

Selenium and Tellurium Tetrachlorides as Reagents for the Conversion of Alcohols to Alkyl Chlorides and Tellurium Tetrachloride as a Lewis Acid Catalyst for Aromatic Alkylation

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Selenium tetrachloride (SeCl_4) reacts smoothly with alcohols in various nonpolar solvents to give the corresponding alkyl chlorides in 44–97% yield. Similar reaction also proceeds with tellurium tetrachloride (TeCl_4), while the treatment of benzyl, 1-phenylethyl, and *t*-butyl alcohols with TeCl_4 in aromatic solvents results in a high yield formation of alkylated aromatics instead of alkyl chlorides. Such Friedel-Crafts aromatic alkylation hardly occurs in the SeCl_4 case. The chlorinating species is not chlorine which might be evolved by dissociation of SeCl_4 or TeCl_4 , but the metal chloride itself. The conversion of optically active (*R*)-(+)-1-phenylethanol to 1-phenylethyl chloride proceeds with nearly complete racemization.

During a search for direct aryl migration method of 2-hydroxypropiophenones to 2-arylpropionic acids by various sulfur, selenium, and tellurium reagents¹⁾ we came across the replacement of hydroxyl group by chlorine when the ketones were treated with selenium or tellurium tetrachloride (SeCl_4 or TeCl_4). Although SeCl_4 has been known as chlorinating agent of olefins,²⁾ acetylenes,³⁾ and isocyanides,³⁾ there is no precedent for the use of TeCl_4 as chlorinating agent as well as the reactions of each reagent with alcohols to our knowledge.⁴⁾ In order to know the scope and limitation of this replacement reaction the reactions of typical primary, secondary, and tertiary alcohols with SeCl_4 or TeCl_4 were carried out in various solvents. It is worthwhile to note that selenium tetrafluoride is known to react with alcohols to give the corresponding alkyl fluorides in good yields.⁵⁾ During this study we also disclosed that TeCl_4 , but not SeCl_4 , works as a

mild Lewis acid catalyst for aromatic alkylation. We report here the details of our new findings.

Results and Discussion

Conversion of Alcohols to Alkyl Chlorides by SeCl_4 or TeCl_4 . Treatment of 1- and 2-phenylethanols, diphenylmethanol, triphenylmethanol, and 1- and 2-octanols with SeCl_4 in toluene, dichloromethane, or 1,2-dichloroethane as solvent at 25–60 °C for 1.5–15 h afforded the corresponding alkyl chlorides respectively in 44–97% yield. The addition of amine sometimes improved the product yield. Selenium tetrafluoride-pyridine complex is known to be a good fluorinating agent of alcohols.⁵⁾ Similar treatment with TeCl_4 also gave alkyl chlorides in 65–86% yield, but the addition of triethylamine or pyridine resulted in lowering the product yield probably because of the

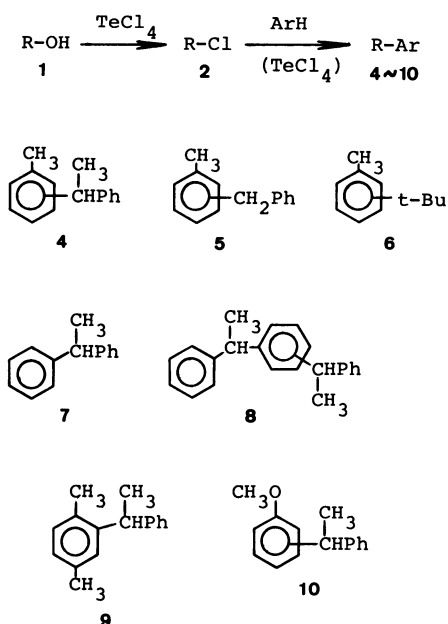
Table 1. Conversion of Alcohols to Alkyl Chlorides Using SeCl_4 or TeCl_4

