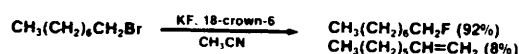


Crown Ethers

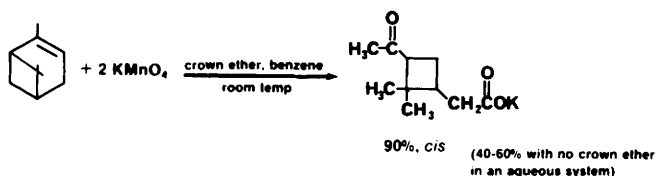


How to dissolve alkali metal salts in organic solvents

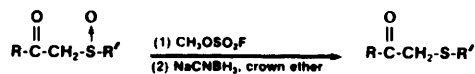
Since the discovery of their remarkable ability to solubilize alkali metal salts in non-polar solvents, crown ethers,^{1a,b} a class of macrocyclic polyethers, have found novel application in synthesis. The new crown ether, **18-crown-6**, promises even greater synthetic utility by virtue of its increased complexing ability.² For example, in acetonitrile or benzene effective solvation of the potassium ion of potassium fluoride by **18-crown-6** results in a highly reactive fluoride ion ("naked" fluoride).² "Naked" fluoride is a potent base and nucleophile,² being capable of converting a variety of alkyl, acyl, or activated aryl halides to their respective fluorides in good yields.



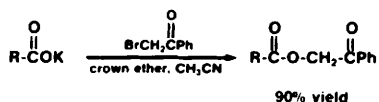
In the presence of **dicyclohexyl-18-crown-6**, potassium permanganate readily dissolves in benzene to form a purple solution ("Purple Benzene")³ which oxidizes alcohols, olefins, aldehydes and aralkyl hydrocarbons in excellent yield under neutral conditions.



Alkoxy-sulfonium salts, formed by alkylation of sulfoxides with **Magic Methyl**[®] (methyl fluorosulfonate), are readily reduced with sodium cyanoborohydride in the presence of crown ethers⁴ to give sulfides in excellent yield. Similarly, β -ketosulfoxides are reduced to β -ketosulfides,⁴ whereas extensive decomposition occurs in the absence of the crown ether.



Phenacyl esters which are difficult to obtain in good yield using classical procedures are easily formed by refluxing a benzene or acetonitrile suspension of acyl salt, crown ether and α -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** markedly changes the rates and stereochemical course⁶ of alkoxide-catalyzed carbanion-generating reactions; e.g., the reaction of 5-decyl tosylate with potassium alkoxides⁷ produces more *trans* olefin in the presence of **dicyclohexyl-18-crown-6**. Crown ethers also find application in the resolution of α -amino acids⁸ and show promise for the preparation of organometallics⁹ by catalyzing the reaction between metals and C-halogen or acidic C-H compounds. The potassium hydroxide complex of **dicyclohexyl-18-crown-6** reacts with *o*-dichlorobenzene¹⁰ to give *o*-chloroanisole in 40-50% through a non-benzyne mechanism. Finally, crown ethers may be contrasted with our α - and β -cyclodextrins. While the cyclodextrins have a lipophilic cavity and hydrophilic shell the reverse is true of the crown ethers.¹¹

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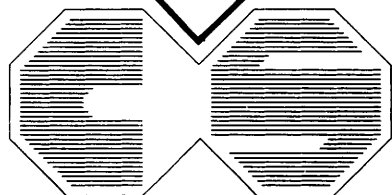
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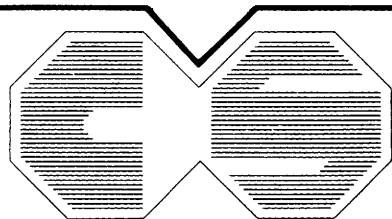
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