An efficient synthesis of 1-chloro-2,2-difluoroethylene via the reductive dechlorination of 1,2,2-trichloro-1,1-difluoroethane

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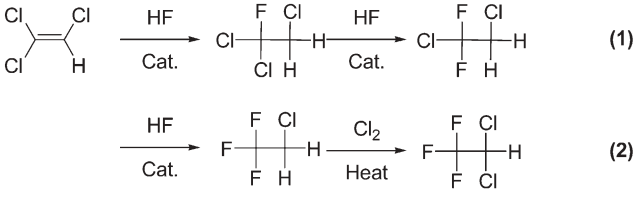
1-Chloro-2,2-difluoroethylene was prepared from 1,2,2-trichloro-1,1-difluoroethane by reductive dechlorination in the presence of zero-valent zinc. Eleven different solvents were investigated and the best results were obtained in methanol, dimethyl formamide and ethanol at 80 °C. A large-scale experiment using ethanol as a solvent gave 1-chloro-2,2-difluoroethylene in high yield. These results provide a method for producing 1-chloro-2,2-difluoroethylene on an industrial scale because 1,2,2-trichloro-1,1-difluoroethane is the waste material arising from 2,2-dichloro-1,1,1-trifluoroethane production. These results can also provide a method for solving the recycling problem of 1,2,2-trichloro-1,1-difluoroethane in 2,2-dichloro-1,1,1-trifluoroethane production.

Keywords green chemistry, 1-chloro-2,2-difluoroethylene, reductive dechlorination, industrial production

1-Chloro-2,2-difluoroethylene is a raw material[1] and key intermediate for the production of fluorine-containing textile finishing agents, fluorosurfactants, organic silicon fluorine modified resins and other fluorine containing fine chemicals.[2,3] These products can be used as heat exchange materials, refrigerants, foaming agents, solvents, cleaning agents, polymerisation media, polyolefin and polyurethane expansion agents, gas dielectrics and flame retardants.[4]

2,2-Dichloro-1,1,1-trifluoroethane is a new type of foaming agent, which is also used as a refrigerant and cleaning agent. Because it has only 0.02 of ozone destruction potential (ODP) and other good properties, it is becoming better known as a replacement for Freon and Halon.[5,6] It also has potential application in the production of fluorine containing medicines and pesticide intermediates.[7] Many companies have successfully set up 2,2-dichloro-1,1,1-trifluoroethane plants. For example, Sinochem Lantian Co., Ltd has the largest single set of production capacity (10000 tons/year) in the world at present. The conventional manufacturing process for 2,2-dichloro-1,1,1-trifluoroethane is shown in Scheme 1. The overall process is divided into two steps. Firstly, trichloroethylene is reacted with hydrogen fluoride forming 2-chloro-1,1,1-trifluoroethane which is then converted in a second step to 2,2-dichloro-1,1,1-trifluoroethane.

In the first step, dehydrohalogenation is suppressed in the presence of hydrogen fluoride. The second stage is a fast reactive free-radical with a poor selectivity,[8] giving side reactions.[9] Besides the target product 2,2-dichloro-1,1,1-trifluoroethane, the gaseous mixture also contains 1,2,2-trichloro-1,1-difluoroethane which is the by-product of a 1,2-dichloro-1,1-difluoroethane chlorination, shown in Eqn (3) of Scheme 2. It may also be a by-product of the addition of hydrogen chloride to 1,1-dichloro-2,2-difluoroethene. 1,1-Dichloro-2,2-difluoroethene is obtained from 2,2-dichloro-1,1,1-trifluoroethane by the elimination of hydrogen fluoride. These proposed reactions are shown in Eqn (4) of Scheme 2.



