0.15 (s, 3 H, $-SiCH_3$). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 101.81 (neg, 1 C, -SeCN), 53.52 (pos, d, 1 C, $-OCH_3$), 53.42 (pos, d, 1 C, $-OCH_3$), 26.51 (pos, 3 C, $-C(CH_3)_3$), 20.32 (pos, d, 1 C, -CHSeCN), 17.80 (neg, 1 C, $-C(CH_3)_3$), -4.76 (pos, 1 C, $-SiCH_3$), -6.37 (pos, 1 C, $-SiCH_3$). FTIR (film, KBr, cm^{-1}): 2860 vs, 2152 m, 1471 s, 1250 vs, 1034 vs, 841 vs. MS (chemical ionization, methane): calcd for $C_{10}H_{22}NO_3PSeSi$ 343, found 344. Exact mass: 343.02704 (calculated), 343.0278 (found).

1-Selenocyanato-1-(trimethylsilyl)ethene (2e). The lithium anion was prepared by addition of 1.1 equiv of *n*-BuLi to a solution of 1-(trimethylsilyl)-1-bromoethene in THF at -78 °C. After stirring for 1 h, the vinyllithium reagent was added to CuCN in THF at -78 °C, and the remainder of the reaction was carried out as described above. Compound **2e** was isolated in 64% yield (109 mg) as a foul-smelling, light yellow oil. ^1H NMR (300 MHz, $CDCl_3$, δ): 4.20 (d, J = 4.4 Hz, 1 H), 3.91 (d, J = 4.4 Hz, 1 H), 0.21 (s, 9 H). FTIR (KBr, film, cm^{-1}): 2960 m, 2163 s, 1585 m, 1432 s, 1245 s, 1001 m. MS: 205 (molecular ion), 190, 179, 162, 150, 125, 113, 97, 85, 73 (base peak). Exact mass: 204.98253 (calculated), 343.0278 (found).

α-Selenocyanatopropiophenone (2f). A THF solution of propiophenone (**1f**) was added to a THF solution of lithium diisopropylamide at -78 °C and stirred for 30 min. The resulting lithium enolate solution was transferred via cannula to CuCN at -78 °C, and the remainder of the reaction was carried out as described above. Compound **2f** was isolated as a pale yellow oil in 68% yield (2.27 g).

^1H NMR (300 MHz, $CDCl_3$, δ): 4.25 (q, J = 7.0 Hz, 2 H), 4.22 (q, J = 7.2 Hz, 1 H), 1.87 (d, J = 7.2 Hz, 3 H), 1.31 (t, J = 7.0 Hz, 3 H). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 169.98 (neg), 100.54 (neg), 62.32 (neg), 40.05 (pos), 18.89 (pos). FTIR (film, KBr, cm^{-1}): 2986 s, 2154 s, 1734 vs, 1450 s, 1381 s, 1323 vs, 1219 vs, 1159 vs, 1074 s, 1018 s, 858 m. MS: 239 (molecular ion), 180, 162, 134, 108 (base peak), 73, 55. Exact mass: 238.98488 (calculated), 238.9851 (found).

9-Selenocyanatofluorene (2g). This compound was isolated as a pale yellow powder in 79% yield (210 mg).

Mp: 109-111 °C. ^1H NMR (300 MHz, $CDCl_3$, δ): 7.31-7.82 (m, 8 H, ArH), 5.66 (s, 1 H, C-9). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 141.76, 140.09, 129.39, 128.01, 120.58, 120.50, 101.90 (1 C, -SeCN), 45.36. IR (KBr, film, cm^{-1}): (SeCN) 2160 s, 1610 s, 1450 s, 1300 m, 1190 m, 915 s, 780 m, 735 vs. MS: 271 (molecular ion), 244, 180, 165 (base peak), 139, 126, 115, 106, 89, 82, 76, 63, 51. Exact mass: 270.98997 (calculated), 270.9877 (found).

