12a. Similar results were obtained from electron impact mass spectrometry. Cryoscopic data for related compounds such as dimethyl selenide dichloride indicate a preferred monomeric state in solution.

A monomeric intermediate could be formed by a nucleophilic attack by the alkene on the dimer forming ion **18** and a $CH_3SeCl_4^-$ counterion. Work continues on this problem.

Experimental Section

All melting points are uncorrected. Microanalyses were carried out by A. B. Gygli Microanalysis Laboratory. ^1H NMR spectra were run on a Varian T-60 or HA-100 spectrometer. ^{13}C NMR spectra were run on a Varian CFT-20 spectrometer using a 16K memory. Chloroform-*d* was used as an internal lock and reference. All spectra were referenced to Me_4Si as an internal standard. The olefins were obtained commercially and their purity verified by GLC and ^1H NMR.

β-Methylselenium trichloride was prepared by the method of Wynne and George.[3a]

Methylene chloride was purified as previously described.[2]

The determination of product compositions and the preparation of analytical samples were carried out as previously described.[6] The elemental analyses for the adducts are given in Table V where available.

No evidence of a molecular ion was found in the mass spectra of the adducts. This is in agreement with previous studies on the mass spectral fragmentation of dialkyl selenide dichlorides.[9] Characteristic peak clusters representative of loss of chlorine radical and molecular chlorine from the molecular ion were observed. For adducts **9b** and **10b**, a cleavage of the $M^+ - Cl_2$ fragment with loss of C_6H_5CHCl to give a $CH_3Se{=}CHCH_3^+$ cation radical at *m/e* 123 was observed. Such a result is consistent with the Markownikoff orientation of the adducts **9b** and **10b**.

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(6) For compound **16:** ^1H NMR δ 1.74 s (3 H), 3.03 s (3 H) (J_{SeCH} = 8 Hz), 3.20, 3.23 AB q (2 H) (J_{HCH} = 12.5, J_{SeCH} = 7 Hz), 3.90, 3.98 AB q (2 H) (J_{HCH} = 13 Hz); MS M^+ *m/e* 220 (calcd, 220.0012).

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Reaction of Crystalline Fluoro Olefins with Bromine Vapor[1]

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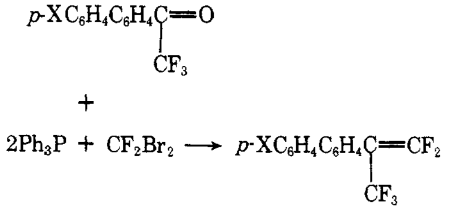
Crystalline fluoro olefins of general structure 4-R-$C_6H_4C(CF_3){=}CF_2$ (R = Ph, 4′-ClC_6H_4, 4′-BrC_6H_4, 4′-MeC_6H_4, 4′-$HO_2CC_6H_4$, and HO_2C) and 3-$HO_2CC_6H_4C(CF_3){=}CF_2$ have been reacted with bromine vapor. Addition to the double bond occurs only in light, while aromatic substitution is a predominant side reaction in R = Ph and 4′-MeC_6H_4. Exposure of any of the first four olefins to bromine vapor results in the formation of a solution of bromine and the olefin. The reactions of the carboxylic acid substituted olefins are true gas–solid processes as a liquid phase is not formed during the reaction. The addition products are formed as a polycrystalline phase.

The gas–solid addition reactions of halogens with crystalline olefins have been reported with increasing frequency. Very early research was performed primarily for synthetic goals;[2] but recent work has been directed at understanding the influence of the crystal lattice upon the course of the reaction.[3] The gas–solid addition of bromine to substituted cinnamic acids was reported to occur without the formation of a liquid phase on the crystals. The reactions were fast and gave the trans adducts.[4] The gas–solid addition of chlorine to *trans*-stilbene was accompanied by the formation of a hard coating on the surface of the crystals which prevented complete reaction.[5] Finally, an asymmetric synthesis was reported for the reaction of bromine vapor with a single crystal of 4,4′-dimethylchalcone ($P2_12_12_1$).[6] Continuation of this work has correlated the absolute configuration of the starting material in the solid with the optical rotation of the product.[7]

The double bond in polyfluorinated olefins is electron poor, such that the usual reactions are attack by nucleophiles, so brominations of fluorinated olefins are usually performed under conditions which favor radical additions.[8] It was of interest to determine if fluorinated olefins would exhibit relatively high solid-state reactivity toward bromine—as has been reported for cinnamic acid derivatives[4]—and what some of the physical characteristics of these reactions would be under different conditions.