R in 1 (2 mmol)	SeCl_4 or TeCl_4 (2.4 mmol)	Base (equiv) ^{a)}	Solvent (4 ml)	Temp/°C	Time/h	Products/% ^{b)}	
						2	1
PhCH_2CH_2	$\text{SeCl}_4[\text{TeCl}_4]$		Toluene	50	4	44[65]	24[20]
PhCH_2CH_2	SeCl_4	Et_3N (1.0)	Toluene	50	4	71[0]	25[94]
Ph_2CH	SeCl_4		Toluene	50	4	90	0
Ph_2CH	TeCl_4		DMF-Toluene ^{c)}	25	3	85	0
Ph_2CH	$\text{SeCl}_4[\text{TeCl}_4]$	Et_3N (1.5)	Toluene	25	3	97[8]	2[90]
$\text{PhCHCH}_3^{\text{d)}$	SeCl_4		Toluene	25	6	96 ^{e)}	— ^{f)}
$\text{PhCHCH}_3^{\text{d)}$	TeCl_4		CH_2Cl_2	–50	3.5	86 ^{e)}	— ^{f)}
$\text{PhCHCH}_3^{\text{d)}$	$\text{SeCl}_4[\text{TeCl}_4]$	Et_3N (1.0)	CH_2Cl_2	25	1.5	96 ^{e)} [39] ^{e)}	— ^{f)} [7] ^{e)}
Ph_3C	$\text{SeCl}_4[\text{TeCl}_4]$		CH_2Cl_2	25	15	95[77]	3[3]
Ph_3C	$\text{SeCl}_4[\text{TeCl}_4]$	$\text{C}_5\text{H}_5\text{N}$ (1.2)	CH_2Cl_2	25	15	92[22]	2[64]
1- C_8H_{17}	$\text{SeCl}_4[\text{TeCl}_4]$		$\text{ClCH}_2\text{CH}_2\text{Cl}$	60	2	92[2]	0[98]
2- C_8H_{17}	$\text{SeCl}_4[\text{TeCl}_4]$		$\text{ClCH}_2\text{CH}_2\text{Cl}$	60	2	49[71]	22[0]

a) Equivalent to SeCl_4 or TeCl_4 . b) GLC yield based on **1** charged unless otherwise stated. c) *N,N*-Dimethylformamide-toluene (2 ml–2 ml). d) **1** (30 mmol), SeCl_4 or TeCl_4 (36 mmol), and solvent (60 ml) were used. e) Isolated yield. f) Not determined.

a) Equivalent to **1**. b) Isolated yield in the case of Cl_2 and GLC yield in the case of SeCl_4 , respectively, based on **1** charged.

anisole, none of *m*-isomer being produced. In the case of benzene as solvent the initially formed product, 1,1-diphenylethane (**7**), was far more reactive than benzene itself and alkylated further to give dialkylated benzene **8** highly selectively. Typical results are summarized in Table 3. The catalytic activity of TeCl₄ seems to be not so strong, as alkylation proceeded only with very reactive (benzyl, 1-phenylethyl, *t*-butyl etc.) alcohol or chloride and even *s*-butyl chloride did not alkylate toluene under similar conditions. It has been known that TeCl₄⁸⁾ and tellurium(IV) oxide (TeO₂)⁹⁾ work as a mild catalyst for aromatic acylation and alkylation respectively. However, no data are so far available on the catalytic activity of TeCl₄ for Friedel-Crafts aromatic alkylation. We are sure that this is a first example of TeCl₄ working as Friedel-Crafts alkylation catalyst, though its activity is mild.



Experimental

General. ¹H NMR spectra were recorded with JEOL FX-90Q (90 MHz) instrument on solutions in CDCl₃ with Me₄Si as an internal standard. GLC analyses were carried out with a Shimadzu 4CMPF apparatus using Thermo-1000(5% or 0.5%)-Chromosorb-W(3 mm×3 m or 1.5 m), SILAR-10C(5%)-Chromosorb-W(3 mm×1 m), PEG 20 M(10%)-Chromosorb-W(3 mm×2 m), Silicone CBP 5-M-25-025(0.2 mm×25 m), and Silicone OV-101(0.24 mm×30 m) columns (N₂ as carrier gas). Optical rotations were measured on a UNION PM-201 automatic polarimeter. All organic and inorganic materials were commercial products of the purest grade and used without further purification. Authentic samples of **2** were all commercially available for GLC analyses.

