Journal of Fluorine Chemistry, *49* (1990) 107–114

Received: November 16, 1989; accepted: March 19, 1990

REDUCTION OF ω-CHLOROPERFLUOROALKYL IODIDES WITH LITHIUM ALUMINIUM HYDRIDE. A SINGLE ELECTRON TRANSFER PROCESS

QING-YUN CHEN* and MING-FANG CHEN

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu, Shanghai 200032 (China)

SUMMARY

The reduction of ω-chloroperfluoroalkyl iodides(1a-b) with $LiAlH_4$ gave ω-chloroperfluoroalkyl hydride(3) and α,ω-dihydroperfluoroalkane (4). However, in the presence of olefin, the addition product (6) was obtained. The reaction can be partly suppressed by p-dinitrobenzene (p-DNB), and tetrahydrofuran derivatives were obtained from the reaction of ω-chloroperfluoroalkyl iodides with diallyl ether. A single electron transfer process was proposed.

INTRODUCTION

The reduction of ketones and alcohols to the corresponding hydrocarbons with hydrogen transfer from main-group metal hydrides such as $LiAlH_4$ is a useful synthetic method [1-3]. In general, $LiAlH_4$ has been thought to react as a nucleophile in transfering a hydride ion to substrates. Recently, some reactions of $LiAlH_4$ have been found to proceed via a single electron transfer(SET) pathway [4-11].

In our study of the reactions of ω-chloroperfluoroalkyl iodides with alkenes, alkynes [12-16] and heterocyclic compounds [17-19], a small amount of by-products ClR_fH(3) was often observed. However, the rather stable $ClCF_2$ group did not participate. The only one exception was the reduction of perfluoroalkyl chlorides with $LiAlH_4$ giving the corresponding hydrides [20-24] . For example, the reduction of ω-chloroperfluorobutyliodobenzene with $LiAlH_4$ afforded ω-chloroperfluorobutyl benzene and ω-hydroperfluorobutylbenzene [20].

0022-1139/90/$3.50

$$m,p\text{-}IC_6H_4(CF_2)_4Cl \xrightarrow[THF]{LiAlH_4} C_6H_5(CF_2)_4Cl + C_6H_5(CF_2)_4H$$

Herein we present a study of the mechanism of reduction of ω-chloroperfluoroalkyl iodides with $LiAlH_4$ in more detail.

RESULTS AND DISCUSSION

ω-Chloroperfluoroalkyl iodide ($\underline{1}$) was added slowly to the solution of $LiAlH_4$($\underline{2}$) in Et_2O or THF at 0°C under N_2, and stirred at room temperature for several hours, yielding ω-chloroperfluoroalkyl hydride ($\underline{3}$) and α,ω-dihydroperfluoroalkane ($\underline{4}$).

$$\underset{\underline{1}}{ClR_fI} + \underset{\underline{2}}{LiAlH_4} \xrightarrow[N_2]{Et_2O\text{ or }THF} \underset{\underline{3}}{ClR_fH} + \underset{\underline{4}}{HR_fH}$$

a: $R_f=(CF_2)_4$; b: $R_f=(CF_2)_6$.

The conversion and product proportion mainly depended on the ratio of reactants used. When the ratio of $\underline{1}$a and $\underline{2}$ was 1:0.83, the conversion was complete and $\underline{3}$a:$\underline{4}$a=2:1, but only 75% of $\underline{1}$a was converted and $\underline{3}$a:$\underline{4}$a=3:1 if $\underline{1}$a:$\underline{2}$=1:0.39 (see Table 1).