Results and Discussion

The initial phase of the work examined the reactions of substituted 2-(4-biphenylyl)-*F*-propenes, **1**, with bromine vapor. These olefins were conveniently prepared from trifluoromethyl ketones via a Wittig reaction with triphenylphosphine and dibromodifluoromethane[9] (cf. Experimental Section). Interestingly, crystals of these olefins could not be grown until traces of unknown impurity were removed by column chromatography. The 4′-carboxylic acid derivative, **1e**, was prepared from **1c** via the Grignard. The physical

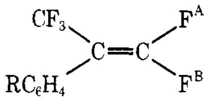


$$p\text{-}XC_6H_4C_6H_4C(CF_3){=}O + 2Ph_3P + CF_2Br_2 \longrightarrow p\text{-}XC_6H_4C_6H_4C(CF_3){=}CF_2$$

1a, X = H
b, X = Cl
c, X = Br
d, X = Me

$$\mathbf{1c} \xrightarrow{Mg} \xrightarrow{CO_2} \xrightarrow[H_2O]{H^+} \mathbf{1e},\ X = HO_2C$$

Table I. Physical Constants of Fluorinated Olefins[a]



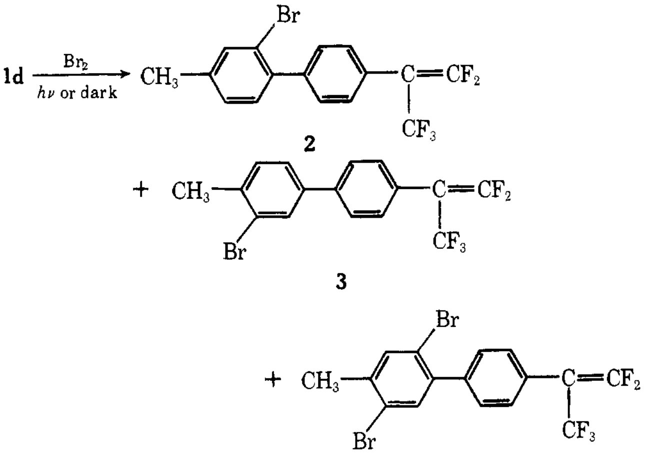
Compd	R	Mp, °C	$\phi^*_{CF_3}$ [b]	ϕ^*_{FA} [b]	ϕ^*_{FB} [b]	J_{FA,CF_3} [c]	J_{FB,CF_3} [c]	$J_{FA,FB}$ [c]
			^{19}F NMR					
1a	p-C_6H_5[d]	85–87	59.8	76.4	78.4	24.2[e]	11.2[e]	12.1
1b	p-(4-ClC_6H_4)[d]	49–52	59.0	75.9	77.1	23.7	11.3	13.9
1c	p-(4-BrC_6H_4)[d]	63–64	59.8	76.1	78.2	24.4	11.4	11.3
1d	p-(4-MeC_6H_4)[d]	92–96	59.0	76.2	77.3	24.6	11.5	15.4
1e	p-(4-$HO_2CC_6H_4$)[f]	216–222	59.0	75.5	77.1	23.3	11.4	11.4
5	p-HO_2C[f]	105–110	59.3	74.5	76.4	23.8	10.0	8.7
6	m-HO_2C[f]	113–115	59.7	75.6	77.1	23.6	10.8	10.8

[a] Satisfactory carbon-hydrogen analysis was obtained for each compound. [b] In parts per million upfield from internal $CFCl_3$, ±0.1 ppm. [c] In hertz, ±0.5 Hz. [d] The crystal morphology was typical for biphenyl derivatives: a fragile leaf. [e] Coupling constants for vinyl fluorines trans to a CF_3 group have been reported in the range of 9–12 Hz, and the cis in the range 21–24 Hz: ref 10. [f] The crystals were elongated plates.

