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Vinylic Substitution of 1,2-Dibromo-1,2-difluoroethylene and Tribromofluoroethylene. An Intramolecular k_{Br}/k_F Element Effect and Apparent Inversion of Configuration in S_NV Reactions[1a]

Bagrat A. Shainyan[1b] and Zvi Rappoport*

Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

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The reactions of (*E*/*Z*)-1,2-dibromo-1,2-difluoroethylene (**1**) and of tribromofluoroethylene (**2**) with alkoxide ions and of **1** with *p*-toluenethiolate ion give multiplicity of products. The reaction of **1** with 1 equiv of NaOMe gives mainly a 2:1 mixture of the product of one bromine displacement, together with methyl dimethoxyacetate (**3**), methyl bromofluoroacetate (**4**), 1,1,2-trifluoro-2-bromoethyl ether (**7**), and 1,1-difluoro-1,2,2-trimethoxyethane (**8**). With 2 equiv of MeO^- **3** and **4** are the main products, and at 130 °C, dimethyl ether **5** is also formed. With $EtOCH_2CH_2O^-$ **1** gave 2-ethoxyethyl bromofluoroacetate (**9**), bis(2-ethoxyethyl) ether (**10**), and *E*/*Z* mixtures of the substitution products $EtOCH_2CH_2OC(F){=}C(F)Br$ (**12**) and $EtOCH_2CH_2OC(Br){=}C(F)Br$ (**13**). Reaction of **2** with excess RO^- (R = Me, Et) gives alkyl dibromoacetates, while with 1 equiv of RO^- only a bromine from the $=C(F)Br$ carbon is displaced. Reaction of **1** with *p*-TolSNa in MeOH gives the reduction–substitution product *p*-TolSC(F)=CHF (**18**), together with $(p\text{-TolS})_2$ (**16**) and *p*-TolSMe (**17**). The same reaction in DMSO gives *E*/*Z* mixtures of the product of displacement of one bromine (**19**) or two bromines (**20**). Formation of the products is rationalized by an initial nucleophilic attack on the vinylic carbon followed by leaving group expulsion, giving, e.g., **12**, **13**, **19**, or **20**. Hydrolysis of the intermediate or addition of HF to the initial substitution product gives saturated products, e.g., **3**, **4**, **7**, or **8**, while S_N2 reactions on the ether oxygen give ethers **5** and **10**. A bromophilic reaction gives the reduction–substitution product **18**, while hydrolysis–decarboxylation leads to **17**. The regiospecificity of the nucleophilic addition is due to polar and hyperconjugative effects. An intramolecular element effect k_{Br}/k_F of >10 is reported for the first time in the reaction of **1** with $EtOCH_2CH_2O^-$. This value and the absence of such effects in other reactions are consistent with a much higher nucleofugality from a $^-CC(F)Br$ system of Br^- compared with F^-. The *E*/*Z* compositions of **18**–**20** indicates an apparent inversion in their formation, but it is not known whether these compositions are thermodynamically or kinetically controlled.

Introduction

Nucleophilic vinylic substitution reactions are usually carried out with systems activated by electron-withdrawing groups at a β-position to the leaving group, which are capable of delocalization of a negative charge by conjugation (NO_2, RCO, CO_2R, etc.).[2] Substitution of unactivated simple vinyl halides under mild conditions is possible only with strong nucleophiles in dipolar aprotic solvents like DMF, DMSO, or HMPA.[3] The substitution is facilitated by using polyhaloalkenes,[3a,4] especially fluorine-substituted ones where the strongly electron-withdrawing fluorine increases the electrophilicity of the attacked carbon and also serves as a leaving group. Substitution of 1,1-dichloroethylene[4a] and tetrachloroethylene[4b] by thiolate anion has been known for a long time, and a facile substitution of the bromine of simple fluorobromoethylenes by sodium thiophenolate was recently reported.[4c]

We report now a study of the reactions of 1,2-dibromo-1,2-difluoroethylene (**1**) with sodium alkoxides and sodium *p*-toluenethiolate and of tribromofluoroethylene (**2**) with sodium alkoxides. Both systems carry the $=C(Br)F$

$$\underset{\mathbf{1}}{BrC(F){=}CF(Br)} \qquad \underset{\mathbf{2}}{Br_2{=}C(Br)F}$$

moiety and therefore are potentially suitable to evaluate the intramolecular element effect[5] k_{Br}/k_F. The regioselectivity of the initial nucleophilic attack on **2** is also of interest.

Results

Synthesis. Both **1** and **2** were synthesized from *sym*-tetrabromoethane by a sequence of fluorination with SbF_3 and bromination–dehydrobromination steps as described by one of us earlier.[6] Compound **1** is formed as a 17:83 equilibrium mixture of the *Z*- to the *E*-isomer, based on integration of the two singlets in the ^{19}F NMR spectrum. The ratio reported previously is 21:79.[7] The literature assignment of the signals to the two isomers[7] is corroborated now by measurements of the F–F coupling on the

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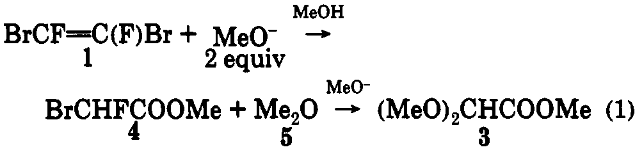
^{13}C satellites. The weaker signal at −95.65 ppm (lit.[7] −95.3 ppm) displays a splitting of 33.90 Hz (lit.[7,8] 34.3 Hz) while for the stronger signal at −113.43 ppm (lit.[7] −113.1 ppm) the splitting is J = 141.21 Hz (lit.[7] J = 141.4 Hz, lit.[8] J = 141.8 Hz) which allows us to assign them to the Z and E isomers of **1**, respectively.

Reactions with Alkoxides. (a) 1 with MeO$^-$. Reaction of **1** with a 2-fold excess of sodium methoxide in methanol at 75 °C in a sealed tube for 40 h results after water–CHCl$_3$ workup in 67% of two products which we failed to separate by distillation. The spectrum of the main product (ca. 65% of the product) displays three singlets in the ^{1}H NMR spectrum at δ(CDCl$_3$) 3.43, 3.81, and 4.83 ppm in a 6:3:1 ratio and coincides with that reported for methyl dimethoxyacetate (**3**).[9] The minor product (35% of the product) displays a doublet at δ 6.60 ppm (J_{HF} = 50.5 Hz) and a singlet at δ 3.91 ppm in a 1:3 ratio in the ^{1}H NMR spectrum and a doublet at −151.12 ppm (J_{HF} = 50.5 Hz) in the ^{19}F NMR spectrum. We assign it to methyl bromofluoroacetate (**4**) which shows similar spectra[10] (^{1}H NMR: 3.95 s, 6.70 d, J_{HF} =50.5 Hz; ^{19}F NMR: −151 d).

GCMS analysis with chemical ionization (CI-GCMS) supports these assignments. Two peaks are observed. The first gives a pair of signals of equal intensities at m/z 171, 173 (M + H for **4** with ^{79}Br, ^{81}Br), while the second gives a single (M + H)$^+$ signal at m/z 135 for **3**. Ester **3** is apparently formed by reaction of MeO$^-$ with the substitution product **4**. Indeed, when a mixture of **3** and **4** was treated with an excess of MeONa in MeOH, the only product isolated was pure **3**: $\nu_{C=O}$ 1773 cm^{-1} (lit.[11] $\nu_{C=O}$ 1771 cm^{-1}).

