18-Crown-6 *(1,4,7,10,13,16-hexaoxacyclooctadecane)*

PRODUCT NO.
18,665-1

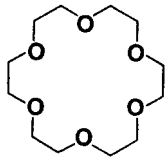
revised 4 / 96

2 pages

Technical Bulletin AL-115

PROPERTIES:

Molecular formula ..... $C_{12}H_24O_6$
F.W. 264.32
m.p. ..... 39-40°
RTECS# MP4500000
CAS No. 17455-13-9



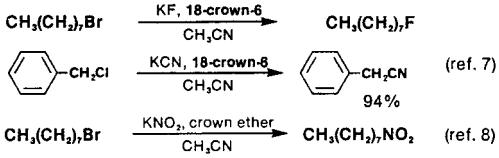
LITERATURE REFERENCES:

Fieser **4**, 142; **5**, 152; **6**, 133; **7**, 76; **8**, 128; **9**, 126

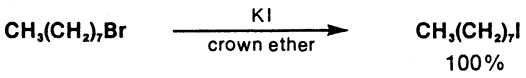
"Crown ethers" is the common name for a group of macrocyclic polyethers which have become valuable tools in organic synthesis as a result of their ability to solvate alkali, alkaline-earth and transition-metal cations in nonpolar, aprotic solvents.[1-3] The selectivity of the crown ethers as complexing agents results from the definite size of the crown cavity, which only admits cations of comparable ionic radii. 18-Crown-6 has an estimated cavity diameter of 2.6 - 3.2Å and is most suitable for complexing with K^+, NH_4^+, and Rb^+ (ionic diameters 2.66, 2.86, and 2.94Å, respectively).[4,5]

When a salt is dissolved in an aprotic solvent using a crown ether, the anion is exposed in such a way that it becomes highly reactive. The nucleophilicities of these exposed ("naked") anions toward organic and inorganic substrates have been the subject of increased research in recent years, as evidenced by the applications below.

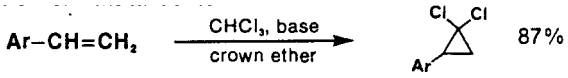
SOLID/LIQUID PHASE-TRANSFER CATALYSIS[6]



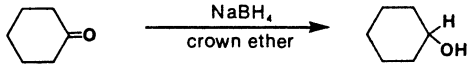
LIQUID/LIQUID PHASE-TRANSFER CATALYSIS[9-11]



FORMATION OF HALOCARBENES[12-14]

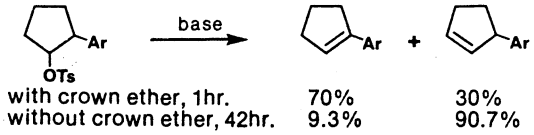


CATALYST IN $NaBH_4$ REDUCTIONS IN AROMATIC SOLVENTS[15]

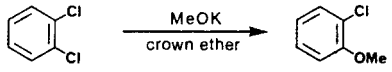


BASE-CATALYZED ELIMINATION REACTIONS[14,17]

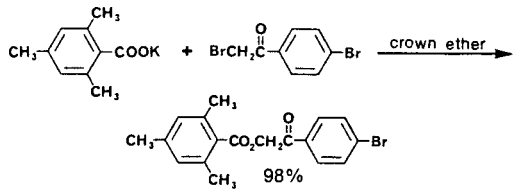
Crown ethers have been found to increase reactivity and influence product geometry.



NUCLEOPHILIC AROMATIC SUBSTITUTION OF UNACTIVATED AROMATIC HALIDES[18]



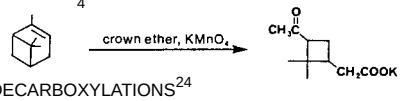
PRODUCTION OF PHENACYL ESTERS[19,20]



FORMATION OF AROMATIC RADICAL IONS[21,22]

Radical anions of benzene and toluene can be generated by adding 18-crown-6 to alkali metals like sodium and potassium in nonpolar solvents.

OXIDATION WITH $KMnO_4$ IN BENZENE[23]

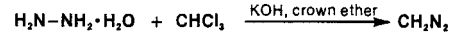


CATALYST FOR DECARBOXYLATIONS[24]

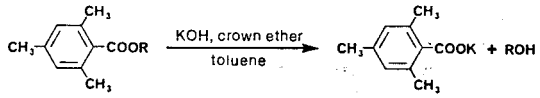
The reaction time has been reported to decrease by a factor of 10^5 when using crown ethers.

CATALYST FOR THE PRODUCTION OF DIAZOMETHANE[25]

Crown ethers simplify the synthesis of diazomethane from hydrazine and chloroform, also increasing the yield.



SAPONIFICATION OF STERICALLY HINDERED ESTERS[26]



PEPTIDE SYNTHESIS[27]

18-Crown-6 was found to function as a catalyst in the quanittative esterification of a chloromethyl resin by the potassium salt of a *t*-Boc amino acid under mild reaction conditions.

TOXICITY AND HANDLING

Very little is known about the biological activity of the crown ethers, but limited acute oral toxicity studies reportedly showed that 18-crown-6 caused CNS effects.[28] It has also been suggested that the crown ethers may be readily absorbed through skin. Since its toxicological properties have not been fully investigated, it is advised that 18-crown-6 be handled with due care by persons wearing gloves and working in a well ventilated fume hood. All contact and inhalation should be avoided.

DISPOSAL

Incineration. Observe all federal, state and local laws.

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