Efficient Carbonyl Addition of Polyfluorochloroethyl, -ethylidene, and -ethenyl Units by Means of 1,1,1-Trichloro-2,2,2-trifluoroethane and Zinc

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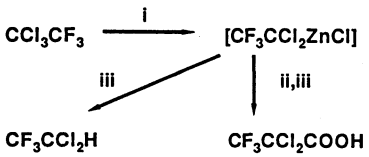
Thermally stable zinc carbenoid CF_3CCl_2ZnCl was prepared from 1,1,1-trichloro-2,2,2-trifluoroethane and zinc powder in *N,N*-dimethylformamide and was allowed to add to carbonyls of aldehydes and α-keto esters in excellent yields to give 1-substituted 2,2-dichloro-3,3,3-trifluoro-1-propanols. Employment of excess zinc induced further reductive β-elimination to afford 1-substituted 2-chloro-3,3,3-trifluoropropenes (**3**) and 1-substituted 2-chloro-3,3-difluoro-2-propen-1-ols (**4**). Exclusive formation of **3** was achieved by use of acetic anhydride as the co-reagent, whereas **4** was produced with an aluminium chloride catalyst highly selectively.

Introduction of fluorine to biologically active compounds often results in remarkable modification of their activity owing to increased stability and lipophilicity as well as to mimic and block effect of fluorine atom.[1] Therefore, various methods have been developed recently for the introduction of fluorinated groups to organic molecules.[2] Readily accessible fluorohalocarbons such as CF_2Br_2, $CFCl_3$, and HCF_2Cl are frequently utilized for this purpose as fluorine-containing building blocks.[3] However, 1,1,1-trifluoro-2,2,2-trihaloethanes (CF_3CX_3, X=Cl, Br) have scarecely been employed as the fluorine source,[4] though they are also commercially available. A carbenoid reagent of type CF_3CX_2-Mtl which might be derived from CF_3CX_3 attracted our interest, as it should provide us a facile way for the nucleophilic introduction of CF_3CX_2 group. In striking contrast to extensive studies on perfluoroalkylmetals,[5] the chemistry of the organo-metallics of the formula CF_3CX_2Mtl remained unexplored at the outset of our study. Only the Grignard reagent CF_3CX_2MgX[6] was recorded which, however, are labile and does not achieve carbonyl addition even at low temperatures. Thus, we searched for a practically stable reagent of this type and found that 1,1-dichloro-2,2,2-trifluoroethylzinc chloride fulfils our criteria.[7] Its preparation and carbonyl addition are described herein.

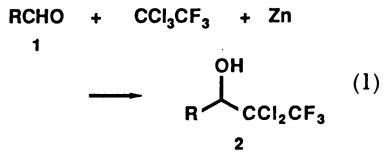
Results and Discussion

Preparation of CF_3CCl_2ZnCl. When 1,1,1-trichloro-2,2,2-trifluoroethane was added to a suspension of small excess of zinc powder in *N,N*-dimethylformamide (DMF) in the presence of copper(I) chloride catalyst[8] at room temperature, exothermic reaction took place, and most of the zinc was consumed within 1 h. At the expense of the peak of CCl_3CF_3(δ=−81.1), a new peak appeared at δ=−72.3, which was assigned as that of CF_3CCl_2ZnCl.[9] Upon hydrolysis CF_3CCl_2H was produced quantitatively. The reaction with carbon dioxide gave 2,2-dichloro-3,3,3-trifluoropropanoic acid (18% yield)[10] (Scheme 1). Thermal stability of the zinc carbenoid deserves particular attention: No decomposition was observed in DMF solution after several days at room temperature. The zinc reagent could be prepared in tetrahydrofuran (THF) solution also in a similar manner.



I: Zn, CuCl cat, DMF (or THF)
II: CO_2
III: H_3O^+

Scheme 1.



a: R = Ph
b: R = 3,4-(OCH_2O)-C_6H_3
c: R = 4-Cl-C_6H_4
d: R = 3,4-Cl_2-C_6H_3
e: R = PhCH=CH
f: R = Me_2C=CH
g: R = PhCH(Me)
h: R = c-C_6H_{11}

2a': PhCH(OH)$CBrClCF_3$
2a": PhCH(OH)CBr_2CF_3

Aldehyde Addition of CF_3CCl_2ZnCl. The synthetic utility of the zinc reagent is demonstrated by an aldehyde addition. Although the pre-prepared reagent does undergo addition to aldehyde carbonyl, the Barbier-type conditions were found more efficient. Treatment of aldehydes (**1**) with 1,1,1-trichloro-2,2,2-trifluoroethane (1.2—1.5 mol) and zinc powder (1.0—1.2 mol) in DMF afforded CF_3CCl_2 adducts **2** (Eq. 1). Results are summarized in Table 1. The reaction with aromatic aldehydes proceeded smoothly in good yields. Though the carbonyl addition to some aliphatic and α,β-unsaturated aldehydes were sluggish, the addition of copper(I) chloride, dichlorobis(triphenylphosphine)palladium(II), or dichlorobis(triphenylphosphine)nickel(II) catalyst or ultrasonic irradiation[5c] improved the yields significantly (Runs 9—12,

Table 1. Aldehyde Addition of CX_3CF_3/Zn Reagent[a]

Run	Aldehyde	CX_3CF_3[b]	Condition	Product	Yield[c] %
1	**1a**	CCl_3CF_3 (1.2)	r.t. 3 h; 50 °C, 2 h	**2a**	86
2	**1a**	CBr_2ClCF_3 (1.2)	0 °C, 0.5 h; 50 °C, 2 h	**2a′**	23[b]
3	**1a**	CBr_3CF_3 (1.5)	0 °C, 0.2 h	**2a″**	27
4	**1b**	CCl_3CF_3 (1.2)	0 °C, 0.2 h; 50 °C, 2 h	**2b**	80
5	**1c**	CCl_3CF_3 (1.5)	0 °C, 0.2 h; 50 °C, 2 h	**2c**	87
6	**1d**	CCl_3CF_3 (1.2)	r.t., 0.5 h; 50 °C, 4.5 h	**2d**	96
7	**1e**	CCl_3CF_3 (1.2)	r.t., 1 h; 50 °C, 17 h	**2e**	82
8	**1f**	CCl_3CF_3 (1.5)	60 °C, 12 h	**2f**	22
9	**1f**	CCl_3CF_3 (1.5)	50 °C, 8 h[e,f]	**2f**	60
10	**1f**	CCl_3CF_3 (1.5)	50 °C, 8 h[g]	**2f**	61[d]
11	**1f**	CCl_3CF_3 (1.5)	50 °C, 8 h[h]	**2f**	72[d]
12	**1f**	CCl_3CF_3 (1.5)	r.t.—50 °C, 8 h[i]	**2f**	83[d]
13	**1g**	CCl_3CF_3 (1.2)	0 °C, 0.3 h; 50 °C, 12 h	**2g**	60
14	**1h**	CCl_3CF_3 (1.2)	0 °C, 0.3 h; 50 °C, 23 h	**2h**	16
15	**1h**	CCl_3CF_3 (1.2)	50 °C, 5 h[f]	**2h**	61

