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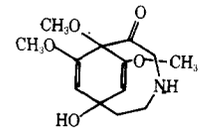

i

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Reaction of Crystalline Fluoro Olefins with Bromine Vapor. 2. Solid-State vs. Solution Stereospecificity for (*E*)- and (*Z*)-1-Substituted-2-chloro-*F*-ethene and -*F*-propene[1]

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Received July 18, 1978

The addition of bromine to (*E*)- and (*Z*)-*p*-$HO_2CC_6H_4CF{=}CFX$ (X = Cl, CF_3) in solution and in the solid has been studied under ionic and radical conditions. For X = Cl, ionic addition leads to the *trans*-dibromo adduct in solution and in the solid–gas reaction. The radical solution reactions show stereoselective formation of the erythro isomer, while the radical solid–gas reactions may indicate a slight preference for cis addition. For X = CF_3, the *Z* isomer preferentially adds bromine cis in the solid state under either ionic or radical conditions. The *E* isomer also shows a preference for cis addition, but the solid-state reaction is complicated by competing mechanisms. The solution reactions for X = CF_3 are mainly nonstereoselective.

The addition of molecular bromine to a polyfluorinated olefin in solution is usually performed under radical conditions which quite often exhibit little stereochemical control over the products.[2] We were interested in the stereospecificity of the solid–gas reaction between a solid fluorinated olefin and bromine vapor to determine the change in stereochemistry due to reaction occurring in the solid state. We now report that the radical reaction between solid fluorinated olefins and bromine vapor shows a preference for cis addition of bromine. In addition, two paths have been observed for the ionic addition, an open cation and a bridged bromonium ion, with each leading to different reaction stereospecificity.

Hadjoudis and Schmidt have reported the ionic addition of bromine vapor to solid α,β-unsaturated acids, amides, and ketones to give the trans adducts.[3] However, this could be expected because of the intermediacy of a bromonium ion in the reaction. Previously it had shown that 2-substituted-*F*-propene derivatives add bromine only under radical conditions and that a carboxy group is necessary to prevent ex-

$$RCF{=}CFX \xrightarrow{Br_2} RCFBrCFBrX$$

1, X = Cl; R = 4-$HO_2CC_6H_4$–
2, X = CF_3; R = 4-$HO_2CC_6H_4$–

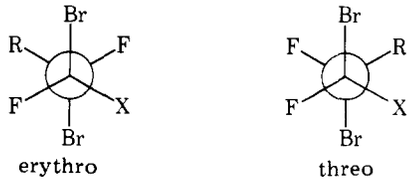

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Table I. Bromination Reactions: Solution and Solid-Gas

		reaction conditions;[a] erythro/threo ratio[b]							
		HOAc[c]		$CF_2ClCFCl_2$[c]		solid-gas[d]			
compd no.	X	dark	$h\nu$	dark	$h\nu$	dark	$h\nu$	$h\nu$ (high int.)[e]	$h\nu$ (5 °C)
(*Z*)-1	Cl	90:10	76:24[j]		77:23	80:20	78:22	70:30	83:17
(*E*)-1	Cl	28:72	74:26	*f*	74:26	28:72	38:62	56:44	21:79
(*E*)-2	CF_3	59:41[g]	53:47[k]	*f*	51:49	46:54	38:62	50:50	50:50[h]
(*Z*)-2	CF_3	55:45[i]	51:49	*f*	48:52	75:25	74:26	71:29	76:24

[a] Reactions were performed at room temperature except for the last column (the incandescent lamp used in the photolytic reactions did not raise the temperature). Reaction times for dark reactions were ~80 h, solution photolytic reactions were ~12 h, and solid-gas photolytic reactions for 1 were 12 h and 2 24 h; yields were ≥ 65% unless noted. [b] ±3%, determined by ^{19}F NMR; isomerization of the starting olefin was not observed under the reaction conditions. [c] Solvent for the reaction. [d] Reactions were performed twice, the average is given; the reactions of (*E*)-2 were performed three times; the diastereomer ratios were found to be independent of the age or batch of the olefin. [e] ~10–12-fold increase in photon flux.. [f] <5% yield. [g] 46% yield. [h] 28% yield. [i] 27% yield. [j] Registry no. 68423-95-0/68423-96-1. [k] Registry no. 68423-97-2/68423-98-3.

tensive solution formation with liquid bromine.[1b] Thus, (*E*)- and (*Z*)-1-(4′-carboxyphenyl)-2-chloro-*F*-ethene (**1**) and (*E*)- and (*Z*)-1-(4′-carboxyphenyl)-*F*-propene (**2**) were selected for examination of the stereospecificity of the addition reaction with bromine.