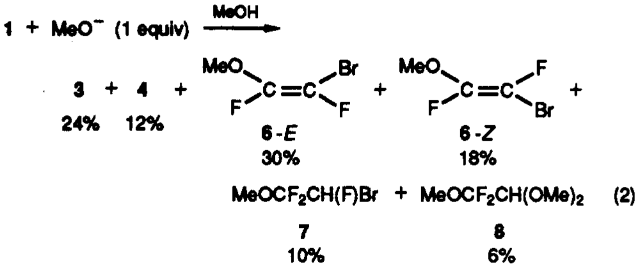
When the same reaction was conducted at 130 °C in a sealed tube, a gas was found to evolve. After it was trapped in CDCl$_3$ it showed one singlet in both the ^{1}H (δ 3.20 ppm) and the ^{13}C (δ 60.66 ppm) NMR spectra, with J(^{13}C–H) 140.9 Hz. These values are in excellent agreement with those reported for dimethyl ether **5** [δ(CDCl$_3$): 3.23 ppm (^{1}H NMR);[12] 59.7 ppm (^{13}C NMR);[12] J(^{13}C–H)=140.2 Hz[13]]. The other products were a 7:4 mixture of **3** and **4** (eq 1).



$$\underset{\mathbf{1}}{\mathrm{BrCF{=}C(F)Br}} + \underset{\text{2 equiv}}{\mathrm{MeO^-}} \xrightarrow{\mathrm{MeOH}} \underset{\mathbf{4}}{\mathrm{BrCHFCOOMe}} + \underset{\mathbf{5}}{\mathrm{Me_2O}} \xrightarrow{\mathrm{MeO^-}} \underset{\mathbf{3}}{\mathrm{(MeO)_2CHCOOMe}} \quad (1)$$

In an attempt to detect the initial substitution intermediate(s) leading to **3** and **4** the reaction of **1** was conducted with an equimolar amount of MeONa at 70–80 °C for 8 h. The mixture was analyzed by ^{1}H and ^{19}F NMR before workup. Except for **1**, **3**, and **4** the two monobromo-substituted products **6**-E and **6**-Z (in a 63:37 ratio) were detected as doublets in the ^{19}F NMR at −102.59 and −134.78 ppm (d, J = 38.1 Hz) (**6**-E) and at −118.94 and −141.16 ppm (d, J = 124.6 Hz) (**6**-Z), respectively.

The ^{19}F NMR spectrum also showed the formation at 10% and 6% (of the total product), respectively, of two other compounds. The first one displayed a doublet of triplets centered at −158.15 ppm with J's of 14.0 (t) and 48.3 Hz (d) and an AB quartet at −87.0 and −87.58 ppm (J = 142.4 Hz). Each line of the latter showed further splitting to a doublet of doublets, J = 14.0 and 5.1 Hz. The ^{1}H NMR shows a doublet of triplets of δ 6.32 (J = 5.1 Hz, t; 48.3 Hz, d). These data are consistent with an ABMX spin system and were attributed to methyl 1,1,2-trifluoro-2-bromoethyl ether (**7**). The δ and J values ascribed to **7** are similar to those observed in the related XCF$_2$CH(F)Br systems (X = Cl, Br).[14] The other compound displayed a doublet centered at −81.53 ppm (J = 5.1 Hz) in the ^{19}F NMR and a triplet at δ 5.65 (J = 5.1 Hz) in the ^{1}H NMR. They are tentatively assigned to the saturated acetal 1,1-difluoro-1,2,2-trimethoxyethane (**8**) (eq 2). The combined results of both integrations are given in eq 2 as relative percentages of the total product.



(2)

(b) 1 with EtOCH$_2$CH$_2$O$^-$. Reaction of **1** with sodium 2-ethoxyethoxide in cellosolve is somewhat different. With a 2-fold excess of EtOCH$_2$CH$_2$ONa the main product at reflux is 2-ethoxyethyl bromofluoroacetate (**9**) as judged by CI-GCMS analysis, which also showed the formation of bis(2-ethoxyethyl) ether (**10**). CI-GCMS and ^{19}FMR revealed the formation of an additional five products including diethyl cellosolve (**11**) (m/z of (M + H)$^+$ 119), E/Z 1,2-difluoro-1-bromovinyl 2-ethoxyethyl ether **12**-E and **12**-Z (for each m/z of (M + H)$^+$ 231, 233), and (E/Z)-1,2-dibromo-1-fluorovinyl 2-ethoxyethyl ethers **13**-E and **13**-Z (m/z of (M + H)$^+$ 291, 293, 295). The latter triplet indicates the presence of two bromines in **13**, showing the displacement of fluorine by the alkoxide. The intensity ratio of the mass spectral signals of **12** to **13** was 6:9.

Under milder conditions (30–40 °C) and with an equimolar ratio of **1** to EtOCH$_2$CH$_2$ONa, a nearly exclusive (ca. 95%) mixture of the monobromo substituion products **12**-E and **12**-Z, has been obtained. The E:Z isomer ratio was 3:2 judging from the ^{19}F NMR spectrum. The low-field signals at −98.98 and −115.87 are attributed to the α-fluorine atoms of **12**-E and **12**-Z, respectively, since they appear as triplets with $^4J_{HF}$ = 1.2 Hz due to a long-range coupling with the OCH$_2$ group.

Two low-intensity singlets (ca. 5%) also appear at −85.30 and −115.77 ppm in a 1:2 ratio. Judging by their multiplicity and their δ's which resemble those of **1**-Z and **1**-E they were tentatively assigned to **13**-Z and **13**-E. An independent evidence for fluorine displacement is that the X-ray powder diffraction patterns of the inorganic precipitate formed in the reaction showed it to be a mixture of both NaF and NaBr (eq 3).

(c) 2 with RO$^-$. Reactions of tribromofluoroethylene **2** with a 4.3 molar excess of sodium methoxide or ethoxide give methyl or ethyl dibromoacetates **14**, respectively,

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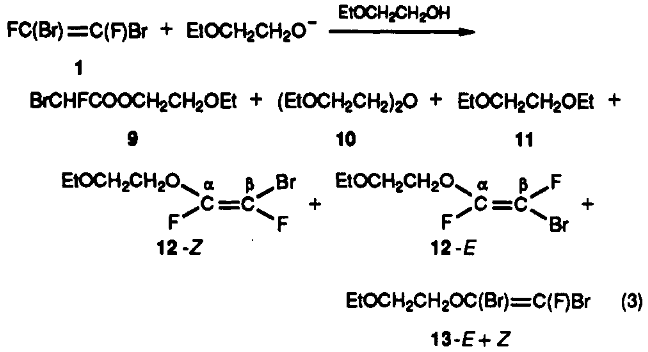


similarly to their formation in the reaction of alkoxides with $PhSO_2CF{=}CBr_2$.[15] With an equimolar amount of MeONa only 1-fluoro-2,2-dibromovinyl methyl ether (15), identical with the reaction product of NaOMe with $PhSO_2CF{=}CBr_2$,[15] was obtained. No substitution product of the fluorine atom was observed (eq 4). The structure

$$\mathrm{Br_2C{=}C(F)Br + MeO^-} \xrightarrow{\mathrm{MeOH}} \underset{15}{\mathrm{Br_2C{=}C(F)OMe}} \rightarrow \underset{14,\ \mathrm{R = Me}}{\mathrm{Br_2CHCOOR}} \quad (4)$$

of 15 was deduced from its ^1H and ^{19}F NMR spectra (($CDCl_3$) δ 3.83; −81.37 ppm, $^4J_{HF}$ 1.2 Hz) and its ^{13}C NMR spectrum which displays two signals for olefinic carbons at 55.29 ppm $^2J(13_{CF})$ = 59.72 Hz, and 127.09 ppm $^1J(13_{CF})$ 372.3 Hz. The high-field geminally coupled signal is probably due to the combined effects of the α-F and α-OMe substituents, as shown by δ of 54.7 ppm for C_β of 1,1-dimethoxyethylene.[16]

