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PRACTICAL WAYS FROM ALDEHYDES TO 2-CHLORO-1,1,1-TRIFLUORO-2-ALKENES AND 2-CHLORO-1,1-DIFLUORO-1-ALKEN-3-OLS

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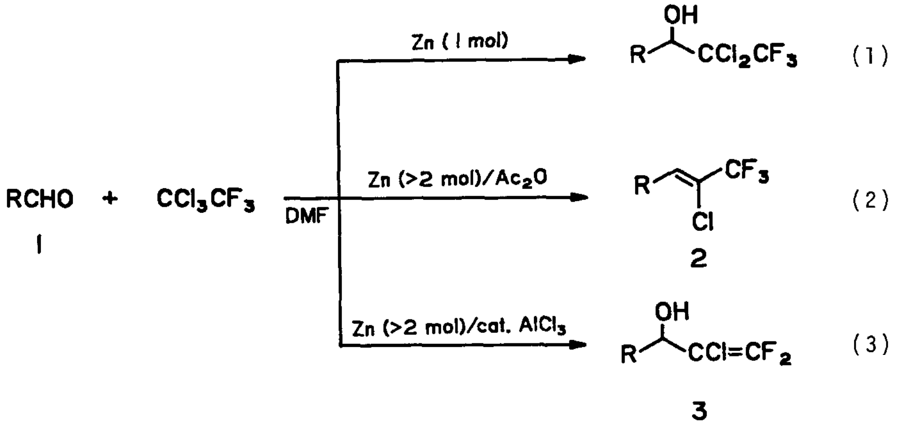
A reagent system $CF_3CCl_3/Zn(>2\ mol)/Ac_2O$ *transformed aldehydes to 2-chloro-1,1,1-trifluoro-2-alkenes exclusively, whereas* $CF_3CCl_3/Zn(>2\ mol)/AlCl_3(cat.)$ *converted aldehydes into 2-chloro-1,1-difluoro-1-alken-3-ols.*

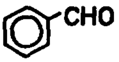
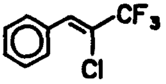
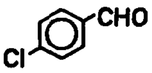
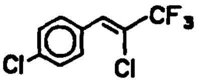
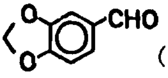
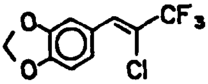
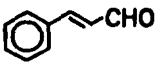
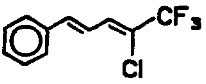
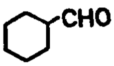
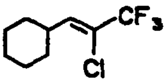
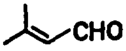
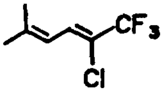
Thermally stable zinc reagent CF_3CCl_2ZnCl prepared from CF_3CCl_3 and slightly excess zinc powder was recently shown to achieve aldehyde addition efficiently (eq 1).[1] The presence of large excess of zinc (>2 mol) might induce further reductive β-elimination to afford 2-chloro-1,1,1-trifluoro-2-alkene (**2**) or 2-chloro-1,1-difluoro-1-alken-3-ol (**3**). The two possible pathways are now found to be controllable by use of either 1.5-1.6 mol of acetic anhydride (eq 2) or $AlCl_3$ catalyst (eq 3), respectively.



A procedure for the selective transformation to **2** is as follows. Benzaldehyde (1 mmol) was treated with CCl_3CF_3 (2 mmol), zinc powder (5 mmol), and acetic anhydride (1.5 mmol) in dimethylformamide (DMF) (1 mL) for 7 h at 50 °C. Usual workup gave **2a** solely in 75% yield as estimated by ^{19}F NMR. The amount of zinc could be reduced to 3.1 mol by a modified two-step procedure: Benzaldehyde was first treated with CF_3CCl_3 (1.2 mol) and zinc (1.1 mol) at 50 °C for 24 h and then with acetic anhydride (1.5 mol) and zinc powder (2 mol) for additional 4 h at 50 °C to give **2a** in 78% yield. In the absence of acetic anhydride, a mixture of **1a** (17%), **2a** (57%), and **3a** (14%) resulted. Such Lewis acids[2] as $TiCl_4$ (1 mol) and $SiCl_4$ (0.3 mol) also were applicable to the selective transformation from **1a** to **2a** (67% and 42%, respectively), but $BF_3{\cdot}OEt_2$ (1 mol) favored the formation of **3a** (**2a**, 30% and **3a**, 52%).

