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REACTIONS OF PERCHLOROFLUORO COMPOUNDS

IV. THE REACTION OF 1,1-DICHLOROHEXAFLUORO-1-BUTENE WITH SOME NUCLEOPHILES

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SUMMARY

Reactions of $CF_3CF_2CF{=}CCl_2$ (**1**) with various nucleophiles such as MeO^-, PhO^-, NH_3, $n\text{-}C_4H_9MgBr$ and $n\text{-}C_4H_9S^-$ were studied. Contrary to a prior report [3], the addition is bidirectional and except for PhO^-, nucleophiles would rather attack the CF= site (path 1) than the $=CCl_2$ site (path 2), no matter whether the base is soft or hard. PhO^- attacked both sites at nearly 1:1 ratio. Temperature had little effect on the direction of MeO^- attack, but solvents could change its reaction rate and the distribution of products. Compared with $CF_2{=}CFCF_2CFCl_2$ (**2**) and $CF_3CF{=}CFCFCl_2$ (trans, **3**), preliminary experiments indicated that the order of reactivity increases along with the series of **1**<**3**<**2**.

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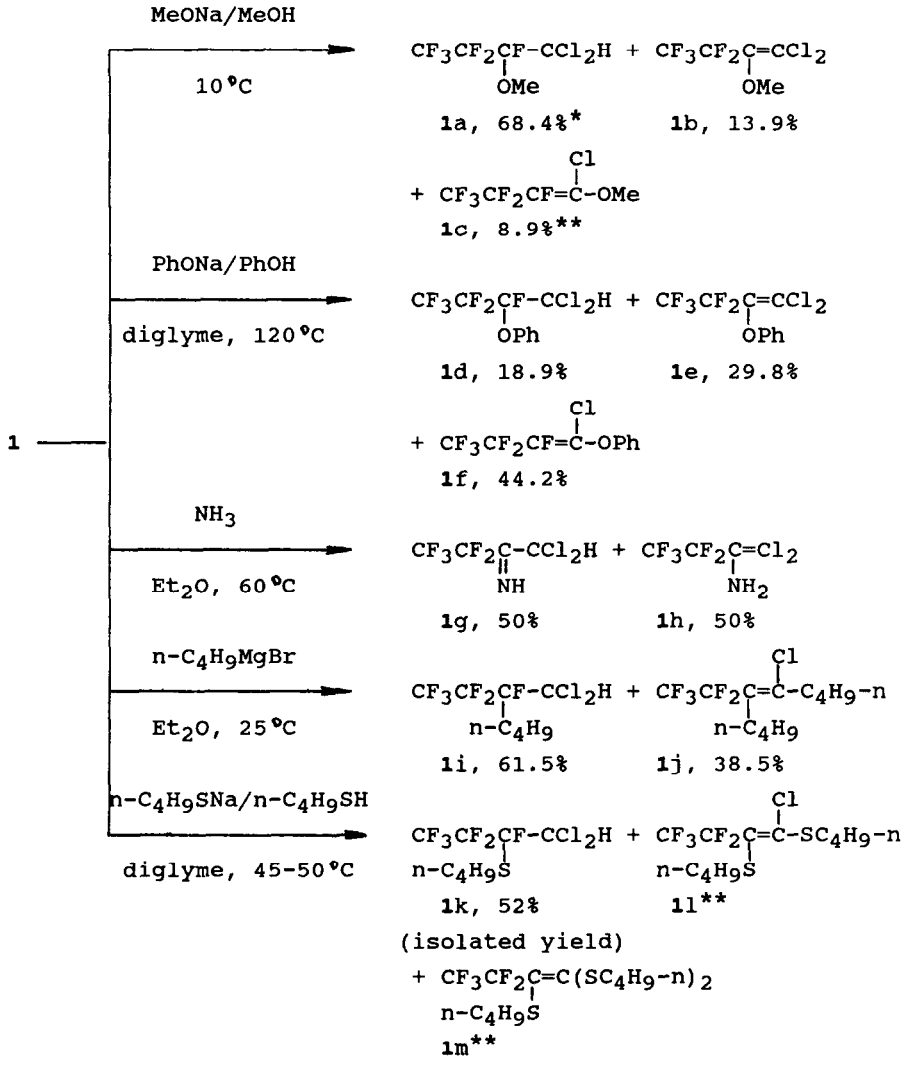
INTRODUCTION

