Synthesis of Fluorinated 1,2,3-Butatrienes from α-Halovinyl Organometallic Reagents

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Abstract: The thermal stability and dimerization reaction of fluorinated α-halovinyl zinc and copper reagents, RR′C=CYM (Y = F, Cl, Br; M = ZnX, Cu), have been explored in detail. Dimerization of these vinyl carbenoids to butatrienes occurred when R was an aromatic (C_6H_5 or C_6F_5) and R′ was a perfluoroalkyl group (CF_3, C_2F_5, C_3F_7). The role of the α-halogen was determined: the α-F vinyl copper reagent (R = C_6H_5, R′ = CF_3) decomposed by oxidative dimerization to 1,3-dienes while the α-Br and -Cl copper reagents dimerized to butatrienes. The fluorinated butatrienes prepared in this study, (*E*)- and (*Z*)-R_1R_2C=C=C=CR_1R_2 (R_1 = CF_3, R_2 = C_6H_5; R_1 = C_2F_5, R_2 = C_6H_5; R_1 = *n*-C_3F_7, R_2 = C_6H_5; R_1 = CF_3, R_2 = C_6F_5) are available on a multigram scale and readily obtained with high isomeric purity. The geometry of one member of each isomeric pair of butatrienes was characterized by X-ray crystallography. The mechanism of the dimerization reaction has been determined to be a nucleophilic displacement/β-elimination process. Diels–Alder (1,2-addition), bromination (1,2-addition), and isomerization reactions are described.

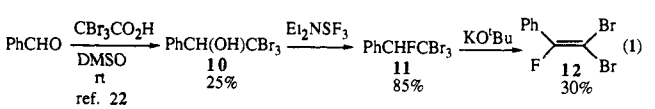
Introduction

Cumulated butatrienes are an interesting class of compounds. The 1,2,3-butatriene moiety has recently been utilized as an intermediate for the preparation of highly unsaturated compounds including radialenes,[1] halo enynes,[2] 1,3-diynes,[3] cyclopentenynes,[4] and hexa-1,5-dien-3-ynes.[5] The cumulene's rigid, conjugated backbone has potential in material science, and some butatrienes have desirable amphoteric properties.[6] The coordination chemistry of cumulenes and transition metals is also of interest.[7] Reports of fluorinated butatrienes, however, have been scarce, even though the incorporation of fluorine into molecules and materials is known to enhance biological activities[8] and thermal properties,[9] respectively. The only fluorinated butatriene to be prepared on a scale amenable to further study is $(CF_3)_2C$=C=C=$C(Ph)_2$.[10,11] The simplest example, CF_2=C=C=CF_2,[12] explodes when liquefied (bp 5 °C). $(CF_3)_2C$=C=C=$C(CF_3)_2$[13] and [*t*-Bu_2C=C=C=CCF_3]$_2$[14] have been reported, but the complexity of their syntheses has precluded additional study. Hartgraves[15] reported the preparation of CF_3CF_2CF=C=C=$C(CH_3)_2$ and $CF_3(CF_2)_3CF_2CF$=C=C=$C(CH_3)_2$ by MeLi-induced elimination of HF from the parent allenes.

Our efforts have been directed at the synthesis of fluorinated building blocks, including organometallic reagents. Since fluorinated organolithium and Grignard reagents are of limited value due to their extremely poor thermal stability, we have developed the chemistry of polyfluorinated vinyl zinc,[16] cadmium,[17] and copper[18] reagents, which exhibit excellent thermal stability. We recently turned our attention to the preparation of fluorinated vinyl zinc and copper reagents with α-halogens other than fluorine, choosing $CF_3(Ph)C$=CYZnX (Y = F, Br) as our model substrate. We were surprised to observe that, while the zinc reagent is stable with an α-F or -Br, the analogous copper reagent was only observed with an α-F: the α-Br analog immediately dimerized to (*E*)- and (*Z*)-$CF_3(Ph)C$=C=C=$C(Ph)CF_3$.[19] We now report the details of our study of fluorinated α-halovinyl organometallic compounds.

Results

Preparation of 1,1-Dihaloalkenes. The 1,1-dibromoalkenes were prepared by Appel reaction of the requisite ketone with CBr_4/PPh_3 (Table I).[20] $PhCF$=CBr_2 (**12**) was prepared by the sequence[21] in eq 1, as the Appel method fails with benzoyl fluoride.



The 1-Br, 1-Y (Y = F, Cl) precursors were prepared by Appel reaction of CF_3COPh with CBr_3Y (Y = F, Cl). $CF_3(Ph)C$=$CFBr$[23] was synthesized selectively from $CFBr_3/PPh_3/CF_3COPh$. The analogous reaction was utilized to prepare $CF_3(Ph)C$=$CClBr$ (**13**), although halogen extraction from $CClBr_3$[24] by PPh_3 was

(1) Iyoda, M.; Tanaka, S.; Otani, H.; Nose, M.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8494–8500.
(2) Ziegler, C. B., Jr. *Tetrahedron Lett.* **1988**, *29*, 411–414.
(3) Ziegler, C. B., Jr.; Harris, S. M.; Baldwin, J. E. *J. Org. Chem.* **1987**, *52*, 443–446.
(4) Ziegler, C. B., Jr. *J. Org. Chem.* **1990**, *55*, 2983–2986.
(5) Kishigami, S.; Tanaka, K.; Toda, F. *Chem. Lett.* **1990**, 1877–1880.
(6) Kawase, T.; Muro, S.; Kurata, H.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1992**, 778–779.
(7) Macomber, R. S.; Hemling, T. C. *Isr. J. Chem.* **1985**, *26*, 136–139. Stang, P. J.; Datta, A. K. *Organometallics* **1989**, *8*, 1024–1029; Joshi, K. K. *J. Chem. Soc. A* **1966**, 594–597, 598–599. Nakamura, A.; Kim, P.-J.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 292.
(8) *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Elsevier Biomedical Press and Kodansha LTD: Amsterdam, 1982.
(9) Emsley, J. *New Sci.* **1989**, *122*, 22 April, 46–50.
(10) Birum, G. H.; Matthews, C. N. *J. Org. Chem.* **1967**, *32*, 3554.
(11) Buddrus, J.; Bauer, H.; Herzog, H. *Chem. Ber.* **1988**, *121*, 295 and references therein.
(12) Martin, E. L.; Sharkey W. H. *J. Am. Chem. Soc.* **1959**, *81*, 5256.
(13) Warrener, R. N.; Nunn, E. E.; Paddon-Row, M. N. *Tetrahedron Lett.* **1976**, 2639.
(14) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527.
(15) Hartgraves, G. H. Ph.D. Thesis, University of Iowa, 1988.
(16) Hansen, S. W.; Spawn, T. S.; Burton, D. J. *J. Fluorine Chem.* **1987**, *35*, 415.
(17) Burton, D. J.; Hansen, S. W. *J. Fluorine Chem.* **1986**, *31*, 461.
(18) Burton, D. J.; Hansen, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 4229.
(19) Morken, P. A.; Baenziger, N. C.; Burton, D. J.; Bachand, P. C.; Davis, C. R.; Pedersen, S. D.; Hansen, S. W. *J. Chem. Soc., Chem. Commun.* **1991**, 566–567.
(20) Ramirez, F.; Desai, N. B.; McKelvie, N. *J. Am. Chem. Soc.* **1962**, *84*, 1745.
(21) RCHO → RCF=CBr_2 has been reported; see: Gajewski, R. P.; Jackson, J. L.; Jones, N. D.; Swartzendruber, J. K.; Deeter, J. B. *J. Org. Chem.* **1989**, *54*, 3311–3317.
(22) Atkins, P. J.; Gold, V.; Wassef, W. N. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1247–1251 (this report does not include data nor a procedure for **10**).
(23) Vanderhaar, R. W.; Burton, D. J.; Naae, D. G. *J. Fluorine Chem.* **1971–1972**, *1*, 381–383.
(24) There has been one report of the Appel chemistry of $CClBr_3$, although there was no experimental detail or indication of purity, selectivity, or yield: Rabinowitz, R. U.S. Patent 3 225 106, 1965; *Chem. Abstr.* **1966**, *64*, 8078h.