Various aldehydes including aromatic, aliphatic, and α,β-unsaturated ones were successfully converted into **2** by the $CF_3CCl_3/Zn/Ac_2O$ reagent (Table I). Acetyl chloride could be employed instead of acetic anhydride in the two-step procedure (run 6).

Table I. Transformation of RCHO to $RCH{=}CH(Cl)CF_3$ with $CCl_3CF_3/Zn/Ac_2O$ reagent.

run	aldehyde (1)	$CCl_3CF_3/Zn/Ac_2O$	conditions	product (2)	% yield[a]
1	 (**1a**)	2.0 5.0 1.5	50 °C, 7 h	 (**2a**)	75 [86:14]
2	**1a**	i: 1.2 1.1 -- ii: -- 2.0 1.6	50 °C, 24 h 50 °C, 4 h	**2a**	78 [87:13]
3	 (**1b**)	2.0 5.0 1.5	50 °C, 4 h	 (**2b**)	73 [88:12]
4	**1b**	i: 1.2 1.1 -- ii: -- 2.0 1.6	50 °C, 24 h 50 °C, 4 h	**2b**	76 [88:12]
5	 (**1c**)	i: 1.2 1.1 -- ii: -- 2.0 1.6	50 °C, 24 h 50 °C, 4 h	 (**2c**)	81 [85:15]
6	**1c**	i: 1.2 1.1 -- ii: -- 2.0 1.6[b]	50 °C, 12 h 50 °C, 4 h	**2c**	63 [86:14]
7		i: 1.2 1.1 -- ii: -- 2.0 1.6	50 °C, 24 h 50 °C, 4 h		72 [89:11]
8		i: 1.2 1.1 -- ii: -- 2.0 1.6	50 °C, 21 h[c] 50 °C, 4 h		50 [85:15]
9		i: 1.2 1.1 -- ii: -- 2.0 1.6	50 °C, 1 h[c] 50 °C, 4 h		53 [88:12]

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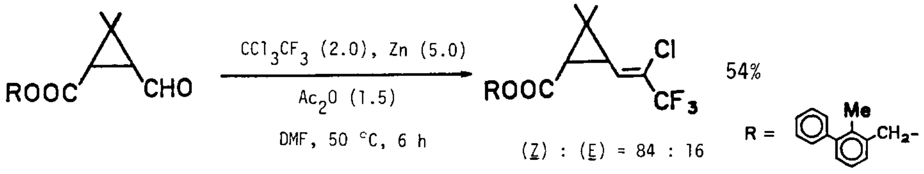
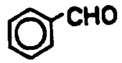
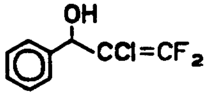
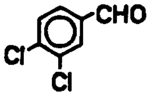
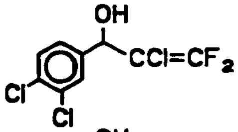
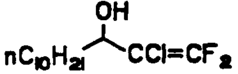
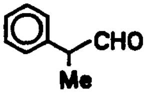
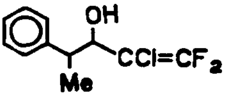
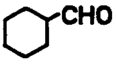
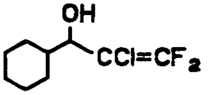
[a] The values in the brackets refer to the (Z) : (E) ratio of **2**. [b] AcCl was employed instead of Ac_2O. [c] $NiCl_2(PPh_3)_2$ (2 mol%) was employed as a catalyst.

Synthetic utility of the present reactions[3] is demonstrated by one-step synthesis of 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate,[4] a recently found highly potent synthetic pyrethroid.[5] Although the same transformation was previously carried out using CF_3CCl_3, PPh_3, and zinc,[6] the method reported here is apparently more practical in view of low cost of reagents and simpler separation procedure.