2-Phenyl-1-selenocyanatoacetylene (2h): This compound was isolated as a pale yellow oil in 77% yield (1.18 g).

^1H NMR (300 MHz, $CDCl_3$, δ): 7.46-7.57 (m, 2 H), 7.28-7.43 (m, 3 H). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 132.23 (pos, 2 C), 130.09 (pos, 1 C), 128.51 (pos, 2 C), 121.00 (neg, 1 C), 104.91 (neg, 1 C, SeCN), 96.57 (neg, 1 C), 68.12 (neg, 1 C). FTIR (NaCl, film, cm^{-1}): 3061 w, 2959 m, 2930 m, 2864 w, 2172 s (C≡C), 2170 m (C≡N), 1717 s, 1487 s, 1443 m, 1281 m, 756 s, 689 s. MS: 207 (molecular ion), 205, 181, 141, 127 (base peak), 117, 100, 89, 74, 63, 51. Exact mass: 206.95869 (calculated), 206.9551 (found).

1-(Dimethylphenylsilyl)-3-selenocyanato-1-propyne (2k). This compound was isolated as a pale yellow oil in 75% yield from the reaction of the cyanocuprate of **1a** with selenocyanogen.

^1H NMR (300 MHz, $CDCl_3$, δ): 7.61-7.66 (m, 2 H, ArH), 7.37-7.42 (m, 3 H, ArH), 4.32 (s, 2 H, CH_2Se), 0.45 (s, 6 H, $-SiMe_2-$). ^{13}C APT NMR (75 MHz, $CDCl_3$, δ): 136.5 (pos, 1 C), 133.0 (neg, 1 C), 129.6 (neg, 1 C), 128.0 (neg, 1 C), 105.7 (pos, 1 C, -SeCN), 89.4 (pos, 1 C), 52.2 (pos, 1 C), -1.1 (pos, 2 C, $-SiMe_2$). FTIR (NaCl, film, cm^{-1}): 3071 w, 2961 m, 2178 s (br), 1591 m, 1429 s, 1250 s, 1117 vs, 984 s, 839 s, 818 vs, 781 s, 733 s, 700 s, 665 s. MS: 279, 241, 173, 137, 136, 135 (base peak), 115, 57. Exact mass: 278.99817 (calculated), 278.9973 (found).

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Registry No. **1a**, 75405-39-9; **1b**, 762-72-1; **1c**, 114083-20-4; **1d**, 114083-21-5; **1e**, 13683-41-5; **1f**, 93-55-0; **1g**, 86-73-7; **1h**, 536-74-3; **1i**, 591-51-5; **1j**, 109-72-8; **1k**, 101150-39-4; **2a**, 114908-22-4; **2b**, 114908-23-5; **2c**, 114083-22-6; **2d**, 114083-23-7; **2e**, 114908-24-6; **2f**, 114908-25-7; **2g**, 114263-69-3; **2h**, 114908-26-8; **2i**, 2179-79-5; **2j**, 4700-45-2; **2k**, 114908-27-9; AgSeCN, 5169-33-5; selenocyanogen, 27151-67-3.

Selenium Dioxide Catalyzed Conversion of Alcohols to Alkyl Chlorides by Chlorotrimethylsilane

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Conversion of alcohols to alkyl chlorides is one of the most frequently used functional group transformation reactions. Thionyl chloride[1] and phosphorus trichloride[2] are the two most popular classical reagents. Triphenylphosphine has been used in combination with carbon tetrachloride,[3] *N*-halo imides,[4] and other chlorine compounds as a mild reagent for the preparation of alkyl chlorides.

More recently, halotrimethylsilanes were found to be useful for halogenation of alcohols. Iodotrimethylsilane converts alcohols to alkyl iodides under mild reaction conditions.[5] Less reactive bromotrimethylsilane needs a higher temperature to react with alcohols to produce alkyl bromides.[6] Chlorotrimethylsilane, on the other hand, generally fails to produce alkyl chlorides. There is only one literature report[7] on the use of chlorotrimethylsilane for the preparation of alkyl chlorides. However, the reaction seems to be limited to some allylic alcohols but not applicable to alcohols in general.