Reactions of 1 with Sodium *p*-Toluenethiolate. Reaction of 1 with *p*-TolSNa in MeOH gave a mixture which was partially separated by distillation. The high-boiling substance was the disulfide 16, whereas the low-boiling fraction was a mixture which was separated by chromatography on silica to methyl *p*-tolyl sulfide (17) and 1,2-difluorovinyl *p*-tolyl sulfide (18) (1:2 ratio before separation). 18 itself was an 18-*Z*:18-*E* mixture of 23:77 judged by ^{19}F NMR (eq 5).

$$\underset{1}{\mathrm{BrC(F){=}C(F)Br}} + p\text{-TolS}^- \xrightarrow{\mathrm{MeOH}} \underset{18}{p\text{-TolSC(F){=}CHF}} + \underset{17}{p\text{-TolSMe}} + \underset{16}{(p\text{-TolS})_2} \quad (5)$$

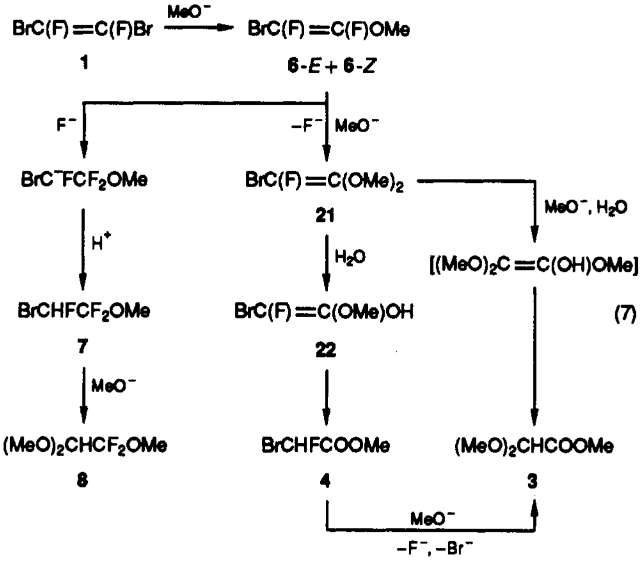
When the methanolic reaction mixture was worked up with an approximately equivalent amount of D_2O instead of H_2O, the intensity of the SMe signal in the proton spectrum of 17 diminished by ca. 2-fold, indicating that 17 is formed by a hydrolysis–decarboxylation sequence.

The reaction of 1 with *p*-TolSNa in dry DMSO took a different course. Neither 17 nor 18 was observed, but the monobromo- (19) and the dibromo-substituted products (20) were isolated by chromatography on silica. Their ratio was dependent upon the concentration of the nucleophile, and when more than 2-fold excess of *p*-TolSNa was used, practically all of 19 was converted to 20. The isomeric ratios were 19-*Z*:19-*E* = 84:16 and 20-*Z*:20-*E* = 14:86 (eq 6). Assignment is based on the F–F couplings measured directly for 19 and on the ^{13}C satellites for 20.

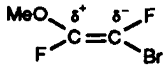
$$\underset{1}{\mathrm{BrC(F){=}C(F)Br}} + p\text{-TolS}^- \xrightarrow{\mathrm{DMSO}} \underset{\text{19-}E\text{:19-}Z\ =\ 16:84}{p\text{-TolSC(F){=}C(F)Br}} \xrightarrow{p\text{-TolS}^-} \underset{\text{20-}E\text{:20-}Z\ =\ 86:14}{p\text{-TolSC(F){=}C(F)STol-}p} \quad (6)$$

Discussion

Reaction with Alkoxides. The only observed monosubstitution products of 1 with MeO^- are 6-*E* and 6-*Z* detected in the reaction with 1 equiv of MeO^-. Addition of a fluoride ion to 6 followed by protonation gives 7, which undergoes two methoxydehalogenations to give 8. Since monofluoro substitution was not detected, we assume that the source of F^- is from the substitution of the fluorine of 6, leading to the ketene acetal 21, where both halogens on one carbon had been replaced. As shown in eq 7, 4 and 3 are formed from 21 by a consecutive sequence of reactions with MeO^- or water or with both MeO^- and water.



The formation of 4 and 7 which retain the CHFBr moiety implies that the attack on 6 occurs at the methoxy-substituted carbon atom. The consecutive attack on the same carbon, which terminates in substitution (21 → 3 + 4) or addition (7 + 8), can be rationalized by the polarization in the monosubstitution product 6. The two fluorine atoms in 6 activate C_α and C_β similarly, but the methoxy group, by virtue of its both inductive and resonance effect, polarizes the double bond in such a way that the carbon atom to which it is attached becomes more electrophilic than the Br-substituted carbon. Consequently, the subsequent nucleophilic attack occurs on the MeO-substituted carbon.



6

Although the *E*/*Z* composition of both 6 and 1 is known, the kinetically controlled stereochemistry of the bromine substitution is unknown, since the *E*/*Z* isomers of 1 equilibrate[7] at an unknown rate and the relative stability of 6-*E* and 6-*Z* is unknown.

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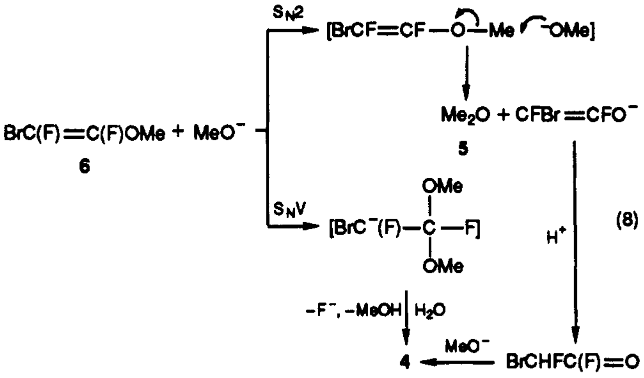
Neither the intermediate acetal **21** nor other intermediates leading to **3** and **4** were isolated or detected. However, several reasonable sequences of consecutive substitutions can be suggested for formation of **3** and **4**. Two of them, shown in eq 7, involve intermediate hemiacetals, e.g., **22**, obtained by reaction of **21** with water present in the commercial methanol. An alternative[17] is a nucleophilic addition of methanol to **21** to give the ortho ester $BrCHFC(OMe)_3$ which on further substitution with MeO^- gives $(MeO)_2CHC(OMe)_3$. Aqueous workup will give **3** or **4**, respectively. Formation of **3** from MeO^- and **4** involves two (presumably S_N2) substitutions on C_α and is corroborated by the **4** + $MeO^- \rightarrow$ **3** transformation.