a) The ratio of CX_3CF_3 to Zn was 1.0 to 1.2. All the reactions were carried out in DMF (1 ml $mmol^{-1}$) of **1**. b) Values in the parentheses are molar equivalents to **1**. c) Isolated yields unless otherwise noted. d) GLC yield. e) The aldehyde **1f** was added dropwise over 1 h after the carbenoid was prepared. f) Copper (I) chloride (5 mol%) was employed. g) A catalyst $PdCl_2(PPh_3)_2$ (1 mol%) was used. h) Carried out in the presence of $NiCl_2(PPh_3)_2$ (1 mol%). i) Ultrasonic irradiation was applied.

Table 2. Transformation of **1** to **3** with CCl_3CF_3, Zn, and Ac_2O[a]

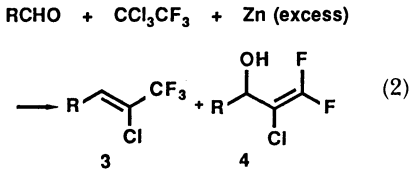
Run	Aldehyde	CCl_3CF_3/Zn/Ac_2O[b]			Reaction condition	Product (yield/%)[c]
1	**1a**	1.5	3.0	—	50 °C, 16 h	**3a** (14) **4a** (57)[d]
2	**1a**	1.5	3.0	1.5	r.t., 5 h; 50 °C, 2 h	**3a** (53) [86 : 14]
3	**1a**	2.0	5.0	1.5	50 °C, 7 h	**3a** (75) [86 : 14]
4	**1a**	2.0	5.0	1.0[e]	50 °C, 7 h	**3a** (67) [86 : 14]
5	**1a**	1.5	3.0	0.3[f]	0 °C, 1 h	**3a** (42) [86 : 14]
6	**1a**	1.5	3.0	0.3[g]	50 °C, 18 h	**3a** (13) [86 : 14] **4a** (54)
7	**1a**	1.5	3.0	1.0[g]	50 °C, 7 h	**3a** (30) [86 : 14] **4a** (52)
8	**1a**	i) 1.2	1.1	—	50 °C, 24 h	**3a** (78)
		ii) —	2.0	1.6	50 °C, 4 h	[87 : 13]
9	**1b**	i) 1.2	1.1	—	50 °C, 24 h	**3b** (81)
		ii) —	2.0	1.6	50 °C, 4 h	[85 : 15]
10	**1b**	i) 1.2	1.1	—	50 °C, 12 h	**3b** (63)
		ii) —	2.0	1.6[h]	50 °C, 4 h	[86 : 14]
11	**1c**	2.0	5.0	1.5	50 °C, 4 h	**3c** (73) [88 : 12]
12	**1c**	i) 1.2	1.1	—	50 °C, 24 h	**3c** (76)
		ii) —	2.0	1.6	50 °C, 4 h	[88 : 12]
13	**1e**	i) 1.2	1.1	—	50 °C, 24 h	**3e** (72)
		ii) —	2.0	1.6	50 °C, 4 h	[89 : 11]
14	**1f**	i) 1.2	1.1	—	50 °C, 1 h[i]	**3f** (53)
		ii) —	2.0	1.6	50 °C, 4 h	[88 : 12]
15	**1h**	i) 1.2	1.1	—	50 °C, 24 h[i]	**3h** (50)
		ii) —	2.0	1.6	50 °C, 4 h	[85 : 15]

a) All the reactions were carried out in DMF (1 ml $mmol^{-1}$). b) Molar ratio of CCl_3CF_3, Zn, and Ac_2O. Single step procedure corresponds to Procedure A, whereas the two-step procedure means Procedure B. c) The values in the brackets are Z/E ratio of **3**. d) Accompanied by **2a** (17—19% yields). e) Titanium-(IV) chloride (0.12 ml, 1.0 mmol) was employed in lieu of acetic anhydride. f) Acetic anhydride was replaced by $SiCl_4$ (0.3 mmol). g) Boron trifluoride etherate (0.3 mmol) was used in place of acetic anhydride. h) Acetyl chloride (0.1 ml, 1.6 mmol) was employed instead of acetic anhydride. i) $NiCl_2(PPh_3)_2$ (2 mol%) was employed as the catalyst.

and 15). Other 1,1,1-trifluoro-2,2,2-trihaloethanes e.g. CBr_2ClCF_3 and CBr_3CF_3 also were applicable, thouth the yields were inferior (Runs 2 and 3). No ketone adducts were isolated under the reaction conditions. Lewis acids such as $AlCl_3$ and $TiCl_4$ were totally ineffective for the ketone addition. DMF solvent is essential to the carbonyl reaction, as in THF the aldehyde addition did not take place.

Attempted reaction of the zinc carbenoid with benzoyl chloride failed. Although benzoyl chloride was consumed immediately in DMF, benzoic acid was isolated after workup with trifluoroacetic acid. Possibly the zinc reagent promoted the reaction of PhCOCl with DMF to give rise to a Vilsmeier reagent $[Me_2N{=}CHOCOPh]^+Cl^-$ or $[Me_2N{=}CHCl]^+PhCOO^-$. Parallel experiment in THF induced ring-opening of the THF ring to yield 4-chlorobutyl benzoate. Thus, strong acid character as well as low nucleophilicity of the zinc carbenoid is now revealed.

Transformation of RCHO (1) into RCH=C(Cl)CF_3 (3). When excess zinc is applied to the aldehyde addition, further reductive β-elimination is expected to afford 2-chloro-1,1,1-trifluoro-2-alkene (**3**) and/or 2-chloro-1,1-difluoro-1-alken-3-ol (**4**) (Eq. 2). Actually, treatment of benzaldehyde with CCl_3CF_3 (1.5 mol) and

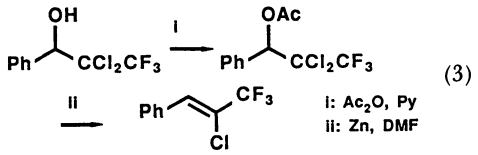


(2)

zinc (3.0 mol) afforded a mixture of **3a** (14%) and **4a** (57%) (Table 2, Run 1). In order to control the two pathways, the effect of various additives was studied.