We now report a simple, inexpensive, and high-yield conversion of alcohols to the corresponding alkyl chlorides. Having a similar property to thionyl chloride, selenium oxychloride is belived to be able to serve as a mild chlorinating agent for alcohols. Unlike gaseous sulfur dioxide, selenium dioxide cannot escape out of the reaction mixture. This suggested that only a catalytic amount of selenium dioxide is needed for the effective chlorination of alcohols to alkyl halides, provided that enough chlorine source is present to convert it back to selenium oxychloride. This was, indeed, found to be true. When benzyl alcohol was mixed with slightly more than 2 equiv of chlorotrimethylsilane and 2-3 mol % of selenium dioxide, hydrogen chloride soon started to evolve. The reaction was complete within an hour at reflux. It took slightly longer at room temperature. The conversion was almost quantitative, and no product other than benzyl chloride was present in the reaction mixture.

$$ROH + 2TMSCl \xrightarrow{SeO_2} RCl + HCl + TMSOTMS$$

The in situ generated selenium oxychloride was found to be very effective for converting a wide variety of alcohols to the corresponding alkyl chlorides. The conversion can

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(2) Patai, S. *The Chemistry of the Hydroxyl Group*; Wiley-Interscience: New York, 1971; Part 1, p 454.
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0022-3263/88/1953-3634$01.50/0

Table I. Selenium Dioxide Catalyzed Reaction of Alcohols with Chlorotrimethylsilane

alcohol	reacn temp, °C	time, h	solvent	product	% yield[a]
benzyl alcohol	25	1	CCl_4	benzyl chloride	97
	60	1	CCl_4		98
	25	3	neat		96
	reflux	40	neat		95
4-methoxybenzyl alcohol	25	1	CCl_4	4-methoxybenzyl chloride	98
2-naphthylmethanol	50	2	CCl_4	2-naphthylmethyl chloride	98
cyclohexylmethanol	25	2	CCl_4	cyclohexylmethyl chloride	93
neopentyl alchol	25	2	CCl_4	neopentyl chloride	96
1-hexanol	50	5	CCl_4	1-chlorohexane	96
2-hexanol	50	5	CCl_4	2-chlorohexane	94
cyclohexanol	50	7	CCl_4	chlorocyclohexane	93
4-*tert*-butylcyclohexanol	50	4	CCl_4	4-*tert*-butylcyclohexyl chloride	98
menthol	reflux	6	CCl_4	menthyl chloride	96
tert-butyl alcohol	60	3	neat	*tert*-butyl chloride[b]	20
	20	3	neat		99
	20	3	CCl_4		99
1,1-diphenylethanol	60	3	CCl_4	1,1-diphenylethyl chloride[c]	5
	20	3	CCl_4		60
cinnamyl alcohol	20	3	CCl_4	cinnamyl chloride	100
2-methyl-3-buten-2-ol	20	3	CCl_4	3-methyl-2-butenyl chloride	96
geraniol	20	3	CCl_4	geranyl chloride + linalyl chloride[d]	98
borneol	reflux	5	CCl_4	bornyl chloride	98
ethylene glycol	reflux	5	CCl_4	1,2-dichloroethane	0
1,4-butanediol	50	5	CCl_4	1,4-dichlorobutane	0

[a] Isolated yield. [b] *tert*-Butyl alcohol was not recovered. [c] 1,1-Diphenylethylene was the exclusive product. [d] A 1:1 mixture was obtained.