Results and Discussion

The results of the solution and solid-gas reactions are given in Table I. The solution reactions were performed in polar (acetic acid) and nonpolar solvents ($CF_2ClCFCl_2$).

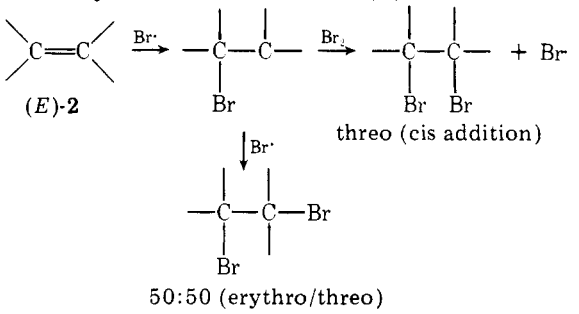
The stereochemistry of the solution reactions of the chloro olefins, (*Z*)-**1** and (*E*)-**1**, reveals a marked dependence upon the reaction conditions. Radical conditions ($h\nu$ in either solvent) led to the preferential formation of the erythro diastereomer from either isomer. Ionic conditions (acetic acid in the dark) resulted in the trans addition of bromine being the major route. This is consistent with a bromonium ion being an intermediate in the reaction.

The solid-gas reactions of (*Z*)-**1** and (*E*)-**1** each showed high reactivity with bromine, even in the dark. This dark reactivity is in sharp contrast with 2-(3′- or 4′-carboxyphenyl)-*F*-propene ($HO_2CC_6H_4C(CF_3)=CF_2$), which was completely unreactive in the dark.[1b] In the dark, each isomer readily added bromine and preferentially formed the trans adduct. In room light, the erythro/threo ratios were only slightly changed from the values for the dark reactions; evidently, the ionic mechanism was competing effectively with the radical pathway for addition to the double bond. Increasing the intensity of the light caused the radical reaction to predominate. For (*E*)-**1** the erythro/threo ratio approached the solution value, while for (*Z*)-**1** the erythro/threo ratio became slightly less than the solution value. This may be due to cis addition of bromine starting to become important (vide infra). In these reactions, in addition to the reactions of **2**, microscopic examination did not reveal any melt formation between liquid bromine and the solid olefin.

The trifluoromethyl olefins, (*E*)-**2** and (*Z*)-**2**, were less reactive than **1** toward ionic bromination in acetic acid. With reaction times comparable to **1** (which gave 75% yields), only yields of 46 and 27% were realized from (*E*)-**2** and (*Z*)-**2**, respectively. In these dark reactions, (*E*)-**2** showed a slight preference for the erythro diastereomer, trans addition of bromine, while (*Z*)-**2** was essentially nonselective. As with (*E*)-**1**, low reactivity was found for the dark reactions in $CF_2ClCFCl_2$, a nonpolar, nonionizing solvent. The photolytic solution reactions in either solvent for (*E*)-**2** and (*Z*)-**2** were nonstereoselective. This would be expected for a radical addition reaction.

The solid-gas reactions of (*Z*)-**2** demonstrated a preference for cis addition of bromine. Both the ionic (dark) and the free-radical ($h\nu$) reactions favored the erythro isomer, ca. 3:1. The ionic reaction cannot involve a bromonium ion, otherwise trans addition would have been expected to predominate. An increase in the intensity of the light did not drastically affect the erythro/threo ratio, as was the case for **1**. (A reported example of cis addition of bromine in solution is the radical, stereospecific bromination of fluorinated norbornenes to yield the *exo-cis*-dibromides.[4]) Curtin and Paul have noted that *trans*-stilbene undergoes a solid-gas reaction with chlorine to give only the *dl*-stilbene dichloride (cis addition of chlorine); in solution a 2:1 mixture of *dl*/meso is formed.[5] The cis addition of bromine to (*Z*)-**2** can be attributed to the decreased molecular freedom in the solid state.

Cis addition was also favored for (*E*)-**2**, but to a lesser degree. The solid-gas reaction, however, is complicated by what appears to be competing processes. The reaction of (*E*)-**2** in the solid state with exposure to more intense light causes a loss of stereospecificity. A possible explanation for this result is two pathways for the bromination of (*E*)-**2**.



