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Synthetic utility of HCFC-123 (2,2-dichloro-1,1,1-trifluoroethane): the reaction between HCFC-123 and aldehydes using zinc

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Abstract

HCFC-123 (2,2-dichloro-1,1,1-trifluoroethane) reacted with zinc and aldehydes to afford predominantly either 1-substituted 2-chloro-3,3-difluoro-2-propen-1-ols or 1-substituted 2,2-dichloro-3,3,3-trifluoro-1-propanols. The reactions proceeded via 1,1-dichloro-2,2,2-trifluoroethylzinc chloride as an organozinc intermediate.

Keywords: 2,2-Dichloro-1,1,1-trifluoroethane; Reaction; Aldehydes; Zinc; 1,1-Dichloro-2,2,2-trifluoroethylzinc chloride

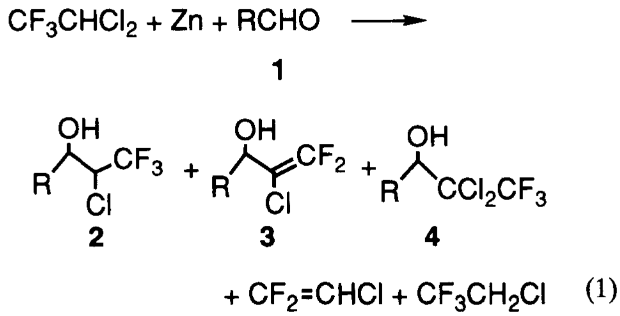
1. Introduction

Chlorofluorocarbons (CFCs) have been used extensively, e.g. as aerosol propellants, blowing agents, cleaning solvents and refrigerants. The decision to phase out their production [1], because their emission causes depletion of the stratospheric ozone layer, has necessitated a search for alternatives such as hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs).

CFCs have also played a very important role as the industrial sources of many fluorine-containing materials. Accordingly, alternatives for CFCs are also needed as new industrial fluorine sources, but their synthetic use has not been investigated. Hence, we have studied the synthetic application of HCFC-123 (CF_3CHCl_2) which is a potential alternative of CFC-11 ($CFCl_3$) [1]. In this paper, we report the reaction of HCFC-123 with zinc and aldehydes to afford fluorine-containing alcohols, and also discuss the reaction route.

2. Results and discussion

Initially the reaction between CF_3CHCl_2, zinc and benzaldehyde (**1a**) was examined[1]. The alcohols **2a**, **3a** and **4a** were obtained as the products of carbonyl addition, and $CF_2{=}CHCl$ and CF_3CH_2Cl were also formed by the reduction of CF_3CHCl_2 (Eq. (1)).



$$CF_3CHCl_2 + Zn + RCHO \longrightarrow$$

1

2 **3** **4**

$$+ CF_2{=}CHCl + CF_3CH_2Cl \qquad (1)$$

(R: **a**, Ph-; **b**, 4-Cl-C_6H_5-; **c**, $PhCH_2CH_2$-; **d**, c-C_6H_{11}-; **e**, PhCH=CH-)

The reaction conditions were varied to improve the yield of alcohol products (Table 1). In this reaction CuCl was effective as the catalyst[2], and **3a** was obtained in 68% yield when the reaction was carried out in *N,N*-dimethylformamide (DMF) at room temperature using 5 mmol of CF_3CHCl_2, 5 mmol of zinc and 1 mmol of aldehyde in the presence of a catalytic amount of CuCl (entry 5, Table 1).

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[1] The carbonyl addition of an organozinc reagent prepared from 1,1,1-trichloro-2,2,2-trifluoroethane has been reported [2].

[2] It has been reported that the addition of a catalytic amount of CuCl to zinc forms a zinc–copper couple and increases the reactivity of zinc, see Ref. [2].

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Table 1
Reaction of HCFC-123 with zinc and benzaldehyde

Entry	Amount (mmol)		Catalyst	Yield [a,b] (%)			Yield [a,c] (%)	
	CF_3CHCl_2	Zn		**2a**	**3a**	**4a**	$CF_2{=}CHCl$	CF_3CH_2Cl
1	2	2.2	none	9	25	8	13	17
2	2	2.2	CuCl	12	37	3	20	24
3	4	2	CuCl	3	18	13	7	16
4	3	3.3	CuCl	9	58	1	21	27
5	5	5	CuCl	8	68 [d]	0	19	30
6 [e]	5	5	CuCl	5	9	60 [f]	21	24

[a] Yield determined by ^{19}F NMR ($C_6H_5CF_3$ used as internal standard).
[b] Yield based on aldehyde.
[c] Yield based on CF_3CHCl_2.
[d] Isolated yield, 62%.
[e] Benzaldehyde added after CF_3CHCl_2 and Zn had been stirred for 24 h.
[f] Isolated yield, 59%.

It was also found that **4a** was obtained predominantly when benzaldehyde was added after the reaction between CF_3CHCl_2 and zinc had occurred. When the reaction of CF_3CHCl_2 (5 mmol) with zinc (5 mmol) was carried out in the presence of a catalytic amount of CuCl in DMF for 24 h, 1.1 mmol of $CF_2{=}CHCl$ and 1.2 mmol of CF_3CH_2Cl were obtained as gaseous products. When benzaldehyde (1 mmol) was added to the residual reaction mixture, **4a** was obtained in 60% yield (entry 6, Table 1). After addition of the aldehyde, no gaseous product was formed.