By use of excess acetic anhydride (1.5—1.6 mol) as the additive, conversion of RCHO into **3** was achieved highly selectively. Various aldehydes including aromatic, aliphatic, and α,β-unsaturated ones were successfully converted into **3**, and the results are summarized in Table 2. Employment of 2 mol of CCl_3CF_3 and large excess of zinc (5 mol) was desirable for giving **3** in satisfactory yields (Procedure A). The amount of zinc could be reduced to 3.1 mol without decrease of the yield by a modified two-step but one-pot procedure (Procdure B): i) Formation of C-C bond with CCl_3CF_3 (1.2 mol) and zinc (1.1 mol) and ii) reduction with zinc (2 mol) and acetic anhydride (1.5 mol). Such Lewis acids as $TiCl_4$ and $SiCl_4$[11] were also effective for exclusive transformation of benzaldehyde into **3a**, whereas boron trifluoride etherate did not significantly affect the selectivity (Runs 6 and 7). Acetyl chloride also could be used in lieu of acetic anhydride for the Procedure B (Run 10).

The reaction pathway should involve formation of an acetate of **2** as the intermediate, since the acetate of **2a** was produced (79% yield) when zinc (1.2 mol), CCl_3CF_3 (1.2 mol), and acetic anhydride (1.2 mol) were employed. Actually, treatment of the acetate with zinc in DMF produced **3a** in good yields (Eq. 3).[14] In order to check an alternative route which goes through a *gem*-dimetallic species like $CF_3CCl(ZnBr)_2$, we allowed CBr_2ClCF_3 to react with zinc at 50 °C and observed a β-elimination to give $CF_2{=}CClBr$. This was successively converted into $CF_2{=}CClZnBr$ under the reaction conditions (Eq. 4). These results contrast sharply to the carbonyl methylenation with $CH_2X_2/Zn/TiCl_4$



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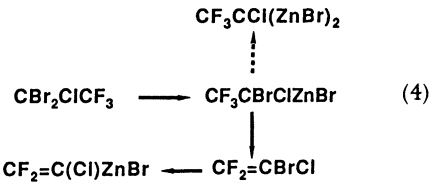


(4)

which involves $CH_2(ZnX)_2$ as the intermediate.[11a]

Synthetic utility of this reaction was demonstrated by a one-pot synthesis of 2-chloro-1,1,1-trifluoro-5-methyl-2,4-hexadiene (**3f**)[12b,c] which is one of key synthetic precursors for artificial pyrethroids containing $CH{=}C(Cl)CF_3$ moiety in common.[12,13] Although the same transformation can be effected with $CCl_3CF_3/PPh_3/Zn$ reagent,[4b] this Wittig type olefination method requires use of 2 mol of triphenylphosphine and tedious separation of triphenylphosphine oxide contaminated in the products and thus is apparently unpractical.

Transformation of RCHO (1) into RCH(OH)CCl=CF_2 (4). In striking contrast, aluminium chloride catalyst promoted highly selective transformation to **4**. For example, in the presence of 10 mol% of aluminium chloride, benzaldehyde was converted into **4a** in 86% yield accompanied by a trace amount of **3a** (<5%). With the increase of the proportion of $AlCl_3$ to 30 mol%, both yield and selectivity decreased considerably. **4a** was no longer produced on employment of 1 mol of $AlCl_3$: A mixture of 2,2-dichloro-3,3,3-trifluoro-1-phenyl-1-propanol (**2a**) (37%) and **3a** (11%) resulted. The effect of $AlCl_3$ may be explained as follows. Catalytic amount of $AlCl_3$ can interact with CF_3 group of the primary adduct and direct the reductive elimination to produce **4**, whereas an equimolar amount of $AlCl_3$ substitutes ZnCl of the primary adduct to weaken the C-O bond of the primary adduct. The $AlCl_3$-catalyzed method was applied to various aldehydes. Results summarized in Table 3 show that 1-substituted 2-chloro-3,3-difluoro-2-propen-1-ols of various kinds are readily accessible through the methodology disclosed herein.

The reaction was monitored by ^{19}F NMR which

Table 3. Transformation of **1** to **4**[a]

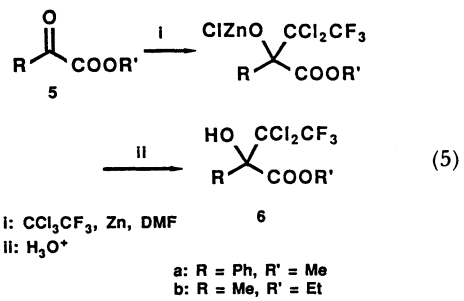
Run	Aldehyde	$AlCl_3$[b]	Reaction time	Product (yield/%)
1	**1a**	0.1	18 h	**4a** (86)
2	**1a**	0.3	18 h	**4a** (80)
3	**1a**	1.0	18 h	**2a** (37)
				3a (11)
				4a (0)
4	**1d**	0.3	3.5 h	**4d** (72)
5	**1g**	0.1	18 h	**4g** (86)[c]
6	**1g**	0.3	19 h	**4g** (39)[c]
7	**1h**	0.1	9 h	**4h** (52)
8	**1h**	0.3	9 h[d]	**4h** (36)
9	**1k**	0.3	18 h	**4k** (41)

a) All the reactions were carried out in DMF (1 ml $mmol^{-1}$) at 50 °C with **1**, CCl_3CF_3, and Zn in a molar ratio of 1 : 1.5 : 3.0. b) Molar equivalents to aldehyde. c) Roughly 1:1 diastereoisomeric mixture. d) Copper(I) chloride catalyst (5 mol%) was used.

showed formation of an aldehyde adduct of CF_3CCl_2ZnCl at the early stage of the reaction. The observation clearly eliminates the possibility of the intermediacy of $CF_2=C(Cl)ZnCl$.