When olefin ($\underline{5}$) was added into the reaction mixture, the adduct($\underline{6}$) was obtained (see Table 2).

$$\underset{\underline{1}}{ClR_fI} + \underset{\underline{2}}{LiAlH_4} + \underset{\underline{5}}{RCH{=}CH_2} \longrightarrow \underset{\underline{3}}{ClR_fH} + \underset{\underline{6}}{ClR_fCH_2CHIR}$$

$\underline{5}$a: $n\text{-}C_6H_{13}CH{=}CH_2$; $\underline{5}$b: $CH_2{=}CHCH_2OCH_2CH{=}CH_2$ (DAE)

TABLE 1

The reaction of ω-chloroperfluoroalkyl iodide(1) with $LiAlH_4$(2)

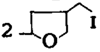
1:2	solvent	T(h)	conversion%^{a}	yield	
				(3+4)^b	(3:4)^a
1a(1:0.39)	Et_2O	15	75	-	(3:1)
1a(1:0.81)	Et_2O	10	100	-	(2:1)
1a(1:1)	Et_2O	13	100	38	(1:1)
1a(1:1)	THF	20	100	52	(2:1)
1b(1:1)	Et_2O	20	100	64	(9.5:0.5)
1b(1:1)	THF	22	100	78	(1:0)

[a] determined by ^{19}F NMR spectroscopy, based on 1.
[b] isolated yield.

TABLE 2

The reduction of ω-chloroperfluoroalkyl iodides with $LiAlH_4$ in the presence of olefins in Et_2O at 10°C[a]

Entry	1:2	Additive^a	T(h)	Conversion%^{c}	Yield%	
					3^c	6^d
1	1a(1:0.53)	5a	18	90	36	18
2	1b(1:0.71)	5b	13	100	27	17^e
3	1b(1:0.71)	5a	13	100	35	17
4	1b(1:0.71)	5a p-DNB^b	12	41	43	26
5	1a(1:1)	5a	17	100	36	18

[a] 1:5=1:2. [b] 50 mol% of p-dinitrobenzene(p-DNB) was used. p-DNB did not react with 2 under the same conditions, [c] determined by ^{19}F NMR, none of 4 was produced. [d] isolated yield. [e] $Cl(CF_2)_6CH_2$ 

The above reaction could be partially suppressed by the SET scavenger p-DNB (Entry 4). The conversion decreased to 41% as compared with that of the control (100% conversion Entry 3). The reaction of ω-chloroperfluoroalkyliodide(1b) with diallyl ether(DAE) afforded a tetrahydrofuran derivative(6b) [16]. All these results and in addition the ability of $LiAlH_4$ to act as an electron donor [4,9-11] indicate the possibility of a SET mechanism as shown in scheme 1. $LiAlH_4$ transfers its electron to the iodide (1) to form a radical anion, which decomposes to produce a radical, then the radical adds olefin to give adduct(6), or abstracts one hydrogen to afford ω-chloroperfluoroalkylhydride (3). 3 was further reduced to 4.

$$\underset{\underline{1}}{IR_fCl} + AlH_4^- \longrightarrow [IR_fCl]^{-\cdot} + 1/2H_2 + AlH_3$$

$$[IR_fCl]^{-\cdot} \longrightarrow [ClR_f]^{\cdot} + I^-$$

$$[ClR_f]^{\cdot} + \underset{\underline{5}}{RCH{=}CH_2} \longrightarrow ClR_fCH_2CHR^{\cdot}$$

$$ClR_fCH_2CHR^{\cdot} + ClR_fI \longrightarrow \underset{\underline{6}}{ClR_fCH_2CHIR} + [ClR_f]^{\cdot}$$

$$[ClR_f]^{\cdot} + \text{"H"} \longrightarrow \underset{\underline{3}}{ClR_fH}$$

$$ClR_fH + H^- \longrightarrow [ClR_fH]^{-\cdot} + H^{\cdot}$$

$$[ClR_fH]^{-\cdot} \longrightarrow [HR_f]^{\cdot} + Cl^-$$

$$[HR_f]^{\cdot} + \text{"H"} \longrightarrow \underset{\underline{4}}{HR_fH}$$

Scheme 1.

That the perfluoroalkyl halides fail to react with nucleophiles by S_N2 can be ascribed to the shielding effect of two α-fluorine atoms but they are able to undergo SET reaction[25]. Because the size of hydrogen is comparable with that of fluorine, the shielding effect in HCF_2 should be more effective than those in ICF_2 and $ClCF_2$ in ω-chloroperfluoroalkyl iodides. Therefore monohydro and/or α,ω-dihydroperfluoroalkanes are the final products in the reaction with $LiAlH_4$ and monohydroperfluoroalkanes are often the by-product with other nucleophiles.

