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OBSERVATION OF A COMPETITIVE PATH IN THE NUCLEOPHILIC ADDITION OF FLUOROOLEFINS: THE BROMOPHILIC REACTION OF THE ADDUCT CARBANION INTERMEDIATE

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SUMMARY

In addition to the hydro-alkoxy-addition products $ROCF_2CFBrH$(**4**), and olefin products ROCF=CFBr(**5**), a new type of product , i.e., the alkoxy-bromo-addition products $ROCF_2CFBr_2$ (**6**) have been obtained in the reactions of bromotrifluoroethene(**3**) with different alkoxides (RO^- = $t\text{-}BuO^-$, $i\text{-}PrO^-$, EtO^- and MeO^-). These products(**6**) are formed from a competitive path involving bromophilic reactions of the intermediate adduct carbanions(**8**). Radicals have been shown to be unlikely intermediates of this competitive reaction path.

INTRODUCTION

Nucleophilic addition reactions of per- or polyfluoroolefins with all kinds of nucleophiles have been studied extensively for several decades [1]. The generally accepted reaction scheme usually reckons (1), (2) and (3) as the main steps of the reaction, as shown in Scheme I. Formally, path (2) will lead to a product with elements of 'Nu' and 'H' added to the double bond, i.e., a product of hydro-nucleophiloaddition.

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$$Nu^- + CF_2{=}CRR' \longrightarrow \underset{\mathbf{1}}{NuCF_2CRR'^-} \quad (1)$$

$$\mathbf{1} + {}'H^+{}' \longrightarrow NuCF_2CRR'H \quad (2)$$

$$\mathbf{1} - \beta\text{-}F^- \longrightarrow NuCF{=}CRR' \quad (3)$$

Scheme I

However, fluoroolefins with their unique intrinsic properties can also react with electron donors via single electron transfer (SET) pathways [2] in addition to the nucleophilic addition. On the other hand, Miller and Becker [3] have briefly reported that the reaction of $CF_3CCl_2^-$ with $CF_2{=}CCl_2$ gave CF_3CCl_3. They believed that the reaction path involved nucleophilic substitution on halogen of $CF_2{=}CCl_2$, but no detailed mechanism and evidence were given. Chambers and Gribble [4] also ascribed the formation of the by-product CF_3CFBr_2 in the reaction of CF_3CFBr^- with pentafluoropyridine to a halogen exchange reaction of CF_3CFBr^- with bromotrifluoroethene. Therefore, reactions of fluoroolefins with nucleophiles are much more diversified than those represented in Scheme I and deserve further exploratory and mechanistic studies [5]. In fact , besides the halophilic reactions, we have also been interested in searching for novel SET reactions of perhalo or polyhaloolefins. The present work represents one of our efforts in that direction; the reactions of bromotrifluoroethene(**3**) with alkoxides(**2**) have been investigated. This has led to the observation that another major product $ROCF_2CFBr_2$(**6**) is formed from a competitive reaction, the bromophilic attack of the adduct carbanion(**8**) on bromotrifluoroethene(**3**).

RESULTS AND DISCUSSION

In the reaction of alkoxides(**2**) with bromotrifluoroethene (**3**) in tetrahydrofuran (THF) (reaction (4)), besides the expected products $ROCF_2CFBrH$(**4**) and $ROCF{=}CFBr$(**5**), a new type of product with elements of "RO" and "Br" added to the double bond, i.e., the product of alkoxy-bromo-addition **6**, is formed.

$$RO^- + CF_2{=}CFBr \longrightarrow ROCF_2CFBrH + ROCF{=}CFBr + ROCF_2CFBr_2 + CF_2{=}CFH + \text{oligomer (or polymer)} \quad (4)$$

2 3 4 5 6 7

RO: a, t-BuO; b, i-PrO; c, EtO; d, MeO.

TABLE 1

Percentage yields of products and product ratios (R = 6/(4+5)) from the reaction of CF_2=CFBr(3) with different alkoxides(2)[a] (room temperature, in THF)

RO	4	5	6	4+5+6	7[d]	R
2a	4.1	51.4	30.4	85.9[b]	1.5	0.55
2b	32.9	29.2	17.2	79.3[c]	2.8	0.28
2c	14.9	68.4	10.4	93.7[c]	1.2	0.12
2d	26.9	55.7	1.5	84.1[c]	0.6	0.02

[a] The molar ratio 2/3 = 0.33, reaction time was 4 h, except for 2a, 1 h.

[b] The yields were determined by GC with ±5 % precision.