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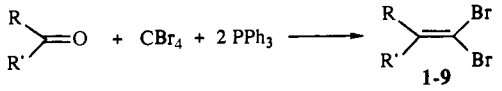
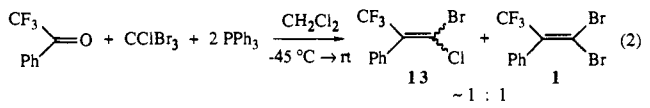
Table I. Preparation of 1,1-Dibromoalkenes

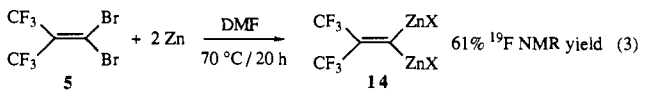


compd	R	R′	yield (%)
1	CF_3	C_6H_5	94
2	C_2F_5	C_6H_5	67
3	C_3F_7	C_6H_5	88
4	CF_3	C_6F_5	76
5	CF_3	CF_3	52
6	CF_2Cl	C_6H_5	67
7	CF_2H	C_6H_5	55
8	CF_3	H	26
9	CF_3	CO_2Et	26

not selective: a 1:1 ratio of **13**:**1** was obtained (eq 2).[25,26] However, chloroalkene **13** was isolable by preparative gas chromatography.

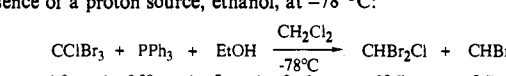


Metalation of 1,1-Dihaloalkenes. The 1,1-dibromoalkenes were metalated with acid-washed zinc metal in DMF solvent. $CF_3(Ph)C{=}CYBr$ (Y = Cl, F) also inserted zinc smoothly into the C–Br bond. Typical conditions for the metalation involved stirring a mixture of the 1,1-dihaloalkene, zinc, and a catalytic amount of mercuric chloride initiator in DMF solvent under N_2 for 1–24 h at room temperature. Attempts to prepare a 1,1-bis(zinc) reagent at room temperature were not successful, and treatment with excess zinc at elevated temperatures (60–80 °C) resulted in decomposition, except in the case of $(CF_3)_2C{=}CBr_2$ (**5**), which gave $(CF_3)_2C{=}C(ZnX)_2$ (**14**) (eq 3).



The zinc reagents were characterized by ^{19}F NMR analysis and hydrolysis experiments. In some instances, the stereochemistry[27] of the zinc reagents could be determined by examination of the coupling constants[28] of the hydrolysis products (Table II). For example, after treatment of $CF_2H(Ph)C{=}CBr_2$ (**7**) with Zn in DMF, two new signals (85:15), each with small downfield shoulders, were observed by ^{19}F NMR analysis (Scheme I). Addition of $ZnBr_2$ to the NMR sample caused the small downfield shoulders to decrease in intensity, prompting their assignment as the bis reagents, $[CF_2H(C_6H_5)C{=}CBr]_2Zn$. After hydrolysis of the sample, two signals in a 85:15 ratio were observed by ^{19}F NMR analysis. Isolation of the isomeric mixture and analysis by GC–MS confirmed the presence of (*E*)- and (*Z*)-CF_2H-(Ph)C=CHBr (**20**, **21**). Examination of the coupling constants

(25) In order to determine if the poor selectivity was occurring during the initial halophilic attack step[26] of the process, the reaction was repeated in the presence of a proton source, ethanol, at –78 °C:



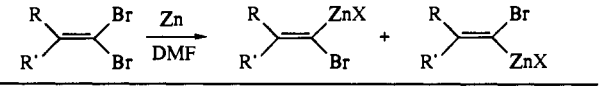
These results imply that there is moderate selectivity in the initial halophilic attack step. Subsequent halogen abstraction from $[Ph_3PCBr_2Cl]^+Br^-$ exhibits little discrimination between between chlorine and bromine.

(26) Burton, D. J. *Actual. Chim.* **1987**, 142–146.

(27) The stereochemistry of the metalation reaction of $RR'C{=}CBr_2$ compounds with *n*-BuLi and *n*-Bu_3ZnLi was recently reported, and metal/halogen exchange was found to take place preferentially at the sterically more hindered bromine atom of $RR'C{=}CBr_2$. However, no such trend was apparent in this study; see: Harada, T.; Katsuhira, T.; Oku, A. *J. Org. Chem.* **1992**, *57*, 5805–5807.

(28) Emsley, J. W.; Phillips, L.; Wray, V. *Prog. Nucl. Magn. Reson. Spectrosc.* **1976**, *10*, 83–756.

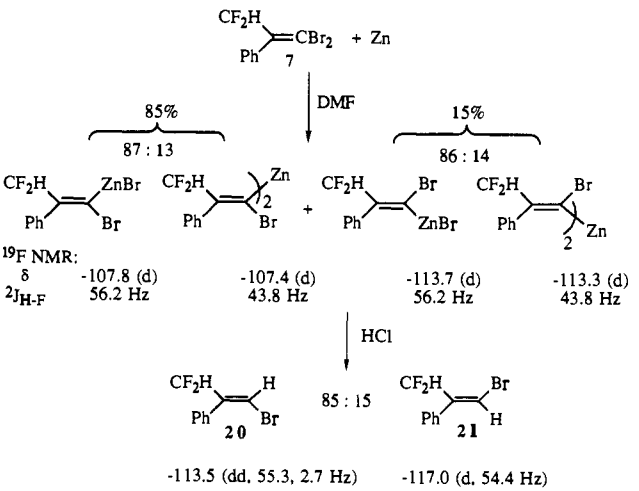
Table II. Ratio of Zinc Reagent Isomers[a]



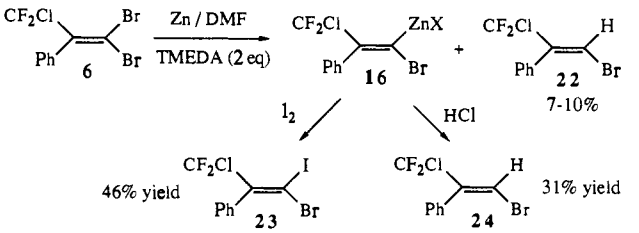
compd	R	R′	%	%
37, **38**	CF_3	C_6H_5	85[b]	15 (86:14)[c]
16	CF_2Cl	C_6H_5	97 (68:32)	3[b]
17	CF_2H	C_6H_5	85 (87:13)	15 (86:14)
18	CF_3	H	29 (80:20)	71 (80:20)
19	F	C_6H_5	0	100[b]

[a] The isomers of the zinc reagents not included in this table were not discernible by NMR. [b] Mono and bis signals overlap. [c] (Mono:bis) mono, X = Br; bis, X = RR′C=CBr.

Scheme I



Scheme II



by ^1H and ^{19}F NMR revealed that the major isomer (85%) exhibited a $^4J_{CF_2-H}$ value of 2.7 Hz, which is assigned to **20**.[29]

The (*E*)-zinc reagent (**16**) derived from $CF_2Cl(Ph)C{=}CBr_2$ (**6**) was formed in DMF solvent, although it decomposed to (*E*)-$CF_2Cl(Ph)C{=}CHBr$ (**22**) after only 1 day at room temperature. Addition of the strongly coordinating *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) ligand[30] increased the thermal stability of zinc reagent **16**, and only 7–10% of **22** was observed after 24 h at room temperature. The insertion was 97% stereoselective for the Br *cis* to the CF_2Cl group in **6**, as determined by iodination (**23**) and hydrolysis (**24**) reactions (Scheme II).

Reaction of $CF_3(CO_2Et)C{=}CBr_2$ (**9**) with Zn gave only complex reaction mixtures as observed by ^{19}F NMR, and no zinc reagent was observed (hydrolysis). Reduction and Barbier-type reactions could be occurring. Treatment of **9** with *t*-BuLi followed by ZnI_2 at –78 °C also failed to give the zinc reagent.[31]

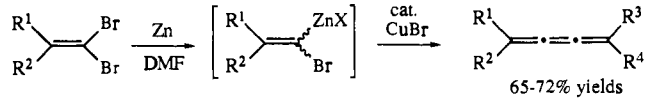
Reaction of α-Halovinyl Zinc Reagents with Cuprous Bromide. Treatment of the zinc reagents listed in Table III with a catalytic amount of CuBr afforded high yields of the corresponding cumulenes in an exothermic reaction. Pure, multigram quantities

(29) Bothner-By, A. A.; Castellano, S.; Gunther, H. *J. Am. Chem. Soc.* **1965**, *87*, 2439–2442.

(30) Jiang, B.; Xu, Y. *J. Org. Chem.* **1991**, *56*, 7336–7340.

