Communications to the Editor

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RADICAL CATION INDUCED REDUCTIVE DEHALOGENATION OF *ORTHO*- AND *PARA*-HALOPHENOLS AND THEIR DERIVATIVES

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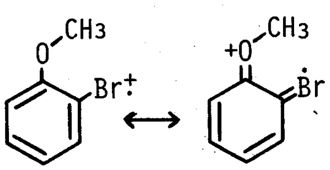
Ortho- as well as *para*- halophenols and their derivatives were reductively dehalogenated in high yields. These reactions proceed through a mechanism which involves initial generation of a radical cation.

KEYWORDS —— reductive dehalogenation; radical cation; hard acid; soft nucleophile; aluminum chloride; ethanethiol; halophenol

Recently, we have developed new reactions such as carbon-oxygen bond cleavage,1) carbon-carbon double bond cleavage,2) preparation of sulfides of polycyclic aromatics3) and the following reductive displacement of alkylthio groups into hydrogen,4) and denitration of primary α-nitroketones5) using a hard acid and soft nucleophile system. Now we wish to report a new type of reductive cleavage of carbon-halogen bond on an aromatic nucleous using this system.

Reaction conditions and yields of the dehalogenated products are listed in Tables I and II.6) Except for phenyl ether (entry 5 in Table II), simultaneous dealkylation (entries 1 and 6 in Table I and 3 in Table II), partial dealkylation (entries 2 and 4 in Table II), or deacylation (entry 3 in Table I) took place to afford the corresponding phenol. In *ortho*-halophenol derivatives, none of the *para*-substituents tested (Me, CH_2CO_2Et, and CO_2Me) prevented the reaction. Corresponding chlorides and fluorides proved to be inert under the same reaction conditions. The reaction of *para*-bromoanisole (1 mmol) with aluminum chloride (1.5 mol eq) in ethanethiol (2.4 ml) for 15 min at 0°C without dichloromethane did not afford dehalogenated products but gave *para*-bromophenol in 67% yield along with a 23% recovery of starting material (compare with entry 2 in Table II). This significant solvent effect can be attributed to the change in the mechanism. It has been reported that aluminum chloride is an effective one-electron oxidant which can oxidize the compound possessing a first ionization potential of ∿ 8 eV.7)



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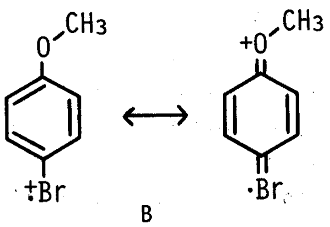

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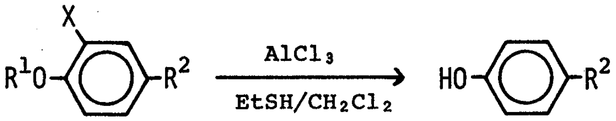
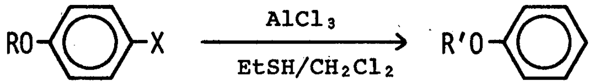
Table I. Reductive Dehalogenation of *ortho*-Halogenated Compounds



Entry	X	R^1	R^2	$AlCl_3$ (mol eq)	Time (h)	Temp. (°C)	Yield (%)
1	Br	Me	H	2.5	1.5	r.t.	94.9
2	Br	H	Me	1.5	0.5	0	94.3
3	Br	Ac	Me	1.5	4.0	0→r.t.	88.6
4	Br	H	CH_2CO_2Et	1.5	17.0	0→r.t.	97.5
5	I	H	H	1.5	0.15	r.t.	86.7
6	I	Me	CO_2Me	5.0	6.5	0→r.t.	95.1

Table II. Reductive Dehalogenation of *para*-Halogenated Compounds



Entry	X	R	$AlCl_3$ (mol eq)	Time (h)	Temp. (°C)	Product (Yield, %)
1	Br	H	1.5	1/4	0	R'=H (89.1)[a,b]
2	Br	Me	1.5	1/4	0	R'=H (45.4), R'=Me (35.8)[a]
3	Br	Me	2.6	1.2	r.t.	R'=H (85.9)
4	Br	Et	1.5	2/3	0	R'=H (63.9), R'=Et (25.1)[a]
5	Br	Ph	1.5	2	0→r.t.	R'=Ph (98.3)
6	I	H	1.5	1/6	r.t.	R'=H (82.0)

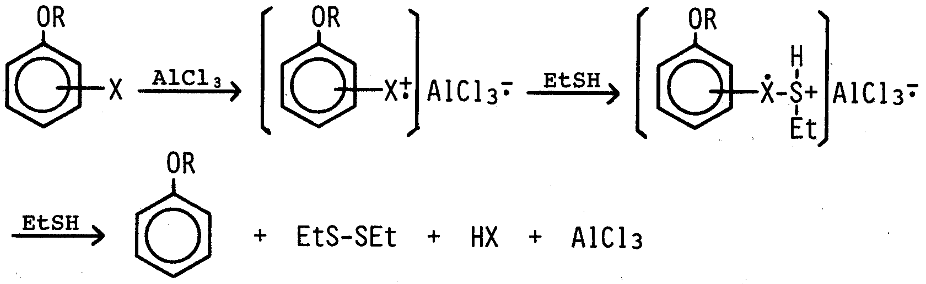
[a] By GLC analysis. [b] 10% of starting material was recovered.

Especially dichloromethane was claimed to be the most satisfactory solvent for this purpose.[8] Thus, it is reasonable to assume that aluminum chloride acts as one-electron oxidant in dichloromethane and as a Lewis acid in ethanethiol. The ESR spectra clearly indicated the formation of the radical cations **A** (g = 2.0040) and **B** (g = 2.0031) from *ortho*- and *para*-bromoanisole, respectively, with aluminum chloride in dichloromethane at room temperature. However the radical cation from *meta*-bromoanisole was not detected by ESR measurement in accord with the fact that the halogens *meta* to an oxygen function were not removed. Therefore, the dehalogenation should involve the initial formation of a radical cation.

Diethyl disulfide was obtained from every reaction. No reductive cleavage of carbon-halogen bond proceeded when diethyl sulfide was used for ethanethiol. Though the fine points of the mechanism still remain to be clarified, the plausible pathway shown in Figure 1 agrees with the above observations.

A huge number of methods for reductive cleavage of the carbon-halogen bond in aromatic compounds have been reported.[9] However, reductive dehalogenation induced by a radical cation has never been described in the literatures. Detailed studies from the mechanistic point of view are currently being pursued.

Figure 1. A Plausible Mechanism of Dehalogenation



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6) A typical experimental procedure for reductive dehalogenation follows (run 2 in Table I): To a stirred solution of 2-bromo-4-methylphenol (1 mmol) in dichloromethane (2 ml) and ethanethiol (0.4 ml) was added aluminum chloride at 0°C. After the mixture was stirred for 30 min at the same temperature, it was poured into ice-water. Extractive work-up followed by chromatographic purification afforded *para*-cresol (94.3%).
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