[c] The yields were determined by ^{19}F NMR, the deviation of calculated yields based on GC and on ^{19}F NMR was about ±3 %.

[d] Approximate yields.

Their yields are listed in Table 1. Various amounts of adducts **4** were formed, presumably from residual alcohols which could not be removed. Notably, the yield of **6a** was as high as 30 % when sublimed t-butyl alkoxide(**2a**) was used. Thus it appeared that **6a** could be turned into another major product and the reaction was studied in more detail.

First, we investigated the dependence of the molar ratio R of product **6a** to products **4a** plus **5a** on the reactant molar

TABLE 2

The dependence of R (**6a**/(**4a**+**5a**)) on R' (**2a**/**3**)[a] (r.t., in THF, 1 h)

R'	Product yields					R
	4a	**5a**	**6a**	**4a**+**5a**+**6a**	**7**	
1.0	1.7	44.0	2.9	48.6	0.01	0.06
0.33	4.1	51.4	30.4	85.9	1.6	0.55

[a] Yields were determined by GC.

$RO^- + CF_2=CFBr \longrightarrow ROCF_2CFBr^-$ (5)
2 **3** **8**

8 + 'H^+' $\longrightarrow ROCF_2CFBrH$ (6)
4

8 − β-F^- $\longrightarrow ROCF=CFBr$ (7)
5

8 + **3** $\xrightarrow[\text{reaction}]{\text{bromophilic}}$ $ROCF_2CFBr_2$ + $CF_2=CF^-$ (8)
6 **9**

2 + **3** $\longrightarrow$ ROBr + **9** (9)
10

8 + **10** $\xrightarrow[\text{reaction}]{\text{bromophilic}}$ **6** + **2** (10)

9 + 'H^+' $\longrightarrow CF_2=CFH$ (11)
7

9 + 3(or **7**) $\longrightarrow$ oligomer (or polymer) (12)

Scheme II

ratio R'(**2a**/**3**) (Table 1). Table 2 shows that R increased from 0.06 to 0.55 when the alkoxide to olefin ratio R' decreased from 1 to 0.33. Since structurally **3** can be a good donor of 'positive' bromine [6], we inferred that the bromine in product

6 might have come from the reactant 3. Thus in addition to reactions (1) to (3) or (5) to (7), other competitive paths are proposed in Scheme II.

However, at this point, Scheme II could not be considered to be the only plausible rationale because 3 could also act as a good electron acceptor. In fact, we have actually found that when sodium naphthalene was used to react with 3, a small amount of trifluoroethene(7) was formed. Thus reactions initiated by electron transfer (SET) and carried on by radical intermediates could be equally viable, as shown in Scheme III. In this scheme, the possibility of the reduction of a perhalogenated radical to the corresponding carbanion is also presented (reaction (20) to (22)).

RO^- (2) + $CF_2=CFBr$ (3) $\xrightarrow{SET}$ $\overline{RO^{\cdot}(CF_2=CFBr)^{\cdot -}}$ (11) (13)

11 $\longrightarrow$ $RO^{\cdot}$ (12) + $(CF_2=CFBr)^{\cdot -}$ (13) (14)

12 + 3 $\longrightarrow$ $ROCF_2\dot{C}FBr$ (15) (15)

15 $\xrightarrow{Br\text{-}abs.}$ $ROCF_2CFBr_2$ (6) (16)

15 $\xrightarrow{H\text{-}abs.}$ $ROCF_2CFBrH$ (4) (17)

13 $\longrightarrow$ $CF_2=\dot{C}F$ (14) + Br^- (18)

14 $\longrightarrow$ $CF_2=CFH$ (7) (19)

15 $\xrightarrow{+e}$ 8 (20)

8 $\xrightarrow[\text{reaction}]{\text{bromophilic}}$ 6 (21)

14 $\xrightarrow{+e}$ $CF_2=CF^-$ (9) (22)

9 $\xrightarrow{\text{proton-abs.}}$ 7 (23)

Scheme III

TABLE 3

Yields of products in the presence of inhibitors or trapping agents[a] (r.t., in THF, 1 h)

Compound added	4a	5a	6a	4a+5a+6a	7	R
None	4.1	51.4	30.4	85.9	1.6	0.55
p-DNB[b]	4.3	40.3	27.4	72.0	5.8	0.61
Air	4.6	41.9	26.9	73.0	9.0	0.58
Cyclohexene	4.9	32.9	24.8	62.6	5.8	0.66
DAE[b]	11.6	15.9	26.5	54.0	2.3	0.96

[a] The yields were determined by GC and the molar ratio of the compound added to **2a** is 1. **2a/3** = 0.33.