Conversion of Alcohols to Alkyl Chlorides by SeCl₄ or TeCl₄ (Table 1). A typical experimental procedure is as follows. To a solution of 2-phenylethanol, [**1**(R=PhCH₂CH₂)], (0.244 g, 2 mmol) in toluene (4 ml) was added selenium tetrachloride (0.533 g, 2.4 mmol) and the resulting mixture was stirred at 50 °C for 4 h. After being cooled down to room temperature, the mixture was added with water (6 ml) and stirred for 0.5 h. The precipitated red-brown solids were filtered off. The organic layer was separated, washed with brine (3 ml), and dried (MgSO₄). GLC analysis using Thermo-1000(5%)-Chromosorb-W(3 mm×3 m) column and propiophenone as an internal standard revealed the presence of 2-phenylethyl chloride, [**2**(R=PhCH₂CH₂)], (0.88 mmol, 44%) and unreacted 2-phenylethanol (0.48 mmol, 24%). The reactions with TeCl₄ were similarly carried out. In the case of 1-phenylethanol the experiment of 15 times scale was carried out and the product 1-phenylethyl chloride was isolated by distillation.

Reaction of 1-Phenylethanol[1**(R=PhCHCH₃)] with Chlorine** (Table 2). To a solution of chlorine (3.06 g, 43.2 mmol) in dichloromethane (30 ml) was added 1-phenylethanol [**1**(R=PhCHCH₃)] (3.67 g, 30 mmol) at -50 °C and the mixture was stirred at the same temperature for 4.5 h. After the addition of 10% aqueous sodium thiosulfate (20 ml) the resulting solution was stirred at room temperature for 0.5 h. The organic layer was separated, washed with brine (10 ml×2), and dried (MgSO₄). Evaporation of the solvent left an oily residue which was subjected to column chromatography on SiO₂ [hexane-ethyl acetate (20:1) as eluent] to give 1-phenylethyl chloride [**2**(R=

Table 3. Aromatic Alkylation Using TeCl₄

1 or 2 (30 mmol)	TeCl ₄ (equiv) ^{a)}	Solvent (30 ml)	Temp/°C	Time/h	Product/% ^{b)} (o/p ratio) ^{c)}
1 (R=PhCHCH ₃)	1.2	Toluene	25	3	4 83 (12/88) ^{d)}
1 (R=PhCHCH ₃)	1.2	Toluene	-50	4	2 (R=PhCHCH ₃) 62 ^{e)} , 4 7
2 (R=PhCHCH ₃)	0.1	Toluene	25	3	4 93 (11/89) ^{d)}
1 (R=PhCH ₂)	1.2	Toluene	25	4	5 87 (35/65)
1 (R= <i>t</i> -Bu)	1.2	Toluene	80	5	6 34 (1/99)
2 (R= <i>t</i> -Bu)	0.2	Toluene	25	20	6 71 ^{e)} (1/99) ^{d)}
1 (R=PhCHCH ₃)	1.2	Benzene	5	1	7 3, 8 44 (24/76)
1 (R=PhCHCH ₃)	1.2	<i>p</i> -Xylene	25	24	9 40
1 (R=PhCHCH ₃)	1.2	Anisole	25	24	10 59 (17/83)

a) Equivalent to **1** or **2**. b) Isolated yield based on **1** or **2** charged. c) Determined by NMR unless otherwise stated. d) Determined by GLC. e) GLC yield based on **1** or **2** charged.

PhCHCH₃)] (0.10 g, 0.71 mmol, 2.4% yield), 1-chloroacetophenone (**3**) (0.73 g, 4.72 mmol, 15.7% yield) and the starting **1** (R=PhCHCH₃) (2.74 g, 22.5 mmol, 74.9% yield), respectively.

Treatment of Optical Active Alcohol with SeCl₄ or TeCl₄. A typical example is as follows. To a solution of commercially available optical active (*R*)-(+)-1-phenylethanol ($[\alpha]_D^{20} +42^\circ$, 1.00 g, 8.19 mmol) in dichloromethane (10 ml) was added tellurium tetrachloride (2.65 g, 9.84 mmol) at -50°C ; the reported maximum optical rotation of the alcohol is $[\alpha]_D^{25} +43.4^\circ$.¹⁰ The resulting mixture was stirred at the same temperature for 6 h. The mixture was then added with water (20 ml) and stirred at room temperature for 10 min. The precipitated white solids were filtered off. The organic layer was separated, washed with brine (20 ml) and dried (MgSO₄). Evaporation of the solvent left an oily residue which was distilled in vacuo to give 1-phenylethyl chloride (1.02 g, 7.26 mmol, 88.6% yield) at bp $64^\circ\text{C}/8\text{ mmHg}$ (1 mmHg=133.322 Pa). It shows the optical rotation of $[\alpha]_D^{20} -0.5^\circ$, the value corresponding to the optical purity of 0.5% calculated from $[\alpha]_D^{20} +109^\circ$ of optically pure (*R*)-(+)-1-phenylethyl chloride.¹¹