Scheme 1

According to a recent survey, the annual production of 10,000 tons of 2,2-dichloro-1,1,1-trifluoroethane, can lead to about 50 tons of 1,2,2-trichloro-1,1-difluoroethane. This has not been utilised efficiently. Burning, which is currently used, is also a tremendous waste of resources. Therefore, the purpose of our study was to solve the recycling problem of 1,2,2-trichloro-1,1-difluoroethane formed during 2,2-dichloro-1,1,1-trifluoroethane production. At present, we have mainly transformed 1,2,2-trichloro-1,1-difluoroethane into the more valuable 1-chloro-2,2-difluoroethylene, by a simple, reliable process to give a product with good stability, selectively and in high yield.

The present methods of producing 1-chloro-2,2-difluoroethylene can be divided into two groups.

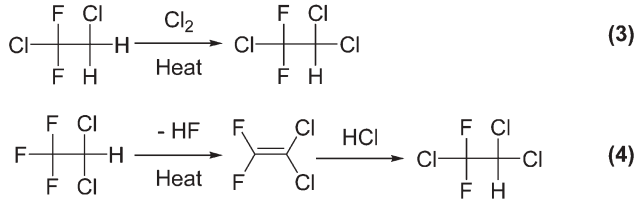
(1) Using 1,2,2-trichloro-1,1-difluoroethane as raw material for preparing 1-chloro-2,2-difluoroethylene:

A catalytic method was reported by Vanlautem *et al.*[10] who used active carbon as the carrier, copper and precious metals of group VIIIB such as Pt to make Cu–Pt binary metal hydrogenation–dechlorination catalyst for preparing 1-chloro-2,2-difluoroethylene from 1,2,2-trichloro-1,1-difluoroethane. This catalytic synthesis was carried out under high temperature and high pressure. Specifically, the hydrogen pressure was 1.0 MPa and reaction temperature was 240 °C as shown in Scheme 3. The cost of producing 1-chloro-2,2-difluoroethylene is high because the catalysts used in this technology comprised VIIIB group precious metal elements. The chlorine atoms within the raw materials were partly reduced by hydrogen atoms and gave impurities such as 1, 1-dichloro-2,2-difluoroethane, 1-chloro-2,2-difluoroethane and 1,1-difluoroethane. This affected the yield of the reaction, and made the products difficult to purify.

(2) Using 1-bromo-1-chloro-2,2,2-trifluoroethane as raw material for preparing 1-chloro-2,2-difluoroethylene:

Hudlicky and Lejhancova have reported a method for producing 1-chloro-2,2-difluoroethylene from 1-bromo-1-chloro-2, 2, 2-trifluoroethane[11] by using zinc powder as a reductant in

Side Reaction



Scheme 2

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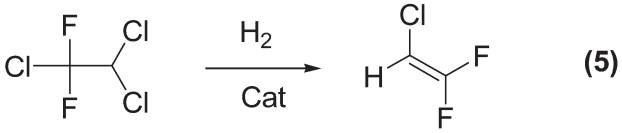


(5)

Scheme 3

1,4-dioxane at temperature of 100 °C, 1-chloro-2,2-difluoroethylene was obtained after reaction for 2 hours in a yield of reaction was 71% as shown in Scheme 4.

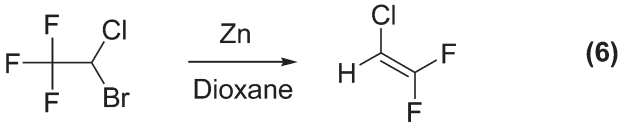
The main problem of this technology is the shortage of raw material 1-bromo-1-chloro-2, 2, 2-trifluoroethane. Hence this synthetic route is not suitable for large scale industrial production.

Thus, the two present methods for preparing 1-chloro-2,2-difluoroethylene have a series of problems: the high price of raw materials and catalysts, the low yield, and the large organic solvent consumption. The cost of production is high. These reactions are hard to convert to the industrial production of 1-chloro-2,2-difluoroethylene. Therefore, it is necessary to explore an industrial process leading to 1-chloro-2,2-difluoroethylene.

