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Facile Synthesis of Alkyl Phenyl Ethers Using Cesium Carbonate

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FACILE SYNTHESIS OF ALKYL PHENYL ETHERS USING
CESIUM CARBONATE

Jong Chan Lee*, Jong Yeob Yuk, and Sung Hye Cho

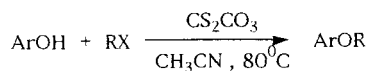
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ABSTRACT: A highly efficient alkylation method of phenols using alkyl halide/cesium carbonate/acetonitrile system is described.

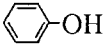
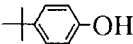
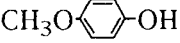
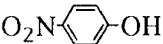
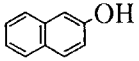


The conversion of phenols to phenyl ethers is an important transformation in organic synthesis and numerous methods have been reported to achieve this goal. However, the reaction of alkylating agents with the phenoxide ions were conventionally required aqueous or phase-transfer catalytic conditions.^{1,2} In general the bases employed in those conditions were limited to NaH, NaOH, and K₂CO₃. These bases' low solubilities in organic solvents often required somewhat longer reaction times and harsh conditions. More soluble tetraalkylammonium fluorides were used for alkylation, however, their hygroscopic nature is highly undesirable.³

Cesium salts assisted cyclization reaction has been often provided higher yields than the methods of using the other alkali metal alternatives.^{4,5}

Table : Yields in Alkylation of Phenols



RX = Methyl iodide (1)
 Allyl bromide (2)
 Benzyl bromide (3)

Entry	ArOH	Phenyl Ether Yield ^a , %		
		with 1 ^b	with 2	with 3
1		39 (13)	84	92
2		82, 55 ^c (69)	94	86
3		83, 72 ^c (45)	88	90
4		96 (88)	98	94
5		91 (84)	98	92
6		80 (65)	98	78
7		84 (80)	98	94

^a Yields of isolated products. ^b Yields in parentheses are obtained in present study with $\text{K}_2\text{CO}_3/\text{CH}_3\text{I}/\text{CH}_3\text{CN}$. ^c Yields obtained with $\text{Cs}_2\text{CO}_3/\text{dimethyl sulfate}/\text{CH}_3\text{CN}$.

To extend applicability of cesium salts and for the search of facile alkylating method, we report in this paper the results on the alkylation of various phenols by use of cesium carbonate as a base. The reaction of a range of substituted phenols with alkyl halides in CH_3CN at 80°C in

the presence of cesium carbonate were studied. The results are summarized in Table.

In the methylation process, methyl iodide exhibited better yields than dimethyl sulfate and the $\text{Cs}_2\text{CO}_3/\text{CH}_3\text{I}/\text{CH}_3\text{CN}$ system gave higher yields than the $\text{K}_2\text{CO}_3/\text{CH}_3\text{I}/\text{acetone}$ combination as illustrated in Table (entry 2, 3). The latter results clearly demonstrated that the use of cesium carbonate leads to improvements in yields compared to the potassium carbonate for the phenyl ether formation. Similarly, allylation and benzylation of phenols were carried out in the $\text{Cs}_2\text{CO}_3/\text{CH}_3\text{CN}$ system. As an alkylating agent, allyl bromide and benzyl bromide were used for allylation and benzylation respectively which provided very high yields for the most cases. Alkylations were completed smoothly within a few hours (4-5h). In the each of alkylation process, phenyl ethers were obtained as a single product. Isolated yields obtained in this study were always comparable or higher than previously reported methods. The high solubility of cesium carbonate in acetonitrile and loose ion-pair formation of phenoxides with cesium cation could be the reasons of these extraordinary high yields of alkylation in non-aqueous system.

In conclusion, we have developed a facile and efficient alkylation method of phenols in high yields with reagent combination of alkyl halide/ Cs_2CO_3 in CH_3CN .

Experimental Section

Melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FT 5300 spectrophotometer. ^1H NMR spectra were determined on Bruker

AMX 500 spectrometer. Elemental analysis was carried out at the KRISS, Taejon, Korea. Cesium carbonate (99.5 %) was purchased from Janssen Chimica. The phenols and alkyl halides were obtained from Aldrich and used without further purification.

General Procedure. The alkyl halide (5.0 equiv.) was added to a solution of phenol (0.10 g, 1.06 mmol) and Cs_2CO_3 (2.0 equiv.) in 40 mL of acetonitrile. The mixture was refluxed for 5h and the solvent was removed in vacuo. The residue was dissolved in diethyl ether (2 x 100 mL), washed with water (3 x 30 mL) and the combined ethereal layers were dried over MgSO_4 , and evaporated. The residue was chromatographed on a short silica gel column with ethyl acetate as eluent to give, after evaporation of ethyl acetate, the pure phenyl ether.

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