The chain propagation step, reaction with Br_2, gives a slight preference to the cis adduct. This is seen in the 38:62 diastereomer ratio for the solid-gas reaction under "normal" illumination. The competing path is a chain termination step where Br· reacts with the radical to give equal amounts of the diastereomers. This path is favored by more intense light as this increases the bromine atom concentration.

This mechanism was supported by additional experiments with (*E*)-**2**. First, the solid-gas reaction at 5 °C gave a 50:50 diastereomer ratio. This loss of stereospecificity is caused by a decrease in the rate of the chain propagation step. This would be expected as the reaction of the intermediate radical with Br_2 would have a higher activation energy than the reaction with Br·. For comparison, the solid-gas reactions at 5 °C for (*E*)-**1**, (*Z*)-**1**, and (*Z*)-**2** resulted in an increase in stereospecificity of the reaction. Second, a decrease of the bromine concentration in the reaction chamber yielded a 47:53 diastereomer ratio. The lower bromine concentration forces the chain termination step to become dominant.

The dibromo adducts from (*E*)-**1**, (*Z*)-**1**, and (*Z*)-**2** were formed as polycrystalline phases during the solid-gas reaction. The X-ray powder pattern of the product formed in the solid-gas reaction was identical with the powder pattern of the product after it had been recrystallized from ether.

Table II. Debromination Studies
p-$RC_6H_4CFBrCFBrX \rightarrow p$-$RC_6H_4CF{=}CFX$

R	X	erythro/threo[a]	reagents	E/Z[b]
H	Cl	78:22[c]	Mg/ether	19:81[e]
		78:22	Zn/dioxane	20:80
		71:29	NaI/acetone	28:72
H	CF_3	48:52[d]	Zn/dioxane	84:16[f]
		48:52	NaI/acetone	48:52
HO_2C	CF_3	74:26	NaI/acetone	71:29

[a] ±3% by ^{19}F NMR analysis. [b] ±3% for R = H by GLC analysis and for R = CO_2H by ^{19}F NMR. [c] Registry no. 68423-99-4/68424-00-0. [d] Registry no. 68424-01-1/68424-02-2. [e] Registry no. 7422-19-7/10575-55-0. [f] Registry no. 4683-67-4/19140-58-0.

The stereochemical structural assignments of the diastereomeric dibromoadducts were accomplished by the E2 debromination reactions listed in Table II. The diastereomers of $C_6H_5CFBrCFBrCl$ were debrominated stereospecifically back to $C_6H_5CF{=}CFCl$ by either Mg, Zn,[6] or NaI.[7] Control experiments showed that neither isomer of the olefin was isomerized by the reaction mixture. The erythro and threo assignments were supported by the observed predominance of the trans addition of bromine to (*Z*)-**1** and (*E*)-**1** in acetic acid in the dark (Table I).

The diastereomers of $C_6H_5CFBrCFBrCF_3$ could only be debrominated stereospecifically by NaI. Debromination with Zn led to stereoselective formation of (*E*)-$C_6H_5CF{=}CFCF_3$. A control reaction showed that neither (*E*)- nor (*Z*)-$C_6H_5CF{=}CFCF_3$ was isomerized by the NaI/acetone reaction mixture.

In conclusion, there is a preference for the cis addition of bromine to (*E*)-**2** and (*Z*)-**2**. The reactions of (*Z*)-**1** and (*E*)-**1** demonstrate the change in stereospecificity with a change from an ionic to a radical reaction mechanism. Finally, a comparison of the ionic brominations of **1** with **2** demonstrates a difference in mechanism. A bromonium ion is involved with **1**, while a nonbridged, open cation is the major intermediate for **2**. Evidently, the highly electronegative trifluoromethyl group decreases the ionic reactivity and also destabilizes the bromonium ion. Steric interactions may also be important as the trifluoromethyl group is larger than the chlorine atom and also about the same as a phenyl group.

Experimental Section

Melting points were determined on a hot stage and are uncorrected. ^{19}F NMR spectra were obtained on a Varian T-60 spectrometer operated at 56.4 MHz. Mass spectral analysis was performed on a Perkin-Elmer Hitachi RMU-7 double-focusing mass spectrometer. X-ray powder photographs were recorded on conventional cameras with nickel-filtered Cu radiation.

F-Propene and chloro-*F*-ethene were obtained from PCR Research Chemicals. *n*-Butyllithium was obtained from Alfa, Ventron.