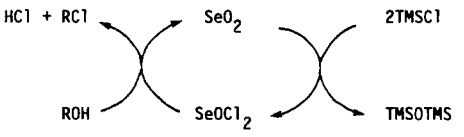
be easily achieved by simply warming the carbon tetrachloride solution of an alcohol and chlorotrimethylsilane containing a catalytic amount of selenium dioxide. For most alcohols, the yield was almost quantitative. The results on the chlorination by this reagent are summarized in Table I.

All benzylic alcohols as well as primary alcohols were efficiently chlorinated. The absence of any skeletal migration and competing elimination during the reaction was proved by recovering neopentyl chloride almost quantitatively from the reaction of neopentyl alcohol.

Cyclohexanol, menthol, and other secondary alcohols were also smoothly converted into the corresponding alkyl chlorides. Alkyl chlorides of rearranged carbon skeleton were not detected. For example, 2-hexanol produced 2-hexyl chloride in almost quantitative yield. This presents a striking contrast to the reactions of thionyl chloride with 2-alkanols to produce 2-chloroalkanes in <30% yield due to the competing elimination and rearrangement.[8] Even borneol, which is very prone to skeletal rearrangement,[9] was found to be chlorinated with the skeleton remaining intact. Bornyl chloride was the only alkyl chloride formed in the reaction.

Reactions of tertiary alcohols, however, presented a problem of the competing elimination. When *tert*-butyl alcohol was reacted with chlorotrimethylsilane and selenium dioxide in refluxing carbon tetrachloride, only *tert*-butyl chloride was detected in the reaction mixture, but the isolated yield did not exceed 30%. The alcohol was believed to be dehydrated to isobutylene, which escaped out of the reaction mixture along with hydrogen chloride. At room temperature, however, *tert*-butyl chloride was obtained in an isolated yield of >99%.[10] Unlike the case for *tert*-butyl alcohol, the dehydration of 1,1-diphenylethanol was not completely suppressed even at room temperature, producing diphenylethyl chloride and 1,1-diphenylethylene in a 3:2 molar ratio.

Scheme I



Allylic alcohols produced allylic chlorides in near-quantitative yields. *trans*-Cinnamyl alcohol was converted to cinnamyl chloride. In the reaction with thionyl chloride, exclusive formation of 3-phenyl-3-chloropropene, and S_N2' product, was observed.[11] For some allylic alcohols, however, the migration of the double bond was also observed with this reagent. Geraniol produced a mixture of geranyl chloride and linallyl chloride. 2-Methyl-3-buten-2-ol, on the other hand, produced only 1-chloro-3-methyl-2-butene, and S_N2' product.

This remarkable reaction was discovered during the course of our study on the insertion reactions of inorganic oxides into silicon–heteroatom bonds. Selenium dioxide was found to react with chlorotrimethylsilane to produce selenium oxychloride. The yield was almost quantitative. Trimethylsilyl chloroselenite, an initial insertion product, could not be detected in the reaction mixture; however, the reaction of this transient insertion product with another equivalent of chlorotrimethylsilane could lead to selenium oxychloride, as we found.[12] This preparation is superior to any other method for preparing selenium oxychloride reported in the literature.[13]

$$2TMSCl + SeO_2 \rightarrow (TMSO(O)SeCl) \rightarrow SeOCl_2 + TMSOTMS$$

Now that chlorotrimethylsilane alone does not produce any alkyl chlorides even after prolonged heating with al-

(8) (a) Cason, J.; Correia, J. S. *J. Org. Chem.* **1961**, *26*, 3645. (b) Yuong, W. E.; Caserio, F. F., Jr.; Brandon, D. D. *J. Am. Chem. Soc.* **1960**, *82*, 6163.

(9) Huckel, W. H. *Chem. Ber.* **1944**, *77*, 805.