(31) Gillet, J. P.; Sauvetre, R.; Normant, J. F. *Synthesis* **1986**, 538–544. Morken, P. A.; Lu, H.; Nakamura, A.; Burton, D. J. *Tetrahedron Lett.* **1991**, *32*, 4271–4274.

Table III. Isolated Butatrienes



compd	R^1	R^2	R^3	R^4	λ_{max} (ϵ)[a]	structure determination
25	CF_3	C_6H_5	CF_3	C_6H_5	376 (27 000)	X-ray
26	CF_3	C_6H_5	C_6H_5	CF_3	388 (32 000)	
27	C_2F_5	C_6H_5	C_2F_5	C_6H_5	376 (21 200)	
28	C_2F_5	C_6H_5	C_6H_5	C_2F_5	377 (37 600)	X-ray
29	C_3F_7	C_6H_5	C_3F_7	C_6H_5	378 (27 500)	
30	C_3F_7	C_6H_5	C_6H_5	C_3F_7	380 (36 800)	X-ray
31	CF_3	C_6F_5	CF_3	C_6F_5	326 (7000)	
32	CF_3	C_6F_5	C_6F_5	CF_3	331 (17 400)	X-ray

[a] λ_{max}, nm, CH_3CN (ϵ, 1 mol^{-1} cm^{-1}).

of (*E*)- and (*Z*)-R(Ph)C=C=C=C(Ph)R (R = CF_3, C_2F_5, C_3F_7) (**25–30**) were readily isolated by silica gel flash chromatography. Unfortunately, (*E*)- and (*Z*)-$CF_3(C_6F_5)C$=C=C=C$(C_6F_5)CF_3$ (**31**, **32**) eluted simultaneously and could not be separated by this technique. However, fractional recrystallization from pentane gave pure **32**. Subsequent recrystallizations afforded **31** in 89% isomeric purity.

The geometries of **25**,[19] **28**,[32] **30**,[32] and **32**[32] were unambiguously determined by X-ray crystallography. The *trans* isomers all exhibited λ_{max} at longer wavelengths with a larger extinction coefficient, ϵ, than their *cis* counterparts. The $\lambda_{max(trans)} > \lambda_{max(cis)}$ trend has been well documented for stilbenes.[33] However, the only reported UV data to our knowledge of an RR′C=C=C=CRR′ (R = alkyl, R′ = aryl) butatriene was consistent with the ϵ but not the λ_{max} trend: R = C_6H_5, R′ = *t*-Bu (*cis* λ_{max} = 332 nm, ϵ = 16 300) (*trans* λ_{max} = 321 nm, ϵ = 20 200).[34]

Surprisingly, substitution of CF_2H for a CF_3 group had a pronounced effect on the product distribution: only traces (4%) of the dimer $CF_2H(Ph)C$=C=C=C$(Ph)CF_2H$ (**54**) were isolated, and the major products were $[CF_2H(Ph)C$=C$]_4$ (**55**) isomers (Scheme VI). The tetramer assignment was made on the basis of HRMS and contains more than one isomer, on the basis of the broad streak on a TLC plate and the complex ^{19}F NMR spectrum. Fractional recrystallization techniques failed to purify a single isomer.

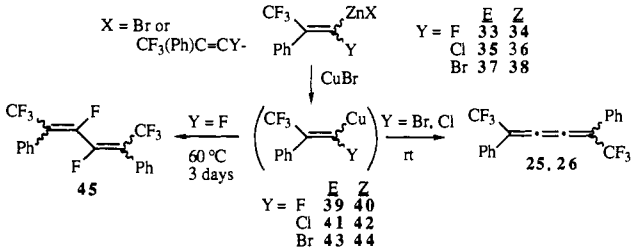
Treatment of $(CF_3)_2C$=CBrZnX, $CF_2Cl(Ph)C$=CBrZnX, or CF_3CH=CBrZnX with CuBr under a variety of conditions afforded complex reaction mixtures as determined by ^{19}F NMR, and no butatrienes or alkynes were detected in the reaction mixtures. Treatment of (*Z*)-PhCF=CBrZnX with CuBr and ^{19}F NMR analysis of the reaction mixture revealed 90% (*E*)-PhCF=CHBr as well as small amounts of several other unidentified products.

The role of the α-halogen was also examined in our model substrate, $CF_3(Ph)C$=CYZnX (Y = Br, Cl, F) (**33–38**). After treatment with CuBr, the α-Cl analog was found to decompose in a manner similar to the α-Br analog, although the dimerization occurred at a slower rate (Scheme III). The α-F copper reagent, however, underwent oxidative dimerization as its major decomposition pathway.

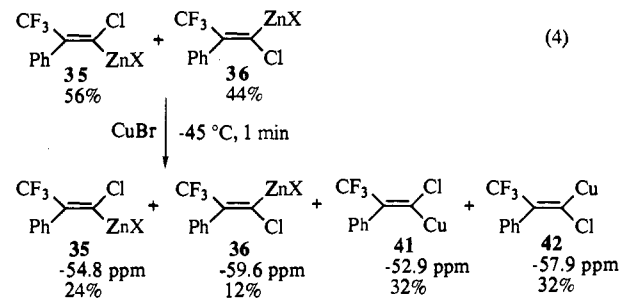
Thermal decomposition (50–60 °C) of the α-halo zinc reagents in the $CF_3(Ph)C$=CYZnX (Y = Br, Cl, F) series was also studied. The α-Br and -Cl analogs decomposed by dimerization to **25**, **26**, and small amounts of $CF_3(C_6H_5)C$=CHY (Y = Cl, Br) while the α-F member gave only $CF_3(C_6H_5)C$=CHF.

Mechanism of Dimerization. Mechanistic studies[35] of reactions with fluorinated substrates offer many advantages. Most importantly, the 100% natural abundance of the NMR active ^{19}F nuclei in conjunction with its broad chemical shift range (>200 ppm) makes ^{19}F NMR a very sensitive probe. A practical advantage is the fact that deuterated solvents are not necessary. A low-temperature NMR study of the CuBr-induced decomposition of $CF_3(Ph)C$=CYZnX (Y = Br, Cl) was undertaken. Addition of 1 equiv of CuBr to a –45 °C 0.25 M solution of $CF_3(Ph)C$=CBrZnX (**37**, **38**) and immediate observation by ^{19}F NMR (–45 °C probe temperature) revealed (*E*)- and (*Z*)-$CF_3(Ph)C$=CBrCu (**43**, **44**), (*E*)- and (*Z*)-$CF_3(Ph)C$=C=C=C$(Ph)CF_3$ (**25**, **26**), and signals attributed to isomers of **46** (Y = Br) (*vide infra*). After warming to 25 °C, **25** and **26** were the sole components of the reaction mixture. The CuBr-induced decomposition of a 0.25 M solution of **37** and **38** in DMF/THF (1:1) was studied at –78 °C. However, at this temperature the CuBr was not soluble. At temperatures where the CuBr was soluble (~–50 °C), the dimerization reaction occurred. Utilization of $CuBr{\cdot}SMe_2$ did not alleviate the solubility problem at low temperature.

Scheme III



The intermediates, however, were observed cleanly when the less labile α-Cl zinc reagent was employed. A 0.25 M solution of (*E*)- and (*Z*)-$CF_3(Ph)C$=CClZnX (**35**, **36**) was treated with 1 equiv of CuBr and monitored by ^{19}F NMR at –45 °C (Figure 1). After 1 min, two new peaks assigned to α-Cl copper reagents **41** and **42** were observed by ^{19}F NMR, as well as unreacted zinc reagent (64% conversion). It appears that (*Z*)-$CF_3(Ph)C$=C(Cl)ZnX (**36**) underwent metathesis reaction at a slightly faster rate than its *E* counterpart (**35**) (eq 4).



(4)

After 5 min at –45 °C, zinc reagents **35** and **36** were consumed, and copper reagents **41** and **42** accounted for 78% of the fluorine by integration. Four broad singlets (22%) in roughly a 1:2:2:1 pattern had appeared (δ –53.9, –54.3, –54.7, –55.2, at –45 °C), which are assigned to the isomers of $CF_3(Ph)C$=C(Cl)C(Cu)=C(Ph)CF_3 (**46**, Y = Cl).[36] After the probe was warmed to 0 °C over a 35-min period, α-Cl copper reagents **41** and **42** were no longer observed by ^{19}F NMR analysis and dienyl isomers **46** (Y = Cl) accounted for 99% of the fluorine by integration. The intermediates at this point were studied by further warming and by trapping with HCl. When the solution was warmed to room temperature, only butatrienes **25** and **26** were observed by ^{19}F NMR analysis.

