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POLYETHYLENE GLYCOL AS A PHASE TRANSFER CATALYST FOR ARYLDIAZONIUM SALT REACTIONS[1]

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Summary. Polyethylene glycol 1000 may be substituted for 18-crown-6 in phase transfer catalyzed reactions of aryldiazonium salts.

In an elegant series of papers, Gokel and coworkers[2,3] have reported new syntheses of aryl bromides, aryl iodides, and unsymmetrical biaryls from aryldiazonium salt reactions in solvents of low polarity. These reactions utilized the crown ether 18-crown-6 to phase transfer aryldiazonium tetrafluoroborates and the reaction-initiating potassium acetate into chloroform and benzene.

Dimethyl ethers of polyethylene glycols have been employed as phase transfer catalysts in reactions involving potassium salts.[4,5] Very recently, we have observed that the complexation constant of 18-crown-6 with p-tert-butylbenzenediazonium tetrafluoroborate is only about five-fold greater than that for certain polyethylene glycols and their dimethyl ethers.[6,7] We now report that inexpensive, commercially-available polyethylene glycol 1000 (PEG 1000) is an effective phase transfer agent for aryldiazonium salt reactions in solvents of low polarity.

Standard reaction conditions were utilized to compare the efficiencies of 18-crown-6 and PEG 1000 as phase transfer catalysts. The aryldiazonium tetrafluoroborate (0.60 mmole), potassium acetate (1.20 mmole), and phase transfer agent (variable amounts), were stirred in 6.0 ml. of the appropriate solvent or solvent combination at room temperature for 120 minutes.[8] The yields of reaction products were determined by gas chromatographic analysis of the reaction mixtures using appropriate internal standards. Yields were reproducible to ± 3%.

Results for the conversion of aryldiazonium tetrafluoroborates into aryl bromides and iodides are recorded in Table I. As might be anticipated, reactions of p-bromobenzenediazonium tetrafluoroborate, potassium acetate, and $CBrCl_3$ employing the same concentrations of 18-crown-6 and PEG 1000 give substantially higher p-dibromobenzene yields with the former. However, increasing the concentration of PEG 1000 provides a yield of p-dibromobenzene equal to the obtained with lower concentrations of crown ether. Utilizing the higher concentration of PEG 1000, yields of aryl bromides and iodides are equal to or greater than those realized with 18-crown-6 (Table I).

Yields of unsymmetrical biaryls formed by aryldiazonium ion reactions in benzene are presented in Table II. As noted with the halogenation reactions, higher product yields are obtained with higher concentrations of PEG 1000. However, in this case, reactions utilizing

Table I. Yields of Aryl Halides from Reactions of Aryldiazonium Tetrafluoroborates with Potassium Acetate and $CBrCl_3$[a] or CH_3I[b] in Chloroform.

Aryl Group	Halogen Atom Source	Phase Transfer Agent (mmole)		Yield (%) ArBr	Yield (%) ArI
p-BrC_6H_4	$CBrCl_3$	18-Crown-6	(0.03)	70 (80[c])	-
"	"	PEG 1000	(0.03)	47[d]	-
"	"	" "	(0.10)	55[d]	-
"	"	" "	(0.20)	67[d]	-
p-$NO_2C_6H_4$	"	18-Crown-6	(0.03)	63 (78[c])	-
"	"	PEG 1000	(0.20)	84	
p-BrC_6H_4	CH_3I	18-Crown-6	(0.03)	-	68 (90[c])
"	"	PEG 1000	(0.20)	-	79
p-$NO_2C_6H_4$	"	18-Crown-6	(0.03)	-	68 (78[c])
"	"	PEG 1000	(0.20)	-	74

[a]Solvent combination was $CBrCl_3$ (1.0 ml.) and $CHCl_3$ (5.0 ml.). [b]Solvent combination was CH_3I (1.5 ml.) and $CHCl_3$ (4.5 ml.). [c]Yield in parentheses was reported in Reference 3. [d]Longer reaction periods did not produce enhanced yields.

PEG 1000 appear to give somewhat lower biaryl yields than found with 18-crown-6 even at the higher PEG 1000 concentrations. Substitution of the dimethyl ether of PEG 1000[7] for PEG 1000 produced a lower yield of biaryl than found with the glycol itself.

Table II. Yields of Unsymmetrical Biaryls from Reactions of Aryldiazonium Tetrafluoroborates with Potassium Acetate in Benzene.

Aryl Group	Phase Transfer Agent (mmole)		Yield of Ar-Ph (%)
p-BrC_6H_4	18-Crown-6	(0.03)	80 (81[a])
"	PEG 1000	(0.03)	28
"	PEG 1000	(0.10)	40
"	PEG 1000	(0.20)	65
"	PEG 1000 DME[b]	(0.20)	52
p-$NO_2C_6H_4$	18-Crown-6	(0.03)	78 (85[a])
"	PEG 1000	(0.20)	65

[a]Yield in parentheses was reported in Reference 2. [b]The dimethyl ether of polyethylene glycol 1000.

Thus, it has been demonstrated that PEG 1000 is an effective agent for phase transfer catalyzed reactions of aryldiazonium salts initiated by potassium acetate in chloroform and benzene. Although substantially higher catalyst concentrations are required to achieve the same yields with PEG 1000 as with 18-crown-6, the low cost of PEG 1000 compared with 18-crown-6 is an important compensating factor.

Reference and Notes

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(8) This period produced maximal yields in the reactions using 18-crown-6.

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