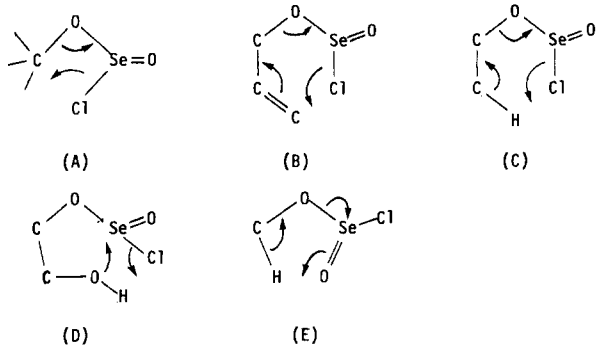
(10) Examples of chlorinating tertiary alcohols with thionyl chloride have seldom been reported in the literature.

(11) (a) Caserio, F. F., Jr.; Dennis, G. E.; De Wolfe, R. H.; Young, W. G. *J. Am. Chem. Soc.* **1955**, *77*, 4182. (b) Catchpole, A. E.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1948**, 8.

(12) Chromium trioxide behaved similarly in the reaction with chlorotrimethylsilane. A trimethylsiloxy group on chromium(VI) is rapidly displaced by a chloride, forming a chlorine–chromium bond. A synthetic application of thus formed Cl–(CrO_2)–Cl will be published soon.

(13) The reaction of selenium tetrachloride with selenium dioxide is the best reported preparation of selenium oxodichloride. Bagnall, K. W. In Bailar, J. C., Ed. *Comprehensive Inorganic Chemistry*; Pergamon: Oxford, 1973; Vol. 2, p 964.

Scheme II



cohols, selenium oxychloride must be the actual chlorinating agent. The role of selenium dioxide is to provide selenium oxychloride in the reaction with chlorotrimethylsilane. It can be regenerated from the reaction with alcohols. Such a role of selenium dioxide can de depicted by the catalytic cycle in Scheme I.

The reaction of thionyl chloride with an alcohol is known to proceed through a fairly unstable alkyl chlorosulfite. By analogy, an alkyl chloroselenite is believed to be formed as an intermediate in the reaction of selenium oxychloride with an alcohol. Being more reactive than thionyl chloride,[13] selenium oxychloride reacts faster with an alcohol. Being less stable than its sulfur analogue, an alkyl chloroselenite degrades faster. Besides, it only exists in very low concentration. This probably explains why this reagent serves better for the chlorination of alcohols. By assuming an alkyl chloroselenite intermediate, one can explain the formation of all types of products observed. Some representative pathways for the decomposition of the intermediates are shown in Scheme II.

Simple substitution (path A) leading to alkyl chlorides is most commonly encountered. The general tendency to retain the configuration at carbon was observed in the chlorination reaction by this reagent. For example, a 9:1 mixture of *trans*- and *cis*-4-*tert*-butylcyclohexanol produced the corresponding trans and cis chloride in the same proportion. (*S*)-Bornyl chloride uncontaminated with the other isomer was obtained from (*S*)-borneol. The formation of these alkyl chlorides with retention can be easily explained in terms of the internal substitution of the alkyl chloroselenite intermediates.

Both allylic substitution leading to allylic halides with a migrated double bond (path B) and elimination leading to olefins (path C) are also observed in the reaction of alcohols with thionyl chloride. However, the tendency of double-bond migration and elimination is greatly diminished as evidenced in the already-mentioned reactions of cinnamyl alcohol and *tert*-butyl alcohol.

Some alkyl chlorosulfites are reported to be stable enough to be isolated and characterized. Following the same procedure,[14] no alkyl chloroselenite could be isolated or detected for any monohydroxy compounds. Vicinal diols, however, are believed to form cyclic selenites (path D). Ethylene dichloride was not produced at all in the selenium dioxide catalyzed reaction of ethylene glycol. With an equimolar amount of selenium dioxide, it seems to be converted to ethylene selenite among other unidentified products.[15] Higher diols such as 1,4-butanediol did not produce the corresponding dichloroalkanes either. Reduced elemental selenium was deposited on standing.