(32) To be published in *Acta Crystallogr., Sect. C.*
(33) Lambert, J. B.; Shurvell, H. F.; Lightner, D. A.; Cooks, R. G. *Introduction to Organic Spectroscopy*; Macmillan: New York, 1987.
(34) Kuhn, R.; Schulz, B. *Chem. Ber.* **1965**, *98*, 3218–3227.
(35) For a recent example, see: Creary, X.; Wang, Y.-Z. *J. Org. Chem.* **1992**, *57*, 4761–4765.
(36) These singlets could not be assigned to any of the four possible diene isomers, each with two unique CF_3's. It could not be determined if only two dienyl cuprate isomers had formed, or if three or four isomers had formed and the chemical shifts of several trifluoromethyl groups had overlapped.

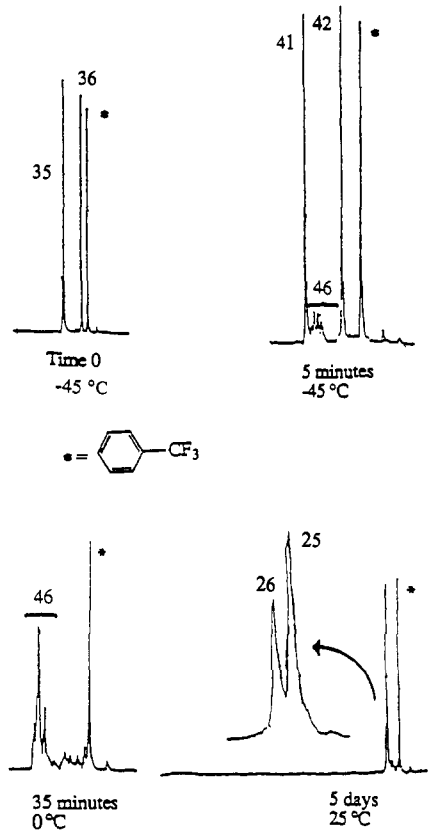
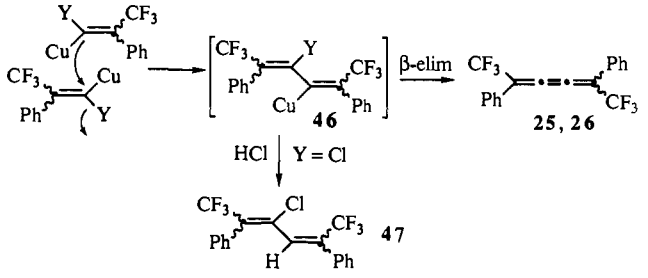


Figure 1. Low-temperature ^{19}F NMR study of $CF_3(Ph)C{=}CClCu$ (**41**,**42**) decomposition.

Scheme IV

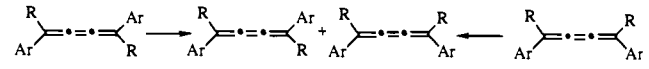


The trapping experiment was carried out by first treating an NMR sample of α-chloro zinc reagents **35** and **36** with 1 equiv of CuBr at −45 °C and then warming to 0 °C over a 35-min period, affording **46** (Y = Cl). Addition of several drops of HCl/Et_2O and examination by GC–MS revealed two isomers of $CF_3(C_6H_5)C{=}CClCH{=}C(C_6H_5)CF_3$ (**47**), and no butatrienes (**25**, **26**) were detected. It could not be determined whether only two isomers had formed or if more than two isomers had formed and were eluting simultaneously during GC–MS analysis. This experiment offers direct proof of the intermediacy of **46** in the dimerization reaction (Scheme IV).

Thermal Isomerization of Butatrienes. The thermal isomerization of the isolated butatrienes was examined in triglyme solvent. In the cases of **25**–**30**, no isomerization was observed up to 50 °C, and thermodynamic equilibrium was achieved after 6 h at 110 °C (Table IV).

Diels–Alder Reaction of (*E*)- and (*Z*)-$CF_3(Ph)C{=}C{=}C{=}C(Ph)CF_3$ (25, 26). The Diels–Alder reaction of butatrienes **25** and **26** with cyclopentadiene was found to proceed under relatively mild conditions: 55 °C/4 h/toluene. These observations were particularly advantageous because no thermal isomerization (Table IV) has been observed under these conditions. Treatment of **25** with cyclopentadiene gave two isomers in a 1.4:1 ratio as determined by ^{19}F NMR (eq 5). Although inseparable by silica gel chromatography, **48** and **48′** could be isolated by preparative HPLC. The cycloaddition was regioselective for 1,2-

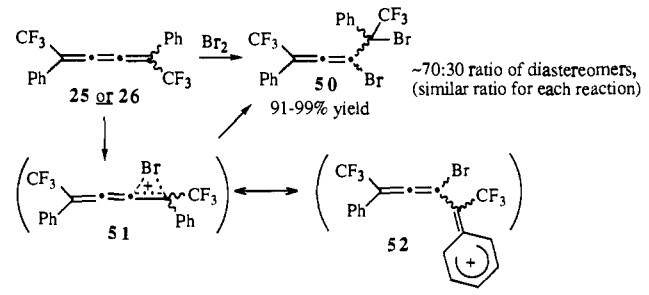
Table IV. Thermal and Photochemical Isomerization of Butatrienes[a]

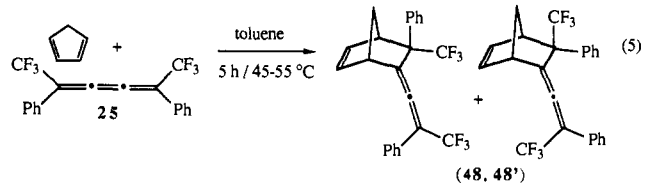


R	Ar	*E*:*Z*
CF_3	C_6H_5	60:40
C_2F_5	C_6H_5	48:52
C_3F_7	C_6H_5	50:50
CF_3	C_6F_5	*b*

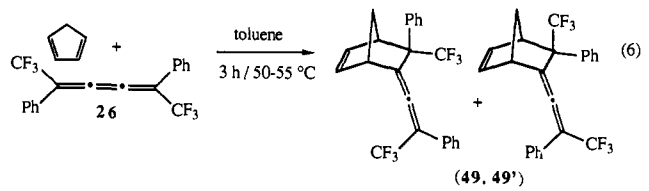
[a] 110 °C/6 h triglyme. [b] Decomposes in triglyme at 50 °C.

Scheme V





attack at the butatriene, as the isomers exhibited characteristic allenic ^{13}C NMR signals at δ 199.8 (q, $^3J_{C-F}$ = 4.3 Hz) for the major isomer (58%) and δ 200.2 (q, $^3J_{C-F}$ = 3.8 Hz) for the minor isomer (42%) as well as FTIR stretches at 1965.2 and 1965.4 cm^{-1}. Diels–Alder reaction of **26** and cyclopentadiene gave two allenic isomers in a 1.3:1 ratio (eq 6). Although these two isomers were not separated, ^{13}C NMR and GC–MS analysis of the mixture demonstrated the presence of two allenes (**49**, **49′**), which were distinguishable from **48** and **48′**.



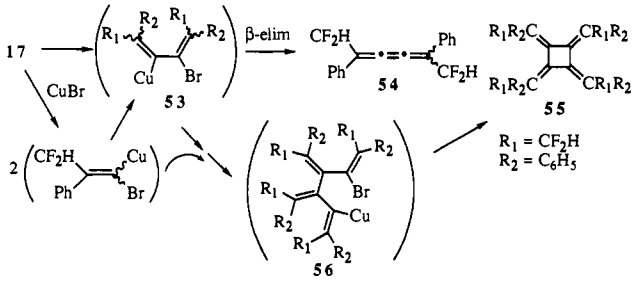
Reaction of (*E*)- and (*Z*)-$CF_3(Ph)C{=}C{=}C{=}C(Ph)CF_3$ (25, 26) with Br_2. Treatment of pure **25** or **26** with Br_2 resulted in 1,2-addition to the terminal double bond as evidenced by the characteristic ^{13}C NMR shifts of the central allenic carbons of **50**. Further, *identical* mixtures of diastereomers were isolated after reaction of pure **25** or **26** with Br_2 (Scheme V). Addition of bromine was regiospecific but not stereospecific.