[b] p-DNB = p-dinitrobenzene, DAE = diallyl ether.

Since Scheme III postulates SET initiation and involvement of radical intermediates(**12** and **15**) in the bulk, experiments with SET inhibitors or radical trapping agents were performed. The results are summarized in Table 3.

Para-dinitrobenzene(p-DNB) is known to inhibit SET reactions, both it and oxygen can retard radical chain reactions, whereas cyclohexene and diallyl ether(DAE) can further form identifiable adducts after trapping the radical intermediates. Table 3 shows that neither the yields nor the product ratios(R) are greatly affected by the addition of inhibitors or trapping agents. Furthermore, no adducts could be found from cyclohexene and DAE. Therefore radical intermediates are most likely not involved and the unusual bromoproducts **6** are formed from a bromophilic attack by the intermediate carbanion **8**, as illustrated by reactions (8) and (10) in Scheme II.

TABLE 4

Percentage yields of products from the reaction of **2a** with 3 in the presence of $BrCCl_3$[a] (r.t., 1 h)

	4a	5a	6a	4a+5a+6a	7	R
2a/$BrCCl_3$ = 1 (in THF)	8.8	4.8	33.5	47.1	0.3	2.5
$BrCCl_3$ as solvent	7.1		26.7	33.8		3.8

[a] The product yields were based on GC.

The validity of the above conclusion has been strengthened by the following experiments: (1) Presence of protic species affects the distribution of products, e.g., when equivalent amounts of t-BuOH and t-BuOK were used, the yield of **4a** increased, but **6a** was still able to form, showing that the bromophilic reaction could compete with the "protophilic" reaction under these circumstances. However, when the reaction was carried out in t-BuOH, **4a** was almost the only product. (2) When $BrCCl_3$ was added or used as the solvent, the R value was raised to 2.5 and 3.8 respectively (Table 4). Furthermore, no trace of CCl_3CCl_3, the coupling product of CCl_3 radicals, could be detected by GC of the crude mixture after reaction.

The use of other solvents, i.e., benzene, THF, N,N-dimethylformamide(DMF), hexamethylphosphoramide(HMPA), diglyme, have been explored and the results are summarized in Table 5. Notably, the addition of the 18-crown-6 brought about a much improved yield [5b], although the R value was not much affected. This result is consistent with our assumption that carbanion intermediates are involved.

TABLE 5

Percentage yields of products from the reactions of **2a** with 3 in different solvents or in the presence of crown ether[a] (r.t., 1 h)

Solvent	**4a**	5a	6a	4a+5a+6a	7	R
Benzene	11.1	50.2	6.1	67.4	2.0	0.10
Diglyme	10.8	16.0	35.9	62.7	0.2	1.34
DMF	24.3	1.1	27.9	53.3	1.7	1.10
HMPA	9.8	17.3	13.5	40.6	0.3	0.50
Benzene+ crown ether	14.8	63.3	8.2	86.1	0.1	0.10
THF+$BrCCl_3$+ crown ether	14.1	2.4	44.6	61.1	0.3	2.70

[a] The yields of products were determined by GC. The molar ratio **2a/3** = 0.33. Crown ether = 18-crown-6.

CONCLUSION

Carbanions are such good halophiles that they may participate in unexpected competitive reaction paths, thus many previously reported nucleophilic additions of perhaloolefins may deserve re-evaluation. More significantly, such reactions, if run in halogen-donating solvents may find synthetic applications (cf. R = 3.8 in $BrCCl_3$), i.e., it might be feasible to add the elements of 'Nu' and 'X' (X = I, Br, Cl) to various kinds of electron-deficient multiple bonds.

EXPERIMENTAL

Melting points were uncorrected. ^{19}F NMR spectra were obtained by using a Varian EM 360 L spectrometer at 56.4 MHz, and ^{1}H NMR spectra were obtained at 60 MHz. The external references trifluoroacetic acid and tetramethylsilane were used for ^{19}F NMR and ^{1}H NMR spectra respectively. Chemical shifts (δ) are reported in parts per million (ppm), and spin-spin coupling constants (J) in Hz. Mass spectra were obtained on a Finnigan 4021 GC-MS spectrometer. Gas chromatography were performed on a Shanghai model 103 gas chromatograph.