Oxidative pathway E was observed only at a high temperature and when equimolar or excess selenium oxychloride was employed. Heating a carbon tetrachloride solution of an equimolar mixture of benzyl alcohol and selenium oxychloride yielded 20–30% of benzaldehyde along with benzyl chloride. Formation of elemental selenium was also observed. Unlike the previous pathway, selenium dioxide cannot be regenerated but reduced to the lower oxidation state. The formation of carbonyl compounds was not detected in any other reactions, where only a catalytic amount of selenium dioxide was present.

The role of chlorotrimethylsilane was proved to convert the selenium dioxide into selenium oxychloride. Having more silicon–chlorine bonds within a molecule, both dichlorodimethylsilane and trichloromethylsilane seem to serve this purpose better. Indeed, they all produced selenium oxychloride in the reaction with selenium dioxide.

As expected, dichlorodimethylsilane converted alcohols to the corresponding alkyl chlorides in the presence of selenium dioxide. Since the reaction produced oligomers and polymers of dimethylsiloxane as the byproducts, it is especially suitable for preparing lower boiling (100 °C or below) alkyl chlorides. However, it was often difficult to purify the higher boiling alkyl chloride in the presence of such siloxanes by distillation. The catalyzed chlorination of alcohols by trichloromethylsilane gave a lower yield of alkyl halides. The reason is not clear yet, but there seems to be a competing reaction of the more reactive trichloromethylsilane with alcohols to produce alkoxysilanes. Authentically prepared alkoxytrimethylsilanes were not cleaved to produce alkyl chlorides by chlorotrimethylsilane–selenium dioxide. Studies on other synthetic uses of selenium oxychloride are in progress.

In summary, in the presence of a catalytic amount of selenium dioxide, chlorotrimethylsilane serves as an efficient chlorinating reagent for a wide variety of alcohols. Selenium oxychloride generated in situ seems to react with alcohols forming unstable alkyl selenites, which rapidly decompose to alkyl chlorides. This reagent is superior to thionyl chloride and other chlorinating agents not only in terms of the yield and mildness of the reaction conditions but also because the competing side reactions are greatly suppressed.

Experimental Section

Selenium(IV) Oxychloride. In a 100-mL, round-bottomed flask was placed 15 g (0.136 mol) of selenium dioxide. Chlorotrimethylsilane (37 g, 0.34 mol) was then added dropwise with stirring at room temperataure. All solid selenium dioxide was dissolved after 2 h of stirring. On standing, the mixture separated into two layers. When carbon tetrachloride was used as a solvent, a homogeneous solution was obtained. After hexamethyldisiloxane was removed, 16.2 g of selenium oxychloride was obtained (74%), bp 170–171 °C (760 mmHg) (lit.[16] bp 176 °C).

Chlorination with Chlorotrimethylsilane. The reaction of benzyl alcohol is representative. In a 50-mL round-bottomed flask equipped with a dropping funnel and a condenser connected to an oil bubbler were placed 10 g (0.18 mol) of chlorotrimethylsilane, 0.2 g of selenium dioxide (2 mol %), and 5 mL of carbon tetrachloride. After several minutes of stirring at room temperature, 5 g (0.0925 mol) of benzyl alcohol was added slowly. Hydrogen chloride soon started to evolve. The resulting mixture was refluxed for 2 h. The flask was then equipped for distillation, and carbon tetrachloride and hexamethyldisiloxane were removed. The residue was distilled to give 5.5 g (95%) of pure benzyl chloride, bp 170–173 °C (760 mmHg).

(14) Gerald, W.; Nechvatal, A.; Wilson, B. M. *J. Chem. Soc.* **1950**, 2088.

(15) For aliphatic cyclic sulfites, see: Chiurdoglu, E.; De Groote, R.; Masschelein, W.; van Rissegheh, M. H. *Bull. Soc. Chim. Belges* **1961**, *70*, 342.

(16) Bagnall, K. W. *The Chemistry of Selenium, Tellurium* and *Polonium*; Elsevier: Amsterdam, 1961; p 14.