Discussion

The mechanism of α-halovinyl organometallic (vinyl carbenoid) dimerization has been reported to occur by a coupling[37]/elimination mechanism and not a free carbene intermediate

(37) The first step of the proposed mechanism, nucleophilic displacement of a vinyl halogen α to a metal, has been studied in detail: Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035–5037.

Scheme VI

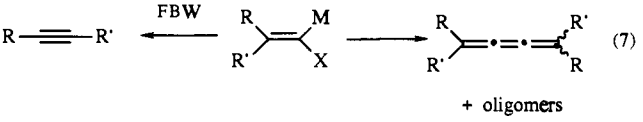


(Scheme IV).[38] However, the experimental evidence to date has mainly been indirect: carbene traps rarely intercept intermediates, and when they do, the yields have been very low.[39] The observation of the intermediates in the dimerization reaction by ^{19}F NMR and isolation of **47** after a trapping experiment with HCl have for the first time provided direct evidence for the intermediacy of **46**. We assume that a similar mechanistic pathway is followed for the thermal dimerization of the α-Cl (**35**, **36**) and α-Br (**37**, **38**) zinc reagents.

The Cu(I)-induced oligomerization of $Ph_2C{=}CBrLi$ to **55** ($R_1 = R_2 = Ph$) and tetraphenylbutatriene has been reported.[40] A similar pathway (Scheme VI) could be occurring in the dimerization/oligomerization of $CF_2H(Ph)C{=}CBrZnX$ (**17**) to **54** and **55**, although we only have molecular formula data (HRMS) and no structural proof for the latter compound.

Treatment of **17** was surprising, since the trifluoromethyl analog (**37**, **38**) gave a good yield (72%) of the butatriene. Perhaps a combination of decreased steric bulk of CF_2H vs CF_3 and increased nucleophilicity of $CF_2H(Ph)C{=}CBrZnX$[41] enables subsequent nucleophilic attack steps of **53** to occur at a faster rate than β-elimination.

Vinyl carbenoids are well-known to undergo Fritsch–Buttenberg–Wiechell (FBW) rearrangement[42] to alkynes (eq 7), although we did not detect alkynes in any of our reaction mixtures.



(7)

+ oligomers

What factors determine which mechanism will be followed for a specific substrate? In general, lithium vinyl carbenoids undergo the FBW rearrangement[42] if a vinyl, aryl, or cyclopropyl group is present and dimerize[43] if two alkyl groups are present. However, vinyl *copper*[6,40,44] carbenoids always dimerize or oligomerize, even with two alkyl groups present. While these generalizations encompass most reported examples, there is an exception: $CH_3(Ph)C{=}CBrLi$ rearranges[45] to $CH_3C{\equiv}CPh$ while $CF_3(Ph)C{=}CBrLi$ dimerizes to **25** and **26**.[19] Since the FBW rearrangement is proposed to involve an accumulation of positive charge in the transition state,[42] it is reasonable to propose that the trifluoromethyl group destabilizes[46] this intermediate, allowing the dimerization reaction to occur.

The α-halogen of the fluorinated α-halovinyl copper reagents was found to affect the mechanism of decomposition. The α-Br and -Cl vinyl copper reagents were unstable at room temperature and decomposed in an exothermic reaction to afford butatrienes in good yields. The α-F vinyl copper reagent, on the other hand, was stable at room temperature and thermally (50–60 °C) decomposed by a well-precedented[47] oxidative dimerization route. We ascribe this change in mechanism to the poor leaving ability of fluoride ion.

The failure of $(CF_3)_2C{=}CBrZnX$ to afford an isolable butatriene after treatment with CuBr could be due to the extremely electrophilic nature of the product. For example, a sample of $(CF_3)_2C{=}C{=}C{=}C(CF_3)_2$ prepared by an alternative method[48] was found to decompose in seconds in DMF at room temperature. However, CuBr-catalyzed decomposition of $(CF_3)_2C{=}CBrZnX$ in the less nucleophilic solvent triglyme still failed to afford an observable butatriene. An attempt to trap the volatile butatriene in a liquid nitrogen trap at low pressure as it was formed was also unsuccessful. It is possible that $CF_2Cl(Ph)C{=}CBrZnX$ (**16**) also fails to dimerize cleanly because the product butatriene has an allylic chlorine that is very susceptible to nucleophilic attack.

The bromination of **25** and **26** occurred selectively at the terminal double bond of the butatriene moiety in a 1,2-fashion.[49] However, **25** and **26** gave identical mixtures of diastereomeric allenes (**50**), which can be rationalized by invoking a cyclic bromonium ion intermediate[50] (**51**) and backside attack by bromide ion to give the *trans* dibromide. However, resonance structure **52** becomes increasingly important for alkenes with aromatic substituents, due to their increased ability to stabilize a positive charge in the transition state.[51] Since structure **52** has the ability to rotate about the C–C bond that is brominated, the anti stereospecificity is lost. A similar result was reported for the bromination of (*E*)- and (*Z*)-β-methylstyrene.[51]

Conclusion

The chemistry of fluorinated α-halovinyl zinc and copper reagents, $RR'C{=}CYM$ (Y = F, Cl, Br; M = ZnX, Cu), has been explored in detail. The α-Cl and -Br zinc reagents were stable at room temperature, while the analogous α-Cl and -Br copper reagents dimerized to butatrienes when R was an aromatic (C_6H_5 or C_6F_5) and R′ was a perfluoroalkyl group (CF_3, C_2F_5, C_3F_7). Direct evidence for a nucleophilic attack/β-elimination pathway for the dimerization reaction has for the first time been obtained. Introduction of substituents such as CO_2Et, H, or CF_3 for R, or F for R′, did not lead to butatriene formation, and side reactions occurred. The α-F vinyl copper reagent ($R = C_6H_5$, $R' = CF_3$) decomposed by oxidative dimerization to 1,3-dienes while α-Br and -Cl copper reagents dimerized to butatrienes. This methodology offers a convenient route to multigram quantities of isomerically pure, thoroughly characterized polyfluorinated butatrienes.

Experimental Section

General. All boiling points are uncorrected. ^{19}F NMR were recorded on a JEOL FX90Q (83.81 MHz) or Bruker AC-300 (282.44 MHz)

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spectrometer, and $\{^1H\}^{13}C$ NMR (75.48 MHz) and ^1H NMR (300.17 MHz) spectra were recorded on the AC-300 spectrometer. All samples were taken in $CDCl_3$ solvent unless noted otherwise. All chemical shifts are reported in parts per million downfield (positive) of the standard: TMS for ^1H and ^{13}C, $CFCl_3$ for ^{19}F NMR. FT-IR spectra were recorded as CCl_4 solutions and reported in wavenumbers (cm^{-1}). GC–MS spectra were obtained at 70 eV in the electron-impact mode. GLPC analyses were performed on a 5% OV-101 column with a thermal conductivity detector. High-resolution mass spectral determinations were made at the University of Iowa High Resolution Mass Spectrometry Facility or the Midwest Center for Mass Spectrometry, the latter with partial support by the National Science Foundation, Biology Division (Grant No. DIR9017262). A Varex preparative scale gas chromatograph with a 1-m $^1/_2$-in. column packed with OV101 and a Beckman-338 binary gradient preparative HPLC system with a 4.6 mm × 250 mm column packed with 5-μm spherical C_{18} particles (Beckman) were utilized. UV measurements were made with a Hewlett-Packard 8452A diode array spectrophotometer in CH_3CN. A 1-ft, silvered, vacuum-jacketed spinning band apparatus with a Teflon band (B/R 8T still) was employed. All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. DMF (CaH_2) and benzonitrile (P_2O_5) were distilled at reduced pressure. TMEDA and CH_2Cl_2 were distilled at atmospheric pressure from CaH_2. Silica gel (EM) was 70–230-mesh ASTM. Zinc (325 mesh, Aldrich) was activated by washing with dilute HCl and then dried *in vacuo* at room temperature. CuBr was treated with aqueous HBr (48% HBr:H_2O = 5:2), precipitated with H_2O, washed with H_2O, acetone, and ether, and then dried *in vacuo*. $CF_3(C_6H_5)C{=}CFBr$[23] and $CF_2HCOC_6H_5$[52] were prepared by literature procedures. $CF_3COC_6F_5$[53] was prepared by a modification of the literature procedure from C_6F_5Li and $CF_3CO_2CH_3$. $RCOC_6H_5$ (R = CF_3, CF_2Cl, C_2F_5, *n*-C_3F_7) were prepared by the method of Dishart and Levine from R_fCO_2H and 2 equiv of C_6H_5MgBr.[54] All reagents were obtained from common commercial sources, except $CF_3CH(OH)OCH_3$ (Central Glass), $CF_3CF(OEt)CO_2Et$ (Du Pont), and CF_3COCF_3 (Daikin).