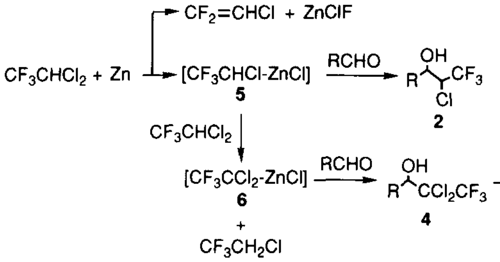
This reaction was applied to various aldehydes using two methods. In method A, CF_3CHCl_2, zinc and aldehyde were stirred in DMF for 12 h, whereas in method B, CF_3CHCl_2 and zinc were stirred in DMF and then aldehyde was added to the reaction mixture. The results are summarized in Table 2. Alcohol **3** was predominantly obtained by method A (entries 1, 5 and 7), while **4** was predominantly obtained by method B (entries 2, 4 and 8). When a halogen-containing aldehyde **1b** was employed, the desired products were not obtained by method A (entry 3), which is ascribed to reaction of the aldehyde with zinc. However, **4** was obtained in good yield by method B (entry 4). When 3-phenylpropanal (**1c**) was employed, the yield of alcohol was decreased because self-condensation of the aldehyde occurred via the abstraction of α-proton (entries 5 and 6). In the case of the α,β-unsaturated aldehyde **1e**, the yield of desired product was very low because of side-reactions of the aldehyde (entries 9 and 10).

Table 2
Reaction of HCFC-123 with zinc and aldehyde

Entry	Aldehyde	Method	Yield [a] (%)		
			2	**3**	**4**
1	**1a**	A	8	62	0
2	**1a**	B	5	9	59
3	**1b**	A	0	0	0
4	**1b**	B	7	11	64
5 [b]	**1c**	A	3	25	0
6 [c]	**1c**	B	1	23	12
7	**1d**	A	2	56	0
8	**1d**	B	3	9	40
9	**1e**	A	0	1 [d]	0
10	**1e**	B	2 [d]	7 [d]	9 [d]

[a] Mixture of **2**, **3** and **4** isolated as one spot by silica gel chromatography. Each yield was determined by ^{19}F NMR analysis of the mixture.
[b] Self-condensation product (23%) formed.
[c] Self-condensation product (14%) formed.
[d] Yield determined by ^{19}F NMR analysis of the crude product.

From the above results, the reaction route is assumed to be as in Scheme 1. CF_3CHCl_2 reacts with zinc and although some $CF_2{=}CHCl$ is afforded via reduction by the zinc, a new organozinc reagent $[CF_3CHCl–ZnCl]$[3] (**5**) is formed. Reaction of **5** with aldehyde gives alcohol **2**, but this reaction is slow and reaction between **5** and unchanged CF_3CHCl_2 proceeds faster to afford a second organozinc reagent $[CF_3CCl_2–ZnCl]$[3] [2] (**6**)[4] and CF_3CH_2Cl. Reagent **6** reacts with aldehyde to afford



Scheme 1.

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[3] The true structure of this chemical species is not clear. It may exist as an aggregated or disproportionated form.

[4] Similar reactions including the formation of organometal species via proton abstraction by other organometallic compounds have been reported, see Ref. [3].

4, followed by reduction of **4** by the remaining zinc to give **3**. When aldehyde was present throughout the reaction, the reduction of **4** to **3** would be fast since a large excess of zinc remained, so that **3** was obtained predominantly. When the aldehyde was added after the reaction of CF_3CHCl_2 with zinc had occurred, the reduction of **4** to **3** would be slower because little zinc remained owing to its reaction with CF_3CHCl_2, and so **4** was obtained as a major product.

The ^{19}F NMR spectrum of the reaction solution between CF_3CHCl_2 and zinc in DMF in the presence of a catalytic amount of CuCl was recorded to confirm the reaction route. ^{19}F signals at δ 63.5 (d, $J=15$ Hz) and 73.4 ppm, assigned to **5** and **6** (lit. value [2], δ 72.3 ppm), respectively, were observed, accompanied by signals due to CF_3CH_2Cl (δ 72.0 ppm, t, $J=9$ Hz) and $CF_2{=}CHCl$ (δ 88.6 ppm, dd, $J=44$, 18 Hz, and δ 92.8 ppm, d, $J=44$ Hz). This result supports the above-mentioned reaction route.

3. Experimental details

Typical experimental procedures were as follows. For method A, a mixture of aldehyde (1 mmol), zinc powder[5] (5 mmol) and CuCl (0.2 mmol) in DMF (2 ml) was placed in the reaction vessel fitted with a glass–Teflon stop valve (Kontes). CF_3CHCl_2 (5 mmol) was introduced into the cooled vessel at −196 °C using a vacuum line system. The reaction mixture was warmed to room temperature, stirred for 12 h and then quenched with aqueous sat. NH_4Cl. It was diluted with water and extracted with ether. The ether layer was washed with water followed by a solution of brine and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the crude product was purified by silica gel column chromatography or preparative thin layer chromatography. In method B, the operation was carried out in a similar manner except that aldehyde was added after a mixture of CF_3CHCl_2, zinc powder and CuCl had been stirred in DMF for 24 h. The products were identified by comparing their IR, ^1H NMR and ^{19}F NMR spectra with those of authentic samples.

4. Conclusions

We have demonstrated the synthetic utility of HCFC-123 as a building block for organofluorine compounds. Fluoroalcohols **3** and **4** have been synthesized from HCFC-123 by reaction with zinc and aldehydes, which proceed via two organozinc species $[CF_3CHCl{-}ZnCl]$ and $[CF_3CCl_2{-}ZnCl]$.

References

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[2] M. Fujita and T. Hiyama, *Bull. Chem. Soc. Jpn.*, *60* (1987) 4377, and references cited therein.

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[5] Commercially available zinc powder was washed successively with dil. HCl, water, ethanol, diethyl ether, and finally absolute diethyl ether and dried under reduced pressure.