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Facile Conversion of Aldehydes into 1-Substituted 2-Chloro-3,3-difluoro-2-propen-1-ols with 1,1-Dibromo-1-chloro-2,2,2-trifluoroethane/Magnesium Reagent

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Synopsis. Aldehydes RCHO are converted in excellent yields into chlorodifluoroallyl alcohols $RCH(OH)CCl=CF_2$ upon treatment with $CClBr_2CF_3$ and magnesium in tetrahydrofuran at 0 °C.

Aldehyde adducts of halogenated ethenyl anions $^{-}CX=CF_2$ ($X=Cl$ or F) have been shown to be useful intermediates for the synthesis of α-halo-α,β-unsaturated ketones and acid derivatives,[1)] as well as artificial pyrethroids.[2)] The aldehyde addition of $CX=CF_2$ anions was earlier realized at −130 °C with $LiCX=CF_2$,[1a−c)] and recently achieved under milder conditions using $R_3SiCX=CF_2/F^-$,[3)] $CF_3CCl_3/Zn/AlCl_3(cat)$,[4)] or CF_3CCl_3/Pb[1h)] reagent. Even these reagents possess problems from practical viewpoints. For example, preparation of the fluorinated vinylsilanes is tedious;[5)] the zinc and lead reagents seem to lack wide applicability.[6)] Reported herein is an alternative facile way to 1-substituted 2-chloro-3,3-difluoro-2-propen-1-ols **2** through the reaction of aldehydes **1** with $CClBr_2CF_3$ and magnesium, both of which are commercially readily available and economical (Eq 1).

$$\underset{\mathbf{1}}{RCHO} + CClBr_2CF_3 \xrightarrow[THF]{Mg} \underset{\mathbf{2}}{RCH(OH)CCl{=}CF_2}$$

a: R = Ph-

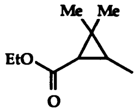
b: R = 4-Cl-C_6H_4-

c: R = PhCH=CH-

d: R = PhCH(CH_3)-

e: R = *c*-C_6H_{11}-

f: R =



Results and Discussion

The adducts **2** were produced in excellent yields, when aldehydes were treated with 3 molar equivalents of 1,1-dibromo-1-chloro-2,2,2-trifluoroethane and 6 mol of magnesium chips in tetrahydrofuran (THF). Results are summarized in Table 1. In addition to common aliphatic and aromatic aldehydes, readily enolizable aldehydes (e.g. **1d** and **1f**) give the desired adducts. Cinnamaldehyde (**1c**) afforded a 1,2-adduct only. The adduct **2f** is a versatile intermediate for synthetic pyrethroids having a $CH=C(Cl)CF_3$ side chain.[2)]

The reaction course of the transformation deserves particular comments. When 1:1 mole ratio of $CClBr_2CF_3$ and Mg was applied, any kinds of aldehyde adducts were not detected, but formation of $CClBr=CF_2$ was observed by ^{19}F NMR of the crude reaction mixture. Thus, the organomagnesium reagent responsible for the carbonyl addition is concluded to be a Grignard reagent $BrMgCCl=CF_2$ generated in situ by the reaction of magnesium metal and the $CClBr=CF_2$.[7)] In this sense, the mechanism of the total transformation contrasts sharply to that of the $CF_3CCl_3/Zn/AlCl_3$ (cat) reagent, which first gives aldehyde adducts $RCH(OH)CCl_2CF_3$ and then reduces the adducts to give products of type **2**.

Although the Grignard reagent $BrMgCCl=CF_2$ is recorded by Stelin et al.,[7)] its carbonyl addition has never been achieved due possibly to the instability of the reagent. Noteworthy is that the in situ prepared reagent can do the transformation at 0 °C as reported herein.

Experimental

Materials. Magnesium chips and 1,1-dibromo-1-chloro-2,2,2-trifluoroethane were purchased from Nakarai Chemicals Co. Ltd. and PCR Co. Ltd., respectively, and used directly. Aldehydes were purchased from Tokyo Kasei Kogyo Co. Ltd. Ethyl 2-formyl-3,3-dimethylcyclopropanecarboxylate was prepared by a procedure previously reported.[2b)] Tetrahydrofuran was dried over benzophenone ketyl and freshly distilled before use.

Reaction of Aldehydes with $CClBr_2CF_3$/Mg Reagent. A Typical Procedure. Magnesium chips 144 mg (6.0 mmol) were suspended in THF 2 mL solution of benzaldehyde (**1a**) 106 mg (1.0 mmol). The whole was cooled at 0 °C, and THF 2 mL solution of 1,1-dibromo-1-chloro-2,2,2-trifluoroethane 825 mg (3.0 mmol) was added dropwise. After 3 h at 0 °C, sat ammonium chloride aq solution 15 mL was added, and the mixture was extracted with diethyl ether (10 mL×3). The ethereal extract was dried over anhydrous magnesium sulfate, concentrated under reduced pressure, and subjected to preparative TLC (silica gel, dichloromethane-hexane 1:1) to give 2-chloro-3,3-difluoro-1-phenyl-2-propen-1-ol 144 mg (**2a**) (70%) as a colorless oil. Spectral data are completely in accord with those of the authentic sample.[4b)]

Table 1. Transformation of RCHO to $RCH(OH)CCl=CF_2$[a)]

Run	Aldehyde	Conditions	Product	Yield/%
1	**1a**	0 °C, 3 h	**2a**	70
2	**1b**	0 °C, 3 h	**2b**	51
3	**1c**	0 °C, 4 h	**2c**	59
4	**1d**	0 °C, 4 h	**2d**	77
5	**1e**	0 °C, 4 h	**2e**	73
6	**1f**	0 °C, 4 h	**2f**	42

a) The molar ratio **1**:$CClBr_2CF_3$:Mg=1:3:6.

In a similar manner, **2b**—**f** were prepared. Physical data of **2d**, **2e**, and **2f** have been already reported.[4b)]

2-Chloro-3,3-difluoro-1-(4-chlorophenyl)-2-propen-1-ol (2b): A colorless oil; ^{1}H NMR ($CDCl_3$) δ=2.20 (broad s, 1H), 5.72 (broad s, 1H), and 7.37 (s, 4H); ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−87.0 (d, J=38 Hz, 1F) and −91.3 (d, J=38 Hz, 1F); IR (neat) 3400, 1746, 1500, 1296, 1096, 1012, 846, and 734 cm^{-1}; MS (70 eV) m/z (rel intensity) 240 (M^++2, 9), 238 (M^+, 10), 220 (64), 218 (100), 183 (45), 182 (29), 154 (20), 143 (41), 120 (43), 99 (21), 77 (20), 75 (30), 74 (21), and 50 (25).

Found: C, 45.09; H, 2.66%. Calcd for $C_9H_6Cl_2F_2O$: C, 45.22; H, 2.53%.

2-Chloro-1,1-difluoro-5-phenyl-1,4-pentadien-3-ol (2c): ^{1}H NMR ($CDCl_3$) δ=2.17 (broad s, 1H), 5.17 (broad s, 1H), 6.20 (dd, J=5.0, 16.0 Hz, 1H), 6.70 (d, J=16.0 Hz, 1H), and 7.20—7.45 (m, 5H). ^{19}F NMR ($CDCl_3$-$CFCl_3$) δ=−86.3 (d, J=40 Hz, 1F) and −90.0 (d, J=40 Hz, 1F); IR (neat) 3380, 1740, 1288, 1012, 993, 965, 753, and 693 cm^{-1}.

Found: m/z 230.0332. Calcd for $C_{11}H_9F_2ClO$: M, 230.0310.

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