A Novel Method for Constructing a CF_2 Group via the Reaction of Alkynes with BrF and IF Prepared Directly from the Corresponding Elements

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Received June 18, 1985

The molecules of IF and BrF as entities, prepared from the respective elements, have practically never been used in organic chemistry. When reacted with various types of alkynes the unknown family of compounds containing CF_2CX_2 (X = I, Br) was obtained in good yields. With phenylacetylenes an additional substitution of one or both X atoms by fluorine was observed. Very deactivated triple bonds, such as **23** and **25**, react successfully only with BrF. Since the starting material is F_2 and most reactions are fast, this method should be suitable for synthesis of biologically interesting ^{18}F-containing compounds. The main method used previously for introducing the elements of XF into organic molecules, namely with *N*-halo amides–anhydrous HF, is not suitable for reaction with alkynes.

Although the halofluorination of double bonds has been known for more than 20 years, the actual XF molecules have not been employed. Instead, halofluorination has been achieved via a series of consecutive reactions involving two different reagents, in particular an *N*-halo amide and anhydrous HF.[1] A few variations have appeared, the most notable ones being the replacement of the strong and unpleasant anhydrous HF with HF·Py complex[2] and those that use a different set of reagents such as AgF and I_2[3] or $Pb(OAc)_4/HF/I_2$.[4] These reactions however, have not been successfully applied to alkynes because of the limited reactivity of the above reagents with the triple bond[5] (see also below).

In keeping with our general aim of demonstrating that elemental fluorine can be widely used in organic chemistry,[6] we have shown that F_2 reacts with either I_2 or with Br_2 at −75 °C to give XF, which can then react rapidly and efficiently with many types of double bonds.[7] Similar addition of XF to alkynes would be efficacious for several reasons, and several goals might be achieved. First, it would constitute a new general route for introduction of the important and not readily obtained CF_2 group, which cannot be easily introduced into organic compounds. Only two somewhat limited methods are currently available for this purpose: the reaction of carbonyl compounds with SF_4 (or its derivative Et_2NSF_3–DAST) and the incorporation of the CF_2 unit into the target molecule with ethyl bromodifluoroacetate[8] or CF_2 containing Freons.[9]

There is high probability that the CF_2 group will either have the characteristic biological properties of an unfluorinated analogue[10] or possess different ones.[11] An additional goal therefore would be the devising of a synthetic route, which would enable radiochemists to construct the $C^{18}F_2$ moiety for use in the rapidly developing positron emitting transaxial tomography (PETT).[12] Since the existing methods are unsuitable for this purpose, an alternative rapid synthesis employing easily achieved starting materials such as ^{18}F–F should be developed. A third goal is the synthesis of compounds that on the one hand, have the desirable CF_2 moiety, while on the other, have the potentially reactive CI_2 or CBr_2 groups serving as handles for further chemical transformations.

In this paper we report the quick and usually quite efficient reaction of BrF and IF with various types of acetylenes meeting the goals outlined above.

When nitrogen-diluted F_2 is passed through a cold suspension (−75 °C) of I_2 in $CFCl_3$, the iodine red is changed to brown. The reaction is almost quantitative, and very little fluorine escapes the reaction vessel. That the major product is indeed IF and not any other iodo fluorides, can be verified by test reactions with olefins which give the corresponding IF adducts almost quantitatively.[7] Molecular F_2 reacts similarly with Br_2, the red solution of the latter in $CFCl_3$ being changed into a pale yellow suspension of BrF. Upon $CHCl_3$ addition a pale orange solution results.[7]

When slightly more than a twofold excess of the IF suspension was allowed to react at −75 °C with 1-hexyne (**1**), 1,1-diiodo-2,2-difluorohexane (**2**) was obtained in good yield and in less than 5 min. It seems likely that the reaction proceeds in an ionic mode. The electrophilic iodine atom in IF attacks initially the more electron-rich terminal carbon of 1-hexyne followed by attack of fluoride on the resulting secondary carbonium ion. The fluoro–iodo olefin thus obtained reacts immediately with a second molecule of IF, which adds in such a way as to produce the more stable carbocation on the carbon attached to the fluorine atom.

