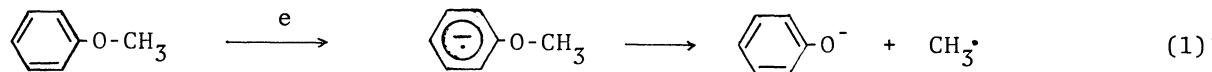


REGIOSELECTIVE CLEAVAGE OF ARYL DECYL ETHERS WITH ALKALI METALS

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Alkali metal cleavage of several types of aryl decyl ethers was conducted in HMPA and THF. Smaller alkali metals in HMPA tend to cleave the bond between the decyl group and oxygen. Potassium in THF cleaves the bond between the aryl group and oxygen in good yields.

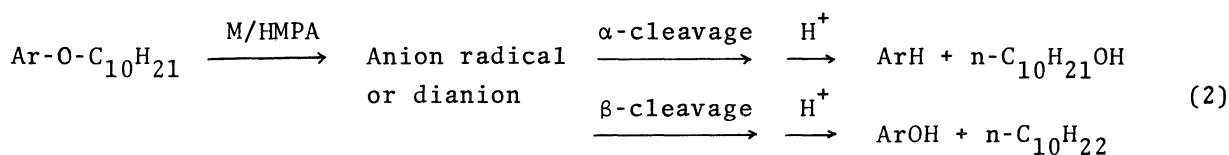
The alkali metal cleavage of bonds between carbon and oxygen atom or other heteroatoms has been proved to be of great value in the synthesis of organometallic reagents¹⁾ and in the degradation of certain organic systems, for example, reductive dealkylation of coals²⁾. Some alkyl aryl ethers were previously cleaved by alkali metals in liquid ammonia³⁾, pyridine⁴⁾, ethylenediamine⁵⁾, hexamethylphosphoric triamide (HMPA)⁶⁾, and tetrahydrofuran (THF)⁷⁾. In the case of anisole, the most likely mechanism is the anion radical reaction. The products of the reaction suggest that cleavage always occurs between the methyl group and oxygen which would also be expected on the basis of bond strengths of the aliphatic vs aromatic carbon to oxygen bonds (eq. 1). However, when the reaction was extended to the cleavage of aryl decyl ethers, the results were highly different and the course



of cleavage markedly depended on alkali metals and solvents used.

In the present paper, in order to gain insight into those factors operative in determining the course, cleavage of several types of aryl decyl ethers was investigated using a variety of methods employing such alkali metals as lithium, sodium, and potassium.

The reactions were first carried out in HMPA which was employed successfully by Normant et al. to the cleavage of anisole and benzyl phenyl ether⁶⁾. Under atmosphere of nitrogen, aryl decyl ethers were added at room temperature into the alkali metal solution of HMPA-THF. After stirring for 2 hr, the reaction mixture was treated with methanol and then with dilute hydrochloric acid. The products of the reaction were, in each case examined, phenol, aromatic hydrocarbon, 1-decanol, decane, and small amounts of reduced products of the aromatic hydrocarbon. Eicosane, a coupling product of decyl radical, was not obtained in any case. Thus the course of cleavage was determined from 1-decanol and decane obtained (eq. 2). Representative results are summarized in Table 1. When sodium was used, the reactions proceeded readily and provided higher yields of cleavage products in a range of 90 to 95 %. The cleavage of ether bond



predominantly occurred between the decyl group and oxygen bond (β -cleavage) which may be expected on the reaction of anisole. However, when potassium was used, α -cleavage (between the aryl group and oxygen) increased to 37-44 %, especially in the case of larger aryl ethers. Low yields may have resulted from low stability of potassium in HMPA⁸) and not from low reactivity.

Table 1. The Cleavage of Aryl Decyl Ethers by Alkali Metal in HMPA/THF^{a)}

Ether	Metal	Total Yield ^{b)}	Course of cleavage (%)	
			β (decane), α (1-decanol)	
Ar-O-C ₁₀ H ₂₁	Na	91	92	8
	K	63	63	37
α -naphthyl	Na	90	92	8
	K	59	56	44
β -naphthyl	Na	90	92	8
p-biphenylyl	Na	93	83	17
phenyl	Na	94	100	0
p-tolyl	Na	94	100	0

a) Reactions were carried out at room temp. for 2 hr using 5 mmol of alkali metal, 1 mmol of aryl decyl ether, 3 ml of HMPA, and 3 ml of THF under nitrogen.

b) Total yields of decane and 1-decanol based on ethers used.

The use of electron carrier such as biphenyl was also effective for the ether cleavage⁷). The homogeneous condition permits the reactions to proceed faster and even the less reactive alkali metal such as lithium, could be employed successfully. To the highly colored solution of 2:1 metal-biphenyl adduct in THF aryl decyl ethers were added at room temperature and was allowed to react for 2 hr. In general, lithium was proved to be far more favorable and better results were obtained with the majority of ethers. Sodium and potassium failed to cleave decyl phenyl ether under these conditions. The results are summarized in Table 2. Under these conditions, α -cleavage increased and it was ascertained that the course of cleavage markedly depended on alkali metals and ethers used.