We ascribe the unexpected formation of dimethyl ether **5** in reaction of **1** with MeO^- under severe conditions to a competition between an S_NV and an S_N2 on the MeO group of **6** (eq 8). The enolate formed in the latter reaction protonates and ketonizes to an acyl fluoride which by hydrolysis gives **4** by an alternative route.



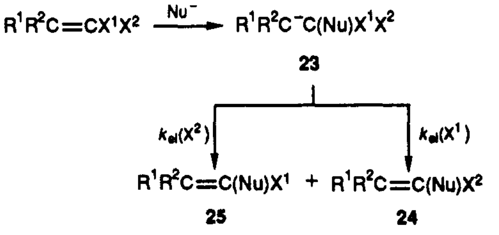
(8)

Formation of dialkyl ethers by reaction of an alkoxide on an aromatic alkoxy group is known to accompany S_NAr reactions[18a] when the leaving group is a phenoxide ion resonatively stabilized by an electron-withdrawing group. A similar S_NV vs S_N2 competition is known for some vinyl sulfides which with an excess of a thiolate ion form dialkyl sulfide and enethiolate ion. As in our case this process predominates under harsher conditions.[3b,d] We know of only one precedent of the formation of dialkyl ethers from alkoxides and vinyl halides.[18b]

The substantial formation of dimethyl ether only at a higher temperature can be rationalized by the different nature of orbitals attacked by the nucleophile. In S_N2 it is a σ^*(O-Alk) orbital, while for S_NV it is a lower lying π^* orbital. Consequently, the S_NV reaction should have a lower activation energy and predominate at a lower temperature.

With a 2-ethoxyethoxide nucleophile, two S_N2 reactions compete with the S_NV process: a nucleophilic attack on a CH_2 carbon of the CH_2CH_2 moiety of **12** gives the ether **10**, whereas attack on the CH_2 carbon of the 2-ethoxy group gives diethyl cellosolve **11**. The latter could also be formed by elimination of a vinyl alcohol molecule from **10**, since such elimination occurs in divinyl ethers of ethylene or diethylene glycol[19].

The Intramolecular Element Effect. A main goal in our work was to search for and evaluate the extent of an intramolecular element effect (IEE)[5] k_{Br}/k_F. If in vinylic substitution two potential leaving groups X^1 and X^2 are attached to the carbon attacked by the nucleophile, both could be displaced. Their relative expulsion rates $k_{el}(X^1)/k_{el}(X^2)$ from the intermediate carbanion **23** could be evaluated from the product ratio[5] (eqs 8 and 9).



(8)

$$k_{el}(X^1)/k_{el}(X^2) = [\mathbf{24}]/[\mathbf{25}] \qquad (9)$$

A priori, the higher nucleofugality of Br^- compared with that of F^- predicts a very high $k_{el}(Br)/k_{el}(F)$ ratio when $X^1 = F$, $X^2 = Br$. While we know of only one (unpublished) precedent of intramolecular Br vs F competition,[20a] for the related substitution of =C(F)Cl moieties, cases were reported where either only Cl^- or both F^- and Cl^- were expelled.[20b-g]

In our systems, two types of behavior were obtained. Both **1** and **2** with MeO^- gave initially only the expected bromine-substitution product. The k_{Br}/k_F ratios were ≥ 100 judged by the intensity of the observed signals and the detection limit in the ^{19}F NMR spectrum. In contrast, in the reaction of **1** with 2-ethoxyethoxide ion, both fluorine and bromine were competitively displaced in the initial step making it the second observation of an intramolecular k_{Br}/k_F element effect. Unfortunately, the accurate ratio of Br^- vs F^- expulsion is unknown due to the low quantity of **13**. In one experiment the [**12**-*E*+*Z*]/[**13**-*E*+*Z*] ratio was obtained only from GC and authentic samples for calibration were not available, so that only the intensities of the signals are known. Those of the fluorine-substitution product are 10–14% of those of the bromine-substitution product and only if the ratio is identical with that of the precursor neutrals, then k_{Br}/k_F = 6–9 in different experiments.

A better estimate is based on the assumption that the two singlets at −85.30 and −115.77 ppm in the ^{19}F NMR spectrum are those for the fluorines of **13**-*Z* and **13**-*E*. If this is the case then the k_{Br}/k_F ratio based on their integration and those of **12** is ca. 20.

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[17] This alternative route was suggested by a reviewer.

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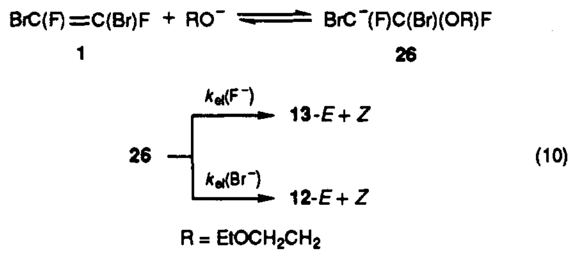
[20] (a) The substitution of (*E*)- and (*Z*)-$PhC(CF_3) = CFBr$ by MeO^- in MeOH gives initially 96–98% of $PhC(CF_3)=C(OMe)F$ and 2–4% of $PhC(CF_3)=C(OMe)Br$. Selective decomposition of the former with the progress of the reaction changes the ratios (Koch, H. F. Unpublished results). (b) Normant, J.; Sauvetre, R.; Villieras, J. *Tetrahedron* **1975**, *31*, 891. (c) Sauvetre, R.; Normant, J.; Villieras, J. *Ibid.* **1975**, 897. (d) Burton, D. J.; Krutzch, H. C. *J. Org. Chem.* **1971**, *36*, 2351. (e) Koch, H. F.; Barness, M. J. 7th IUPAC Conference on Physical Organic Chemistry; Auckland, New Zealand, 20–24 Aug 1984. (f) Koch, H. F.; Koch, J. G. In *Molecular Structure and Energetics: Fluorine Containing Molecules*; Liebman, F., Greenberg, A., Dolbier, W. R., Eds.; VCH Publishers: New York, 1988; Chapter 6. (g) Zakharkin, L. J.; Lebedev, V. N. *Zh. Obshch. Khim.* **1978**, *42*, 558; *Engl. Transl.* **1978**, *42*, 556; *Zh. Obshch. Khim.* **1971**, *41*, 817; *Engl. Transl.* **1971**, *41*, 824.

The IEE from carbanion **26** (eq 10) depends on (a) the nucleofugalities of Br^- vs F^- and (b) the relative stabilization of the transition state for expulsion of one halide ion by the second, nonexpelled halogen present in the transition state.



(10)

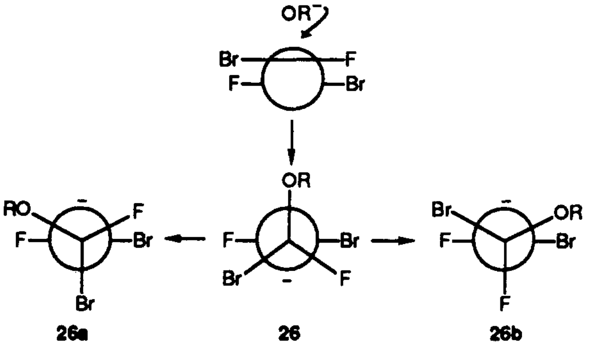
Concerning nucleofugality, the higher C–F compared with the C–Br heterolytic bond dissociation energy should make the bromide a much better leaving group. However, in our protic media (ROH), this effect is partially balanced by the higher solvation energy of F^- compared with Br^-.