Table II. Reaction of 1a with Bromine

Solvent	Conditions	Products, % yield[a]: p-BrC_6H_4-C_6H_4C(CF_3)=CF_2	$C_6H_5C_6H_4$-C(CF_3)Br-CF_2Br	p-BrC_6H_4-$C_6H_4C(CF)_3$-$BrCF_2Br$
HOAc	hν, 12 h		75	
	Dark, 5 days	7		
CF_2ClC-FCl_2	hν, 1 day		95	
	dark, 5 days		Trace	
Solid–gas	hν, 3 days[b]	35		65
	Dark, 6 h[b]	93	6	<1

[a] GLC yields based on **1a**. [b] Time for complete reaction.



4

properties of these and two other olefins are listed in Table I.

First, the reactivity of **1a** toward bromine was determined in a polar (acetic acid) and a nonpolar solvent ($CF_2ClCFCl_2$). The products, as shown in Table II, indicate that addition to the double bond occurs under only radical conditions (i.e., in the presence of diffuse room light and in either solvent). Aromatic substitution, however, is an ionic reaction and occurs only to a slight extent in acetic acid.

When solid **1a** was exposed to bromine vapor, it quickly dissolved in the bromine which had condensed on the surface of the crystal and aromatic bromination occurred very quickly. This is not unexpected in view of the ease with which biphenyl itself is brominated when exposed to bromine vapor.[11] Bromine addition was a slower reaction and occurred only in the presence of light. Thus, the relative reactivity of addition vs. substitution had been reversed from that observed for the solution reactions.

The competition of the aromatic substitution reaction was eliminated in **1b** by the presence of the chloro substituent. Exposures of crystals of **1b** to bromine vapor again resulted in the formation of a liquid phase. Complete addition of bromine to the double bond occurred after 2 days exposure to room light. In the dark, no reaction was detected after 1 week.

The methyl substituted olefin, **1d**, gave unexpected results. In either the dark or the light, three products were formed initially. These were isolated and each was identified as an aromatic bromide, **2–4**. The mass spectrum of each product had a substantial peak at m/e 207, which was due to the $[C_6H_4C(CF_3){=}CF_2]^+$ ion. This fragment was not present in the spectrum of **1d** and indicated that bromine substitution had occurred in the p-tolyl part of **1d**. The bromine positions were determined by ^{13}C NMR chemical shift assignments (see Table III).

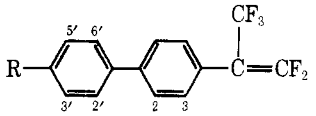
Approximately equal amounts of **2** and **3** were always found. This is not unusual as the directing effects of the methyl substituent and the aryl group would be opposed. Normally the phenyl group would predominate,[14] but the presence of the 2-F-propenyl group would decrease its directing power. Thus, the aryl group and the methyl are observed to be approximately equal in directing ability.

Disappointingly, the reactions of **1a–d** were liquid phase reactions. Attempts to use very low concentrations of bromine vapor still led to the formation of liquid on the surface of the crystals. The apparent solution was to have a substituent which could form strong, intermolecular associations and not form a solution with bromine. Thus, the reaction of **1e** was examined.

Powdered crystals of **1e** reacted slowly with bromine vapor; after 10 days ^{19}F NMR analysis showed a 60% yield of a 1,2-dibromo adduct. Mass spectral data, however, indicated that aromatic substitution had also taken place as the 100% peaks were at m/e 406, 408 ($C_{16}H_8BrF_5O_2$). Two possible structures of the product are given in Table IV. (The exact structure was not determined as the product could not be separated from **1e**. Attempts to completely react **1e** led to the formation of products which contained two aromatic bromines.) The reaction was a true solid–gas reaction as a liquid phase was not formed during the reaction.