The achievement of the practical transformation of aldehydes to **4** is of great value from synthetic viewpoint, as the aldehyde adducts of $CX=CF_2$ group (X=F, Cl) are key intermediates for a number of fluorine containing carbonyl compounds.[14] Whereas the carbonyl addition is usually carried out with labile $LiCX=CF_2$[15,16] below −100 °C, the $CX_3CF_3/Zn/AlCl_3$ (cat) reagent can do the same transformation at 50 °C.[17]

Addition of CF_3CCl_2ZnCl to α-Keto Esters and DMF. Although the zinc carbenoid did not add across ketone carbonyls, the reagent reacted with α-keto esters **5** (Eq. 5). The yields of the aducts **6** were moderate even in the presence of large excess of the reagent. The conversion-based yields were quantitative, though. Possibly the intermediate adduct is in equilibrium between **5** and the zinc reagent which gradually decomposes to shift the equilibrium to the starting material.



(5)

Attempted Reaction with Chlorosilanes. In the presence of chlorosilanes, the CF_3CCl_2ZnCl reagent reacted with DMF to give α-silyloxy *N,N*-dimethylamines **7** in good yields (Eq. 6). As CF_3CCl_2ZnCl alone does not interact with DMF, **7** may be derived from a Vilsmeier type reagent $[Me_2N^+=CHOSiR_3]Cl^-$ generated in situ from R_3SiCl and DMF.

$$HCONMe_2 + R_3SiCl + CCl_3CF_3 \longrightarrow CF_3CCl_2CH(NMe_2)OSiR_3 \quad (6)$$

7

a: $SiR_3 = SiMe_2t\text{-}Bu$
b: $SiR_3 = SiEt_3$

A new zinc carbenoid reagent CF_3CCl_2ZnCl is readily prepared from commercially available CCl_3CF_3 and zinc and is shown to undergo carbonyl addition. Although it did not exhibit enough reactivity to achieve coupling with a wide variety of electrophiles, the zinc reagent allowed us to introduce three kinds of C_2 units containing both chlorine and flourine atoms. Synthetic application to artificial pyrethroids is disclosed in following article.[18]

Experimental

Melting points and boiling points are uncorrected. Bulb-to-bulb distillation was carried out by use of Büchi Kugelrohr or Glass Tube Oven (Shibata GTO 250R). ^1H NMR spectra (tetramethylsilane as an internal standard) were obtained with a Varian EM-390, Varian XL-100A, Hitachi R-90H, or Bruker AM-400 spectrometer, chemical shifts being given in ppm units, ^{19}F NMR spectra (trichlorofluoromethane as an internal standard) with a Hitachi R-20B or Varian XL-100A spectrometer, ^{13}C NMR spectra with a Bruker AM-400. IR data of neat liquid film samples (unless otherwise noted) were recorded with a JASCO A-202. Mass spectra (70 eV unless otherwise noted) were recorded with a RMU-6MG, high mass with a Hitachi M-80A spectrometer. GLC analyses were performed with a Shimadzu GC-7A chromatograph (FID detector). Preparative GLC were carried out with a Shimadzu GC-3Bt chromatograph (TCD detector). TLC analyses were performed by means of Merck Silica Gel 60 F_{254} (0.25 mm thick). Preparative TLC plates were prepared with Merck Kiesel-Gel PF_{254}. Column chromatography was carried out with silica-gel (Wakogel C-200) at atmospheric pressure. Ultrasonic irradiation was performed with a Wakenyaku UW-10 (250 W, 28 KHz) cleaner. DMF was distilled over calcium hydride and stored over Molecular Sieve 4A. Zinc powder purchased from Wako Pure Chemical Industries, Ltd. was washed successively with dil hydrochloric acid, water, ethanol, diethyl ether and finally with absolute diethyl ether, and dried under reduced pressure. 1,1,1-Trichloro-2,2,2-trifluoroethane was purchased from Tokyo Kasei Kogyo Co. and used directly.

A Typical Procedure for Generation of CF_3CCl_2ZnCl and Its Aldehyde Addition. To a solution of benzaldehyde (**1a**) (2.12 g, 20.0 mmol) in DMF (20 ml) were added 1,1,1-trichloro-2,2,2-trifluoroethane (4.52 g, 24.1 mmol) and zinc powder (1.44 g, 22.1 mmol), and the resulting mixture was stirred for 3 h at room temperature and for 2 h at 50 °C before treatment with sat aq ammonium chloride solution (30 ml). Extraction with diethyl ether (2×30 ml), drying the ethereal extract over magnesium sulfate, concentration, followed by distillation, gave 2,2-dichloro-3,3,3-trifluoro-1-phenyl-1-propanol (**2a**) (4.49 g, 86% yield) as a colorless oil. Bp 100 °C (bath temp)/1 Torr;† ^1H NMR ($CDCl_3$) δ=2.90 (d, *J*=5 Hz, 1H), 5.20 (d, *J*=5 Hz, 1H), 7.25—7.55 (m 5 H); ^{19}F NMR

† 1 Torr=133.322 Pa.

($CDCl_3$-$CFCl_3$) δ=−74.4 (s); IR 3460, 1248, 1188, 1061, 874, 766, 712, 700, 666, 612 cm^{-1}; MS *m/z* (rel intensity) 260 (M^++2, trace), 258 (M^+, trace), 107 (100), 79 (55), 77 (30), and 51 (13).

Found: C, 41.44; H, 2.82%. Calcd for $C_9H_7Cl_2F_3O$: C, 41.73; H, 2.72%.

2-Bromo-2-chloro-3,3,3-trifluoro-1-phenyl-1-propanol (2a'): A colorles oil. ^1H NMR ($CDCl_3$) (a 1 : 1 mixture of two steteoisomers) δ=2.83 (d, *J*=5 Hz, 1 H), 5.20, 5.25 (d, *J*=5 Hz, 1 H), and 7.3—7.7 (m, 5 H); MS *m/z* (rel intensity) 304 (M^++2, trace), 302 (M^+, trace), 107 (100), 79 (43), 77 (20), 51 (8).

Found: *m/z* 301.9299. Calcd for $C_9H_7BrClF_3O$: M, 301.9320.

Formation of **4a** (12%) was shown by GLC assay of the crude reaction mixture.

2,2-Dibromo-3,3,3-trifluoro-1-phenyl-1-propanol (2a''): A colorless oil. ^1H NMR ($CDCl_3$) δ=2.86 (br s, 1 H), 5.11 (s, 1 H), and 7.25—7.65 (m, 5 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−70.1 (s); IR 3455, 1236, 1188, 1172, 698 cm^{-1}; MS *m/z* (rel intensity) 250 (2), 107 (100), 79 (39), 77 (21), and 51 (11).