There are existing methods using zinc powder as a reducing agent for preparing similar fluoroalkenes by reductive dechlorination:

Edward *et al.* prepared 1,1-dichlone-2,2-difluoroethylene from 1,1,1,2-tetrachloro-2,2-difluoroethane using zinc powder in methanol for a reductive dechlorination reaction at a temperature of 60–63 °C.[12] Sauer optimized and improved this method,[13] and by adding small amounts of zinc chloride in the initial stage of the reaction increased the reaction yield to 89–95% (Scheme 5).

Maynard *et al.*[14,15] used zinc as a reducing agent in ethanol to prepare 1-chloro-2,3,3-trifluorocyclobutene from 1,1,2-trichloro-2,3,3-trifluorocyclobutane by reductive dechlorination reactions, after backflow for an hour, the yield was about 70% (Scheme 6).



(6)

Scheme 4

Experimental

The ^{19}F NMR spectra were recorded on a Varian 400MHz spectrometer. The chemical shifts were referenced to TMS for ^{1}H NMR and $CFCl_3$ for ^{19}F NMR respectively. Gas chromatography was as follows: gas chromatograph GC-2010, (Shimadzu) Qualitative analysis used GC-MS Voyager mass spectrometer_Trace 2000.

All solvents were dried with a molecular sieve and were of analytical grade, and the zinc powder (325 mesh)was pretreated before use by literature procedures.[16,17]

Small-scale preparation of 1-chloro-2,2-difluorothylene

Powdered zinc (0.13g, 2.0 mmol) was added to a 50 mL upright flask. After evacuating the flask, the solvent (1 mL) was injected into the flask using a syringe. The mixture was heated to 80 °C (or 120 °C) with magnetic stirrer, and 1,2,2-trichloro-1,1-difluoroethane 0.167 g (1.0 mmol) was added using a syringe. The reaction was followed by GC and ^{19}F NMR. 1-Chloro-2,2-difluoroethylene was obtained as a colorless gas.

Spectroscopic data for 1-chloro-2,2-difluoroethylene: MS (M_r = 98.1), *m/z* (% relative intensity), EI: 48.2(43), 50.2(23), 63.2(49), 67.1(23), 69.1(8), 79.1(22), 81.1(8),98.1(100), 100.1(78). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.295(dd, J_1 = 17.2 Hz, J_2 = 1.2 Hz)ppm. ^{19}F NMR (376.4 MHz, $CDCl_3$): δ –86.836 (dd, J_{HF} = 19.2 Hz, J_{HF} = 42.7 Hz), –91.084 (d, J_{HF} = 42.9 Hz)ppm.

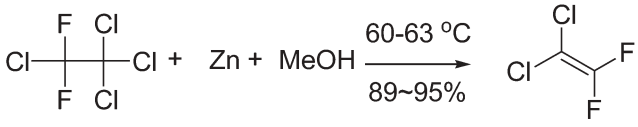
Large-scale preparation of 1-chloro-2,2-difluorothylene

Ethanol (3135 mL) and 1,2,2-trichloro-1,1-difluoroethane (2099g) was mixed. The pretreated Zinc powder (325 mesh) was added in batches to a 5L three-necked flask at 80 °C. After all the starting material had been added, it was refluxed for another 2 hours and the 1-chloro-2,2-difluoroethylene was collected by –60 ~ –80 °C freezing circular ethanol, 1127g crude product was obtained, the GC content is as high as 95% of 1-chloro-2,2-difluoroethylene with a yield of 92.3%.

Results and discussion

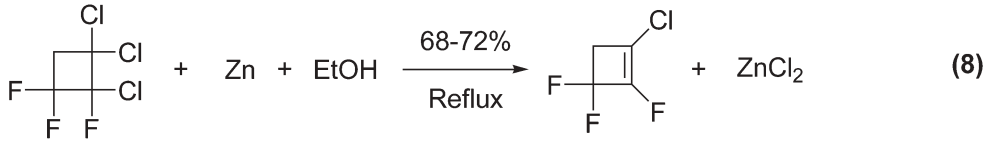
The synthetic reaction is shown in Scheme 7. We have investigated the reactions of 1,2,2-trichloro-1,1-difluoroethane in a series of solvents at temperatures of 80–120 °C. The GC data and ^{19}F NMR data of the liquid phases of the reaction are summarised in Tables 1 and 2, respectively.