As the reaction time was long, it was felt that the rate might be increased if the molecular size of the compound could be

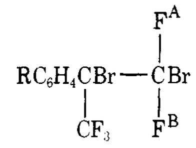
Table III. ^{13}Chemical Shifts of Some Biphenyl Derivatives[a]



Compd	C-2	C-3	C-2′	C-3′	C-5′	C-6′	R	Substituents
1a[b]	−127.46	−130.36	−127.83	−128.90	−128.90	−127.83	H,	None
1b[b]	−127.34	−130.48	−128.41	−129.10	−129.10	−128.41	Cl,	None
1d[c]	(−127.03)[d]	−130.28	(−127.24)[d]	−129.66	−129.66	(−127.24)[d]	Me, −21.10	None
2[c]	(−128.31)[d]	−130.94		−133.69	(−129.50)[d]	−129.88	Me, −20.71	2′-Br
3[c]	−127.25	−130.44	−125.87	−131.14		−130.86	Me, −22.63	5′-Br
4[e]	−129.6	−129.6		−134.78		−134.21	Me, −22.20	2′,5′-Br$_2$

[a] Expressed in δ values (ppm) downfield from Me_4Si (0.0). [b] Assignments are based on comparisons with $PhC(CF_3)=CF_2$ (δ_{ortho} −130.65, δ_{meta} −129.29, δ_{para} −129.97) and the substituent chemical shifts of biphenyl and 4-chlorobiphenyl: ref 12. [c] Assignments based on **1a** plus the substituent chemical shifts for methyl and bromo substituents: ref 13. [d] Similar values in parentheses may be interchanged. [e] Assignments based on substituent chemical shifts observed for **2** and **3** and checked with known methyl and bromo substituent chemical shifts: ref 13.

Table IV. Dibromo Adducts



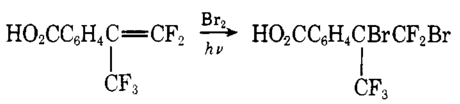
$$RC_6H_4\underset{CF_3}{CBr}-\overset{F^A}{\underset{F^B}{CBr}}$$

Registry no.	R	Mp, °C	^{19}F NMR $\phi^*_{CF_3}$[a]	ϕ^*_{FA}	ϕ^*_{FB}	J_{F,CF_3}[b]	$J_{F,F}$	Mass spectral analysis[c]
61587-29-9	p-C_6H_5	<40	64.6	45.0	50.8	11.7	164.9	$M^+\cdot$ 7%, (p-Br)$^+$ 7%
61587-30-2	p-(4-ClC_6H_4)	*d*	63.8	45.1	50.7	11.9	168.4	$M^+\cdot$, (p-Br)$^+$ not detected
61618-19-7	p-(4-BrC_6H_4)	*d*	63.8	45.1	50.8	12.2	167.4	$M^+\cdot$ not detected, (p-Br)$^+$ 0.7%
61649-92-1	p-(4-$HO_2CC_6H_3Br$)[e]	*f*	63.7	45.2	50.8	13.3	168.9	$M^+\cdot$, (p-Br)$^+$ not detected
61688-30-0[e]								
61587-31-3	p-HO_2C	118–112	63.7	45.3	51.0	12.3	169.2	$M^+\cdot$, (p-Br)$^+$ not detected
61587-32-4	m-HO_2C	148–151	63.8	45.4	51.2	11.6	168.2	$M^+\cdot$ 0.3%, (p-Br)$^+$ 1%

[a] In parts per million upfield from internal $CFCl_3$, ±0.1 ppm. [b] In hertz, ±0.5 Hz. [c] For each compound, the 100% peak was due to $(p\text{-}Br_2)^+\cdot$. [d] The compound is viscous liquid. [e] The isomeric structure, $HO_2CC_6H_4C_6H_3BrCBr(CF_3)CF_2Br$, also fits the observed data. [f] A mixture containing **1e**.

decreased. Thus, **5** and **6** were prepared in a manner analogous for **1e**. These olefins had the additional feature that aromatic bromination should be suppressed as two deactivating substituents were present on the benzene ring.

