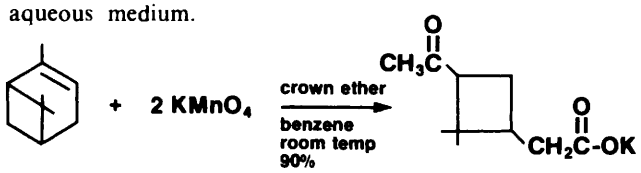
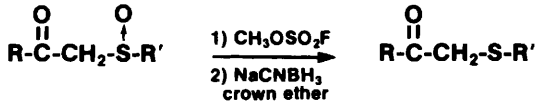
A Royal Method for Improving Reactions that Utilize Potassium Salts:

Crown Ethers

Since the discovery of their remarkable ability to solubilize alkali metal salts in non-polar solvents, crown ethers,[1] a class of macrocyclic polyethers, have found novel application in synthesis. For instance, potassium permanganate readily dissolves in benzene in the presence of dicyclohexyl-18-crown-6 to form a purple solution ("Purple Benzene") which oxidizes alcohols, olefins, aldehydes and aralkyl hydrocarbons in excellent yield under neutral conditions.[2] α-Pinene is oxidized in 90% yield[2] in contrast to only 40-60% yield in an aqueous medium.

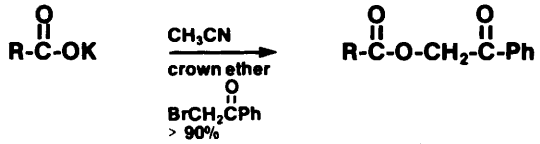


Reduction of alkoxysulfonium salts formed by alkylation of sulfoxides with Magic Methyl® (methyl fluorosulfonate) proceeds readily with sodium cyanoborohydride in the presence of crown ethers[3] to give the sulfides in excellent yield. β-Ketosulfoxides are reduced to β-ketosulfides[3] whereas extensive decomposition occurs in the absence of the crown ether:



Also, sodium borohydride reduces ketones in aromatic hydrocarbon solvents in the presence of dibenzo-18-crown-6.[4]

Phenacyl esters which are difficult to obtain in good yield using classical procedures are easily formed[3] by refluxing a benzene or acetonitrile suspension of the aryl salt, crown ether and the β-bromoacetophenone:



The alkylation of acetoacetic ester enolates gives less *O*-alkylated product in the presence of a crown ether[5] especially in weakly polar solvents. Dicyclohexyl-18-crown-6 also markedly changes the rates and stereochemical course[6] of alkoxide-catalyzed carbanion-generating reactions. Moreover, the reaction of 5-decyl tosylate with potassium alkoxides[7] produces more *trans* olefin in the presence of dicyclohexyl-18-crown-6. In a similar fashion the stereochemical course of the reaction of potassium *tert*-butoxide with *trans*-2-phenylcyclopentyl tosylate[8] is markedly changed by the addition of dicyclohexyl-18-crown-6.

Crown ethers also find application in the resolution of α-amino acids,[9] in the manufacture of an ion-selective electrode,[10] and in studies of ion-transport mechanisms.[1]

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