Addition of nucleophiles to fluoroolefins has been studied extensively and reviewed comprehensively[1]. The fact that a nucleophile almost invariably becomes attached to the terminal difluoromethylene group in a terminal fluoroolefin or at position 2 for linear internal perfluoro-2-olefins ($CF_3CF=CF-$) is explained by a combination of $+I\pi$ repulsion and steric factors [2]. Park et al.[3]once reported that for the reaction of $CF_3CF=CCl_2$ with MeONa/MeOH the nucleophile attacked the dichloromethylene site and only $CF_3CFHCCl_2OMe$ was formed. Such a conclusion, which seems to be contradictory with the above explanation, prompted us to reexamine this kind of reaction.

RESULTS AND DISCUSSION

1,1-Dichlorohexafluoro-1-butene (**1**) was obtained by treatment of 4,4-dichlorohexafluoro-1-butene (**2**, $CF_2=CFCF_2CFCl_2$) with $AlCl_3$ [4], while **2** was isolated from the pyrolyzate of polytrifluorochloroethylene[5]. The reactions of **1** with various nucleophiles such as MeO^-, PhO^-, NH_3, $n\text{-}C_4H_9MgX$ and $n\text{-}C_4H_9S^-$ were studied. The results are summarized in Scheme 1.

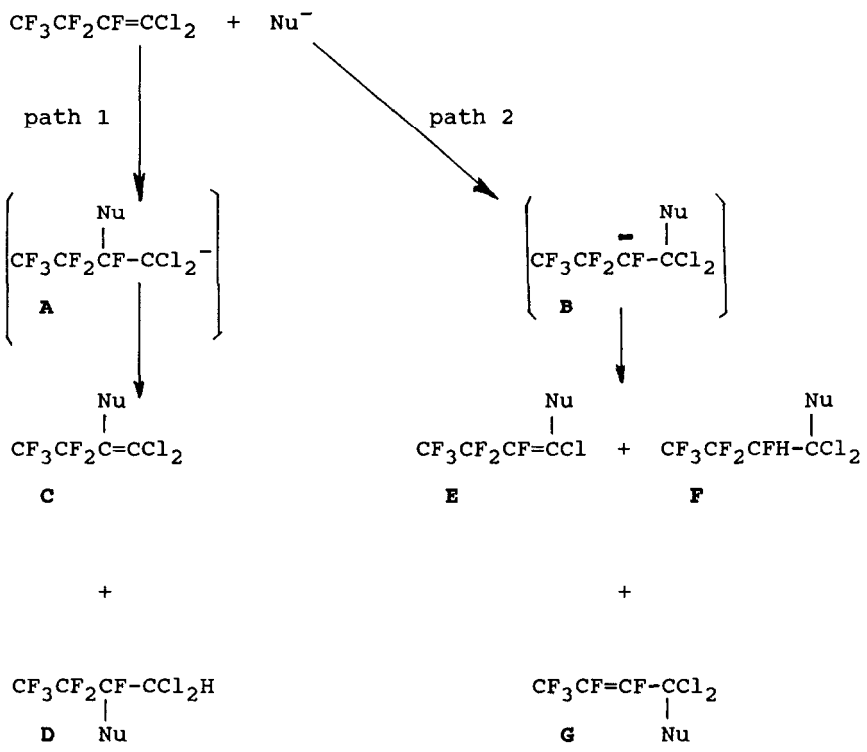
1 was recovered after it was mixed with PhONa/PhOH in diglyme and heated at 80°C for 24h, or with NH_3 at 20°C for 12h. But the reaction of **2** and **3**($CF_3CF=CFCFCl_2$, trans) with PhONa/PhOH proceeded smoothly at 40°C and 70°C, or with NH_3 at -78°C and 0°C to r.t., respectively[6]. These preliminary experiments showed that the order of reactivity increases along the series **1**≪**3**≪**2**.