The conditions used for the preparation of alkyl halides from alcohols were identical with or similar to those illustrated in the preparation of benzyl chloride. The yields, reaction temperature, times are compiled in Table I. Most alkyl chlorides were fractionally distilled by using a 20-cm Vigreux column. 1-Hexyl chloride, 2-hexyl chloride, cyclohexyl chloride, 2-methyl-3-buten-2-ol, and neopentyl chloride were distilled by using a spinning-band still. The identity of the alkyl chloride was confirmed by comparing proton NMR data[17] and gas chromatographic retention times with those of authentic samples.

Chlorination with Dichlorodimethylsilane. Selenium dioxide (0.18 g) was added to 13.5 g of dichlorodimethylsilane (105 mmol) in 10 mL of carbon tetrachloride, and the mixture was stirred until it became homogeneous. *tert*-Butyl alcohol (7.4 g, 100 mmol) was slowly added. After standing for 2 h at 20 °C, the mixture was slowly distilled through a fractionating column to obtain 8.6 g (93%) of 2-chloro-2-methylpropane, bp 51–52 °C. Following the same procedure, benzyl chloride was prepared in 95% yield.

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Registry No. Chlorotrimethylsilane, 75-77-4; selenium dioxide, 7446-08-4; benzyl alcohol, 100-51-6; 4-methoxybenzyl alcohol, 105-13-5; 2-naphthylmethanol, 1592-38-7; cyclohexylmethanol, 100-49-2; neopentyl alcohol, 75-84-3; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; cyclohexanol, 108-93-0; 4-*tert*-butylcyclohexanol, 98-52-2; menthol, 89-78-1; *tert*-butyl alcohol, 75-65-0; 1,1-diphenylethanol, 599-67-7; (*E*)-cinnamyl alcohol, 4407-36-7; 2-methyl-3-buten-2-ol, 115-18-4; geraniol, 106-24-1; borneol, 507-70-0; ethylene glycol, 107-21-1; 1,4-butanediol, 110-63-4; benzyl chloride, 100-44-7; 4-methoxybenzyl chloride, 824-94-2; 2-naphthylmethyl chloride, 2506-41-4; cyclohexylmethyl chloride, 1072-95-3; neopentyl chloride, 753-89-9; 1-chlorohexane, 544-10-5; 2-chlorohexane, 638-28-8; chlorocyclohexane, 542-18-7; 4-*tert*-butylcyclohexyl chloride, 62056-46-6; menthyl chloride, 16052-42-9; *tert*-butyl chloride, 507-20-0; (*E*)-cinnamyl chloride, 21087-29-6; 3-methyl-2-butenyl chloride, 503-60-6; linalyl chloride, 471-10-3; bornyl chloride, 464-41-5; selenium(IV) oxychloride, 7791-23-3; 1,1-diphenylethyl chloride, 947-40-0; 1,1-diphenylethylene, 530-48-3; geranyl chloride, 5389-87-7; dichlorodimethylsilane, 75-78-5.

(17) Pruchert, C. J. *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1983.

Synthesis of (2,2,2-Trifluoroethyl)benzene Derivatives[1]

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Introduction

Organic fluorine compounds containing a trifluoromethyl group have lately attracted considerable attention because of their biological activities.[2] In previous papers, we reported the trifluoromethylation[3] of aromatic halides with trifluoromethyl copper and the trifluoropropylation[4] of aromatic compounds by the Friedel–Crafts reaction of trifluoropropene in the presence of HBF_4 as a catalyst. In the former, the trifluoromethyl group was directly attached to an aromatic ring, while in the latter, it was linked by a two-methylene bridge to an aromatic ring. Aromatic trifluoromethyl compounds were widely used as medicines or agricultural chemicals.[2] Trifluoropropyl compounds showed interesting physicochemical and physiological properties, also.[5] Therefore, we were interested in the property of trifluoroethyl compounds, since a trifluoroethyl group is located between the lower (CF_3) and the higher ($CH_2CH_2CF_3$) analogues and also represents a CF_3 group connected to the aromatic ring by a methylene bridge. Although various methods for the synthesis of trifluoroethyl compounds have been reported,[6] they have disadvantages such as use of a highly toxic reagent, low yields, and/or multistep procedures. No convenient routes to trifluoroethyl compounds were available. Now, we report the synthesis of trifluoroethyl compounds from aromatic amines by trichloroethylation followed by the Cl to F halogen exchange reaction of the trichloroethyl derivatives.

