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Mild Chlorination of Aromatic Compounds with Tin(IV) Chloride and Lead Tetraacetate

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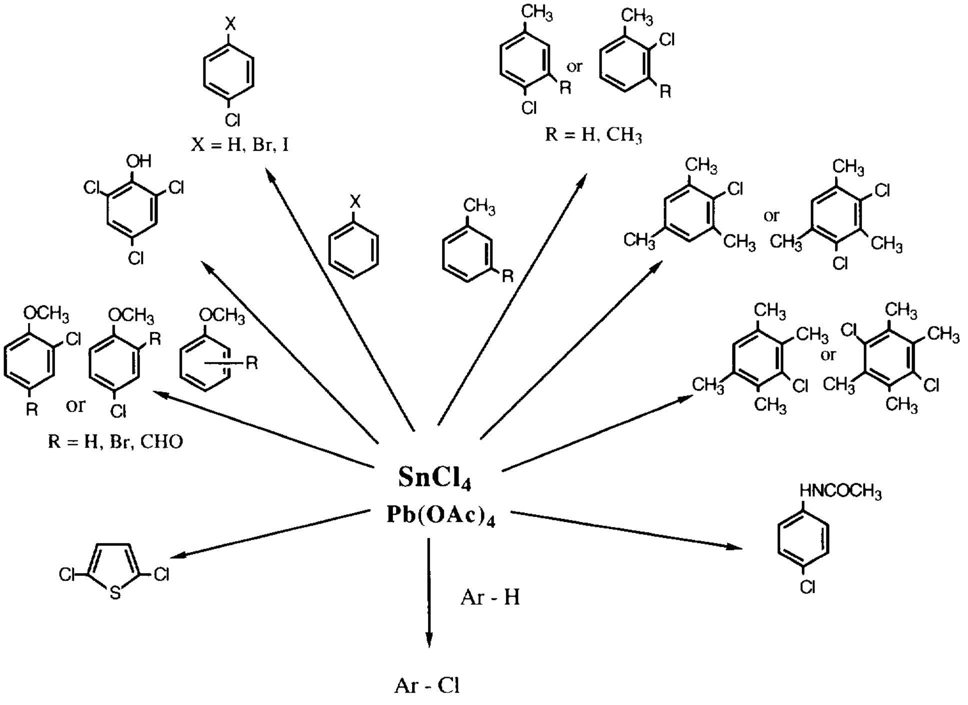
Abstract - $SnCl_4/Pb(OAc)_4$ acts as a safe source of Cl_2 for the chlorination of aromatic compounds. A variety of aromatic compounds are effectively chlorinated with $SnCl_4/Pb(OAc)_4$ under mild conditions. The mixture is a selective chlorinating agent, particularly with polyalkylbenzenes, polycyclic aromatic compounds and anisoles. Copyright © 1996 Elsevier Science Ltd

Chlorination of aromatic compounds with elemental chlorine is a well-known reaction.[1] Owing to the hazards associated with chlorine gas, several alternative approaches to aromatic chlorination have appeared in the literature.[2,3] One of these approaches is the use of metal chlorides as chlorinating agents.[4] Certain metal chlorides, e.g. iron(III), copper(II) and antimony(V) chlorides have received particular attention.[5-7] In addition to halogenation, the reaction of these metal chlorides is sometimes accompanied by other transformations, like



Ar = 4-biphenylyl-, 1-naphthyl-, 1-(2-methylnaphthyl)-,
1-(4-methylnaphthyl)-, 9-anthryl-, 9-phenanthryl-

side-chain attack in alkylbenzenes, disproportionation, metallation or polymerization.[8-10]

Other metal chlorides have also been used, in the presence of oxidizing agents. For example, titanium (IV) chloride and peroxytrifluoroacetic acid[11] and aluminum chloride in the presence of NO_2 and O_2.[12] However , both methods have limited application and require *in situ* generation of the oxidizing agent.

We now report a more convenient method for aromatic chlorination using more readily available reagents. We have found that the combination of tin (IV) chloride and lead tetraacetate (LTA) effectively chlorinates both monocyclic and polycyclic aromatic compounds in high yields under mild conditions.