EXPERIMENTAL

All boiling points are uncorrected. The infrared spectra were recorded on a Carl Shimadzu IR-440 spectrometer. NMR spectra (chemical shift in ppm from external TMS for ^1H, and from TFA for ^{19}F NMR, positive for upfield shifts) were recorded on an EM-360 NMR spectrometer (60 MHz). Mass spectra were taken on a Finnigan GC-MS-4021.

All solvents and reagents were purified prior to use. All reactions were carried out under the atmosphere of pure nitrogen.

General procedure

The following procedure for the reaction of ω-chloroperfluoroalkyl iodide with $LiAlH_4$ is typical. In a 200 mL three-necked flask fitted with a magnetic stirrer, a reflux condenser, and a N_2 inlet, was placed 1.140 g (30 mmol) of $LiAlH_4$ and 60 ml of dry THF under N_2. 10.8g (30 mmol) of **1a** in 20 mL of dry THF was added dropwise at 0°C with stirring. After the addition, the mixture was allowed to stir for an additional 15 min at 0°C, then was stirred for 20 h at 10°C. ^{19}F NMR spectra showed that the conversion was 100% and **3a**:**4a** = 2:1.

The mixture was cooled in ice and dilute hydrochloric acid was added cautiously until the metallic hydroxide was dissolved. The organic layer was separated and washed , dried over $MgSO_4$. Distillation of the organic layer gave 3.4g of colorless liquid. The yield was 52%. b.p. 46-48°C. ^{19}F NMR show that 3a:4a = 2:1. All the products were identified by their b.p., ^1H and ^{19}F NMR, and MS by comparison with the authentic samples[26].

3a b.p. 44-46°C. ^1H NMR δ 6.20(t-t,J_{H-F}=52.3 Hz); ^{19}F δ -8.0(2F,t), 45.0(2F, m), 52.0(2F, m), 61.3(2F,d, J_{H-F}=52.1 Hz) [27].

3b b.p. 78-80°C. ^1H NMR δ 6.00(t-t,J_{H-F} = 53.0 Hz); ^{19}F δ -7.3(2F,t), 43.2(2F,m), 45.3(2F, m), 47.3(2F, m), 53.5(2F, m), 62.2(2F, d, J_{H-F}=53.0 Hz)[27].

Reaction of 1 with 2 in the presence of olefin

Typical procedure. In a 250 mL three-necked flask, fitted with magnetic stirrer, N_2-inlet and condenser, 810 mg (21.3 mmol) of $LiAlH_4$, 70 mL of absolute ether, and 6.7 g (60 mmol) of 5a were placed under N_2. 13.8 g (30 mmol) of 1b in 30 mL of absolute ether was added slowly at 0°C with stirring, then the mixture was stirred at room temperature for 13 h. ^{19}F NMR showed that the reaction was complete and contained 35% of 3b. The mixture was treated as above. 1.9g (3.3 mmol) of 6a was obtained. Yield 17.0%. b.p. 118-121°C/1mmHg. ^1H NMR 4.25(m, 1H), 3.10(m, 2H), 1.40-1.00(m, 13H); ^{19}F NMR -9.0(2F, t), 36.3(2F, m), 43.0(2F,m), 44.3(4F, m), 45.3(2F,m). IR(neat): 2900, 2850, 1470, 1200, 1140 cm^{-1}. m/e: 574, 447, 405, 71,57. Analysis, Found: C,28.9, H,2.7, Cl, 6.15, F, 39.74, I, 22.21; $C_{14}H_{16}ClF_{12}I$, Calc., C, 29.26, H, 2.81, Cl, 6.17, F, 39.67, I, 22.08%.