The effect of the remaining halogen involves its interaction with the negative charge on a carbon β to it and the anomeric interaction between the two α-halogens, one of which is only partially bound in the transition state.

MO calculations on the model anions **27**, X = F, Br, had shown that the overall stabilizing negative hyperconjugative interaction between C–Br and the p(C^-) orbital is much larger than that between C–F and p(C^-).[21] In the intramolecular rotation in **26** (drawn here for simplicity as planar at C_β), the hyperconjugative driving force will lead preferentially to conformer **26a** with eclipsed C–Br and p(C^-) orbitals than to **26b** with eclipsing C–F and p(C^-) (eq 11). Consequently, regardless of whether X^- expulsion from **26a** or **26b** is faster or slower than internal rotation which equilibrates **26a** and **26b**, Br^- should be expelled much faster than F^-. The anomeric effect, which involves bromine, a third raw element, seems to be much less important.[22]

$$^{-}CH_2CH_2X$$

27



(11)

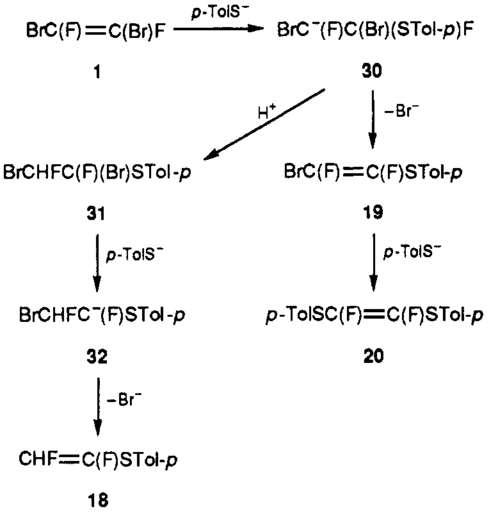
We conclude that Br^- is predicted to be a better nucleofuge than F^- from an intermediate $C^-C(Br)F$ carbanion. All our results are consistent with this conclusion, although neither the magnitude of the IEE with $EtOCH_2CH_2O^-$ nor why it is not observed in the reactions with MeO^- could have been predicted.

Formation of the dibromo ester **14** (R = Me) from **15** demonstrates again the tendency of the second nucleophile to attack the alkoxy-substituted carbon atom. In **15** the regiospecificity involves competition between reactions of $Br_2C=$ and the more electrophilic (MeO)FC= carbon (cf. **6**). The negative hyperconjugation stabilizes the β,β-dibromo carbanion **28** much more than the β-fluoro-β-methoxy carbanion **29**.[21] However, **28** will be more destabilized than **29** by the two four-electron repulsions between p(C^-) and its substituents, i.e., the nonbonding electron pairs of F and O, vs those of the two bromines. The interplay between the effects leads to preferential formation of **29** over **28**.

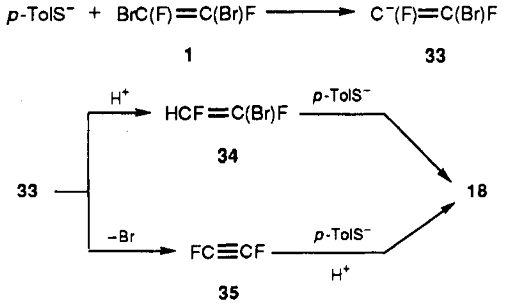
$MeOCBr_2C^-(F)OMe$ **28** $\qquad Br_2C^-C(F)(OMe)_2$ **29**

Reactions with *p*-Toluenethiolate. The reaction with *p*-$TolS^-$ is strongly dependent on the solvent. Only nucleophilic vinylic substitution is observed in the dipolar aprotic DMSO, while in a protic solvent a bromophilic reduction accompanies the formation of the hydrolysis–decarboxylation product **17**. Competition is known between these two routes in the reactions of thiolates with other fluorobromoethylenes in MeOH.[4,15,23]

Two mechanisms can be suggested for the formation of the reduction product **18**. In the first one (eq 12), an initial nucleophilic addition gives carbanion **30** which can either expel Br^- leading to **19** (substitution) or undergo protonation to give the adduct **31** (addition). Attack of the thiolate on a bromine in **31** can give carbanion **32** which loses Br^- to form **18**. The other product *p*-TolSBr reacts



(12)



(13)

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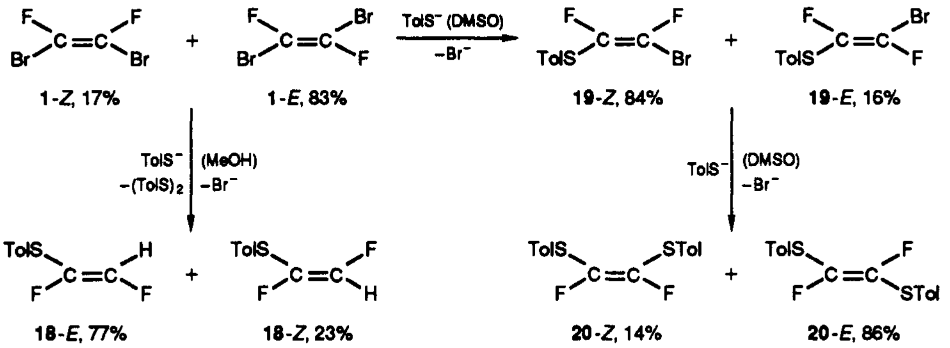

(14)

with p-TolS$^-$ to give the disulfide **16**. According to this mechanism the [**18**]/([**19**] + [**20**]) ratio is the ratio for the competitive protonation of vs bromide expulsion from **30**. Other β-fluoro carbanions formed in vinylic substitution show similar competition,[24] but the adduct of a β-bromo carbanion was never observed.

This mechanism is consistent with the absence of reduction products in the aprotic solvent, and is corroborated by a similar debromination of analogs of **31**, such as $PhSCF(Br)CHBr_2$[15] or $BrCF_2CH_2Br$[25] by thiolates.

The alternative mechanism (eq 13) involves a bromophilic reaction on **1** to give the vinyl carbanion **33** which is either protonated to **34** and then undergoes substitution to **18** or eliminates Br$^-$ to give difluoroacetylene **35** which adds p-TolS$^-$ and H$^+$ to give **18**.

Stereochemistry of the Substitutions. The stereochemical outcome of both the substitution and the reduction is known unequivocally from the ^{19}F NMR spectra of **18**–**20**. 1,2-Dibromo-1,2-difluoroethylene is configurationally unstable,[7] and the reactant is an equilibrium mixture of 17% **1**-*Z*/83% **1**-*E*. The products of tolylthio–demonobromination are apparently of an inverted configuration, 84% **19**-*Z*/16% **19**-*E*. Moreover, the further substitution products **20** have a 14% **20**-*Z*/86% **20**-*E* composition, consistent with an inversion in the second tolylthio–debromination reaction. The reduction also proceeded with apparent inversion, the **18**-*E*/**18**-*Z* ratio being 77:23 (eq 14).