In the absence of electron carrier, lithium or sodium in THF was inert to these ethers even at higher temperatures, but potassium reacted readily. The tendency of α -cleavage was significantly increased to 70-85 % as described in Table 3.

At present, two possible mechanisms were reported for the cleavage of ethers. The first is an anion radical mechanism elucidated by Angelo⁹) and Evans¹⁰). The second is the dianion mechanism reported by Eargle¹¹) and Eisch⁷).

Table 2. The Cleavage of Aryl Decyl Ethers by Alkali Metal-Biphenyl Solutions in THF^{a)}

Ether Ar-O-C ₁₀ H ₂₁	Metal	Total Yield ^{b)}	Course of cleavage (%)	
			β(decane), α(1-decanol)	
α-naphthyl	Li	97	54	46
	Na	78	18	82
	K	67	54	46
β-naphthyl	Li	85	36	64
	Na	58	34	66
	K	61	44	56
p-biphenyl	Li	78	69	31
	Na	74	5	95
	K	92	7	93
phenyl	Li	67	79	21
	Na, K	0	-	-

a) Reactions were conducted at room temp. for 2 hr using 5 mmol of alkali metal, 1 mmol of ether, 0.25 mmol of biphenyl, and 6 ml of THF.

b) Total yields of decane and 1-decanol based on ethers used.

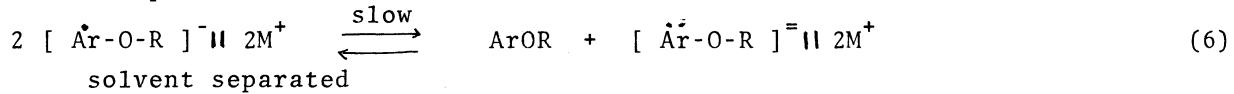
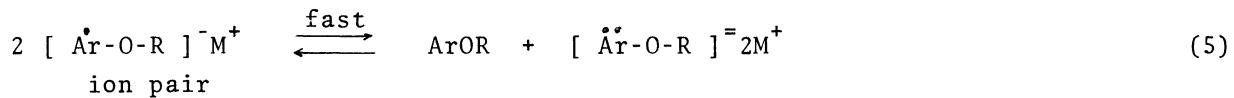
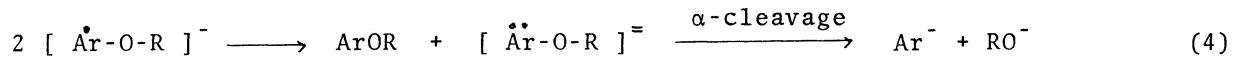
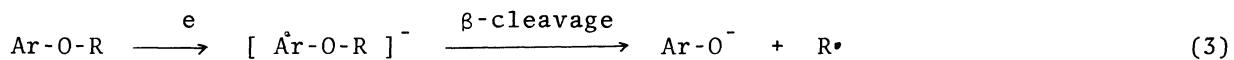
Table 3. The Cleavage of Aryl Decyl Ethers by Potassium in THF^{a)}

Ether Ar-O-C ₁₀ H ₂₁	Temp. °C	Time hr	Total Yield ^{b)}	Course of cleavage (%)	
				β(decane), α(1-decanol)	
α-naphthyl	35	1	78	29	71
β-naphthyl	35	1	71	30	70
p-biphenyl	35	2	76	15	85
phenyl	60	4	trace	-	-

a) Reactions were conducted using 1 mmol of ether, 10 ml of THF, and 2.5 mmol of potassium under nitrogen.

b) Total yields of decane and 1-decanol based on ethers used.

Our results may be most likely interpreted by the two mechanistic possibilities (eq. 3, 4). One electron transfer to the ether formed the anion radical in which the added electron is in the aromatic ring. Ejection of alkyl radical would cause the β-cleavage, which upon reduction and protonation is converted to decane. The solvent such as HMPA which forms strong associations with the cations, favors formation of the solvent separated anion radicals, which does not disproportionate to dianion owing to its higher reduction potential than ion pairs (eq. 6).¹²⁾ A less polar solvent such as THF does not bind strongly with the cation, hence



dianion formation is correspondingly more favorable (eq. 5), and causes α -cleavage. The influence of alkali metals on the course of cleavage may be also interpreted by solvation. Hence the smallest cation, lithium, which strongly associates with the solvent because of the higher heat of solvation ($\text{Li} > \text{Na} > \text{K}$), would form solvent separated anion radicals. Conversely, potassium tends to form dianions¹³⁾. However, whether the predominant pathway is anion radical or dianion mechanism would also depend upon the aromatic rings used for cleavage of ethers. The reduction potential of aromatic hydrocarbon suggests that biphenyl ether is most easily reduced¹³⁾. Indeed, the order for ease of α -cleavage is biphenyl, naphthyl, and phenyl ether.

Our present observations suggest that regioselective cleavage of alkyl aryl ethers is possibly achieved by changing the metal and solvent. Highly polar solvent and smaller alkali metals favor cleavage of the bond between alkyl group and oxygen. And less polar solvent and potassium tends to cleave the bond between the aryl group and oxygen.

Other polar solvents such as dimethoxyethane are under investigation.

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