Table : Chlorination of Aromatic Compounds with $SnCl_4$-$Pb(OAc)_4$

No	Substrate	Product	time/h	molar ratio subs:$SnCl_4$:LTA	yield %[a]	mp,°C or bp,°C/Torr	
						found	lit[13-16]
1	benzene	chlorobenzene	2[b]	1:2:1	(76)	132/760	132/760
2	toluene	o,p-chlorotoluene(55:45%)	1[b]	1:2:1	(80)	---	---
3	m-xylene	4-chloro-1,3-dimethylbenzene	0.5	1:2:1	(74)	186-188/760	187-188/760
4	mesitylene	2-chloromesitylene	0.25	1:2:1	86	101-103/25	104/25
		2,4-dichloromesitylene	0.5	1:4:2	88	59-61	58-59
5	durene	3-chlorodurene	0.25	1:2:1	77	47-50	47.5-48
		3,6-dichlorodurene	0.5	1:4:2	90	186-188	189-189.5
6	bromobenzene	4-bromochlorobenzene	20	1:2:1	56	66-68	67
7	iodobenzene	4-chloroiodobenzene	20	1:2:1	58	54-56	57
8	anisole	4-chloroanisole	0.25	1:2:1	80	71-72/9	71.5/9
		2,4-dichloroanisole	3	1:4:2	77	124-126/10	125/10
		2,4,6-trichloroanisole	12[b]	1:6:3	87	59-62	61-62
9	4-bromoanisole	4-bromo-2-chloroanisole	3	1:2:1	84	66-68	69
10	anisaldehyde	5-chloroanisaldehyde	15	1:2:1	72	79-82	79-81
11	phenol	2,4,6-trichlorophenol	2	1:6:3	71	67-69	69-70
12	salicylic acid	5-chlorosalicylic acid	2[c]	1:2:1	77	169-171	172
		3,5-dichlorosalicylic acid	2	1:4:2	65	218-220	219-220
13	acetanilide	4-chloroacetanilide	20[c]	1:2:1	78	173-175	172-173
14	naphthalene	1-chloronaphthalene	0.25	1:2:1	87	112-113/5	111-113/5
		1,4-dichloronaphthalene	0.25	1:4:2	(65)	67-69	67-68
15	1-methylnaphthalene	1-chloro-4-methylnaphthalene	0.25	1:2:1	85	125-127/6	124-128/6
16	2-methylnaphthalene	1-chloro-2-methylnaphthalene	0.25	1:2:1	84	158-160/25	159-161/25
17	acenaphthene	5-chloroacenaphthene	0.25	1:2:1	76	67-69	70-71
18	fluorene	2-chlorofluorene	0.25[c]	1:2:1	(67)	93-96	96-97
19	anthracene	9-chloroanthracene	0.25[c]	1:2:1	68	101-103	104-106
		9,10-dichloroanthracene	0.5[c]	1:4:2	78	212-214	212-213
20	phenanthrene	9-chlorophenanthrene	0.25	1:2:1	85	52-54	53-54
21	pyrene	1-chloropyrene	0.25	1:2:1	85	118-121	119-121
22	biphenyl	4-chlorobiphenyl	0.25	1:2:1	(70)	74-76	77
23	thiophene	2,5-dichlorothiophene	0.25[c]	1:4:2	75	162/760	162/760

[a] yields of isolated pure products; values in parenthesis were determined by GLC.

[b] solvent : trifluoroacetic acid.

[c] solvent : ethyl acetate

Results and Discussion

A standard reaction was set up in which a solution of the aromatic substrate and two equivalents of anhydrous $SnCl_4$ is stirred while one equivalent of $Pb(OAc)_4$ is added portionwise. In general, the chlorination reactions were carried out in dichloromethane. In a few cases, other solvents, like trifluoroacetic acid or ethyl acetate, were used. The reaction was monitored by a moist starch-iodide paper held over the mixture. The blue colour indicates presence of chlorine.

The results of aromatic chlorination with the $SnCl_4$ - $Pb(OAc)_4$ system are summarized in the Table. The reaction with alkylbenzenes gave only nuclear-chlorinated compounds and no side-chain attack was observed. Toluene gave nearly a 1:1 mixture of o- and p-chlorotoluene while m-xylene gave mainly 4-chloro-1,3-dimethylbenzene and traces of the 2-chloro derivative. As a result of increasing reactivity with increasing number of alkyl groups, mesitylene and durene were readily chlorinated to the mono and dichloro derivatives under the same conditions by the use of the corresponding amount of the chlorinating mixture.

$SnCl_4$- $Pb(OAc)_4$ system shows high regioselectivity towards aromatic ethers. Treatment of anisoles with one equivalent of the chlorinating mixture gave the para derivative in high yield when this position was available. 2,4-Dichloroanisole and 2,4,6-tri- chloroanisole were also selectively obtained in high yield depending upon the molar ratio of the chlorinating mixture.

Monochlorophenols could not be obtained, presumably owing to the greater reactivity of phenols compared to anisole. A less reactive phenol, i.e. salicylic acid, was chlorinated with $SnCl_4$-$Pb(OAc)_4$ to give 3-chloro- salicylic acid in high yield. 3,5-Dichlorosalicylic acid was also obtained in good yield by the use of the corresponding amount of the mixture.

Although direct chlorination of aniline resulted in extensive oxidation, acetanilide underwent nuclear chlorination after prolonged treatment due to complex ing with $SnCl_4$ which caused the ring to become deactivated towards electrophilic substitution.[11]

The reaction of $SnCl_4$- $Pb(OAc)_4$ with polycyclic aromatic compounds is fast and regioselective. Naphthalene and methylnaphthalenes gave 1-chloro derivatives in high yields when this position was available. Dichlorination is also possible in the case of naphthalene and anthracene. 1,4-Dichloronaphthalene was isolated in 60% by fractional recrystalization while 9,10-dichloroanthracene was obtained as the only product.

Although a detailed mechanism of the reaction is not available, detection of chlorine allows the author to speculate the reaction to proceed according to the following steps:

$$2\,SnCl_4 + Pb(OAc)_4 \longrightarrow Cl_2 + 2\,Cl_3SnOAc + Pb(OAc)_2$$
$$Ar\text{-}H + Cl_2 \longrightarrow Ar\text{-}Cl + HCl$$

Experimental

All melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. Dichloromethane was dried with calcium chloride and distilled. The ^1H NMR spectra were determined in $CDCl_3$ on a Varian Model E390 90MHz spectrometer using tetramethylsilane as an internal standard. Product mixtures were analyzed by GLC on a Hitachi Model 163 flame ionization instrument equipped with a SE-30 on Chromosorb WAW column.

General Procedure for Chlorination with $SnCl_4$ and $Pb(OAc)_4$.

Lead tetraacetate (2.6 g, 5 mmol) was added portionwise over 5 minutes to a vigorously stirred solution of the aromatic substrate (5 mmol) and anhydrous tin(IV) chloride (2.65 g, 10 mmol) in dry dichloromethane (25 ml). The mixture was stirred for the specified time and then diluted with ether (25 ml). The resultant solid was filtered off and the filtrate was washed successively with 5% HCl and aqueous $NaHCO_3$ and dried (Na_2SO_4). Evaporation in vacuo afforded the chloro compound.

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