$$\underset{\mathbf{1}}{CH_3(CH_2)_3C{\equiv}CH} + \underset{X = I,\ Br}{XF} \rightarrow \underset{\mathbf{4},\ X = Br}{CH_3(CH_2)_3CF{=}CHX} \xrightarrow{XF}$$

$$[CH_3(CH_2)_3C^+F\text{–}CHX_2] \xrightarrow{F^-} \underset{\substack{\mathbf{2},\ X = I \\ \mathbf{3},\ X = Br}}{CH_3(CH_2)_3CF_2CHX_2}$$

$$\underset{\mathbf{5}}{CH_3C{\equiv}CCH_3} + IF \rightarrow \underset{\mathbf{6}}{CH_3CF_2CI_2CH_3}$$

(1) See, for example: (a) Djerassi, C., Ed. "Steroid Reactions"; Holden-Day: San Francisco, 1963. (b) Heasley, V. L.; Gipe, R. K.; Martin, J. L.; Wiese, H. C.; Oakes, M. L.; Shellhamer, D. F. *J. Org. Chem.* **1983**, *48*, 3195.

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(5) Dear, R. E. A. *J. Org. Chem.* **1970**, *35*, 1703.

(6) See, for example: (a) Gal, C.; Rozen, S. *Tetrahedron Lett.* **1984**, *25*, 449. (b) Lerman, O.; Tor, Y.; Hebel, D.; Rozen, S. *J. Org. Chem.* **1984**, *49*, 806. (c) Rozen, S.; Lerman, O. *J. Org. Chem.* **1980**, *45*, 672.

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(10) Fried, J.; Halinan, E. A.; Szwedo, M. J., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3871 and references therein.

(11) See, for example: Middleton, W. J.; Bingham, E. M. *J. Org. Chem.* **1980**, *45*, 2883. Cross, B. E.; Erasmunson, A.; Filippone, P. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1293.

(12) For an interesting review on PETT and on the role of ^{18}F in this field, see: Degani, R. *Chem. Eng. News* **1981**, *63* (Nov 9), 30.

0022-3263/86/1951-0222$01.50/0

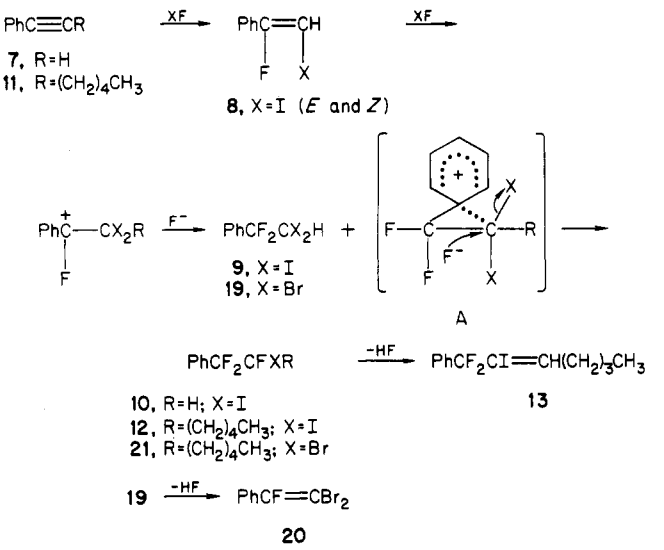
A suspension of BrF in $CFCl_3$ alone proved to be too reactive with alkynes, and only tars were obtained even at −75 °C. The addition of a small amount of a proton donor such as EtOH has a strong taming effect on the reagent, either through hydrogen bonding or through the formation of the corresponding hypobromite.[7,13] When 1 was added to an excess of BrF in an EtOH-containing $CFCl_3$ solution, 1,1-dibromo-2,2-difluorohexane (3) was obtained in 60% yield. When only 1 equiv of BrF was used, (*E*)-1-bromo-2-fluoro-1-hexene (4)[5] was formed in 50% yield, along with a 25% yield of 3. Dear prepared compound 4 by reacting 1 with a mixture of *N*-bromoacetamide and anhydrous HF. However the formal addition of a second mole of "BrF" was not achieved.[5] This fact illustrates one of the major differences between the real BrF and those reagents that serve as a formal source of BrF.

The addition of XF is not confined to terminal acetylenes. Thus 2-butyne (5) reacts cleanly with IF to give 2,2-difluoro-3,3-diiodobutane (6) in better than 85% yield. It is easy to show by NMR spectroscopy that the unsymmetrical isomer was obtained since one of the methyl groups gives rise to a triplet at 2.12 ppm (J_{HF} = 18 Hz) while the other appears as a singlet at 2.98 ppm.