Preparation of 1-(4′-Bromophenyl)-2-chlorodifluoroethylene. A procedure similar to that described for the preparation of $C_6H_5CF{=}CFCl$ and $C_6H_5CF{=}CFCF_3$[8] was followed. Thus, *n*-butyllithium (50 mmol, 20.8 mL of a 2.4 M solution in hexane) was added to 50 mmol (11.8 g) of *p*-dibromobenzene in 50 mL of anhydrous ether at 0 °C. The resultant solution was then slowly added to a solution of 0.100 mol (11.65 g) of chloro-*F*-ethene in 50 mL of anhydrous ether at −30 °C. After addition of the organolithium, the solution was allowed to warm to room temperature. The reaction mixture was hydrolyzed with aqueous acid, the ether layer was washed and dried (molecular sieves), and the ether was removed.

The *E* and *Z* isomers of $BrC_6H_4CF{=}CFCl$ (and also of $BrC_6H_4CF{=}CFCF_3$) were separated by preparative GLC on an 8-ft 20% Apeizon-L column at 195 °C.[9]

Preparation of the Carboxy-Substituted Olefins (*E*)-1, (*Z*)-1, (*E*)-2, and (*Z*)-2. The procedure described previously was followed.[1b] The physical properties of the olefins are given in Table III.

General Procedure for the Gas–Solid Reactions. A 50-mg amount of the olefin was powdered and placed in one side of a heavily creased 20-mL flask. The flask was flushed with nitrogen, and ca. 0.5 mL of liquid bromine was placed in the other side of the flask. The sample was dissolved in acetone, and the ^{19}F NMR spectrum was recorded.

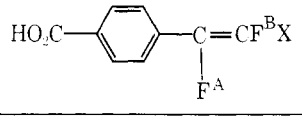
E2 Debromination with Zinc. An *E*/*Z* mixture of $C_6H_5CF{=}CFCl$ (1.18 mmol, 207 mg) was mixed with 3 mL of $CF_2ClCFCl_2$. Several drops of bromine were added, and the solution was irradiated. After GLC analysis showed complete consumption of the olefin, trimethylethylene was added to scavenge excess bromine. Volatiles were removed, and the residue was dissolved in dioxane. ^{19}F NMR indicated a 78:22 erythro/threo product distribution.

Additional dioxane was added to bring the volume to 3 mL, and ca. 0.6 g of Zn dust was added. The solution was gently heated and stirred overnight under nitrogen. GLC analysis using naphthalene as an internal standard revealed 0.79 mmol of (*Z*)-$C_6H_5CF{=}CFCl$ and 0.20 mmol of (*E*)-$C_6H_5CH{=}CFCl$ (80:20 *Z*/*E*).

E2 Debromination with NaI.[7] Approximately 50 mg of (*Z*)-$HO_2CC_6H_5CF{=}CFCF_3$ was allowed to react with bromine vapor in a gas–solid reaction as described above. ^{19}F NMR analysis in acetone showed a 74:26 erythro/threo ratio and no unreacted olefin.

The solution was diluted to 15 mL in acetone, ca. 1 g of NaI was added, and the solution was refluxed overnight. The reaction mixture was cooled, extracted into ether, washed with $Na_2S_2O_3$ solution, and dried (molecular sieves), and the ether removed. ^{19}F NMR analysis

Table III. Physical Constants of Fluorinated Olefins[a]



compd	X	mp, °C	^{19}F NMR[b] ϕ^*_{FA}	ϕ^*_{FB}	$\phi^*_{CF_3}$	$J_{FA,FB}$	J_{FA,CF_3}	J_{FB,CF_3}
(*E*)-1	Cl[c]	165–167[d]	134.1	101.2		13.9		
(*Z*)-1	Cl[c]	215–218	148.6	114.6		127.4		
(*E*)-2	CF_3[e]	206–210	145.0	167.0	66.1	132.8	22.6	10.7
(*Z*)-2	CF_3[e]	125–127	108.5	154.1	65.0	8.1	8.4	12.4