In striking contrast, aluminium chloride preferred **3a** formation. When benzaldehyde was allowed to react with CF_3CCl_3 (1.5 mol) and Zn (3 mol) in the presence of $AlCl_3$ (0.1 mol) at 50 °C for 18 h, formation of **3a** (86%) along with a trace amount of **2a** (<5%) was observed[7] by ^{19}F NMR analysis. Results applied to various aldehydes are summarized in Table II, which shows that this reaction is practical for the introduction of $CCl{=}CF_2$ moiety to aldehyde carbonyls in a single step.[8,9] The aldehyde adducts of $CX{=}CF_2$ groups (X = F, Cl) are key synthetic intermediates for various fluorine-containing compounds.[12,13]

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

run	aldehyde (**1**)	$AlCl_3$[b]	conditions	product (**3**)	% yield
1	 (1a)	0.1	50 °C, 18 h	 (3a)	86
2	**1a**	0.3	50 °C, 18 h	**3a**	80
3		0.3	50 °C, 3.5 h		72
4	$nC_{10}H_{21}CHO$	0.3	50 °C, 18 h		41
5		0.1	50 °C, 18 h		86
6		0.1	50 °C, 9 h		52

[a] RCHO : CCl_3CF_3 : Zn = 1 : 1.5 : 3.0. [b] Mol-equiv to **1**.

Acknowledgment. We thank FMC Corporation for a generous gift of (2-methyl-3-phenylphenyl)methanol.

References and Notes

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2. Similar deoxygenative behavior of Lewis acids is observed in the carbonyl methylenation with CH_2CX_2/Zn/Lewis acid reagent: (a) K. Takai, Y. Hotta, K. Oshima, and H. Nozaki, Tetrahedron Lett., **1978**, 2417; idem, Bull. Chem. Soc. Jpn., **53**, 1698 (1980). (b) J. Hibino, T. Okazoe, K. Takai, and H. Nozaki, Tetrahedron Lett., **26**, 5579 (1985). (c) T. Okazoe, J. Hibino, K. Takai, and H. Nozaki, ibid., **26**, 5581 (1985).
3. The product 2-chloro-1,1,1-trifluoro-5-methyl-2,4-hexadiene (**2d**) is also known as a key precursor of 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate: see ref. 5a.
4. Only the (1R*,3S*) isomer was afforded though the starting aldehyde was a mixture of (1R*,3R*) and (1R*,3S*) isomers (6 : 1). See ref 1b.
5. (a) D. Holland and D. A. Laidler, J. Mol. Cat., **11**, 119 (1981). (b) D. Bellus, Pure Appl. Chem., **57**, 1827 (1985). (c) Japan Kokai Tokkyo Koho 53-95945; 54-112820; 54-130537; 55-59142; 55-89248; 55-111488; 59-92830.
6. Anon. (UK), Res. Discl., **219**, 239 (1982); Chem. Abstr., **98**, 16322r (1983).
7. On the employment of 1 mol of $AlCl_3$, 2,2-dichloro-3,3,3-trifluoro-1-phenyl-1-propanol and **2a** were afforded in 37% and 11% yield, respectively; Formation of **3a** was not detected.
8. We have recently reported fluoride ion catalyzed aldehyde addition of polyhalovinylsilanes under mild conditions: M. Fujita and T. Hiyama, J. Am. Chem. Soc., **107**, 4085 (1985).
9. The same transformation was carried out with $IMgCCl=CF_2$[10] or $LiCCl=CF_2$,[11] but its thermal instability or use of unavailable olefins limited the synthetic application.
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12. M. Fujita and T. Hiyama, an accompanying paper.
13. (a) J. F. Normant, J. P. Foulon, D. Masure, R. Sauvetre, and J. Villieras, Synthesis, **1975**, 122. (b) C. Chuit, R. Sauvetre, D. Masure, M. Baudry, J. F. Normant, and J. Villieras, J. Chem. Res. (S), **1977**, 104. (c) R. Sauvetre, D. Masure, C. Chet, and J. F. Normant, Synthesis, **1978**, 128. (d) J. P. Gillet, R. Sauvetre, and J. F. Normant, Tetrahedron Lett., **26**, 3999 (1985). (e) F. Tellier, R. Sauvetre, and J. F. Normant, J. Organomet. Chem., **292**, 19 (1985).

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