Reaction of 1b with 2 in the presence of p-DNB

To a cooled mixture of $LiAlH_4$(135 mg, 3.55 mmol), 5a(1.1g, 10mmol), p-DNB(420 mg, 2.5 mmol) and Et_2O(20 mL), was added 1b(2.3 g, 5 mmol) in Et_2O(5mL) dropwise under N_2. The mixture was stirred at room temperature for 12h when ^{19}F NMR spectroscopic analysis showed that 41% of 1b was converted and the amount of 3b reached 44%. Treatment of the mixture gave 170mg of 6a. yield: 26%.

ACKNOWLEDGEMENT

We would like to thank Professor Wei-Yuang Huang for his encouragement of this work. Thanks are also owed to the Chinese National Science Found for support.

REFERENCES

1 N. G. Gaylord, 'Reduction with Complex Metal Hydrides', Wiley-Interscience, New York, 1956.

2 H. O. House, 'Modern Synthetic Reactions', W. A. Benjamin, Menlo Park, CA, 1972.

3 A. J. Birch and M. Slaytor, Chem & Ind., (1956) 1524.

4 E. C. Ashby, A. B. Goel and R. N. DePriest, J. Am. Chem. Soc., **102**(1980)7779.

5 J. Hatem and B. Waegell, Tetrahedron Lett., (1973) 2033.

6 S. K. Chung and F. F. Chung, Tetrahedron Lett., (1979)2473.

7 P. R. Singh, Alok Nigam and J. M. Khurana, Tetrahedron Lett., **21** (1980)4753.

8 P. R. Singh, J. M. Khurana and Alok Nigam, Tetrahedron Lett., **22** (1981) 2901.

9 E. C. Ashby and A. B. Goel, Tetrahedron Lett., **22** (1981)1879.

10 E. C. Ashby, A. B. Goel and R. N. DePriest, J. Org. Chem., **53** (1988)6156.

11 E. C. Ashby, A. B. Goel and R. N. DePriest, Tetrahedron Lett., **22** (1981) 3729..

12 Q. Y. Chen and Z. Y. Yang, J. Fluorine Chem., **28** (1985) 399.

13 Q, Y. Chen, Y. B. He and Z. Y. Yang, J. Fluorine Chem., **34** (1986) 255.

14 Q. Y. Chen and J. G. Chen, Huaxue Xuebao, **46**(1988) 301.

15 Q. Y. Chen, Z. M. Ming and Z. Y. Yang, J. Fluorine Chem., **36** (1987) 149.

16 Q. Y. Chen, Z. Y. Yang, C. X. Zhao and Z. M. Qiu, J. Chem. Soc., Perkin Trans. I., (1988) 563.

17 Q. Y. Chen and Z. M. Qiu, Youji Huaxue, (1987) 364.

18 Q. Y. Chen and Z. M. Qiu, Huaxue Xuebao, **46** (1988) 258.

19 Q. Y. Chen and Z. M. Qiu, J. Chem. Soc., Chem. Comm., (1987)1240

20 Q. Y. Chen. Y. X. Chen and W. Y. Huang, Huaxue Xuebao, **42** (1984) 906.

21 Q. Y. Chen and Y. X. Chen, Youji Huaxue, **6** (1985) 464.

22 R. N. Haszeldine and J. E. Osborne, J. Chem. Soc., (1956) 61.

23 M. W. Buxton and J. C. Tatlow, J. Chem. Soc., (1954) 1177.

24 J. C. Tatlow and R. E. Worthington, J. Chem. Soc., (1952) 1251.

25 a) Q. Y. Chen, X. K. Jiang, B. C. Chen and M. L. Liang, Sci. Sin. 15 (1966) 498; b) R. D. Chambers, 'Fluorine in Organic Chemistry', Wiley, 1973; c) C. G. Krespan, J. Org. Chem., **43**(1978)637; d) Q. Y. Chen and Z. M. Qiu, J. Fluorine Chem., **31**(1986)301 and the references therein. e) Q. Y. Chen and S. Z. Zhu, Acta Chim. Sin. 41 (1983) 1044.

26 R.N. Haszeldine and R. J. Marklow, J. Chem. Soc., (1956) 962.

27 Z. M. Qiu, Doctoral Thesis, Shanghai Institute of Organic Chemistry,Academia Sinica, China, 1987.