$CF_3(C_6H_5)C{=}CBr_2$ (1). A 1-L flask with three necks was equipped with a Teflon-coated stir bar, septum, N_2 tee, low-temperature thermometer, triphenylphosphine (115.6 g, 0.441 mol), and CH_2Cl_2 (400 mL) and then cooled to –48 °C. CBr_4 (73.37 g, 0.221 mol) was added all at once *via* a solid addition tube. The solution immediately changed from colorless to yellow and finally to an orange color. After stirring for 30 min at –40 °C, α,α,α-trifluoroacetophenone (35.02 g, 0.201 mol, 100% GLPC purity) was added *via* syringe, and the solution was allowed to warm to room temperature overnight. The reaction mixture was poured into a 2-L flask and steam distilled for 4 h, producing 2 L of distillate. The organic and aqueous layers of the distillate were separated, and the organic layer was dried over Na_2SO_4 and filtered, and the CH_2Cl_2 was removed by rotary evaporation to afford the bulk of the product. The aqueous layer was extracted with ether (3 × 200 mL), the organic layers were combined, dried over Na_2SO_4, and filtered, and the solvent was removed by rotary evaporation. Distillation afforded 62.47 g of **1** (94%, 99.4% GLPC purity): bp 94–104 °C/11 mmHg; GC–MS 333 ($M^{\bullet+}$ + 1, 22), 331 ($M^{\bullet+}$ + 1, 35), 329 ($M^{\bullet+}$ + 1, 22), 170 (100), 151 (44), 101 (29), 75 (59), 69 (39); FTIR 3065.4 (vw), 1585.2 (s), 1293.2 (vs), 1184.1 (vs), 784.2 (s); ^1H NMR (acetone-d_6) δ 7.45–7.29 (m); ^{19}F NMR (acetone-d_6) δ –58.0 (s); ^{13}C NMR (neat) δ 142.3 (q, J = 32.6 Hz), 140.0, 133.7, 133.2, 133.0, 126.5 (q, J = 276 Hz), 106.1 (bs).

$CF_3CF_2(C_6H_5)C{=}CBr_2$ (2). Compound **2** was prepared from triphenylphosphine (114.6 g, 0.437 mol), CBr_4 (73.48 g, 0.222 mol), and $CF_3CF_2(Ph)C{=}O$ (45.05 g, 0.201 mol) by the procedure described for **1**, affording 51.95 g (67% yield, 99.3% GLPC purity) of **2**: bp 108–109 °C/6–7 mmHg; FTIR 628.4 (s), 1148.3 (vs), 1155.6 (vs), 1170.2 (vs), 1321.9 (vs), 1493.6 (m), 1600.3 (m), 1806.1 (w), 1951.6 (w), 3062.3 (w); GC–MS 382 ($M^{\bullet+}$, 15), 380 ($M^{\bullet+}$, 34), 378 ($M^{\bullet+}$, 18), 311 (14), 231 (11), 229 (11), 182 (16), 180 (16), 151 (100), 101 (26), 75 (23), 69 (7.9); HRMS calc for $C_{10}H_5F_5{}^{79}Br^{81}Br$ 377.8678, obs 377.8662; ^1H NMR δ 7.16 (m, 2 H), 7.34 (m, 3 H); ^{19}F NMR δ –81.4 (t, J = 3–3.5 Hz, 3 F), –107.1 (q, J = 3–3.5 Hz, 2 F); ^{13}C NMR δ 136.3, 135.9 (t, J = 23.8 Hz), 129.5, 128.8 (overlapping carbons), 119.2 (qt, J = 288, 37.8 Hz), 112.7 (tq, J = 259, 39.5 Hz), 103.3 (t, J = 3.5 Hz).

$CF_3CF_2CF_2(C_6H_5)C{=}CBr_2$ (3). Compound **3** was prepared from triphenylphosphine (80.3 g, 306 mmol), CBr_4 (50.8 g, 153 mmol), and *n*-C_3F_7COPh (37.65 g, 137.4 mmol) by the procedure described for **1**, affording 51.81 g (88% yield) of **3**: bp 66–75 °C/0.5 mmHg (100% GLPC pure); GC–MS 432 ($M^{\bullet+}$, 11), 430 ($M^{\bullet+}$, 26), 428 ($M^{\bullet+}$, 14), 351 (1.1), 349 (1.1), 313 (11), 311 (26), 309 (13), 230 (10), 232 (9), 151 (100), 101 (18), 69 (11); FTIR 3064.1 (vw), 1600.1 (w), 1582.4 (w), 1445.1 (m), 1344.0 (s), 1262.4 (vs), 1229.7 (vs), 1212.6 (vs), 1188.5 (vs), 1117.7 (vs), 698.1 (s); HRMS calc for $C_{11}H_5F_7{}^{79}Br_2$ 427.8647, obs 427.8629; ^1H NMR δ 7.4 (m, 3 H), 7.3 (m, 2 H); ^{19}F NMR δ –80.9 (t, J = 10 Hz, 3 F), –104.2 (q, J = 10 Hz, 2 F), –123.2 (s, 2 F); ^{13}C NMR δ 137.0, 136.4 (t, J = 24.0 Hz), 130.2 (overlapping carbons), 129.5, 118.6 (qt, J = 288, 34.2 Hz), 115.0 (tt, J = 259, 33 Hz), 104.8 (t, J = 4 Hz).

$CF_3(C_6F_5)C{=}CBr_2$ (4). Reaction of triphenylphosphine (26.22 g, 99.7 mmol), CBr_4 (33.23 g, 100 mmol), and octafluoroacetophenone (12.10 g, 45.8 mmol) was carried out as described for **1**. The CH_2Cl_2 was removed with a rotary evaporator, and then the residue was distilled at 130 °C/0.1 mmHg to yield 60 g of distillate which contained CH_2Cl_2. The CH_2Cl_2 was removed by rotary evaporation to afford 22 g of crude product, contaminated by CBr_4. The crude mixture was distilled through a Bantam-ware (Kontes) distillation apparatus with a 6-in. vacuum-jacketed Vigreux column. The first fraction contained CBr_4, and no water was passed through the condenser as the CBr_4 (mp 88–90 °C) distilled at 50–52 °C/43 mmHg. After all of the CBr_4 had distilled, ice water was passed through the condenser, the pressure was lowered to 24 mmHg, and 14.69 g (76% yield, 99% GLPC pure) of **4**, bp 106–107 °C/24 mmHg, was collected: GC–MS 422 ($M^{\bullet+}$, 36), 420 ($M^{\bullet+}$, 68), 418 ($M^{\bullet+}$, 38), 341 (35), 339 (34), 272 (38), 270 (37), 260 (100), 241 (56), 210 (41), 141 (65), 69 (53); FTIR 1653.8 (vw), 1503.6 (s), 1269.8 (s), 1162.4 (vs), 683.1 (m); HRMS calc for $C_9F_8{}^{79}Br_2$ 417.8239, obs 417.8257; ^{19}F NMR δ –60.2 (s, 3 F), –138.3 (m, 2 F), –150.1 (m, 2 F), –160.6 (m, 1 F); ^{13}C NMR (acetone-d_6) δ 145.1 (dm, J = 250 Hz), 144.0 (dtt, J = 257, 13.4, 5.1 Hz), 139.2 (dm, J = 250 Hz), 125.6 (q, J = 35.9 Hz), 122.3 (q, J = 276 Hz), 111.2 (td, J = 19, 3.9 Hz), 110.7 (bs).