* the percentage yields of these compounds were estimated by GLC analysis. ** Compounds **1c**, **1l** and **1m** were very difficult to get pure and so only MS and ^{19}F NMR data were recorded.

Scheme 1

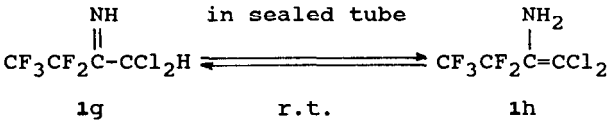
These experiments showed that the addition of certain nucleophiles to olefin 1 is bidirectional; thus the nucleophiles could attack both C-1 and C-2 of **1** with the possible formation of products **C-G** through intermediates **A** and **B** (in Scheme 2).



Scheme 2

None of the mixtures showed any -CFH- signal in their ^{19}F NMR spectra. **1a** and **1b**, **1d** and **1e**, **1g** and **1h**, **1i** and **1k** were formed via intermediate **A** (path 1); while **1c** and **1f** arose via interme-

diate **B**(path 2). **1j**, **1l** and **1m** were presumably formed by further reaction with the nucleophiles. Pure **1g** and **1h** can isomerize with each other in sealed glass tube at r.t.to give a 1:1 mixture.



The foregoing results implied that the nucleophiles (MeO^-, NH_3, $n\text{-}C_4H_9^-$, $n\text{-}C_4H_9S^-$) would rather attack the CF= site (path 1) than the $=CCl_2$ site (path 2), no matter whether the base is soft or hard. Such findings are not surprising, considering the +I effect repulsion and the steric factors. In addition, intermediate **A** (in Scheme 2), an anion with a dichloromethylene group, should be more stable than **B**[7]. Only with PhO^- does the reaction proceed through both path 1 and path 2 in almost 1:1 ratio (in Scheme 1). As chloride ion is a good leaving group, it is reasonable that no addition product **F** or S_N2' product **G** (in Scheme 2), but only **E** (**1c** and **1f**) was found in the reaction mixture.

In order to make sure whether the direction of attack would be affected by temperature[8], the reactions of MeO^- with **1** at various temperatures were examined. Experiments showed that only **1b** was increased at the expense of **1a** with the rise in temperature and **1c** was little affected (in Table 1). However, in diglyme the rate of reaction was slower and no **1c** was detected.

At present we have no adequate explanation to advance for the unusual addition of PhO^- and effect of solvents on the reaction of nucleophiles with fluoroolefins.

TABLE 1

Effect of Temperature and Solvents on the Reaction of **1** with MeONa [a]

1 (mmol)	MeONa (mmol)	MeOH (mmol)	Solvent	Temp. (°C)	Time (h)	**1**	**1a**	**1b**	**1c**
21.5	64.5		MeOH	10	12	----	75.0	15.2	9.8
21.5	21.5		MeOH	45-50	4	14.6	53.7	22.0	9.8
21.5	21.5	44.0	Diglyme	45-50	7	80	----	20	---
21.5	21.5	44.0	diglyme	90	12	----	55.6	44.4	---

[a] The composition of products was determined by ^{19}F NMR

EXPERIMENTAL

Boiling points were uncorrected. A Zeiss Specord-75 was used to record infrared spectra of samples as films. ^{1}H NMR (with chemical shifts in ppm from external TMS) and ^{19}F NMR (with chemical shifts reported in ppm from external TFA and positive for upfield shifts) were determined at 60MHz on a Varian EM-360 Spectrometer. Mass spectra were measured with a Finnigan 4021 Mass Spectrometer. The GLC analysis were performed with a 102 G (Shanghai Analytic Faculty) using 3-6m long column packed with DNP (dinonyl phthalate, 15%), APZ(Apiezon, saturated hydrocarbon, 15%) or SE-30 (methyl siloxane polymer, 15%).

The chemical reagents used were A.R. grade. Diglyme (DG) (A.R.) was treated with $LiAlH_4$, distilled under reduced pressure and then dried over metal Na. Et_2O was also treated with $LiAlH_4$. All products described below are new.