This result is surprising. Vinylic substitution of bromine in slightly and moderately activated systems proceeds with retention of configuration whereas highly activated systems give partial or complete stereoconvergence.[2] Apparent inversion in vinylic substitution is rare and was observed in three types of cases: (a) in ring opening of thiirenes and selenirenes, where there is a high vinyl cation character of the attacked carbon;[26] (b) when the reaction leads to stereoconvergence and one of the isomers is the thermodynamically controlled product, where one isomeric vinyl halide gives inversion and the other isomer gives retention;[27] and (c) in the substitution of the non-β-activated (*E*)-β-alkylvinyl iodonium tetrafluoroborates with halides which may involve the intermediacy of a vinyl iodonium halide.[28]

These situations do not apply in our system. The observed inversion of configuration in the substitution could therefore result from two mechanistic routes. First, an authentic in-plane S_N2 reaction takes place, in spite of calculations in other systems which indicate that this is a higher energy process compared with a perpendicular attack.[2,29] Second, if the substitution products isomerize under the reaction conditions the product composition will be thermodynamically controlled. Since the isomers of **1** are configurationally unstable[7] (although the mechanism for their mutual isomerization is unknown), $E \rightleftharpoons Z$ isomerization for **18**–**20** is possible.

We have no information on the thermodynamic equilibria for the *E*/*Z* pairs of **18**–**20**. Unfortunately, we could not separate the *E*/*Z* isomers so we do not know if their isomerization is facile under our conditions. We know, however, that with polyhaloalkenes, especially those substituted by two vicinal fluorines, both nonbonded interactions of vicinal substituents and the relative bulk of the halogens affect the equilibria.[30] For example, with 1,2-dihaloethylenes $HCF{=}CHX$ (X = F, Cl, Br, I) the *Z* isomer predominates at equilibrium, and the more so, the higher is the atomic number of X.[31] In contrast, both with **1** and with $HCBr{=}C(F)Br$,[6,32] the *E* isomer predominates in the equilibrium, suggesting predominance of the steric factor over the electronic factor.

The relative energies of these isomeric pairs were calculated by ab initio methods using different basis sets.[33] The higher stability of **1**-*E* is reproduced by the MP2/LANL1DZ method (ΔE(cis–trans) = −2.2 kcal mol^{-1}) but the method failed to predict the correct stability order for 1,2-difluoroethylenes, or for (*E*/*Z*)-$HSC(F){=}C(F)Br$. Calculations at the highest level available (MP2/6-311G** for H, C, and F atoms, MP2/MC-311G for S, and MP2/LANL1DZ for Br) which give the correct order for 1,2-difluoroethylene (ΔE(cis–trans) = −0.2 kcal mol^{-1}) gave lower stability by 2.1 and 2.4 kcal mol^{-1} for (*Z*)-$HSC(F){=}C(F)Br$ or (*E*)-$HSC(F){=}CHF$, respectively. Unfortunately, we do not know whether the discrepancy between the calculated and observed *E*/*Z* ratios is due to a shortcoming of the calculation or to the fact that the experimental ratios are kinetically rather than thermodynamically controlled.

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Comparison of the Sulfur and the Oxygen Nucleophiles. There are three differences in the behavior of the sulfur and the oxygen nucleophiles toward 1. (a) The regioselectivity of the attack on the initial substitution product is different. The second RO^- attacks the same carbon attacked by the first RO^-, whereas the second RS^- attacks the other carbon of the C=C bond.

This difference amounts to higher stabilization of the transition state leading to carbanion **36** than to its isomer **37**, giving rise to **20** rather than to $BrCF{=}C(STol\text{-}p)_2$.

$$\underset{\mathbf{36}}{RSC^-(F)C(F)(Br)SR} \qquad \underset{\mathbf{37}}{(RS)_2C(F)C^-(F)Br}$$

The higher hyperconjugative C–Br–p(C^-) stabilization of **36** compared with that of C–SR–p(C^-) in **37**[21] also favors the former. Destabilization of the charge by an α-F is present in both **36** and **37**. That the stabilizing effect of the α-RS group can exceed the destabilization by the α-F in an $RSC^-(F)$ moiety is supported by the regiochemistry of the monosubstitution of $PhSC(F){=}CCl_2$ by PhS^- which gives $PhSC(F){=}C(Cl)SPh$ via $PhSC^-(F)CCl_2SPh$.[34]

(b) In reaction with $EtOCH_2CH_2O^-$ some fluoride is expelled, although bromide expulsion predominates, whereas with p-$TolS^-$ no fluorine-displacement product was observed. This difference is consistent with the HSAB theory, as reflected in symbiotic effects in substitution.[35] The hard RO^- is more inclined to substitute the fluorine than the soft RS^-. Lower intermolecular element effects k_F/k_{Cl} or k_F/k_{Br} with RS^- compared with RO^- were previously observed in S_NV reactions.[2c,36]

(c) Reduction products are formed only with RS^- but not with RO^- ions. Formation of products derived formally from halophilic reduction is well known in S_NV reactions with soft nucleophiles, e.g., ArS^-, I^-, etc.[3d,4,15,23,37] We know of no similar reduction of vinyl halides which accompany an S_NV reaction with alkoxides. Bromophilic reactions by ArO^- or RO^- on saturated polyhaloalkanes are known,[38] and since the facility of halophilic reduction increases from haloalkanes to haloalkenes and haloalkynes,[39] the absence of reduction products with haloalkenes is surprising. A possible explanation is that a four-electron repulsive F–p(C^-) interaction destabilizes the incipient vinyl anion.[33] Indeed, the reactivity in halophilic reactions depends on both the number and the location of fluorine atoms in the substrate.[38] If this is the case, formation of **18** is more plausible via adduct **31** (eq 12) than via the sequence of eq 13.

Formation of Methyl *p*-Tolyl Sulfide. The formation of sulfide **17** is ascribed to the sequence of steps initiated from the reduction/substitution product **18**. Initial vinylic substitution gives the dithio derivative **38**, which by water workup apparently gives fluorine substitution to **39**, followed by ketonization to **40** which hydrolyzes to **41** and decarboxylates to **17** (eq 15).

$$\underset{\mathbf{18}}{FCH{=}CF(STol\text{-}p)} + p\text{-}TolS^- \xrightarrow[-F^-]{}$$
$$\underset{\mathbf{38}}{p\text{-}TolSCH{=}C(F)STol\text{-}p} \xrightarrow[-F^-]{H_2O}$$
$$\underset{\mathbf{39}}{p\text{-}TolSCH{=}C(OH)STol\text{-}p} \rightarrow$$
$$\underset{\mathbf{40}}{p\text{-}TolSCH_2C(STol\text{-}p){=}O} \xrightarrow{H_2O}$$
$$\underset{\mathbf{41}}{p\text{-}TolSCH_2COOH} \xrightarrow{-CO_2} \underset{\mathbf{17}}{p\text{-}TolSCH_3} \quad (15)$$

Consequently, two of the hydrogens of the aliphatic CH_3 group arise from the water and the third one probably arises from MeOH in the formation of **18**. Indeed, workup with D_2O resulted in a decrease in the intensity of the CH_3 signal in the ^1H NMR spectrum. A similar formation of $ArSO_2CH_3$ from $ArSO_2CH{=}CX_2$ under basic conditions was likewise rationalized.[40]