Powdered crystals of **5** and **6** reacted smoothly with bromine vapor and formed the dibromo adduct as a polycrystalline



$$HO_2CC_6H_4\underset{CF_3}{C}=CF_2 \xrightarrow[h\nu]{Br_2} HO_2CC_6H_4\underset{CF_3}{C}BrCF_2Br$$

5, para
6, meta

phase. Complete reaction required 4 days. The structure of the dibromo adduct was easily confirmed by ^{19}F NMR and mass spectral analysis (see Table IV). The x-ray powder pattern of the product (as formed in the solid–gas reaction) was identical with the powder pattern of the product after it had been recrystallized.

Exposure of powdered crystals of **6** to bromine vapor in the dark resulted in no reaction after 7 days. After this period, the x-ray powder pattern of the reactant was unchanged and was identical with that of original **6**.

Microscopic examination of single crystals of **5** and **6**, when exposed to bromine vapor, did not reveal the formation of a liquid phase on the surface of the crystals. The rate of attack of bromine at each crystal face appeared to be equal.[15]

When $CF_2ClCFCl_2$ was used as a reaction solvent, **5** and **6** were each completely brominated in about 30 h. When this reaction was attempted in the dark, addition did not occur. Thus, the solid-state reactivities of **5** and **6** are roughly comparable to the solution reactivities.

This work is being extended to related systems and will be reported in due course.

Experimental Section

Melting points were determined on a hot stage and are uncorrected. ^{19}F NMR spectra were obtained on a Varian HA-60-IL spectrometer operated at 56.4 MHz; ^{13}C NMR spectra were obtained on a Varian CFT-20 spectrometer. Mass spectral analysis was performed on a Perkin-Elmer Hitachi RMU-7 double focusing mass spectrometer. Infrared spectra were either of neat liquids or KBr disks and were recorded on a Beckman 20 A-X. X-ray powder photographs were recorded on conventional cameras with nickel-filtered Cu radiation.

Dibromodifluoromethane was obtained from Du Pont, and diglyme from Ansul. Sodium trifluoroacetate was vacuum dried at 70 °C for 3 days.

Preparation of p-(p'-Chlorophenyl)trifluoroacetophenone. In a nitrogen-swept flask were placed 250 mL of dry THF and 0.13 mol (3.16 g) of Mg turnings and the mixture was heated to 60 °C. 4-Chloro-4′-bromobiphenyl (0.10 mol, 26.8 g) was dissolved in THF and slowly dripped into hot solution. After addition was completed, the mixture was heated for an additional 1 h and then allowed to cool to room temperature. The solution was transfered to a clean flask and 0.10 mol (13.6 g) of sodium trifluoroacetate was added in two portions with *vigorous stirring.* An hour later, the reaction mixture was poured into ice and HCl, extracted into ether, and dried ($CaCl_2$), and the ether was removed. The solid ketone was purified by fractional sublimation at ca. 1 mmHg, yield 14.2 g (50%), mp 96–102 °C.

Note. Addition of CF_3CO_2Na to the Grignard causes formation of a very thick solution; good stirring is essential.

Preparation of 2-[4′-Chloro-(4-biphenylyl)]-*F*-propene (1b).[9] To 110 mL of dry diglyme were added 0.074 mol (19.4 g) of triphenylphosphine, 0.050 mol (14.2 g) of the ketone prepared above, and 0.037 mol (7.76 g) of dibromodifluoromethane. The mixture was heated at 70 °C for 24 h under nitrogen. The mixture was extracted into hexane, washed, and dried ($CaCl_2$), and the hexane removed. The olefin was purified by column chromatography with silica gel/hexane, yield of **1b** 5.4 g (45%).

Preparation of 2-[4′-Chloro-(4-biphenyl)]-1,2-dibromo-*F*-propane from 1b. In 8 mL of $CF_2ClCFCl_2$ was placed 0.5 g of **1b.** Several drops of bromine were added and the solution was allowed to stand for several days until complete addition to the double bond had occurred. The solvent was removed. GLC analysis showed the residual liquid to be exclusively the desired product. The structure was confirmed by ^{19}F NMR, Table IV.