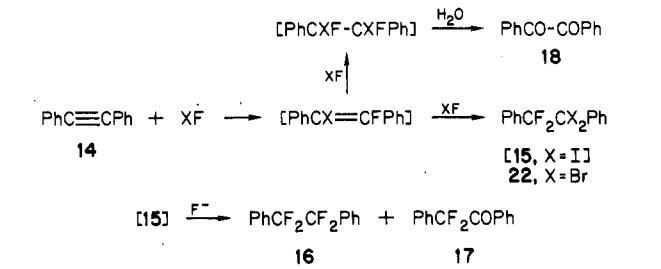
Phenylalkynes gave slightly different results. When only 1 mol equiv of IF was allowed to react with phenylacetylene (7), the expected mixture of the two known (*E*)- and (*Z*)-1-fluoro-1-phenyl-2-iodoethanes (8) were eventually formed in 1:1 ratio.[14] If however, an excess of IF was used, apart from the expected 1,1-difluoro-1-phenyl-2,2-diiodoethane (9), 1,1,2-trifluoro-1-phenyl-2-iodoethane (10) was isolated as well. Since replacement of the iodine atom by fluorine is confined to the arylalkynes, it seems likely that the neighboring arene ring plays some role in this substitution. In principle, the crowded carbon atom bearing two iodine atoms should be susceptable to facile nucleophilic attack. We suggest that, in the transition state, the phenonium ion A is involved. Similar intermediates have already been proposed in several cases.[15] Such participation of the phenyl ring stabilizes a partially positive charge on the carbon α to the fluorine atoms—usually a very unstable and short lived species—to the extent that it will enable a nearby fluoride from another XF molecule to substitute one of the weakly bonded iodine atoms, producing thus the more stable and less sterically hindered 10.

This phenomenon is even more noticeable with the secondary phenylalkyne 11. When it was allowed to react with IF, no difluoro diiodo compound of type 9 was isolated. Since in this case, the carbon atom bearing two iodine atoms would be more crowded than before and the positive charge more stabilized, the transition state A would be more easily achieved, consistent with the fact that only 1,1,2-trifluoro-1-phenyl-2-iodoheptane (12) was obtained. This compound, however, was always accompanied by its dehydrofluorinated product, 1,1-difluoro-1-phenyl-2-iodo-2-heptene (13). It is clear that the dehydrofluorination took place after the reaction was completed since 13 itself reacts readily with IF, producing many unidentified products.

The substitution of iodine by fluorine reaches its zenith with diphenylacetylene (14). We assume that also in this



case the 1,1-difluoro-2,2-diiododiphenylethane (15) was first obtained. However, the two benzylic C–I bonds are very weak, and the stability of a positive charge on this carbon is greater than in any other similar case. As a result both iodine atoms are easily replaced by fluoride, and 1,1,2,2-tetrafluorodiphenylethane (16)[16] was obtained in 60% yield. This behavior resembles the reaction of IF with various stilbenes, which give only difluorobibenzyl derivatives.[7] That the first reaction is indeed the addition of IF to 14 is supported by the fact that 16 was accompanied by a 20% yield of difluorobenzyl phenyl ketone (17),[17] a species that can originate from hydrolysis of 15 at any stage of the reaction. Benzil (18), which was also isolated in



10% yield, originated probably from the symmetrical addition of IF to the triple bond and a subsequent hydrolysis. Such symmetrical addition would be possible only in systems like 14 which can stabilize more than usual the corresponding α-fluorocarbocation. The addition of trifluoroacetyl hypofluorite, CF_3COOF, to diphenylacetylene to give benzil has been reported.[6c]

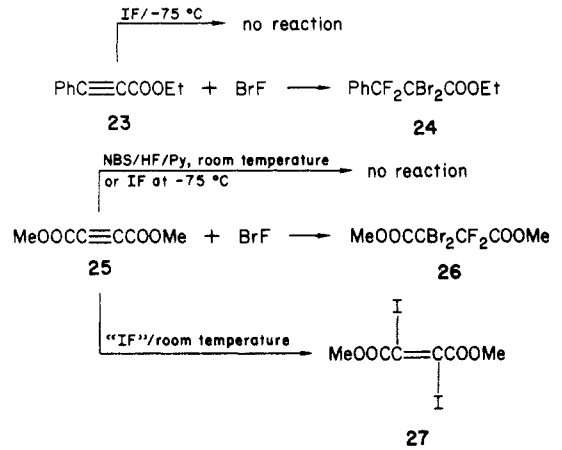
The parallel reactions with BrF seem to be governed by the fact that the C–Br bond is stronger than the C–I bond and that the CBr_2 group is less crowded than the CI_2 one. Thus, phenylacetylene (7) gave the expected 1,1-difluoro-1-phenyl-2,2-dibromoethane (19), although an elimination of HF producing 1-fluoro-1-phenyl-2,2-dibromoethene (20) was also observed since the aliphatic hydrogen in 19 is more acidic than that in compound 9. Compound 20 can also be obtained by treating 19 with ethanolic KOH.