Found: C, 31.33; H, 1.96%. Calcd for $C_9H_7Br_2F_3O$: C, 31.07; H, 2.03%.

2,2-Dichloro-3,3,3-trifluoro-(3,4-methylenedioxyphenyl)-1-propanol (2b): A colorless oil. ^1H NMR ($CDCl_3$) δ=3.12 (d, *J*=5 Hz, 1 H), 5.20 (d, *J*=5Hz, 1 H), 6.00 (s, 2 H), 6.75—7.55 (m, 3 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75 (s); IR 3500, 1490, 1450, 1250, 1200, 1029 cm^{-1}; MS *m/z* (rel intensity) 306 (M^++4, trace), 304 (M^++2, 4,) 302 (M^+, 6), 151 (100), 149 (12), 123 (11), 93 (59), 65 (33), 63 (10), 39 (10).

Found: C, 39.86; H, 2.30%. Calcd for $C_{10}H_6Cl_2F_3O_3$: C, 39.63; H, 2.33%.

2,2-Dichloro-3,3,3-trifluoro-(4-chlorophenyl)-1-propanol (2c): Colorless crystals, mp 85 °C. ^1H NMR ($CDCl_3$) δ=2.93 (d, *J*=5 Hz, 1 H), 5.21 (d, *J*=5 Hz, 1 H), 7.25—7.60 (m, 4 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.0 (s); IR (KBr) 3480, 1241, 1209, 1185, 881, 831 cm^{-1}; MS *m/z* (rel intensity) 294 (M^++2, trace), 292 (M^+, trace), 143 (36), 141 (100), 113 (19), 77 (67).

Found: C, 36.65; H, 2.07%. Calcd for $C_9H_6Cl_3F_3O$: C, 36.83; H, 2.06%.

2,2-Dichloro-3,3,3-trifluoro-1-(3,4-dichlorophenyl)-1-propanol (2d): A colorless oil. ^1H NMR ($CDCl_3$) δ=2.97 (br d, *J*=4 Hz, 1 H), 5.17 (br d, *J*=4 Hz, 1H), 7.2—7.8 (m, 3 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.2 (s); IR 3480, 1473, 1253, 1188, 1033, 884, 866, 824, 713, 659 cm^{-1}; MS *m/z* (rel intensity) 330 (M^++4, trace), 328 (M^++2, trace), 326 (M^+, trace), 179 (11), 177 (66), 175 (100), 149 (12), 147 (22), 113 (17), 111 (54), 75 (14).

Found: C, 32.81; H, 1.41%. Calcd for $C_9H_5OCl_4F_3$: C, 32.96; H, 1.54%.

4,4-Dichloro-5,5,5-trifluoro-1-phenyl-1-penten-3-ol (2e): A colorless oil. ^1H NMR ($CDCl_3$) δ=2.53 (br s, 1 H), 4.80 (d, *J*=5 Hz, 1 H), 6.27 (dd, *J*=5 and 16 Hz, 1H), 6.82 (d, *J*=16 Hz, 1H), 7.20—7.50 (m, 5 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−73.9 (s); IR 3450, 1257, 1195, 969, 870, 751, 722, 694 cm^{-1}; MS *m/z* (rel intensity) 286 (M^++2, trace), 284 (M^+, 2), 134 (11), 133 (100), 115 (22), 103 (10), 77 (15), 55 (37).

Found: C, 46.35; H, 3.02%. Calcd for $C_{11}H_9Cl_2F_3O$: C, 46.34; H, 3.18%.

2,2-Dichloro-1,1,1-trifluoro-5-methyl-4-hexen-3-ol (2f). Zinc powder (1.50 g, 24 mmol) and copper(I) chloride (99 mg, 1.00 mmol) were suspended in DMF (20 ml) at room temperature. After 5 min, 1,1,1-trichlorotrifluoroethane (4.75 ml, 40 mmol) was added, and the whole was stirred for 20 min at room temperature. Exothermic reaction soon took place, and the vessel was occasionally cooled with ice-water bath. Then, 3-methyl-2-butenal (**1f**) (1.81 g, 21.5 mmol) was added over 10 min to this mixture at 60 °C. Workup and purification by column chromatography (CH_2Cl_2-hexane 1 : 2 to 2 : 1) gave **2f** (3.0 g, 60% yield) as a colorless oil, bp 65—67 °C/0.6 Torr. ^1H NMR ($CDCl_3$) δ=1.77(d, *J*=1.4 Hz, 3 H), 1.81 (d, *J*=1.4 Hz, 3 H), 2.08 (br s, 1 H), 4.80 (d, *J*=9.1 Hz, 1 H), 5.33 (d, *J*=9.1Hz, 1H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.6 (s); IR 3420, 1258, 1204, 1052, 872, 724 cm^{-1}; MS *m/z* (rel intensity) 221 (trace), 219 (trace), 85 (100), 55 (10), 41 (29), 39 (12), 29 (15).

Found: C, 35.30; H, 3.83%. Calcd for $C_7H_9Cl_2F_3O$: C, 35.47; H, 3.83%.

A control experiment in the absence of copper(I) chloride catalyst gave **2f** in 16% yield.

An experiment which employed dichloro[bis(triphenylphosphine)]palladium was carried out by adding 1,1,1-trichloro-2,2,2-trifluoroethane (0.18 ml, 1.5 mmol), $PdCl_2(PPh_3)_2$ (7.5 mg, 0.011 mmol) and zinc powder (78 mg, 1.2 mmol) to a solution of **1f** (86 mg, 1.0 mmol) in DMF (1 ml) and by stirring the reaction mixture at room temperature for 1 h and at 50 °C for 8 h. The yield of **2f** was estimated to be 61% by GLC assay (internal standard: tridecane; column: 5% silicone SE-30 on Uniport HP, 2 m; carrier gas: N_2, 50 ml min^{-1}): R_t 2.97 min.

The adduct **2f** was alternatively prepared by ultrasonic irradiation. To a solution of **1f** (84 mg, 1.0 mmol) in DMF (1 ml) was added 1,1,1-trichloro-2,2,2-trifluoroethane (0.18 ml, 1.5 mmol) and zinc powder (78 mg, 1.2 mmol), and the mixture was allowed to warm gradually to 50 °C under ultrasoic irradiation which was continued for 2 h at 50 °C. The yield was estimated by GLC.