Reaction of **1** with MeONa/MeOH: 5.0g (21.5mmol) **1** in 10ml MeOH was added dropwise to the solution of MeONa/MeOH [from 1.5g (65 mmol) metal Na and 25ml MeOH] with stirring for 12 h at 10°C. The solution was poured into 80ml water. The separated organic layer was washed with dil.HCl and then a water solution saturated with NaCl. Distillation of the dried crude product gave 3.1g of a mixture of **1a-1c** at 90-114°C. From this mixture **1a** and **1b** were isolated by semipreparative GLC (column: APZ; temp.: 80°C).

Compound **1a**: $C_5H_4Cl_2F_6O$ (calculated: C, 22.65; H, 1.52; F,43.00. Found: C,22.40; H,1.43; F,43.00). IR(cm^{-1}): 3000m, 2954s, 2850w, 1200s. MS m/e (intens., assign.): 69(31.9,CF_3), 83(12.8, $CHCl_2$), 85(16.3,CF_2Cl), 119(52.5,C_2F_5), 181(100,M-$CHCl_2$), 229(3.4,M-Cl), 245(1.8,M-F). ^1H NMR: 3.85(s,3H,OCH_3); 6.08(d,1H,J=4.0Hz,CCl_2H) ppm. ^{19}F NMR: 3.3(d,3F,J=11.3Hz,CF_3), 44.1(s,2F,CF_2), 48.8(q,1F, J=11.3Hz,CF)ppm.

Compound **1b**: $C_5H_3Cl_2F_5O$ (calculated: C, 24.50; H, 1.23; F, 38.76. Found: C, 24.38; H, 1.19; F, 39.74). IR: 2937m, 2833w, 1609m(C=C) MS: 69(26.6,CF_3),85(34.4,CF_2Cl),125(17.7,M-C_2F_5),175(47.2,M-CF_3), 225(31.6,M-F),229(19.7,M-CH_3),244(100,M). ^1H NMR: 3.77(s,OCH_3) ppm. ^{19}F NMR: 6.3(s,3F,CF_3), 36.8(s,2F,CF_2)ppm.

Compound **1c**: MS: 69(26.9,CF_3), 85(13.1,CF_2Cl),109(100,C_3F_3O),159 (85.5,M-CF_3), 193(1.0,M-Cl), 209(3.1,M-F), 228(17.3,M). ^{19}F NMR: 7.5(s,3F,CF_3), 39.6(d,2F,J=9.4Hz,CF_2), 63.5(t,1F,J=9.4Hz,CF)ppm.

Reaction with C_6H_5ONa/C_6H_5OH: A solution of PhONa/PhOH in 10ml DG [from 0.5g (21.5mmol) Na and 6.1g (64.5mmol) PhOH] and 5.0g (21.5mmol) **1** were placed in a 60ml stainless steel bomb, and shaken at 120°C for 11.5h. The contents were poured into ice water. The separated organic layer was washed with aq.NaOH to remove the unreacted PhOH, then washed with H_2O and dried. Distillation gave 5.8g products at 80-105°C/12mmHg. **1d**, **1e** and **1f** were isolated by semipreparative GLC (column: SE-30; temp.: 110°C).

Compound **1d**: $C_{10}H_6Cl_2F_6O$ (calculated: C,36.71; H,1.85; F, 34.95. Found: C,36.72; H,1.84; F,35.61). IR: 3060w, 1591s, 1491vs. MS: 51(24.7,C_4H_3), 65(53.3,C_5H_5), 77(100,C_6H_5), 94(23.0,C_6H_5OH), 243 (43.11, M-CCl_2), 255(26.0, M-2Cl), 291(15.7, M-Cl), 326(48.2,M). ^1H NMR: 5.83(d,1H,J=3Hz,CCl_2H), 7.23(s,5H,C_6H_5)ppm. ^{19}F NMR: 2.3 (d,3F,J=11.3Hz,CF_3), 35.6(q,1F,J=11.3Hz,CF), 41.8(s,2F,CF_2)ppm.