Nucleophilic substitution of the bromine atom by fluoride was detected only in the case of 11, which was converted to 1,1,2-trifluoro-1-phenyl-2-bromoheptane (21)

(13) Brand, M.; Rozen, S. *J. Fluorine Chem.* **1982**, *20*, 419.
(14) Zupan, M. *Synthesis* **1976**, 473. The reagent in this case was $MeIF_2$/HF, but as with the other older methods it will not react further with the relatively deactivated olefin 8, in sharp contrast to the molecular IF and BrF.
(15) See, for example: Barton, D. H. R.; Hesse, R. H.; Jackmann, G. P.; Ogunkoya, L.; Pechet, M. M. *J. Chem. Soc., Perkin Trans. 1* **1974**, 739.
(16) It is worth noting that 15 was prepared directly by reacting F_2 with 14 in 23% yield: Merritt, R. F. *J. Org. Chem.* **1967**, *32*, 4124. See also: Mcewen, W. E.; Guzikowski, A. P.; Wolf, A. P. *J. Fluorine Chem.* **1984**, *25*, 169.
(17) Merritt, R. F. *J. Org. Chem.* **1967**, *32*, 4124.

in good yield. It seems likely that the driving force for this substitution is the release of steric hindrance about the homobenzylic carbon atom. That the stability of the partially positive-charged carbon does not play a major role in this case is evident from the reaction of BrF with diphenylacetylene (14) which gives 1,1-difluoro-2,2-dibromobibenzyl (22) in 65% yield and a 15% yield of benzil (18).

Conjugated acetylenic carbonyl systems could not be successfully halofluorinated by the old methods and their variations. Treatment of ethyl phenylpropiolate (23) with an excess of NBS/HF/Py failed to result in a full addition of the elements of Br and F to the triple bond. However, when this compound was treated with molecular BrF at −75 °C, the reaction was complete in less than 5 min and ethyl 2,2-dibromo-3,3-difluoro phenylpropionate (24) was obtained in 70% yield. IF did not react with 23, even after 16 h at −75 °C, and only the starting material was recovered.



Dimethyl acetylenedicarboxylate (25) contains one of the most unreactive triple bonds toward electrophilic attack. When it was treated with NBS/HF/Py, no reaction was observed. The same was true when molecular IF was brought in contact with 25 for 3 days at −75 °C. However, even this acetylenic derivative was not resistant toward BrF and, after 12 h at −75 °C, dimethyl 2,2-dibromo-3,3-difluorosuccinate (26) was obtained in 70% yield. The addition mode of BrF to both 23 and 25 was evident either from the ^{19}F NMR, which showed only singlets at −93 and −101 ppm, respectively, or from the ^{13}C NMR which exhibited triplets for the CF_2 carbon at 116.1 ($^1J_{CF}$ = 256 Hz) and at 110.4 ppm ($^1J_{CF}$ = 265 Hz), respectively.

Although 25 did not react with IF at −75 °C, it did react when the reaction mixture was allowed to warm to room temperature. Methyl diiodofumarate (27)[18] was isolated after 16 h in 70% yield. We do not know much about the mechanism of this unusual reaction. It is likely that iodine monofluoride is not involved since, above −40 °C, it undergoes disproportionation to IF_3 and IF_5.[19]

In conclusion, we believe that the method described herein provides a unique route for the gentle introduction of the important CF_2 group into various organic substrates. The speed of the reaction, usually less than 5 min, and the readily available starting materials make this reaction suitable for the introduction of the important ^{18}F radioisotope into many organic molecules.

We hope that in the near future, the iodine and/or bromine atoms will prove to be reactive handles that will enable synthesis of other fluorine containing compounds which are now difficult to obtain.

(18) Bruck, B. *Ber.* **1893**, *26*, 846.
(19) Schmeisser, M.; Sartori, P.; Naumann, D. *Chem. Ber.* **1970**, *103*, 880.