The characterization of each dibromo addition compound prepared for this study is given in Table IV. Mass spectrometry was of limited value as most of the compounds debrominated once ionized. However, the ^{19}F NMR spectrum of each was consistent with the proposed structure.

Preparation of *m*-(*F*-2-Propenyl)benzoic Acid (6). 2-(*m*-Bromo)phenyl-*F*-propene[9,15] (0.022 mol, 6.30 g), 0.035 mol (0.85 g) of Mg turnings, and 35 mL of dry ether were mixed under dry nitrogen. The reaction was initiated and maintained by addition of small amounts of 1,2-dibromoethane. When all of the aryl bromide had reacted, the reaction solution was transferred to a clean flask, and carbon dioxide bubbled through the solution for 30 min. The mixture was acidified, washed, and dried (molecular sieves) and the ether was removed. The solid product was purified by fractional sublimation, yield 1.4 g (25%).

General Procedure for the Gas–Solid Reaction of Olefins with Bromine. Crystals of the olefin were powdered and placed in one side of a small flask which was heavily creased. A few drops of bromine were placed in the other side; the flask was stoppered and either set in a light-tight container or on the bench. Progress of the reaction was determined by removing small samples, mixing them with trimethylethylene, and analyzing by gas chromatography on a 5-ft 2% OV-101 column.

Microscopic analysis of the reactions of single crystals was performed on a microscope slide in a small covered dish.

Reaction of 2[4′-Methyl(4-biphenylyl)]-*F*-propene (1d) with Bromine. The olefin **1d** was reacted as described above and three products were detected by GLC. These were separated by preparative GLC on a 5-ft 5% SE-30 column at 200 °C. The structure of each product was assigned based on the following spectral data.

The reactant olefin, **1d**, had a strong absorption in the IR at 1742 cm^{-1} due to $>C{=}CF_2$.[16,17] Mass spectral analysis revealed *m/e* 298 (100%, $M^{+\cdot}$) and 207 [2%, $(C_6H_4C_3F_5)^+$].

The product with the shortest retention time, **2**, a liquid, had a strong IR absorption at 1740 cm^{-1}; mass spectrum *m/e* 376, 378 (58%, $M^{+\cdot}$), 297 [100%, $(p\text{-Br})^+$], 207 [86%, $(C_6H_4C_3F_5)^+$].

The second product, **3**, a liquid, had a strong IR absorption at 1744 cm^{-1}; mass spectrum *m/e* 376, 378 (100%, $M^{+\cdot}$), 297 [54%, $(p\text{-Br})^+$], 207 [83%, $(C_6H_4C_3F_5)^+$]. Thus **2** and **3** were isomers with formula $BrC_7H_6C_6H_4C(CF_3){=}CF_2$. The final positional assignment of the bromine was done by ^{13}C NMR; see Table III.

The product with the longest retention time, **4**, mp 99–101 °C, had a strong IR absorption at 1725 cm^{-1}; mass spectrum *m/e* 454, 456, 458 (100%, $M^{+\cdot}$), 375, 377 [22%, $(p\text{-Br})^+$], 207 [22%, $(C_6H_4C_3F_5)^+$]. Analysis of the reaction revealed that **4** was formed from **2** and **3**. Thus only two structures were possible for **4**; the final choice was made by ^{13}C NMR, Table III.

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Registry No.—**1a,** 61587-19-7; **1b,** 61587-20-0; **1c,** 61587-21-1; **1d,** 61587-22-2; **1e,** 61587-23-3; **2,** 61587-24-4; **3,** 61587-25-5; **4,** 61587-26-6; **5,** 61587-27-7; **6,** 61587-28-8; *p*-(*p*′-chlorophenyl)trifluoroacetophenone, 61587-33-5; 4-chloro-4′-bromobiphenyl, 23055-77-8; dibromodifluoromethane, 75-61-6; 2-(*m*-bromo)phenyl-*F*-propene, 61587-34-6.

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