2,2-Dichloro-1,1,1-trifluoro-4-phenyl-3-pentanol (2g): A colorless oil. ^1H NMR ($CDCl_3$), δ=1.46 (d, *J*=7.0, Hz, 3 H), 2.37 (d, *J*=8.1 Hz, 1 H), 3.52 (dq, *J*=2.1 and 7.0 Hz, 1 H), 4.31 (dd, *J*=2.1 and 8.1 Hz, 1 H), 7.33 (s, 5 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.8 (s); IR 3550, 1250, 1194, 870, 704 cm^{-1}; MS *m/z* (rel intensity) 288 (M^++2, trace), 286 (M^+, trace), 106 (10), 105 (100), 103 (5), 79 (9), 77 (7).

Found: C, 46.02; H, 3.97%. Calcd for $C_{11}H_{11}Cl_2F_3O$: C, 46.02; H, 3.86%.

2,2-Dichloro-1-cyclohexyl-3,3,3-trifluoro-1-propanol (2h). Cyclohexanecarbaldehyde (**1h**) (112 mg, 1.00 mmol) and 1,1,1-trichloro-2,2,2-trifluoroethane (0.18 ml, 1.5 mmol) were added to a suspension of zinc powder (78 mg, 1.20 mmol) and copper(I) chloride (5 mg, 0.05 mmol) in DMF (1 ml), and then the reaction mixture was stirred for 5 h at 50 °C. Workup followed by preparative TLC (CH_2Cl_2) gave **2h** (156 mg, 61% yield) as a colorless oil. ^1H NMR ($CDCl_3$) δ=1.0—2.3 (m, 12H), 3.94 (br s, 1H); ^{19}F NMR ($CDCl_3$-$CFCl_3$): δ=−75.1 (s); IR 3490, 2950, 2875, 1252, 1200 cm^{-1}; MS *m/z* (rel intensity) 245 (M^+−19, trace), 113 (19), 95 (60), 83 (100), 82 (18), 67 (17), 55 (84), 41 (39).

Found: C, 40.90; H, 5.08%. Cacld for $C_9H_{13}Cl_2F_3O$: C, 40.78; H, 4.94%.

In the absence of the copper catalyst, the yield of **2h** was 16%.

2,2-Dichloro-3,3,3-trifluoro-1-phenylpropyl Acetate. A solution of 2,2-dichloro-3,3,3-trifluoro-1-phenyl-1-propanol (0.62 g, 2.4 mmol) in pyridine (1 ml) and acetic anhydride (1

ml) was allowed to react for 4 h at room temperature. Work-up and purification by preparative TLC (CH_2Cl_2-hexane 1:2) gave the desired acetate (0.69 g, 96% yield) as a colorless oil. ^1H NMR ($CDCl_3$) δ=2.15 (s, 3 H), 6.35 (s, 1 H), 7.3—7.6 (m, 5 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−74.7 (s); IR 1767, 1373, 1248, 1204, 1040,1028, 938, 840, and 699 cm^{-1}; MS *m/z* (rel intensity) 302 (M^++2, trace), 300 (M^+, trace), 149 (27), 107 (87), 79 (14), 77 (13), 43 (100).

Found: C, 43.79; H, 2.79%. Calcd for $C_{11}H_9Cl_2F_3O_2$: C, 43.88; H, 3.01%.

Zinc Reduction of 2,2-Dichloro-3,3,3-trifluoro-1-phenyl-1-propyl Acetate. Zinc powder (40 mg, 0.61 mmol) was added to a DMF (0.5 ml) solution of the acetate (0.150 g, 0.50 mmol), and the mixture was stirred for 2 h at 50 °C. GLC assay (dodecane as the internal standard; 5% SE-30, 2 m; 120 °C; N_2 50 ml min^{-1}, R_t 5.81 min for **3a** and 12.0 min for the standard) revealed **3a** was produced in 88% yield.

Transformation of 1c to 3c. A Typical Procedure A for the Preparation of 3. To a solution of 4-chlorobenzaldehyde (**1c**) (139 mg, 0.99 mmol) in DMF (1 ml) was added 1,1,1-trichloro-2,2,2-trifluoroethane (0.24 ml, 2.0 mmol) and zinc powder (0.33 g, 5.0 mmol), and the mixture was stirred for 10 min at 0 °C and for 4 h at 50 °C. Water (10 ml) was added, and the resulting mixture was extracted with diethyl ether (3×10 ml). The ethereal extract was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Purification by preparative TLC (CH_2Cl_2-hexane 1:2) afforded 2-chloro-1-(4-chlorophenyl)-3,3,3-trifluoropropene (**3c**) (175 mg, a mixture of (Z)- and (E)-isomers, 73% yield) as a colorless oil. Bp 75 °C (bath temp)/1 Torr. ^1H NMR ($CDCl_3$) δ=7.25 (s, 1 H), 7.40 (d, *J*=10 Hz, 2 H), 7.67 (d, *J*=10 Hz, 2 H) were attributed to the (Z) isomer. ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−69.1 (s, for (Z)-isomer) and −61.7 (s, for (E)-isomer) with the intensity ratio of 88:12. IR 1495, 1307, 1288, 1173, 1140, 1106, 962 cm^{-1}; MS *m/z* (rel intensity) 244 (M^++4, 11), 242 (M^++2, 66), 241 (M^++1, 10), 240 (M^+, 100), 207 (10), 205 (28), 187 (13), 185 (38), 170 (14), 169 (23), 136 (15), 75 (16), 74 (10), 50 (12).

Procedure B Exemplified by the Preparation of 3a. To a solution of benzaldehyde (**1a**, 105 mg, 0.99 mmol) in DMF (1 ml) were added 1,1,1-trichlorotrifluoroethane (0.142 ml, 1.2 mmol) and zinc powder (72 mg, 1.1 mmol). The mixture was stirred for 1 h at room temperature and for 24 h at 50 °C before the addition of acetic anhydride (0.15 ml) and zinc powder (131 mg, 2.0 mmol). Stirring was continued for 4 h at 50 °C. Water (1 ml) and 5 drops of conc hydrochloric acid were added to quench the reaction. Extraction with diethyl ether (3×3 ml), concentration, followed by ^{19}F NMR assay ($CDCl_3$-$CFCl_3$, internal standard: 1,3,5-trichloro-2,4,6-trifluorobenzene), showed two doublets at δ=−69.9 (d, *J*=0.8 Hz) and −62.1 (s) attributed to (*Z*)- and (*E*)-**3a** respectively in a ratio of 87:13 and 87% yield. ^1H NMR ($CDCl_3$) δ=7.2—7.5 (m, 4 H), 7.5—7.8 (m, 2 H); IR 1287, 1216, 1176, 1140, 692 cm^{-1}; MS *m/z* (rel intensity) 208 (M^++2, 34), 207 (M^++1, 10), 206 (M^+, 100), 171 (39), 151 (59), 102 (16), 75 (11), 51 (15), 50 (10).