Experimental Section

^1H and proton broad band decoupled ^{13}C NMR spectra were recorded with a Bruker WH-360 spectrometer at 360 and 90.56 MHz, respectively, with $CDCl_3$ as a solvent and Me_4Si as an internal standard. The ^{19}F NMR spectra were recorded on a Bruker WH-90 spectrometer at 84.67 MHz and are reported in ppm upfield from $CFCl_3$, which also served as an internal standard. Mass spectra were measured with a Du Pont 21-491B spectrometer. IR spectra were recorded on a Perkin-Elmer 177 spectrometer.

General Fluorination Procedure. A description of the setup and the procedure for working with elemental fluorine has previously been described.[6c] It should, however, be remembered that the reactions described herein should be conducted with care since F_2 is a strong oxidant and not much is known about IF and BrF. If elementary precautions are taken, however, the work with fluorine and its derivatives is safe and relatively simple. In the past, we have never had any accidents while working with it. A detailed procedure for working with IF and BrF can be found in ref 7. Unless otherwise stated, a cold 40–80-ml $CHCl_3$ solution of 40 mmol of the alkyne is added in one portion to ca. 100 mmol of IF, suspended in $CFCl_3$ at −75 °C. The BrF suspension was prepared in $CFCl_3$, but prior to use, 200 mL of precooled, commercial $CHCl_3$ containing EtOH was added, and a solution was obtained after being stirred for 15 min. Subsequently, a cold $CHCl_3$ solution of the appropriate alkyne was added in such an amount as to keep 10–20% excess of BrF. Unless otherwise stated, in both cases the reaction was stopped after 5 min and worked up as usual, which means by pouring the mixture into 500 mL of dilute thiosulfate solution, washing with water until neutral, drying over $MgSO_4$, and evaporating the solvent. The crude product was usually purified by chromatography on a short silica gel column and, if needed, also by HPLC (LiChrosorb Si 60, Merck). Unless a melting point is given, the products are liquids. For the few compounds that are already known, only that physical data which have not previously been published are given. Microanalyses also confirm the correct composition of the new fluorinated derivatives.

Reaction of 1-Hexyne (1) with IF and BrF. A cold $CHCl_3$ solution of 3.3 g of 1 was allowed to react with the IF suspension. After the usual workup, the crude product was chromatographed with petroleum ether as eluent. The oily 2 was thus isolated in 80% yield: ^1H NMR δ 5.26 (1 H, t, J_{HF} = 13 Hz), 2.30 (2 H, m), 1.51–1.36 (4 H, m), 0.94 (3 H, t, J = 7 Hz); ^{19}F NMR −96 ppm (q, J_{HF} = 13 Hz); ^{13}C NMR 119.36 (CF_2, t, $^1J_{CF}$ = 247 Hz), 32.69 (C_3, t, $^2J_{CF}$ = 24 Hz), 24.08 (C_4), 22.19 (C_5), 13.45 (C_6), 5.17 ppm (CHI_2, t, $^2J_{CF}$ = 34 Hz); MS, m/e 374 (M^+), 267 ($(CHI_2)^+$). Anal. Calcd for $C_6H_{10}F_2I_2$: C, 19.25; H, 2.67. Found: C, 19.83; H, 2.61. The parallel reaction with BrF produced 3 in 60% yield and was purified by chromatography using petroleum ether as eluent: ^1H NMR δ 5.61 (1 H, t, J_{HF} = 12 Hz), 2.36–1.2 (6 H, m), 0.96 (3 H, t, J = 6 Hz); ^{19}F NMR −102 ppm (m, $W_{h/2}$ = 67 Hz); ^{13}C NMR 119.76 (CF_2, t, $^1J_{CF}$ = 250 Hz), 41.63 ($CHBr_2$, t, $^2J_{CF}$ = 40 Hz), 33.85 (C_3, t, $^2J_{CF}$ = 19 Hz), 23.65 (C_4), 21.55 (C_5), 12.85 ppm (C_6); MS, m/e 107 ($[CH_3(CH_2)_3CF_2]^+$). Anal. Calcd for $C_6H_{10}Br_2F_2$: C, 25.71; H, 3.57. Found: C, 25.36; H, 3.79.