Conclusion. The reactions of **1** and **2** with RO^- and p-$TolS^-$ are far from simple substitution processes. Nucleophilic reactions at the vinylic carbon compete with S_N2 reactions on sp^3-hybridized carbons and with bromophilic reactions. The initial substitution products further react to give a multiplicity of products including those of bromophilic reduction. Two unique features observed in this work are the still large but observable k_{Br}/k_F intramolecular element effect and apparent inversion of configuration in the substitution of **1** by p-$TolS^-$ in DMSO.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on the neat samples with a Perkin-Elmer IR 157G instrument, and NMR analysis was performed with a Bruker AMX 400 instrument at 400, 100, and 376 MHz for ^1H, ^{13}C, and ^{19}F nuclei, respectively, in $CDCl_3$ solutions. Mass spectra were recorded with a Varian MAT 311 instrument at 70 eV. GCMS and CI-GCMS analyses were carried out on a Finnigan ITS 40 mass spectrometer with a capillary SE 30 column and isobutane as an ionizing gas in the CI experiments. X-ray powder diffraction patterns were taken on a Phillips PW 1710 diffractometer with Ni-filtered Cu-K_α radiation (40 kV and 35 mA). Column chromatography was performed on dry silica column (Kieselgel 60) using petroleum ether as an eluent. 1,2-Dibromo-1,2-difluoroethylene (**1**) and tribromofluoroethylene (**2**) were prepared from *sym*-tetrabromoethane according to the literature.[6] Compound **1**, bp 70 °C, was purified by distillation which gave a mixture of the *E*/*Z* isomers, which showed only two peaks on a 5% SE-30 GC column and two signals in the ^{19}F spectrum. The presence of impurities, such as $CF_2{=}CFBr$ (bp −2.5 °C), is therefore excluded.

Reactions of 1 with Sodium Methoxide. (a) **1** (1.1 g, 5 mmol) was dissolved in a solution of 1 M NaOMe in MeOH (10 mL), and the tube was sealed. The mixture was heated in an oil bath (75–80 °C) for 40 h, cooled, poured into ice–water, and extracted with $CHCl_3$. After evaporation of the solvent distillation at 130–150 °C yielded 0.5 g (67%) of a 2:1 mixture of methyl dimethoxyacetate (**3**)[9] [^1H NMR ($CDCl_3$) δ: 3.43 (6H, s, $(MeO)_2C$), 3.81 (3H, s, OMe), 4.83 (1H, s, CH)] and methyl bromofluoroacetate **4**.[10] ^1H NMR ($CDCl_3$) δ: 3.91 (3H, s, Me), 6.60 (1H, d, J_{HF} = 50.5 Hz, CH). ^{19}F NMR ($CDCl_3$) δ: −151.12 (d, J_{HF} = 50.5 Hz).

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(b) A similar reaction mixture was kept in a thick-wall sealed tube at 130 °C for 15 h, cooled to −30 °C, and opened, and the gas evolved was trapped in a dry ice cooled $CDCl_3$/TMS in an NMR tube which was then sealed. ^1H NMR [($CDCl_3$) δ 3.20] and ^{13}C NMR [($CDCl_3$) δ 60.66] identified the compound as dimethyl ether **5**. The residue after evaporation of **5** contained both **3** and **4** as in part a above.

(c) A solution of **1** (0.45 g, 2 mmol) in 0.64 M MeONa in MeOH (3 mL) was kept in a sealed ampule at 70–80 °C for 8 h. After cooling, the mixture was divided to two parts. The first one was diluted with $CDCl_3$ (1:1) and analyzed by ^{19}F NMR. The second one was diluted with water (15 mL), extracted with $CDCl_3$, washed with water (5 mL), dried, and analyzed by ^1H and ^{19}F NMR. Compounds **3**, **4**, and **6**–**8** were detected. The results of the analysis are given in the Results.

Reaction of 2 with Sodium Alkoxides. (a) **2** (1.4 g, 5 mmol) was dissolved in 1 M NaOMe solution in MeOH (5 mL) and kept overnight at 30–40 °C until all the alkali was consumed. After conventional water–ether workup and distillation at 50 °C at 18 mm 1-fluoro-2,2-dibromovinyl methyl ether (**15**)[15] (0.8 g, 68%) was obtained. ^1H NMR ($CDCl_3$) δ: 3.83 (d). ^{19}F NMR ($CDCl_3$) δ: −81.37 (q, $^4J_{HF}$ = 1.2 Hz) (lit.[15] ^1H NMR 3.81; ^{19}F NMR −80.7; $^4J_{HF}$ = 1.2).

(b) **2** (2.8 g, 10 mmol) was dissolved in a 1.1 M solution of RONa (R = Me, Et) in ROH (40 mL). The reactions were performed and worked up as for **1** in part a above. The esters **14** were obtained in 80–85% yield and identified by comparison with authentic samples prepared previously.[15] ^1H NMR ($CDCl_3$) δ: **14** (R = Me) 3.88 (3H, s, Me), 5.83 (1H, s, $CHBr_2$); **14** (R = Et) 1.33 (3H, t, Me), 4.31 (2H, q, J = 7.0 Hz), 5.82 (1H, s, $CHBr_2$).

Reactions of 1 with Sodium 2-Ethoxyethoxide. Sodium metal (0.23 g, 10 mmol) was dissolved in cellosolve (20 mL), and **1** (2.2 g, 10 mmol) was added. The reaction mixture was kept overnight at 30–40 °C until the consumption of all the alkali, most of the solvent was then evaporated under vacuo, and the residue was distilled off to dryness under vacuo. The remainder was a mixture of NaF and NaBr by X-ray powder diffraction. The distillate was diluted with water (100 mL), and the organic layer was separated, washed with water (10 mL), and dried ($CaCl_2$), giving 1.2 g (52%) of a Z/E mixture of ether **12**, bp 65–70 °C/120 mm. The low yield is probably due to the close boiling points of **12** and cellosolve and a low solubility of **12** in water–cellosolve mixtures. ^1H NMR ($CDCl_3$) δ: 1.22 (3H, t, CH_3), 3.55 (4H, m, CH_2CH_2), 3.72 (2H, m, CH_2). ^{19}F NMR ($CDCl_3$) δ: −98.98 (d of t, $^4J_{HF}$ = 1.2 Hz, α-F in **12**-E), −115.87 (d of t, $^4J_{HF}$ = 1.2 Hz, α-F in **12**-Z), −132.51 (d, β-F in **12**-E, J_{FF} = 37.8 Hz), −138.83 (d, β-F in **12**-Z, J_{FF} = 124.0 Hz). Mass spectrum m/z (relative abundance, assignment): 232, 230 (8, 7, M), 185, 183, (7, 6, M − H − EtOH), 160, 158 (72, 84, M − $EtOCH{=}CH_2$), 159, 157 (20, 20, C_2BrF_2O), 140, 138 (45, 45, C_2BrFO), 131, 129 (100, 99, CF_2Br). High resolution of parent peaks: 229.9757; 231.9764. Calcd for $C_6H_9BrF_2O_2$: 229.9754, 231.9754. The compound was purified by preparative GC on a 10- × 22-mm 5% XE-60 or chezasorb column at 120 °C. Anal. Calcd for $C_6H_9BrF_2O_2$: C, 31.19; H, 3.93; Br, 34.59; F, 16.45. Found: C, 31.09; H, 3.67; Br, 34.89; F, 16.86.

