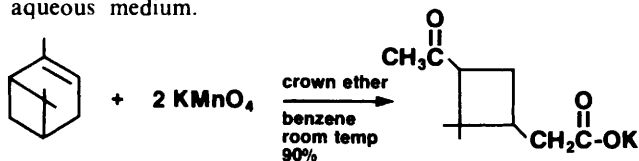




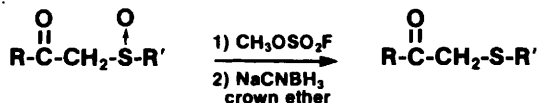
A Royal Method for Improving Reactions that Utilize Potassium Salts: Crown Ethers



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% yield² in contrast to only 40-60% yield in an aqueous medium.

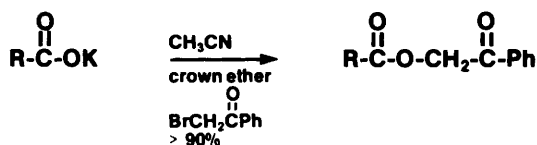


Reduction of alkoxy-sulfonium salts formed by alkylation of sulfoxides with Magic Methyl® (methyl fluorosulfonate) proceeds readily with sodium cyanoborohydride in the presence of crown ethers³ to give the sulfides in excellent yield. β -Ketosulfoxides are reduced to β -ketosulfides³ whereas extensive 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 formed⁵ 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 ether⁵ especially in weakly polar solvents. Dicyclohexyl-18-crown-6 also markedly changes the rates and stereochemical course⁶ of alkoxide-catalyzed carbanion-generating reactions. Moreover, the reaction of 5-decyl tosylate with potassium alkoxides⁷ 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 tosylate⁸ 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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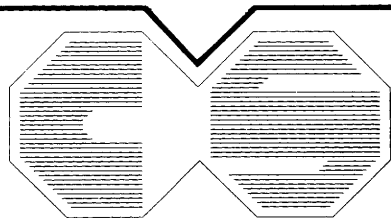
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