The analytical conditions of the gas chromatograph for liquid phase products were: a 2 m 0.5 cm column of 15 % PEG-1500 on 60/80 mesh 102 support. Nitrogen carrier velocity, 20 mL/min., hydrogen, 30 mL/min., air 275 mL/min., column temperature 100° C, n-dodecane as internal standard. The conditions for gas phase products were: a 2 m 0.5 cm column of 10 % SE-30 on 60/80 mesh 102 support. Nitrogen carrier velocity, 20 mL/min., hydrogen, 30 mL/min., air, 275 mL/min., column temperature 45° C and chlorotrifluoroethene as internal standard. A flame ionization detector was used.

Trifluorotoluene was used as internal standard for ^{19}F NMR spectra analysis.

All solvents were purified according to standard procedures [7].

Low temperature distillation of bromotrifluoroethene(3)

Distillation was carried out under nitrogen atmosphere with a 1.5 m × 1.5 cm column packed with 0.2 cm diameter steel springs. Bromotrifluoroethene (300 mL) was charged to a 500 mL flask cooled by a dry ice-acetone bath. The temperature of the fractional head was maintained at -25° C and the temperature of the bath was controlled by varying the ratio of dry ice to acetone. The distillate was collected at -5° to -4° C.

The preparations of alkoxides(2)

The t-BuOK used was prepared and sublimed according to Bunnett and Scamhorn [8]. The other sodium alkoxides were prepared in the same way and dried at 70° C/1 torr for 24 h.

General procedure for the sealed-tube reactions

The tube with the alkoxide and solvent was degassed and refilled with pure N_2 three times before CF_2=CFBr(3) was introduced by a vacuum line system. The amount of 3 was calculated by the ideal gas equation. The sealed tube was shaken for specified time (1 to 4 h) at room temperature.

The reaction of 3 with sodium naphthalene

To a 25 mL flask were added 10 mL of THF, 0.26 g (11.2 mmol) of sodium and 1.44 g (11.2 mmol) of naphthalene. The reaction was carried out at room temperature for 6 h. One-sixth of the liquid (1.88 mmol) was added to a tube with 5 mL of THF and 0.10 g (0.63 mmol) of 3. After 1.5 h, about 1-2 percent of trifluoroethene(7) was found in gas phase.

The reaction of 2a with 3 (cf. general procedure)

The amounts of reactants and solvent used were: **2a**: 0.21 g (1.88 mmol), **3**: 0.91 g (5.63 mmol), and THF 7 mL. After reacting at room temperature for 1 h, the products were **4a**, **5a**, **6a**, and **7**. The spectra data of the products: **4a**: ^{19}F NMR 1.1 (2F,J = 15 Hz, $-CF_2-$); 78.5 (1F, J = 48 Hz, -CFBrH); ^{1}H NMR 1.3 (3H,$-CH_3$); 6.1 (1H, J = 6 Hz, -CFBrH). m/z (assign., rel. intens.): 219 (M^+-CH_3, 17); 161 (M^+-CF_2CFBr, 8); 111 (M^+ -CFBrH, 3); 57 ($C(CH_3)_3$, 80); 59 ($(CH_3)_2COH$, 100). **5a**: ^{19}F NMR 24.8 (1F, J = 128 Hz, =CFBr, E); 57.6 (1F, J = 128 Hz, ROCF=, E); 8.8 (1F, J = 38 Hz, =CFBr, Z); 52.1 (1F, J = 38 Hz, ROCF=, Z). m/z (assign., rel. intens.): 214 (M^+, 0.01); 199 (M^+-CH_3, 5); 158 (FCOCFBrH, 0.5); 57 ($C(CH_3)_3$, 100). **6a**: ^{19}F NMR 2.0

(2F, J = 11 Hz, $-CF_2-$); -4.3 (1F, J = 11 Hz, -CF-); ^1H NMR 1.5 (9H, $-C(CH_3)_3$). m/z (assign., rel. intens.): 297 (M^+-CH_3, 5); 239 ($M^+-C(CH_3)_3$, 4); 189 ($M^+-(CH_3)_3COCF_2$, 1); 123 (M^+-CFBr_2, 5); 57 ($C(CH_3)_3$, 100). **7**: m/z (assign., rel. intens.): 82 (M^+, 56); 63 (M^+-F,31); 51 (M^+-CF, 100).