[a] Satisfactory carbon–hydrogen analysis was obtained for each compound; each compound gave a mass spectrum consistent with its structure. [b] Chemical shifts are in parts per million upfield from internal $CFCl_3$, ±0.1 ppm; coupling constants are in hertz, ±0.5 Hz. [c] Consistent with the ^{19}F NMR values reported for (*E*)- and (*Z*)-$C_6H_5CF{=}CFCl$.[9,10] [d] Lit.[11] mp 165–166 °C for HO_2C-$C_6H_4CF{=}CFCl$ (stereochemistry not specified). [e] Consistent with the ^{19}F NMR values reported for (*E*)- and (*Z*)-$C_6H_5CF{=}CFCF_3$.[12]

Table IV. ^{19}F NMR Data of Dibromo Diastereomers [a]

$RC_6H_4CBrCBrX$
F^A F^B

compd	R	X	$\phi^*_{F^A}$	$\phi^*_{F^B}$	$\phi^*_{CF_3}$	J_{F^A,F^B}	J_{F^A,CF_3}	J_{F^B,CF_3}
erythro[b]	H	Cl	113.6	66.8		25.3		
threo[b]	H	Cl	112.1	65.5		25.2		
erythro	4-CO_2H	Cl	109.8	59.2		25.3		
threo	4-CO_2H	Cl	106.7	57.1		25.2		
erythro	H	CF_3	125.0[c,d]	115.0[c]	69.1	22.9	9.0	14.3
threo	H	CF_3	125.0	111.4	69.7	27.5	10.7	10.7
erythro	4-CO_2H	CF_3	122.6	116.7	69.9	23.7	9.2	14.7
threo	4-CO_2H	CF_3	122.6	112.8	70.5	26.4	10.8	10.8

[a] See footnote *b* of Table III; recorded as erythro/threo mixtures; all spectra were first order in appearance. [b] Chemical shifts and coupling constants are in agreement with those reported for *erythro*- and *threo*-ClCFBrCFBrCF=CFCl.[13] [c] Chemical shift assignments for F^A and F^B are based on $J_{F^A,CF_3} < J_{F^B,CF_3}$.[14] [d] Overlap of the F^A peaks for erythro and threo occurred.

showed a 71:29 mixture of (*E*/*Z*)-$HO_2CC_6H_4CF{=}CFCF_3$. No other resonances were observed in the spectrum. The experiment was repeated with the same results.

Reaction of (*Z*)-$C_6H_5CF{=}CFCF_3$ with NaI and Br_2 in Acetone. In a 50-mL flask were placed 0.148 mmol of (*Z*)-$C_6H_5CF{=}CFCF_3$ (30.8 mg), 20 mL of acetone, and 6.7 mmol (1 g) of NaI. The solution was stirred, and 0.50 mmol (80 mg, 26 μL) of bromine was introduced. The mixture was refluxed under nitrogen. After 30 h 0.180 mmol (28.9 mg, 25 μL) of mesitylene was added as an internal standard. GLC analysis then showed a 96% recovery of (*Z*)-$C_6H_5CF{=}CFCF_3$ and no (*E*)-$C_6H_5CF{=}CFCF_3$.

Similar experiments with (*E*)-$C_6H_5CF{=}CFCF_3$ and $C_6H_5CF{=}CFCl$ demonstrated that isomerization did not occur in the reaction solution.

Characterization of Dibromo Adducts. The adducts were prepared in $CF_2ClCFCl_2$ from samples of **1**, **2**, $C_6H_5CF{=}CFCl$, and $C_6H_5CF{=}CFCF_3$. After removal of the solvent, the adducts were purified by fractional sublimation or flash distillation. Mass spectral analysis of $C_6H_5CFBrCFBrCl$ and $C_6H_5CFBrCFBrCF_3$ had $M^{+\cdot}$ peaks of 3 and 1%, respectively, at 15 eV. However, the adducts from **1** and **2** had the $(p\text{-}Br_2)^{+\cdot}$ ion as the highest *m*/*e* peak. In each of these adducts the 100% peak was $(p\text{-}Br_2)^{+\cdot}$.[1b] The ^{19}F NMR spectrum of each adduct is listed in Table IV.

Acknowledgment. The author would like to thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No.—(*Z*)-**1**, 68423-92-7; (*E*)-**1**, 68423-93-8; (*Z*)-**2**, 68423-94-9; (*E*)-**2**, 955-42-0; (*E*)-1-(4′-bromophenyl)-2-chlorodifluoroethylene, 7422-21-1; (*Z*)-1-(4′-bromophenyl)-2-chlorodifluoroethylene, 7422-44-8; *p*-dibromobenzene, 106-37-6; chloro-*F*-ethene, 79-38-9.

References and Notes

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