Reaction of 2-Butyne (5) with IF. To 100 mmol of cold (−75 °C) IF suspension in $CFCl_3$ was added 2 g of 5, dissolved in cold $CHCl_3$, in one portion. After 5 min the reaction was stopped and worked up as usual. The crude reaction mixture was chromatographed with petroleum ether as eluent, and the pure 2,2-difluoro-3,3-diiodobutane (6) was obtained in 85% yield: ^1H NMR δ 2.98 (3 H, s), 2.12 (3 H, t, J_{HF} = 18 Hz); ^{19}F NMR −93.5 (q, J = 18 Hz); MS, m/e 346 (M^+), 219 ($(M - I)^+$), 65 ($(CH_3CF_2)^+$). Anal. Calcd for $C_4H_6F_2I_2$: C, 13.87; H, 1.73. Found: C, 13.80; H, 1.70.

Reaction of Phenylacetylene (7) with IF and BrF. 7 (2.5 g) was reacted with approximately 100 mmol of IF suspended in $CFCl_3$. After 5 min at −75 °C, the reaction was worked up as usual and chromatographed with petroleum ether as eluent. The first fraction proved to be compound 10: 45% yield; ^1H NMR δ 7.87–7.33 (5 H, m) 6.91 (1 H, ddd, J_1 = 47 Hz, J_2 = 12 Hz, J_3 =

6 Hz); ^{19}F NMR −161.5 (1 F, the X portion of an ABX system, quintetlike, $^2J_{HF}$ = 47 Hz, $^3J_{FF}$ = $^3J_{FF'}$ = 23 Hz), −100.26 and −95.94 ppm (2 F, the AB portion of the ABX system, $J_{FF(AB)}$ = 273 Hz, $J_{FF(AX)}$ + $J_{FF(BX)}$ = 46 Hz); ^{13}C NMR 131–126 (C_{Ar}), 116.92 (CF_2, dt, $^1J_{CF}$ = 265 Hz, $^2J_{CF}$ = 31 Hz), 70.31 ppm (CHIF, dt, $^1J_{CF}$ = 265 Hz, $^2J_{CF}$ = 31 Hz); MS, *m/e* 286 (M^+), 159 ($(CHIF)^+$), 127 ($(PhCF_2)^+$). Anal. Calcd for $C_8H_6F_3I$: C, 33.57; H, 2.10. Found: C, 33.86; H, 2.06. The second fraction eluted was identified as **9**: 40% yield; ^1H NMR δ 7.60–7.39 (5 H, m), 5.40 (1 H, t, J_{HF} = 13 Hz); ^{19}F NMR −92 ppm (d, J_{HF} = 13 Hz); ^{13}C NMR 131–126 (C_{Ar}), 116.92 (CF_2, t, $^1J_{CF}$ = 255 Hz), −29.29 ppm (CHI_2, t, $^2J_{CF}$ = 39 Hz); MS, *m/e* 394 (M^+), 267 ($(CHI_2)^+$), 140 ($(PhCF_2CH)^+$), 127 ($(PhCF_2)^+$). Anal. Calcd for $C_8H_6F_2I_2$: C, 24.37; H, 1.52; I, 64.47. Found: C, 24.08; H, 1.77; I, 64.24. Phenylacetylene (**7**) was also reacted with BrF in the usual way. The crude reaction mixture was chromatographed with petroleum ether, and two main fractions were collected. The first one proved to be the dibromo olefin **20**: 45% yield; ^1H NMR δ 7.80–7.20 (m); ^{19}F NMR −77 ppm (s); ^{13}C NMR 156.17 (CBr_2, d, $^2J_{CF}$ = 274 Hz), 131–126 (C_{Ar}), 117.29 ppm (CF, d, $^1J_{CF}$ = 334 Hz); MS, *m/e* 278, 280, 282 (M^+). Anal. Calcd for $C_8H_5FBr_2$: C, 34.29; H, 1.79. Found: C, 34.40; H, 1.96. The second fraction, also isolated in 45% yield, was found to be 1,1-difluoro-1-phenyl-2,2-dibromoethane (**19**): ^1H NMR δ 7.70–7.35 (5 H, m), 5.80 (1 H, t, *J* = 9 Hz); ^{19}F NMR −99.0 ppm (d, *J* = 9 Hz); ^{13}C NMR 133–126 (C_{Ar}), 117.29 (CF_2, t, $^1J_{CF}$ = 249 Hz), 42.69 ppm (CBr_2, t, $^2J_{CF}$ = 40 Hz); MS, *m/e* 302, 300, 298 (M^+), 127 ($(PhCF_2)^+$). Anal. Calcd for $C_8H_6Br_2F_2$: C, 32.00; H, 2.00. Found: C, 32.18; H, 2.01.