^{19}F NMR of the crude material before distillations displayed, besides the four doublets of **12**-E/Z, two singlets in 1:2 ratio at −85.30 and −115.77 ppm, whose integration was ca. 5% of that of the signals of **12**. They were tentatively assigned to **13**-E and -Z.

2-Ethoxyethyl Bromofluoroacetate (9). A solution of **1** (1.1 g, 5 mmol) in cellosolve ((30 mL) to which Na (0.23 g, 10 mmol) was added was refluxed for 1 h. The mixture was poured into water (150 mL) and extracted with $CHCl_3$ (30 mL), and the organic phase was dried ($CaCl_2$). Fractional distillation gave 2-ethoxyethyl bromofluoroacetate (**9**) (0.8 g, 70%). Bp: 70–75 °C at 80 mm. ^1H NMR ($CDCl_3$) δ: 1.23 (3H, t, Me), 4.16 (4H, m, CH_2OCH_2), 4.43 (2H, t, $COOCH_2$), 6.62 (2H, d, J_{HF} = 50.5 Hz, CHFBr). ^{19}F NMR ($CDCl_3$) δ: −151.13 (d, J_{HF} = 50.5 Hz). CIMS (isobutane): 231, 229 (100, 99, M), 185, 183 (9, 9, M − EtOH). Anal. Calcd for $C_6H_{10}BrFO_3$: C, 31.46; H, 4.40; Br, 34.89; F, 8.29. Found: C, 31.17; H, 4.60; Br, 35.17; F, 8.64. Compound purified for analysis as for **12** above.

Reactions of 1 with Sodium *p*-Toluenethiolate in MeOH. 1,2-Dibromo-1,2-difluoroethylene (**1**) (2.2 g, 10 mmol) was added to a solution of *p*-toluenethiol (2.4 g, 20 mmol) in a 1 M MeONa solution (20 mL), and the mixture was refluxed for 1 h until all the alkali was consumed. After water–ether workup the organic solvent was dried ($CaCl_2$), the solvent was evaporated, and the residue was distilled in vacuo giving two fractions. The fraction boiling at 140 °C at 0.5 mm (0.8 g, 33%) is di-*p*-tolyl disulfide (**16**). Mp: 41–3 °C. ^1H NMR ($CDCl_3$) δ: 2.30 (2H, s, Me), 7.37, 7.08 (4H, AB q, Ar, J = 8.3 Hz) (lit.[41] ^1H NMR 2.32, 7.1, 7.4). Mass spectrum m/z (relative abundance, assignement): 246 (41, M), 123 (78, TolS), 91 (100, C_7H_7).

The low-boiling fraction (45 °C at 0.5 mm, 2.0 g) was separated by column chromatography to two products, methyl *p*-tolyl sulfide (**17**) (0.5 g, 37%) and 1,2-difluorovinyl *p*-tolyl sulfide (**18**) (1.35 g, 73%).

17. ^1H NMR ($CDCl_3$) δ: 2.31 (3H, s, CH_2), 7.11, 7.18, (4H, AB q, J = 8.3 Hz, Ar) (lit.[42] ^1H NMR 7.15, Ar). Mass spectrum m/z (relative abundance, assignment): 138 (46, M), 123 (100, TolS), 91 (76, C_7H_7), 77 (31, Ph).

18. Colorless oil. ^1H NMR ($CDCl_3$) δ: 2.35 (3H, s, CH_3), 6.78 (0.8H, d of d, ═CH in **18**-E, $^2J_{HF}$ = 74.72 Hz; $^3J_{HF}$ = 12.39 Hz), 7.16, 7.33 (4H, AB q, J = 8.4 Hz, Ar), 7.41 (0.2 H, d of d, ═CH in **18**-Z, $^2J_{HF}$ = 77.5 Hz, $^3J_{HF}$ = 0.28 Hz). ^{19}F NMR ($CDCl_3$) δ: −114.51 (d of d, α-F in **18**-E, J_{HF} = 12.4 Hz; J_{FF} = 14.07 Hz), −158.24 (d of d, β-F in **18**-E, J_{HF} = 74.72 Hz, J_{FF} = 14.07 Hz), −138.31 (d, α-F in **18**-Z, J_{FF} = 145.55 Hz), − 158.24 (d of d, β-F in **18**-Z, J_{HF} = 77.5 Hz, J_{FF} = 145.55 Hz). Mass spectrum m/z (relative abundance, assignment): 186 (100, M), 171 (25, M − Me), 123 (73, TolS), 91 (31, C_7H_7), 77 (15, Ph), 63 (16, C_2HF_2). Anal. Calcd for $C_9H_8F_2S$: C, 58.05; H, 4.33; F, 20.41; S, 17.21. Found: C, 58.14; H, 4.27; F, 20.23; S, 17.04%.

Reactions of 1 with Sodium *p*-Toluenethiolate in DMSO. To a solution of **1** (2.2 g, 10 mmol) in dry DMSO (20 mL) was added dry *p*-TolSNa (2.9 g, 20 mmol). The mixture was kept for 0.5 h at rt, poured into water (200 mL), and extracted with $CHCl_3$ (2 × 15 mL), the extract was washed with water (10 mL) and dried ($CaCl_2$), and the solvent was evaporated. The residue was chromatographed on a silica column giving 1-bromo-1,2-difluorovinyl *p*-tolyl sulfide **19** as a yellow oil (0.8 g, 30%) and 1,2-difluoro-1,2-bis(*p*-tolylthio)ethylene (**20**), mp 87–88 °C (1.1 g, 35%), each as an E/Z mixture. We failed to separate the E/Z mixtures of **18**–**20** by chromatography on silica, using 0:100 to 30:70 $CHCl_3$–petroleum ether eluent.

19. ^1H NMR ($CDCl_3$) δ: 2.35 (3H, s, Me), 7.17, 7.35 (4H, AB q, J = 7.5 Hz, Ar). ^{19}F NMR ($CDCl_3$) δ: −83.82 (d, α-F in **19**-Z), −106.84 (d, β-F in **19**-Z; J_{FF} = 16.15 Hz); −102.34 (d, α-F in **19**-E), −118.62 (d, β-F in **19**-E, J_{FF} = 146.48 Hz). Mass spectrum m/z (relative abundance, assignment): 266, 264 (66, 68, M), 251, 249 (7, 7, M − Me), 185 (30, M − Br), 170 (58, M − Br − Me), 143, 141 (100, 98, M − TolS), 123 (21, TolS), 51 (15, C_7H_7). Anal. Calcd for $C_9H_7BrF_2S$: C, 40.77; H, 2.66; Br, 30.14; F, 14.33; S, 12.09. Found: C, 40.89; H, 2.78; Br, 29.91; F, 14.18; S, 12.28.

20. ^1H NMR ($CDCl_3$) δ: 2.34 (3H, s, Me), 7.14, 7.34 (4H, AB q, J = 8.2 Hz, Ar). ^{19}F NMR ($CDCl_3$) δ: −98.93 (s, **20**-Z), −114.42 (s, **20**-E). Mass spectrum m/z (relative abundance, assignment): 308 (59, M), 185 (100, M − TolS), 170 (13, M − TolS − Me), 141 (56, $C_8H_7F_2$), 123 (29, TolS), 91 (35, C_7H_7). Anal. Calcd for $C_{16}H_{14}F_2S_2$: C, 62.31; H, 4.58; F, 12.32; S, 20.79. Found: C, 62.16; 4.45; F, 12.40; S, 20.58.

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