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NEW REAGENTS 3[1a,b] : ALUMINIUM IODIDE - A HIGHLY REGIOSELECTIVE ETHER-CLEAVING REAGENT WITH NOVEL CLEAVAGE PATTERN

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Abstract: AlI_3 is an easily accessible and versatile ether-cleaving reagent.

Boron and silicon halides have been widely used for the cleavage of dialkyl and aryl alkyl ethers.[1a,b,2,3,4] Although $AlCl_3$[5] has been employed for the cleavage of certain types of ethers, its usefulness for ether cleavage is rather limited. Brief reports on the ether-cleaving property of $AlBr_3$ and AlI_3 have not been followed up to explore the full synthetic potential of these reagents.[6,7,8]

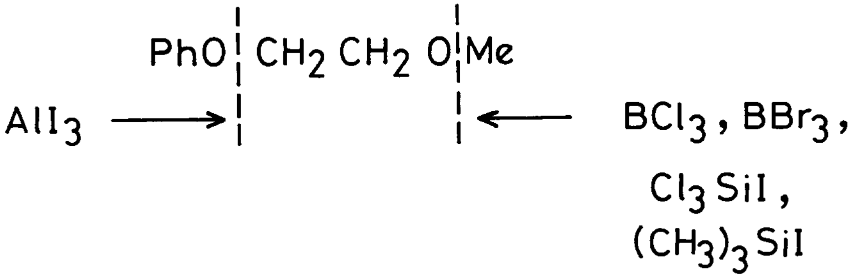
The Lewis acid strength of aluminium halides increase in the order[9]

$$AlCl_3 < AlBr_3 < AlI_3 .$$

One could expect AlI_3 to be a highly reactive reagent.

Inverse reactivity pattern:

In CH_3CN, AlI_3 cleaves aromatic aliphatic ethers much faster than dialkyl ethers. For example, anisole is cleaved in 12 hr. at 80°C, whereas cyclohexyl methyl ether requires 52 hr. under the same conditions. This is further illustrated in the case of 1-methoxy-2-phenoxy ethane. We find AlI_3 alone gives phenol, whereas other reagents give 2-phenoxy ethanol (see Table I). This behaviour of AlI_3 is in contrast to the normal reactivity pattern of silicon and boron reagents (Scheme I).



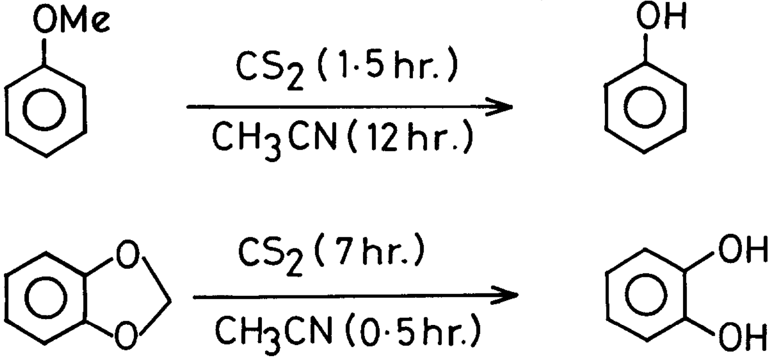
Scheme I

TABLE I. Cleavage of $PhOCH_2CH_2OMe$ with various reagents

Reagent	Mole ratio substrate: reagent	Time hr./temp. °C	Solvent	Products isolated yield (%)		
				PhOH	$PhOCH_2CH_2OH$	Starting material
AlI_3	1:1	4/82	CH_3CN	75.7	-	-
BCl_3	3:1	15/65	$CHCl_3$	traces	47	25.4
BCl_3	1:1	11/65	$CHCl_3$	33	58.7	-
BBr_3	3:1	22/25	CH_2Cl_2	traces	44.3	19.4
$(CH_3)_3SiCl$/ NaI	1:1	12/25	CH_3CN	traces	55.1	33.5
$SiCl_4$/NaI	1:1	16/25	CH_3CN: CH_2Cl_2 1:1	traces	75	6

<u>Novel solvent effects</u>:

Another noteworthy feature is that the rates of cleavage of certain ethers are reversed in CS_2 and in CH_3CN. 1,3-Benzodioxzole (0.5hr.) and o-dimethoxybenzene (0.5hr.) are cleaved faster than anisole (12hr.) in CH_3CN, whereas the reverse is observed in CS_2(1,3-benzodioxzole 7hr., o-dimethoxybenzene 19hr., anisole 1.5hr.) (see Table II, entry 1,4&7) (Scheme II).