The reaction of 2b with 3 (cf. general procedure)

The amounts of reactants and solvent used were: 2b: 0.15 g (1.83 mmol), **3**: 0.91 g (5.63 mmol), and THF 2 mL. After reacting at room temperature for 4 h, the products were **4b**, **5b**, **6b** and **7**. The spectra data of the products: **4b**: ^{19}F NMR 6.5 (2F, J = 13 Hz, $-CF_2-$); 80.0 (1F, J = 47 Hz, -CF-). m/z (assign., rel. intens.): 219 (M^+-1, 0.2); 205 (M^+-CH_3, 19); 161 ($M^+-(CH_3)_2CHO$, 15); 109 (M^+-CFBrH, 2); 43 ($(CH_3)_2CH$, 100). **5b**: ^{19}F NMR 34.8 (1F, J = 145 Hz, =CFBr, E); 61.9 (1F, J = 145 Hz ROCF=, E); 17.8 (1F, J = 37 Hz, =CFBr, Z); 55.3 (1F, J = 37 Hz, ROCF=, Z). m/z (assign., rel. intens.): 200 (M^+, 1.2); 158 (FCOCFBrH, 0.9); 43 ($(CH_3)_2CH$, 100). **6b**: ^{19}F NMR -2.34 (1F, J = 13 Hz, -CF-); 7.0 (2F, J = 13.2 Hz, $-CF_2-$). m/z (assign., rel. intens.): 283 (M^+-CH_3, 1.3); 239 ($M^+-(CH_3)_2CHO$, 2.4); 219 (M^+-Br, 0.9); 189 ($CFBr_2$, 0.5); 109 (M^+-CFBr_2, 5); 43 ($(CH_3)_2CH$, 100).

The reaction of 2c with 3 (cf. general procedure)

The amounts of reactants and solvent used were **2c**: 0.13 g (1.91 mmol), 3: 0.91 g (5.63 mmol), and THF 2mL. after reacting at room temperature for 4 h, the products were **4c**, **5c**, **6c** and **7**. The spectra data of the products: **4c**: ^{19}F NMR 8.93 (2F, J = 14 Hz, $-CF_2-$); 80.0 (1F, J = 48 Hz, -CF-). m/z (assign., rel. intens.): 205 (M^+-1, 0.5); 191 (M^+-CH_3, 0.8); 187 (M^+-F, 1.6); 161 ($M^+-C_2H_5O$, 18); 95 (M^+-CFBrH, 100); 45 (C_2H_5O, 9). **5c**: ^{19}F NMR 37.6 (1F, J = 126 Hz, =CFBr, E); 62.6 (1F, J = 126 Hz, ROCF=, E); 20.9 (1F, J = 35 Hz, =CFBr, Z);

55.9 (1F, J = 35 Hz, ROCF=, Z). m/z (assign., rel. intens.): 186 (M^+,19.6); 158 (FCOCFBrH, 100); 141 (CF=CFBr, 2); 110 (CFBr, 13). **6c**: ^{19}F NMR -2.4 (1F, J = 13 Hz, -CF-); 9.3 (2F, J = 13 Hz, $-CF_2-$). m/z (assign., rel. intens.): 239 ($M^+-C_2H_5O$, 6); 205 (M^+-Br, 10); 189 ($CFBr_2$, 8); 95 (M^+-CFBr_2, 100); 45 (C_2H_5O, 6).

The reaction of 2d with 3 (cf. general procedure)

The amounts of reactants and solvent used were: **2d**: 0.1 g (1.85 mmol), **3**: 0.91 g (5.63 mmol) and THF 2mL. After reacting at room temperature for 4 h, the products were **4d**, **5d**, **6d** and **7**. The spectra data of the products: **4d**: ^{19}F NMR 12.0 (2F, J = 14 Hz, $-CF_2-$); 80.6 (1F, J = 50 Hz, -CF-). m/z (assign., rel. intens.): 192 (M^+, 0.6); 161 (M^+-CH_3O, 2); 173 (M^+-F, 1.2); 81 (M^+-CFBrH, 100). **5d**: ^{19}F NMR 40.8 (1F, J = 137 Hz, =CFBr, E); 63.6 (1F, J = 137 Hz, ROCF=, E); 24.4 (1F, J = 41 Hz, =CFBr, Z); 58.0 (1F, J = 41 Hz, ROCF=, Z). m/z (assign., rel. intens.): 172 (M^+, 6); 157 (M^+-CH_3, 5); 138 (M^+-CH_3-F, 2); 110 (CFBr, 1.2); **6d**: ^{19}F NMR -1.8 (1F, J = 14 Hz, -CF-); 12.6 (2F, J = 14 Hz, $-CF_2-$). m/z (assign., rel. intens.): 191 (M^+-Br, 76); 160 (M^+-CH_3O-Br, 9); 81 (M^+-CFBr_2, 100).

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