$(CF_3)_2C{=}CBr_2$ (5). A three-neck 2-L flask equipped with a Teflon-coated stir bar, solid addition tube, and a condenser (methanol/Neslab bath cooler) further attached to a N_2 tee was charged with triphenylphosphine (262.2 g, 1.00 mol) and benzonitrile (1 L). The flask was cooled to 10 °C with an ice water bath, and then CBr_4 (165.8 g, 0.500 mol) was added over a 10-min period from the solid addition tube. After stirring for 1 h at 10 °C, the condenser was cooled to –100 °C and hexafluoroacetone (91 g, 0.55 mol) was condensed into the solution over a 45-min period. The viscous mixture was stirred for 4 h at room temperature, and then the magnetic stir bar was removed and a mechanical stirrer was connected to the apparatus. The volatile materials were distilled from the flask at 85 °C/15 mmHg and were collected in two –196 °C traps. The distillate was redistilled through a Bantam-ware (Kontes) apparatus equipped with a vacuum-jacketed 6-in. Vigreux column, collecting 84.37 g (52% yield, 98.4% GLPC purity) of **5**: bp 56–61 °C/120–125 mmHg; GC–MS 324 ($M^{\bullet+}$, 34), 322 ($M^{\bullet+}$, 67), 320 ($M^{\bullet+}$, 35), 243 (44), 241 (42), 155 (32), 153 (32), 131 (22), 129 (23), 93 (36), 69 (100); FTIR 1622.1 (w), 1582.0 (m), 1296.7 (s), 1232.8 (s), 1175.8 (s), 783.2 (s); ^{19}F NMR (C_6H_5CN) δ –59.4 (s) (lit.[55] –57.5); ^{13}C NMR (neat) δ 126.9 (m), 120.3 (q, J = 278 Hz), 108.8 (bs).

$CF_2Cl(C_6H_5)C{=}CBr_2$ (6). A procedure analogous to that for **1** was followed, employing triphenylphosphine (107.5 g, 0.410 mol), CBr_4 (68.0 g, 0.205 mol), $CF_2ClC(Ph){=}O$ (35.4 g, 0.186 mol), and 400 mL of CH_2Cl_2. Compound **6** (45.6 g, 67% yield, 95.4% GLPC purity), bp 132–134 °C/4.0 mmHg, was isolated: GC–MS 350 ($M^{\bullet+}$, 2.9), 348 ($M^{\bullet+}$, 15), 346 ($M^{\bullet+}$, 22), 344 ($M^{\bullet+}$, 9.7), 313 (19), 311 (39), 309 (20), 269 (4.0), 267 (17), 265 (13), 151 (100), 75 (42); FTIR 3063.8 (vw), 1949.9 (vw), 1587.9 (s), 1493.5 (m), 1267.3 (vs), 1157.2 (vs), 1131.3 (vs); ^1H NMR (acetone-d_6) δ 7.24–7.39 (m); ^{19}F NMR (DMF) δ –43.9 (s); ^{13}C NMR (acetone-d_6) δ 142.2 (t, J = 28 Hz), 141.9, 129.8, 129.1 (overlapping carbons), 124.5 (t, J = 293 Hz), 101.0 (bs).

$CF_2H(C_6H_5)C{=}CBr_2$ (7). Reaction of triphenylphosphine (16.53 g, 63.0 mmol), CBr_4 (10.49 g, 31.6 mmol), and α,α-difluoroacetophenone (3.85 g, 24.7 mmol) was carried out as described for **1**. The CH_2Cl_2 layer of the resulting heterogeneous reaction mixture was decanted, and the solids were washed with CH_2Cl_2 (3 × 30 mL). The CH_2Cl_2 was removed by rotary evaporation, and then the involatile residue was dry-loaded onto a silica gel (200 g) column and eluted with pentane, isolating 4.21 g (55% yield) of **7**, 100% GLPC pure: GC–MS 314 ($M^{\bullet+}$, 54), 312 ($M^{\bullet+}$, 100), 310 ($M^{\bullet+}$, 48), 233 (10), 231 (11), 213 (14), 211 (15), 182 (23), 180 (23), 152 (69), 151 (100), 101 (21), 51 (26); FTIR 3038.5 (vw), 1604.6 (w), 1444.7 (w), 1365.9 (m), 1123.5 (m), 1044.0 (s), 802.8 (vs),

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740 (vs); ^{1}H NMR δ 7.6 (m, 3 H), 7.2 (m, 2 H), 6.77 (t, J = 55 Hz, 1 H); ^{19}F NMR δ −114.1 (d, J = 54 Hz); ^{13}C NMR δ 140.3 (t, J = 25.6 Hz), 133.9, 129.1, 129.0, 128.5, 113.2 (t, J = 239 Hz), 100.0 (t, J = 11 Hz).

$CF_3CH{=}CBr_2$ (8). A three-neck 2-L flask (flask 1) equipped with a Teflon-coated stir bar, two septa, and a dry ice/isopropyl alcohol condenser connected at the top to a N_2 bubbler was charged with benzonitrile (600 mL) and triphenylphosphine (79.1 g, 302 mmol) and cooled to 15 °C. Carbon tetrabromide (49.9 g, 150 mmol) was added all at once, and the solution was stirred for 30 min. Another three-neck 2-L flask (flask 2) equipped with a Teflon-coated stir bar, two septa, and a 12-in. uncooled condenser, was charged with concentrated H_2SO_4 (400 mL) and heated to 100–110 °C with an oil bath. An outlet at the top of flask 2's condenser was connected *via* Tygon tubing to an inlet at the bottom of the dry ice condenser of flask 1. The H_2SO_4 solution was stirred vigorously, and then trifluoroacetaldehyde methyl hemiacetal, $CF_3CH(OH)OCH_3$ (50.2 g, 386 mmol), was added *via* syringe to flask 2 over a 30-min period, with gaseous $CF_3CH{=}O$ rapidly boiling into flask 1 under the reaction conditions. The contents of flask 1 were stirred at room temperature for another 4 h, and then the volatiles were removed at reduced pressure (65 °C/0.8 mmHg). The distillate was redistilled, producing 9.73 g (26% yield, 99% GLPC purity) of **8**: bp 41–55 °C/95–100 mmHg; GC–MS 256 ($M^{\bullet+}$, 17), 254 ($M^{\bullet+}$, 33), 252 ($M^{\bullet+}$, 18), 175 (56), 173 (57), 75 (32), 69 (100); FTIR (3070.0 (vw), 1629.7 (m), 1605.0 (w), 1294.4 (vs), 1258.5 (s), 1149.6 (vs), 656.1 (s); ^{1}H NMR δ 6.84 (q, J = 6.6 Hz); ^{19}F NMR δ −61.1 (d, J = 6.6 Hz); ^{13}C NMR δ 127.4 (q, J = 37 Hz), 121.6 (q, J = 272 Hz), 102.7 (q, J = 6.7 Hz).

$EtO_2CC(CF_3){=}CBr_2$ (9). A 50-mL flask equipped with a Teflon-coated stir bar and a distillation apparatus was charged with 1 g of silica gel, 10 mL of concentrated H_2SO_4, and 14.20 g (65.1 mmol) of $CF_3CF(OEt)CO_2Et$. The solution was stirred and heated to 140 °C with an oil bath. At this temperature $CF_3C(O)CO_2Et$[56] begins to distill. Three fractions were collected: bp 80–96 °C (2.53 g, 91% GLPC pure), 96–103 °C (4.22 g, 95% GLPC pure), and 103–105 °C (3.05 g, 88% GLPC pure). The combined yield was 89%, with 88–95% GLPC purity: ^{1}H NMR δ 4.46 (q, J = 7.0 Hz, 2 H), 1.42 (t, J = 7.0 Hz, 3 H); ^{19}F NMR δ −76.1 (s). It was critical in this procedure to promptly (25 → 140 °C/10 min) heat the solution to 140 °C and begin the distillation. It was apparent after several trials that purity and yield suffered when the mixture was gradually warmed to 140 °C (the impurities have not been identified).

Reaction of triphenylphosphine (33.35 g, 127 mmol), CBr_4 (21.00 g, 63.3 mmol), and CF_3COCO_2Et (10.8 g, 63.5 mmol) was carried out as described for **1**. The following isolation was performed with rigorous exclusion of air and moisture from the hygroscopic **9** using inert atmosphere Schlenk techniques. The CH_2Cl_2 was removed by low-pressure distillation. Anhydrous Et_2O (150 mL) was added to the flask, and then the resulting slurry was stirred vigorously for 10 min. The slurry was filtered through a 200-mL Schlenk funnel with a coarse frit. The solid was transferred back to the flask, and the extraction procedure was repeated three times. The Et_2O was removed by low-pressure distillation (25 °C/100 mmHg). Distillation of the residue afforded 5.43 g (26% yield, 99% GLPC pure) of **9**: bp 116–119 °C/70–75 mmHg; FTIR 1162.4 (vs), 1238.1 (vs), 1246.42 (vs), 1282.35 (vs), 1291.43 (vs), 1600.69 (m), 1745.02 (s), 1753.03 (s), 2986.28 (w); GC–MS 328 ($M^{\bullet+}$, 1.1), 326 ($M^{\bullet+}$, 2.1), 324 ($M^{\bullet+}$, 1.0), 300 (19), 298 (37), 296 (19), 283 (44), 281 (100), 279 (61), 259 (28), 257 (47), 255 (30), 93 (62), 69 (50), 45 (34); HRMS calc for $C_6H_5{}^{81}Br_2F_3O_2$ 327.8568, obs 327.8578; ^{1}H NMR δ 4.36 (q, J = 7 Hz, 2 H), 1.36 (t, J = 7 Hz, 3 H); ^{19}F NMR δ −60.4 (s); ^{13}C NMR (neat) δ 160.9 (bs), 133.0 (q, J = 35.2 Hz), 120.3 (q, J = 275 Hz), 103.5 (q, J = 4.5 Hz), 63.0, 13.1.