Reaction of 1-Phenyl-1-heptyne (11) with IF and BrF. A cold $CHCl_3$ solution of 4.0 g of **11** was allowed to react for 5 min with 50 mmols of IF suspended in cold $CFCl_3$. After the usual workup, the crude product was chromatographed with petroleum ether as eluent. Compound **13** was first eluted in 45% yield: ^1H NMR δ 7.50–7.40 (5 H, m), 6.11 (1 H, tt, J_{HH} = 7 Hz, $^4J_{HF}$ = 2 Hz), 2.37–2.01 (2 H, m), 1.54–1.31 (4 H, m), 0.90 (3 H, t, *J* = 7 Hz); ^{19}F NMR −87.0 ppm (s); MS, *m/e* 336 $(M)^+$, 279 $((M - C_4H_9)^+)$, 127 ($(PhCF_2)^+$). Anal. Calcd for $C_{13}H_{15}F_2I$: C, 46.43; H, 4.46; I, 37.80. Found: C, 46.18; H, 4.24; I, 37.44. The second fraction proved to be the trifluoro derivative **12**, which was obtained in 20% yield: ^1H NMR δ 7.70–7.40 (5 H, m), 2.46 (2 H, t, *J* = 6 Hz), 1.93–1.18 (6 H, m), 0.89 (3 H, t, *J* = 7 Hz); ^{19}F NMR −121 (1 F, m, $W_{h/2}$ = 40 Hz), −103.5 (1 F, dd, $^2J_{FF}$ = 251 Hz, $^3J_{FF}$ = 11 Hz), −97.0 ppm (1 F, dd, $^2J_{FF}$ = 251 Hz, $^3J_{FF}$ = 13 Hz); MS, *m/e* 318 $((M - 2 F)^+)$, 229 $([CH_3(CH_2)_3CH_2IF]^+)$, 127 ($(PhCF_2)^+$). Anal. Calcd for $C_{13}H_{16}F_3I$: C, 43.82; H, 4.49; I, 35.67. Found: C, 44.55; H, 4.76; I, 35.22. A similar reaction was performed with BrF. The adduct **21** was obtained after chromatography with petroleum ether in 45% yield: ^1H NMR δ 7.82–7.08 (5 H, m), 2.51–1.03 (8 H, m), 0.90 (3 H, t, *J* = 6 Hz); ^{19}F NMR −120 (1 F, m, $W_{h/2}$ = 60 Hz), −103 ppm (2 F, br s, $W_{h/2}$ = 30 Hz); MS, *m/e* 308, 310 (M^+), 127 ($(PhCF_2)^+$). Anal. Calcd for $C_{13}H_{16}BrF_3$: C, 50.49; H, 5.18. Found: C, 50.10; H, 5.21.

Reaction of Diphenylacetylene (14) with IF and BrF. Diphenylacetylene (**14**; 3.5 g) in cold $CHCl_3$ solution was reacted with 100 mmol of IF. The crude reaction mixture was chromatographed with 5% EtOAc in petroleum ether as eluent. The first compound was obtained in 60% yield and proved to be the known 1,1,2,2-tetrafluorodiphenylethane (**16**): mp 120 °C (from MeOH);[16] ^{19}F NMR −112 ppm (s); MS, *m/e* 254 (M^+), 127 ($(PhCF_2)^+$), 126 ($(PhCF_2 - H)^+$). The ketone **17**[17] was eluted next in 20% yield: ^{19}F NMR −98.0 ppm (s); MS, *m/e* 232 (M^+), 127 ($(PhCF_2)^+$), 105 $((PhCO)^+)$. The most polar compound, which was obtained in 10% yield, was identified as benzil (**18**). When the reaction was performed with BrF and the crude reaction mixture was subjected to chromatography, a 65% yield of the 1,1-difluoro-2,2-dibromobibenzyl (**22**) was obtained: ^1H NMR δ 7.73–6.98 (m); ^{19}F NMR 93.5 ppm (s); ^{13}C NMR 132–126 (C_{Ar}), 118 (CF_2, t, $^1J_{CF}$ = 262 Hz), 42.15 ppm (CBr_2, t, $^2J_{CF}$ = 40 Hz); MS, *m/e* 378, 376, 374 (M^+), 127 ($(PhCF_2)^+$). Anal. Calcd for $C_{14}H_{10}Br_2F_2$: C, 44.68; H, 2.66. Found: C, 44.98; H, 2.61. Further elution with 5% EtOAc in petroleum ether furnished additional 15% benzil (**18**).