Found: C, 52.05; H, 2.89%. Calcd for $C_9H_6ClF_3$: C, 52.32; H, 2.93%.

Followings were synthesized by the Procedure B.

2-Chloro-3,3,3-trifluoro-1-(3,4-methylenedioxyphenyl)propene (3b): Z:E=85:15, a colorless oil, bp 70 °C (bath temp)/0.1 Torr. ^1H NMR ($CDCl_3$) (a Z/E mixture) δ=6.03 (s, 2 H), 6.7—7.4 (m, 3 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−68.4 (s) for the (Z)-isomer and δ=6.00 (s, 2 H); −61.2 (s) respectively for the (E)-isomer. IR 1507, 1496, 1450, 1291, 1262, 1251, 1174, 1133, 1040 cm^{-1}; MS *m/z* (rel intensity) 252 (M^++2, 34), 251 (M^++1, 39), 250 (M^+, 100), 249 (87), 157 (26), 137 (16), 107 (12), 87 (12), 63 (11), 62 (13).

Found: C, 47.81; H, 2.47%. Calcd for $C_{10}H_6ClF_3O_2$: C, 47.93; H, 2.41%.

4-Chloro-5,5,5-trifluoro-1-phenyl-1,3-pentadiene (3e): Z:E=89:11, a colorless oil, bp 60—70 °C (bath temp)/0.1 Torr. ^1H NMR ($CDCl_3$) δ=6.6—7.2 (m, 2 H), 7.2—7.6 (m, 6 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−68.5 (s) for the (Z)-isomer and δ=−61.8 (s) for the (E)-isomer. MS *m/z* (rel intensity) 234 (M^++2, 17), 232 (M^+, 50), 197 (31), 178 (14), 177 (100), 146 (10), 129 (14), 128 (61), 127 (16), 77 (10), 63 (11), 51 (15).

Found: C, 56.74; H, 3.25%. Calcd for $C_{11}H_8ClF_3$: C, 56.79; H, 3.47%.

1-Cyclohexyl-2-chloro-3,3,3-trifluoropropene (3h): Z:E=85:15, a colorless oil, bp 70 °C (bath temp)/12 Torr; ^1H NMR ($CDCl_3$) δ=1.1—2.0 (m, 10 H), 2.3—2.7 (m, 1 H), 6.32 (d, *J*=9.0 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−69.2 (s) for the (Z)-isomer and δ=6.05 (d, *J*=9 Hz, 1 H); −62.2(s) respectively for the (E)-isomer.

Found: C, 50.82; H, 5.64%. Calcd for $C_9H_{12}ClF_3$: C, 50.84; H,5.69%

Transformation of 1 to 4. A Typical Procedure. Zinc powder (194 mg, 2.97 mmol) was added to a DMF (3 ml) solution of 3,4-dichlorobenzaldehyde (**1d**) (174 mg. 0.99 mmol), 1,1,1-trichloro-2,2,2-trifluoroethane (0.18 ml, 1.5 mmol), and aluminium chloride (39 mg, 0.3 mmol) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and for 3.5 h at 50 °C, treated with sat ammonium chloride aq solution (4 ml), and extracted with diethyl ether (3×10 ml). The ethereal extract was dried over anhydrous magnesium sulfate and concentrated in vacuo. Purification by preparative TLC gave 2-chloro-1-(3,4-dichlorophenyl)-3,3-difluoro-2-propen-1-ol (**4d**, 193 mg, 72% yield) as a colorless oil, bp 130 °C (bath temp)/1 Torr. ^1H NMR ($CDCl_3$) δ=2.48 (br s, 1 H), 5.70 (br s, 1 H), 7.1—7.6 (m, 3 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−85.1 (d, *J*=40 Hz, 1 F), −89.4 (d, *J*=40 Hz, 1 F); IR 3400, 1747, 1394, 1290, 1132, 1032, 1010, 885, 827, 717 cm^{-1}; MS *m/z* (rel intensity) 276 (M^++4; 14), 274 (M^++2, 43), 270 (M^+, 45), 239 (25), 237 (38), 219 (24), 217 (25), 177 (63), 175 (100), 149 (32), 147 (52), 127 (37), 125 (41), 113 (29), 111 (89), 91 (34), 75 (35), 74 (25).

Found: C, 39.32; H, 1.96%. Calcd for $C_9H_5Cl_3F_2$: C, 39.53; H, 1.84%.

2-Chloro-3,3-difluoro-1-phenyl-2-propen-1-ol (4a): ^1H NMR ($CDCl_3$) δ=2.88 (br s, 1 H), 5.67 (br s, 1 H), 7.36 (s, 5 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−86.6 (dd, *J*=2 and 20 Hz, 1F), −90.4 (dd, *J*=3 and 20 Hz, 1 F); IR 3400, 1744, 1292, 1008, 701 cm^{-1}; MS *m/z* (rel intensity) 206 (M^++2, 11), 204 (M^+, 34), 186 (12), 185 (11), 184 (31), 183 (22), 169 (29), 151 (16), 149 (10), 127 (10), 125 (17), 107 (99), 105 (26), 91 (32), 79 (100), 78 (30), 77 (59), 75 (10), 51 (42), 50 (19), 39 (12), 28 (17), 18 (27).

Found: *m/z* 204.0137. Calcd for $C_9H_7ClF_2O$: M^+, 204.0152.

2-Chloro-1,1-difluoro-4-phenyl-1-penten-3-ol (4g): A colorless oil. ^1H NMR ($CDCl_3$) δ=1.42 (d, *J*=7.2 Hz, 3 H), 2.25 (br s, 1 H), 2.97 and 3.08 (q, *J*=7.2 Hz, 1 H), 4.53 (dt, *J*=10 and 3 Hz, 1 H), 7.1—7.4 (m, 5H) for the Z/E isomer mixture. ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−87.5 (dd, *J*=2 and 38 Hz, 1F), −90.5 (dd, *J*=3 and 38 Hz, 1 F); MS *m/z* (rel inten-

sity) 232 (M^+, trace), 106 (23), 105 (100), 103 (7), 79 (13), 77 (15), 51 (7).