Friedel-Crafts Aromatic Alkylation Catalyzed by TeCl₄ (Table 3). A typical experimental procedure starting from alcohol is as follows. To a solution of 1-phenylethanol, **1** (R=PhCHCH₃), (3.7 g, 30 mmol) in toluene (30 ml) was added slowly tellurium tetrachloride (9.7 g, 36 mmol) keeping the reaction temperature at 25°C (exothermic reaction). Small amounts of white precipitates appeared immediately and then the color of the mixture turned dark-brown in a few minutes. The mixture was stirred for 3 h and then quenched with water (20 ml). The organic layer was separated, washed with brine (20 ml $\times$ 2) and dried (MgSO₄). Evaporation of the solvent left an oily residue which was distilled in vacuo to afford a mixture of 1-phenyl-1-tolylethanes (**4**) (4.9 g, 25 mmol, 83.3% yield) at bp $117\text{--}128^\circ\text{C}/1\text{ mmHg}$. GLC analysis of **4** using Silicone OV-101 (0.24 mm $\times$ 30 m) capillary column at $100\text{--}260^\circ\text{C}$ (4°C min^{-1}) revealed the presence of two isomers of ortho/para=12/88: ¹H NMR, para-isomer, $\delta=1.57$ (d, $J=7\text{ Hz}$, 3H), 2.26 (s, 3H), 4.07 (q, $J=7\text{ Hz}$, 1H), 7.05 (m, 4H), 7.18 (m, 5H); ortho-isomer, 2.19 (s, 3H). Found: C, 91.92; H, 8.08%. Calcd for C₁₅H₁₆: C, 91.78; H, 8.22%.

Analytical data of other alkylated aromatics are as follows.

Benzyltoluenes (5): A colorless liquid of o/p=35/65 by ¹H NMR; ¹H NMR, para-isomer, $\delta=2.40$ (s, 3H), 4.02 (s,

2H), 7.14–7.28 (m, 9H); ortho-isomer, 2.35 (s, 3H), 4.06 (s, 2H).

***t*-Butyltoluenes (6):** A colorless liquid, bp $38^\circ\text{C}/1\text{ mmHg}$; ¹H NMR $\delta=1.25$ (s, 9H), 2.24 (s, 3H), 6.98 (d, 2H), 7.17 (d, 2H). The isomer ratio (o/p) was determined by GLC using Silicone OV-101 capillary column as 1/99.

1,1-Diphenylethane (7): A colorless liquid isolated by column chromatography on SiO₂ (hexane as eluent); ¹H NMR $\delta=1.57$ (d, 3H), 4.03 (q, 1H), 6.92–7.32 (m, 10H).

Bis(1-phenylethyl)benzenes (8): A colorless liquid isolated by column chromatography on SiO₂ (hexane as eluent), o/p=24/76 by ¹H NMR; ¹H NMR, para-isomer, $\delta=1.65$ (d, 6H), 4.87 (q, 2H), 6.88–7.24 (m, 14H); ortho-isomer, 1.46 (d, 6H), 3.95 (q, 2H).

1,4-Dimethyl-2-(1-phenylethyl)benzene (9): A colorless liquid, bp $129^\circ\text{C}/2\text{ mmHg}$; ¹H NMR, $\delta=1.55$ (d, 3H), 2.13 (s, 3H), 2.47 (s, 3H), 4.22 (q, 1H), 6.80–7.24 (m, 8H).

(1-Phenylethyl)anisoles (10): A colorless liquid of o/p=17/83 by ¹H NMR, bp $156^\circ\text{C}/5\text{ mmHg}$; ¹H NMR, para-isomer, $\delta=1.58$ (d, 3H), 3.71 (s, 3H), 4.05 (q, 1H), 6.68–7.20 (m, 9H); ortho-isomer, 1.55 (d, 3H).

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