Reaction of Ethyl Phenylpropiolate (23) with BrF. A cold solution of 3.5 g of **23** in $CHCl_3$ was added to 50 mmol of BrF solution in $CFCl_3/CHCl_3$. The reaction was stopped after 5 min and worked up as usual. The oily adduct **24**, obtained in 70% yield, was purified by chromatography using 5% EtOAc in petroleum ether: IR 1730 cm^{-1}; ^1H NMR δ 7.65–7.44 (5 H, m), 4.29 (2 H, q, *J* = 7 Hz), 1.3 (3 H, t, *J* = 7 Hz); ^{19}F NMR −93.0 ppm (s); ^{13}C NMR 160 (CO), 131–126 (C_{Ar}), 116.1 (CF_2, t, $^1J_{CF}$ = 256 Hz), 64.62 (OCH_2), 58.25 (CBr_2, t, $^2J_{CF}$ = 35 Hz), 13.63 ppm (CH_3); MS, *m/e* 374, 372, 370 (M^+). Anal. Calcd for $C_{11}H_{10}Br_2F_2O_2$: C, 35.48; H, 2.69; Br, 43.01. Found: C, 35.43; H, 2.79; Br, 42.73.

Reaction of Dimethyl Acetylenedicarboxylate (25) with BrF and IF. 25 (2.8 g) dissolved in 50 mL of cold $CHCl_3$ was added to more than 50 mmol of BrF dissolved in a cold mixture of $CFCl_3$ and $CHCl_3$ (1:1). The reaction was monitored by GC, and after 5 min practically no reaction was observed. The reaction mixture was stirred overnight at −75 °C and then worked up as usual. Chromatography of the crude product with 30% EtOAc in petroleum ether purified the 2,2-dibromo-3,3-difluorosuccinate **26**, which was obtained in 70% yield: IR 1730 cm^{-1}; ^1H NMR δ 3.938 (s), 3.941 (s); ^{19}F NMR −101.0 ppm (s); ^{13}C NMR 110.39 (CF_2, t, $^1J_{CF}$ = 265 Hz), 55.0 (CH_3O), 54.1 (CH_3O), 53.64 ppm (CBr_2, t, $^2J_{CF}$ = 29 Hz); MS, *m/e* 296, 294, 292 $([M - ((CH_3O) - (CH_3)]^+)$, 218, 216, 214 $((CBr_2COO)^+)$. Anal. Calcd for $C_6H_6Br_2F_2O_4$: C, 21.18; H, 1.76; Br, 47.06. Found: C, 21.24; H, 1.75; Br, 46.70. When IF was applied to **25** following the usual conditions, no reaction was observed even after 3 days. When, however, the reaction mixture was allowed to warm up and then kept at room temperature for 16 h, the known dimethyl 2,3-diiodofumarate (**27**) was obtained in 70% yield: mp 125 °C (from MeOH–H_2O);[18] ^1H NMR δ 3.90 (s); ^{13}C NMR 165.05 (CO), 88.01 (CI), 53.60 ppm (CH_3O); MS, *m/e* 396 (M^+). There are certain spectral evidences pointing to the fact that the crude reaction mixture contains some additional 10–15% of dimethyl 2,3-diiodomaleate which was not isolated in a pure form.

Acknowledgment. We thank the Fund for Basic Research administrated by the Israel Academy of Science and Humanities, for supporting this research.

Registry No. **1**, 693-02-7; **2**, 99686-81-4; **3**, 99686-82-5; **5**, 503-17-3; **6**, 99686-83-6; **7**, 536-74-3; **9**, 99686-85-8; **10**, 99686-84-7; **11**, 14374-45-9; **12**, 99686-88-1; **13**, 99725-81-2; **14**, 501-65-5; **16**, 425-32-1; **19**, 99686-87-0; **20**, 99686-86-9; **21**, 99686-89-2; **22**, 99686-90-5; **23**, 2216-94-6; **24**, 99686-91-6; **25**, 762-42-5; **26**, 99686-92-7; **27**, 16141-19-8; IF, 13873-84-2; BrF, 59680-92-1; dimethyl 2,3-diiodomaleate, 71264-48-7.