Scheme I

$$\underset{1}{ArNH_2} + CH_2{=}CCl_2 \xrightarrow[CuCl_2\text{-}CH_3CN]{t\text{-}BuONO} \underset{2}{ArCH_2CCl_3}$$

Scheme II

$$\underset{2a}{p\text{-}NO_2C_6H_4CH_2CCl_3} \xrightarrow[DMF]{KF} \text{decomposed}$$

$$\mathbf{2a} \xrightarrow{HF} \underset{4a}{p\text{-}NO_2C_6H_4CH_2CF_2Cl} + \underset{5}{p\text{-}NO_2C_6H_4CH_2COOH}$$

Scheme III

$$\underset{2a\text{-}d}{ArCH_2Cl_3} \xrightarrow{SbF_3\text{-}SbCl_5} \underset{3}{ArCH_2CF_3} + \underset{4}{ArCH_2CF_2Cl} + \underset{6}{ArCHClCF_2Cl} + \underset{7}{ArCH{=}CCl_2} + \underset{8}{ArCCl{=}CCl_2}$$

Table I. Trichloroethylation of Aromatic Amines 1

Ar	yield of 2 (%)	Ar	yield of 2 (%)
a 4-NO_2Ph	64	**d** 4-CH_3Ph	57
b 3-NO_2Ph	71	**e** 3-ClPh	65
c 3-CF_3Ph	73	**f** 4-ClPh	61

Discussion

Trichloroethyl derivatives were reported to have been prepared by the Meerwein arylation of aromatic amines.[7] However, a straight application of the general procedure of this reaction gave low yields of trichloroethyl compounds **2**. Doyle and his co-workers reported the similar reaction of acrylonitrile.[8] They treated aromatic amines with *tert*-butyl nitrite followed by the reaction with acrylonitrile in acetonitrile. We applied this modified procedure to 1,1-dichloroethylene (Scheme I) and isolated in fairly good yield compound **2**, irrespective of the electronic properties of the substituents on the starting arylamines. The results are shown in Table I.

Next, we attempted to convert the trichloroethyl group into a trifluoroethyl group.[9] When the *p*-nitro trichloro compound **2a** was heated with potassium fluoride in di-

(1) A part of this work was presented in the International Symposium to mark the Centenary of the Isolation of Fluorine, Paris, August 1986.
(2) *Biomedical Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Kodansha Ltd.; Tokyo, 1982.
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(6) (a) Dmowski, W. *Rocz. Chem.* **1974**, *48*, 1697. (b) Eliseenkov, E. V.; Koginov, A. S. *Zh. Org. Khim.* **1978**, *14*, 781. (c) DePuy, C. H.; Schultz, A. L. *J. Org. Chem.* **1974**, *39*, 878. (d) McLoughlin, V. C. R.; Thrower, J. *Tetrahedron* **1969**, *25*, 5921.
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(8) Doyle, M. P.; Siegfried, B.; Elliott, R. C.; Dellaria, J. F., Jr. *J. Org. Chem.* **1977**, *42*, 2431.
(9) For the replacement of chlorine atoms with fluorine atoms, several methods were reported. See: *Chemistry of Organic Fluorine Compounds*; Hudlicky, M., Ed., Ellis Horwood Ltd.; Chichester, 1976.

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