Scheme II

In CS_2 and in C_6H_6 secondary alkyl groups, after they are converted to the corresponding iodides during ether cleavage undergo isomerisation to give a mixture of products. This does not take place in CH_3CN medium in which even labile ethers like allyl phenyl ether gives phenol and allyl iodide. No ring alkylation products could be detected (see Table II, entry 3).

<u>Preparation of AlI_3:</u>

Dry aluminium foil (250 mg, 9.3 mmol) and iodine (1.9 g, 15 mmol) were refluxed in dry CS_2 (10 ml) or dry CH_3CN (8 ml) till the iodine colour disappeared (~3 hr.).

TABLE II. Cleavage of ethers with AlI_3

Entry	Substrate	Substrate: reagent ratio	Product[c]	Solvent system[a]	Time of reflux hr.	Yield[b] (%)
1	Anisole	1:1	Phenol	A	12	94
		1:1	Phenol	B	1	90.3
		1:1	Phenol	C	1.5	90.4
2	p-Dimethoxybenzene	1:1	p-Methoxyphenol	C	3	74.2
		2:1	Hydroquinone	C	4	85
3	Allyl phenyl ether	1:1	o-Allylphenol	C	d	26
			Phenol			4.5
		1:1	Phenol	A	5	89
4	1,3-Benzodioxzole	1:1	Catechol	A	0.5	70.5
		2:1	Catechol	B	5.5	68.0
		2:1	Catechol	C	7	80
5	Methyl-o-methoxybenzoate	1:1	Methyl salicylate	C	0.9	76
6	Methyl-p-methoxybenzoate	2:1	Methyl-p--hydroxybenzoate	C	6	68
7	o-Dimethoxybenzene	3:1	Catechol	C	19	84
			Guaiacol			2
		2:1	Catechol	B	7.5	91
		1:1	Catechol	A	0.5	93
8	1-(2-Methoxyethoxy)--2-methoxy benzene	1:1	Catechol	A	0.75	80
9	Tetrahydrofuran	1:1	4-Iodobutanol	A	5	70
			1,4-Diiodobutane			5.8
10	Cyclohexyl-n-butyl ether	1:1	Cyclohexanol	A	24[e]	37.8[f]
			Cyclohexyl iodide			2.6
			starting material			25.3

a)Solvent system - A-Acetonitrile; B-Benzene; C-Carbondisulphide. b)all yields were isolated yields. c)the products were identified by spectroscopic data and physical constants. d)3.5 hr at ~ -70°C. e)sealed tube at 90-95°C. f)yield calculated by GLC analysis.

Cleavage of 1,3-benzodioxzole in CS_2:

To a freshly prepared solution of AlI_3 (10 mmol) in CS_2, 1,3-benzodioxzole (610 mg, 5 mmol) in CS_2 (2 ml) was added and refluxed till there was no more starting material (7 hr. TLC). The cooled reaction mixture was decomposed with ice, extracted with ether and washed with thiosulphate solution. The thiosulphate solution was extracted once again with ether and the combined ether extract was dried over anhydrous $MgSO_4$. The solvent was removed and the product was chromatographed (TLC silica gel; 3:1 hexane: ethylacetate) to obtain catechol, 440 mg (80%); m.p. 106°C (Lit.[10] m.p.104.8 - 105.8°C).

Cleavage of allyl phenyl ether in CH_3CN:

To a freshly prepared solution of AlI_3 (5 mmol) in CH_3CN, allyl phenyl ether (670 mg, 5 mmol) in CH_3CN was added and the concentration of the solution was adjusted to ~1M with respect to both reagent and reactant. The reaction mixture was refluxed till there was no more starting material (5 hr. TLC), cooled and poured into water. The mixture was extracted with ether and the aqueous extract was washed with 5% sodium hydroxide solution. After acidification of the alkaline aqueous solution, it was extracted into ether, dried over anhydrous $MgSO_4$ and the solvent was removed. The crude product after short path distillation yielded phenol; 418 mg (89%).

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