Our experimental results show that the reactions with MeOH and DMF as solvent gave selectively 1-chloro-2,2-difluoroethylene in good yield (Table 1). There was almost no reaction in



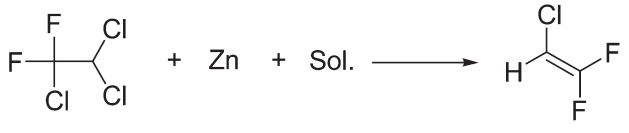
(7)

Scheme 5



(8)

Scheme 6



(9)

Scheme 7

Table 1 Gas phase content of reaction mixtures

Sol.	R1122/%	R122/%	Impurity[a]	T/°C
MeOH	98.4	0.23	0	80
EtOH	95.6	1.30	0	80
THF	97.6	0.37	1	80
CH_3CN	91.1	0.85	2	80
DME	75.1	0.18	3	80
Dioxane	92.2	0.90	1	80
	0	86.2	4	80
Morpholine	37.4	1.94	7	80
DMF	98.4	0.04	0	80
D.G.	52.1	29.6	3	80
DMAC	96.8	1.89	1	80
	74.0	0.49	4	120
D.G.	94.7	1.07	1	120
DMAC	94.9	0.60	2	120

[a]Impurities representing more than 1% by area of the GC (R1122:1-chloro-2,2-difluoroethylene, R122: 1,2,2-trichloro-1,1-difluoroethane).

Table 2 ^{19}F NMR data of reaction liquid phase mixtures

Sol.	R1122/R122	Impurity/ppm[a]
MeOH	100/433	–
EtOH	100/400	–
THF	100/823	–
CH_3CN	100/168	–
DME	100/83	–
Dioxane	0/136	–
	0/55	–83.96(d)
Morpholine	–	–
DMF	100/58	–82.52(d)
D.G.	0/155	–
DMAC	100/190	–82.53(d)

[a]Chemical shift of impurities representing more than 5% by ^{19}F NMR area compared to the 1-chloro-2,2-difluoroethylene. (R1122:1-chloro-2,2-difluoroethylene, R122: 1,2,2-trichloro-1,1-difluoroethane).

4-methylmorpholine or DMAC at temperature 80 °C. Moreover, the reactions gave a better yield at 120 °C than 80 °C with 4-methylmorpholine, D.G. or DMAC as the solvent. The ^{19}F NMR results also indicate that the reactions in MeOH or DMF gave the best results (Table 2), whereas morpholine was the worst. It formed a by-product by reacting with 1-chloro-2,2-difluoroethylene and 1,2,2-trichloro-1,1-difluoroethane. It also can be seen from Tables 1 and 2 that the reactions also gave a good yield by using ethanol as solvent. Because ethanol is cheaper and safer than any other solvents and it is environmentally friendly, the scale-up experiment used ethanol as a solvent.

Conclusion

In conclusion, 1-chloro-2,2-difluoroethylene has been synthesised from 1,2,2-trichloro-1,1-difluoroethane which was a by-product from the waste material of 2,2-dichloro-1,1,1-trifluoroethane production process. The reductive dechlorinations of 1,2,2-trichloro-1,1-difluoroethane by zinc in eleven different solvents was investigated, and the reactions in MeOH and DMF as solvent had good stability and gave 1-chloro-2,2-difluoroethylene in high yield. The scale-up experiments using ethanol as a solvent also gave a good yield. These results provide a method for producing 1-chloro-2,2-difluoroethylene and to solve the recycling problems of 1,2,2-trichloro-1,1-difluoroethane derived from 2,2-dichloro-1,1,1-trifluoroethane production, compatible with industrial methodology.

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