dinitrophenyl hydrazone.	With $\text{Bu}_4\text{NHSO}_4$ as PTC, 76%, estd. by VPC (ref. 7).
3. $\text{PhCOOCH}_2\text{Ph} + \text{KOH}$ (5 mM) (10 mM) → $\text{PhCOOH}$	PEG-400 (15 mM) neat, 1 ml water. 30 min. stirring at room temp.	80% isolated yield.	
4. $\beta$ -naphthol (10 mM) + $\text{PhCH}_2\text{Cl}$ (20 mM) → $\beta$ -Naphthyl benzyl ether.	See text.	83% isolated after silica gel chromato- graphic puri- fication.	This reaction not reported but similar ones yield 80% with other PTC (ref. 7).

We have found that PEG of molecular weight 400 or above can be used as PTC (PEG-200 is not efficient in ion binding<sup>2</sup>). PEG-400 is advantageous since it can be directly used as the solvent in several cases. Also, since PEG is as easily soluble in many organic solvents as in water, it can solubilize immiscible organic solutions into water to produce a homogeneous liquid phase. Studies on such phase-mixing catalytic features of PEG will be reported soon.

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