Compound **1e**: $C_{10}H_5Cl_2F_5O$ (calculated: C, 39.10; H,1.64; F,30.93. Found: C,39.19; H,1.64;F,30.82). IR: 1609m (C=C), 1595s, 1491vs. MS: 51(48.5,C_4H_3), 65(25.8,C_5H_5), 77(100,C_6H_5), 154(10.7,M-CF_3-CCl_2), 243(28.2,M-COCl), 271(9.5,M-Cl),306(36.6,M). ^1H NMR: 6.97 (d,J=6.0Hz,C_6H_5)ppm. ^{19}F NMR: 5.2(s,3F,CF_3), 35.3(s,2F,CF_2)ppm.

Compound **1f**: $C_{10}H_5ClF_6O$ (calculated: C, 41.35; H,1.73; F, 39.22. Found: C,41.44; H,1.78; F,39.36). IR: 1687s (C=C), 1600s,1496vs. MS: 77(100,C_6H_5), 154(45.9,M-C_2F_4Cl), 227(14.3,M-COCl),255(11.5, M-Cl), 271(8.2,M-F), 290(49.4,M). ^1H NMR: 7.00(d, J=6.0Hz, C_6H_5)

ppm. ^{19}F NMR: 7.0(s,3F,CF_3), 39.8(d,2F,J=9.4Hz,CF_2), 64.0(t,1F, J=9.4Hz,CF)ppm.

Reaction with NH_3: 5.0g (21.5mmol) **1**, 40ml Et_2O and about 10ml liquid NH_3 were mixed in a 250ml stainless steel bomb at -78°C, then shaken at 60°C for 23.5h. The contents were poured into 30 ml H_2O. The separated ether layer was washed with H_2O, and dried. Distillation gave 2.4g of a liquid at 106-108°C. Pure **1g** and **1h** were obtained by semipreparative GLC (column: APZ; temp.: 100°C).

Compound **1g**: $C_4H_2Cl_2F_5N$ (calculated: C,20.88; H,0.87; N,6.09; F, 41.29. Found: C,21.94; H,1.22; N,6.98; F,40.90). IR: 3275m (NH), 3020w, 1682m (C=C). MS: 69(44.7,CF_3), 83(23.2,CCl_2H), 110(12.3, $CCl_2H-\underset{\underset{NH}{\|}}{C}$), 146(10.5, M-$CCl_2H$), 230(100, M+1). ^1H NMR: 6.43(s,NH, CCl_2H)ppm. ^{19}F NMR: 4.7(s,3F,CF_3), 38.3(s,2F,CF_2)ppm.

Compound **1h**: IR: 3500s (NH_2), 3400s (NH_2), 1640s (NH_2 bending vibration), 1609s (C=C). MS: 69(25.0, CF_3), 110(39.9, $CCl_2=\underset{\underset{NH_2}{|}}{C}$), 160(62.8,M-$CF_3$), 229(100,M). ^1H NMR: 3.97(s,NH_2)ppm. ^{19}F NMR: 5.7(s,3F,CF_3), 37.7(s,2F,CF_2)ppm.

Reaction with n-C_4H_9MgBr: 5.0g (21.5mmol) **1** was added dropwise at 25°C, while stirring, into a Grignard solution made from 1.52g (65.2mmol) magnesium turnings and 4.42g (32.3mmol) n-C_4H_9Br in 35ml Et_2O. This mixture was allowed to react for 24h. After gener-

al work-up, 3.6g products with b.p. ranging 70-85°C/40mmHg were separated. Then **1i** and **1j** were isolated by semipreparative GLC (column: DNP; temp.: 100°C).

Compound **1i**: $C_8H_{10}Cl_2F_6$ (calculated: C,33.00; H, 3.46; F, 39.15. Found: C,33.96; H,3.49; F,40.41). IR: 2958m, 2862m, 1200vs. MS: 43(100,C_3H_7), 69(7.72,CF_3), 83(16.21,CCl_2H), 208(18.38, M-CCl_2), 262(13.40,M-C_2H_4), 290(1.01,M). ^1H NMR: 1.20(t, 2H, J=4Hz, CH_3), 1.68(m,4H,CH_2CH_2), 2.50(m,2H,CH_2-CF), 6.23(d,1H,J=3Hz,CCl_2H)ppm. ^{19}F NMR: 3.7(d,3F,J=15.0Hz,CF_3), 39.9, 43.8(AB, 2F, J=282Hz,CF_2), 84.8(q,1F,J=15.0Hz,CF)ppm.