Found: C, 57.01; H, 4.84%. Calcd for $C_{11}H_{11}OClF_2$: C, 56.79; H, 4.76%.

1-Cyclohexyl-2-chloro-3,3-difluoro-2-propen-1-ol (4h): A colorless oil. ^1H NMR ($CDCl_3$) δ=0.5—1.8 (m, 10 H), 2.03 (br d, J=10 Hz, 1 H), 4.07 (d, J=10 Hz, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−82.1 (dd, J=2 and 40 Hz, 1 F), −91.8 (m of dd, J=3 and 40 Hz, 1 F); IR 2950, 1746, 1287, 996 cm^{-1}; MS m/z (rel intensity) 210 (M^+, trace), 127 (9), 84 (7), 83 (99), 82 (22), 67 (8), 56 (5), 55 (100), 53 (5), 41 (50), 39 (16), 29 (10), 27 (12).

Found: m/z 210.0612. Calcd for $C_9H_{13}OClF_2$: M, 210.0621.

2-Chloro-1,1-difluoro-1-tridecen-3-ol (4k): ^1H NMR ($CDCl_3$) δ=0.7—1.0 (m, 3 H), 1.25 (s, 16 H), 1.45—1.9 (m, 2H), 1.77 (br s, 1 H), 4.35—4.6 (m, 1H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−87.0 (dd, J=39 and 2 Hz, 1 F), −91.0 (dd J=39 and 3 Hz, 1F); IR 3380, 2945, 2875, 1747, 1288 cm^{-1}; MS m/z (rel intensity) 250 (M^+, trace), 129 (34), 127 (100), 57 (22), 55 (14), 43 (39), 41 (25), 29 (15).

Found: m/z 250.1326. Calcd for $C_{13}H_{21}ClF_2O$: M, 250.1299.

Addition of CF_3CCl_2ZnCl to α-Keto Esters. A Typical Procedure. Zinc powder (125 mg, 2.0 mmol) and copper(I) iodide (5 mg, 0.05 mmol) were added to a DMF (1 ml) solution of methyl phenylglyoxylate (**5a**) (164 mg, 1.0 mmol). To this mixture was added 1,1,1-trichloro-2,2,2-trifluoroethane (0.18 ml, 1.5 mmol) drop by drop at room temperature. The reaction mixture was stirred for 10 min, treated with saturated ammonium chloride aq solution (10 ml), and then extracted with diethyl ether (2×10 ml). The ethereal extract was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Purification by preparative TLC (silica gel, CH_2Cl_2) afforded methyl 3,3-dichloro-4,4,4-trifluoro-2-hydroxy-2-phenylbutanoate (**6a**, 175 mg, 55% yield) as a colorless oil, bp 70 °C (bath temp)/0.2 Torr. ^1H NMR ($CDCl_3$) δ=4.00 (s, 3 H), 4.72 (s, 1 H), 7.3—7.5 (m, 3 H), 7.9—8.2 (m, 2 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−70.6 (s); IR 3490, 1732, 1272, 1240, 1206 cm^{-1}; MS m/z (rel intensity) 259 (M^++2−COOMe, 7), 257 (M^+−COOMe, 11), 193 (6), 165 (25), 153 (5), 151 (7), 106 (8), 105 (100), 78 (12), 77, (29), 59 (6), 51 (10), 15 (8).

Found: C, 41.55; H, 2.97%. Calcd for $C_{11}H_9Cl_2F_3O_3$: C, 41.67; H, 2.86%.

Ethyl 3,3-Dichloro-4,4,4-trifluoro-2-hydroxy-2-methylbutanoate (6b): A colorless oil. ^1H NMR ($CDCl_3$) δ=1.35 (t, J=7.0 Hz, 3H), 1.78 (s, 3 H), 4.11 (s, 1 H), 4.35 (q, J=7.0 Hz, 2 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−72.4 (s); IR 3500, 1734, 1241, 1200, 1187 cm^{-1}; MS m/z (rel intensity) 197 (M^++2−COOEt, 13), 195 (M^+−COOEt, 20), 160 (18), 142 (5), 140 (14), 131 (6), 117 (6), 67 (6), 45 (7), 43 (100), 29 (47), 27 (11), 18 (12).

Found: C, 31.37; H, 3.44%. Calcd for $C_7H_9Cl_2F_3O_3$: C, 31.25; H, 3.37%.

Reaction of CF_3CCl_2ZnCl with DMF and Chlorotrialkylsilanes. A Typical Procedure. Zinc powder (0.78 g, 12 mmol) and 1,1,1-trichloro-2,2,2-trifluoroethane (1.42 ml, 12 mmol) were added slowly to a solution of t-butylchlorodimethylsilane (1.52 ml, 10 mmol) in DMF (10 ml) under cooling with water bath. The mixture was stirred for 1 h at room temperature. The whole was charged on a short silica gel (20 g) column and eluted with hexane (ca. 100 ml). The eluate was concentrated and again subjected to colum chromatography (silica gel, 10 g, hexane). Concentration of the hexane eluate and distillation gave 1-(t-butyldimethylsiloxy)-2,2-dichloro-3,3,3-trifluoro-1-dimethyl-1-propanamine (**7a**, 2.02 g, 60% yield) as a colorless oil, bp 50 °C (bath temp)/0.15 Torr. ^1H NMR ($CDCl_3$) δ=0.16 (s, 6 H), 0.98 (s, 9 H), 2.53 (s, 6 H), 4.71 (s, 1 H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−75.2 (s); IR 1257, 1198, 1184, 1088, 1061, 840, 783 cm^{-1}; MS m/z (rel intensity) 324 (M^+−Me, trace), 208 (29), 188 (68), 131 (45), 130 (23), 116 (26), 102 (39), 85 (37), 83 (54), 75 (32), 74 (22), 73 (100), 59 (28).

Found: C, 38.83; H, 6.52; N, 4.12%. Calcd for $C_{11}H_{22}Cl_2F_3NOSi$: C, 38.93; H, 6.58; N, 4.07%.

2,2-Dichloro-1-triethylsiloxy-3,3,3-trifluoro-*N*,*N*-dimethyl-1-propanamine (7b): Bp 95 °C (bath temp)/0.3 Torr. ^1H NMR ($CDCl_3$) δ=0.2—1.2 (m, 15 H), 2.50 (s, 6 H), 4.70 (s, 1 H); IR 2975, 2899, 1260, 1196, 1182, 1068, 1008, 942, 902, 812, 742 cm^{-1}.

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