Compound **1j**: $C_{12}H_{18}ClF_5$ (calculated: C, 49.23; H,6.20; F, 32.45. Found: C,49.07; H,6.18; F,32.12). IR: 2948s, 2865vs, 1655w (C=C). MS: 43(100,C_3H_7), 56(39.39,C_4H_8), 81(19.23,C_2F_3), 131(4.92,C_3F_5), 185(6.96,$C_7H_6F_5$), 250(0.1,M-42). ^1H NMR: 0.8(t, 6H, J=4Hz,$2CH_3$), 1.43(m,8H,$4CH_2$), 2.22(t,2H,J=5.5Hz,CH_2), 3.33(t,2H,J=6Hz,CH_2)ppm. ^{19}F NMR: 10.5(s,3F,CF_3), 24.8(s,2F,CF_2)ppm.

Reaction with n-C_4H_9SNa/n-C_4H_9SH: 5.0g (21.5mmol) **1** in 5ml DG was added dropwise into 15ml DG containing 30mmol n-C_4H_9SNa and 34.5 mmol n-C_4H_9SH at 35-40°C for 9h. After work-up as usual, distillation gave 3.6g **1k** at 69-75°C/3mmHg(yield 52%) and 1.5g residue. After this residue was chromatographed on silica gel and eluted with petroleum, 0.8g mixture of **1l** and **1m** was obtained and determined by GC-MS and ^{19}F NMR.

Compound **1k**: $C_8H_{10}Cl_2F_6S$ (calculated: C, 29.73; H,3.12; F,35.27. Found: C, 29.89; H,3.18; F, 35.22). MS: 57(100,C_4H_9), 89(32.63,

C_4H_9S), 279(0.9, M-C_3H_7), 287(0.46,M-Cl), 322(1.28,M), 323(2.10, M+1). ^1H NMR: 1.13(t,3H,J=6Hz,CH_3), 1.77(m,4H,$2CH_2$), 3.15(t,2H, J=7Hz,SCH_2), 6.47(d,1H,J=3Hz,CCl_2H)ppm. ^{19}F NMR: 2.7(t,3F,J=15.0 Hz,CF_3), 37.4, 39.7(AB,2F,J=282Hz,CF_2), 67.2(m,1F,CF)ppm.

Compound **1l**: MS: 57(100,C_4H_9), 147(44.85,$C_8H_{18}S$+1), 324(1.82,M-S) 358(5.73,M+2). ^1H NMR: 0.97(t,6H, J=6Hz, $2CH_3$), 1.53(m,8H,$4CH_2$), 2.80(f,4H,J=6Hz,$2CH_2S$)ppm. ^{19}F NMR: 6.2(s,3F,CF_3), 28.7(s,2F,CF_2) ppm.

Compound **1m**: MS: 146(22.67,$C_8H_{18}S$+1),323(100,M-C_4H_9S), 355(14.03, M-2HF-Me), 375(19.01, M-HF-Me), 391(21.34, M-F), 412(47.31, M+2). ^1H NMR: 0.98(t,9H,J=6Hz,$3CH_3$), 1.47(m,12H,$6CH_2$), 2.93(m,6H,$3CH_2S$) ppm. ^{19}F NMR: 6.7(s,3F,CF_3), 33.3(s,2F,CF_2)ppm.

Reaction with MeONa/MeOH in DG: A solution of 5.0g (21.5mmol) **1** and 15ml DG containing 21.5mmol MeONa and 44.0mmol MeOH was placed into a 60ml stainless steel bomb and stirred at 90°C for 12h. After the general work-up, 4.7g organic matter was obtained and ^{19}F NMR showed that **1a**:**1b** was 55.6:44.4.

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