$C_6H_5CH(OH)CBr_3$ (10).[22] Tribromoacetic acid (18.2 g, 61.3 mmol) was added over a 1-h period to a solution of benzaldehyde (4.26 g, 40.2 mmol) and DMSO (50 mL), then the mixture was stirred overnight at room temperature. The reaction mixture was poured into 300 mL of ice water and extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were combined, dried over $MgSO_4$, and filtered, and the solvent was removed by rotary evaporation to afford 15 g of crude product. The crude material was purified by silica gel (600 g) chromatography, with 1:1 pentane:CH_2Cl_2 eluent. Fractions containing a mixture (5.67 g) of benzaldehyde and product were combined and recrystallized from pentane, and the crystals were evacuated at 75 °C/1.5 mmHg/2 h to remove residual benzaldehyde to afford 3.6 g of **10** (25% yield): R_f (1:1 pentane:CH_2Cl_2) = 0.20; mp 78 °C; DIP-MS 362 ($M^{\bullet+}$, 0.02), 360 ($M^{\bullet+}$, 0.11), 358 ($M^{\bullet+}$, 0.14), 356 ($M^{\bullet+}$, 0.02), 255 (0.13), 253 (0.41), 251 (0.48), 249 (0.27), 107 (100), 79 (29), 77 (17); FTIR 3574.4 (br, w), 3037.7 (vw), 2337.5 (vw), 1454.6 (w), 1058.4 (m), 825.6 (s), 729.5 (vs); ^{1}H NMR (DMSO-d_6) δ 7.7 (m, 2 H), 7.4 (m, 3 H), 7.2 (d, J = 5–6 Hz, 1 H), 5.1 (d, J = 5–6 Hz, 1 H); ^{13}C NMR δ 135.2, 129.6, 129.4. 127.6, 85.8, 54.5.

$C_6H_5CHFCBr_3$ (11). (Diethylamido)sulfur trifluoride (1.69 g, 10.5 mmol) was added *via* syringe over a 10-min period to a solution of $C_6H_5CH(OH)CBr_3$ (2.86 g, 7.97 mmol) and CH_2Cl_2 (25 mL), and then the mixture was stirred for 1 h at room temperature. The reaction mixture was washed with ice water (3 × 20 mL), dried over $MgSO_4$, and filtered, and the solvent was removed by rotary evaporation. The residue was purified by silica gel (150 g) chromatography with hexane eluent, isolating 2.43 g (85% yield) of solid product: R_f = 0.38; mp = 48–52 °C; GC–MS 358 ($M^{\bullet+}$, 0.13), 360 ($M^{\bullet+}$, 0.36), 362 ($M^{\bullet+}$, 0.31), 364 ($M^{\bullet+}$, 0.11), 202 (**4**), 200 (4), 109 (100), 101 (12), 51 (11); FTIR 3038.5 (vw), 1455.2 (w), 1282.6 (w), 1045.4 (m), 794.1 (vs), 723.7 (vs); HRMS calc for $C_8H_6{}^{79}Br^{81}Br_2F$ 361.7963, obs 361.7965; ^{19}F NMR δ −155.3 (d, J = 44 Hz); ^{1}H NMR δ 7.7 (m, 2 H), 7.4 (m, 3 H), 5.78 (d, J = 43 Hz, 1 H); ^{13}C NMR δ 132.6 (d, J = 21 Hz), 130.1, 129.3 (d, J = 6.5 Hz), 127.7, 99.3 (d, J = 197 Hz), 44.4 (d, J = 33.7 Hz).

$C_6H_5CF{=}CBr_2$ (12). KO^{t}Bu (1.08 g, 9.62 mmol) was added over a 1-h period to a 0 °C solution of **11** (1.96 g, 5.43 mmol) in hexane (30 mL), CH_2Cl_2 (5 mL), and methanol (5 mL), and then the mixture was stirred overnight at room temperature. The mixture was filtered, the filtrate was washed with H_2O (3 × 30 mL), dried over $MgSO_4$, and filtered, and the solvent was removed by rotary evaporation. The residue was dried over activated 4-Å molecular sieves and then distilled to afford 0.46 g (30% yield) of **12**, bp 76–100 °C/0.5 mmHg (unreacted **11** was also distilling at later stages; however, this compound solidified in the condenser and the liquid distillate was pure **12**): GC–MS 282 ($M^{\bullet+}$, 18), 280 ($M^{\bullet+}$, 38), 278 ($M^{\bullet+}$, 19), 201 (8), 199 (8), 120 (100), 100 (12), 99 (14), 74 (10); FTIR 3065.1 (vw), 2361.8 (vw), 1624.5 (w), 1267.1 (m), 1070.6 (s), 892.2 (vs); HRMS calc for $C_8H_5F^{79}Br_2$ 277.8742, obs 277.8745. The purity was determined to be >98% by NMR analysis: ^{19}F NMR δ −77.0 (s) (lit.[57] −77 (s)); ^{1}H NMR δ 7.7 (m, 2 H), 7.4 (m, 3 H); ^{13}C NMR δ 156.3 (d, J = 257 Hz), 130.4, 129.9 (d, J = 27 Hz), 128.5 (d, J = 4 Hz), 128.3, 76.4 (m, this C exhibits δ 77.1 (d, J = 50 Hz) in acetone-d_6).

Chlorotribromomethane.[58] Sodium hypochlorite was prepared by the literature procedure[59] in a 3-L flask from NaOH (218 g, 5.5 mol), H_2O (300 mL), ice (1.25 kg), and Cl_2 (161 g, 2.3 mol). The reaction flask was equipped with a mechanical stirrer and septa, then $CHBr_3$ (255 g, 1.01 mol) was added, and the mixture was stirred vigorously for 3 days at room temperature. The solids were washed with water in a Buchner funnel to afford 281 g (97%) of crude product. GC–MS of the solid material revealed 82% $CClBr_3$, with a 96:4 ratio of $CClBr_3$ to CBr_4. Small amounts of $CHBr_3$ and $CHBr_2Cl$ were also present. Spinning band distillation gave 172 g (59%) of $CClBr_3$, bp 160–161 °C. Recrystallization of the light orange solid from pentane gave 31.1 g (11%) of solid white $CClBr_3$, mp 55–56 °C (lit.[58] mp 53 °C), which was contaminated by traces of CBr_4 as determined by ^{13}C NMR and GC–MS techniques: ^{13}C NMR $CClBr_3$ δ +4.6 (lit.[60] + 3.9); CBr_4 δ −29.8; $CHBr_3$ δ +9.6; GC–MS $CClBr_3$ 288 ($M^{\bullet+}$, 0.07), 286 ($M^{\bullet+}$, 0.06), 211 (16), 209 (72), 207 (100), 205 (47), 81 (18), 79 (18).

$CF_3(C_6H_5)C{=}CBrCl$ (13). A procedure analogous to that for **1** was followed, employing 17.30 g (65.6 mmol) of triphenylphosphine, $CClBr_3$ (9.30 g, 32.4 mmol, 1–5% CBr_4), and trifluoroacetophenone (5.25 g, 30.2 mmol). Usual workup and distillation gave 5.10 g of material, bp 99–110 °C/12 mmHg. ^{19}F NMR and GC–MS analysis of the distillate indicated that 50% **1**, 28% *E*-**13**, and 22% *Z*-**13** had formed. The *E* and *Z* isomers of **13** were separated from **1** by preparative scale GC to afford a 99% GLPC pure sample of (*E*)- and (*Z*)-**13**. A typical GC–MS for (*E*)- or (*Z*)-$CF_3(C_6H_5)C{=}CBrCl$ follows: 288 ($M^{\bullet+}$, 22), 286 ($M^{\bullet+}$, 90), 284 ($M^{\bullet+}$, 81), 207 (27), 205 (86), 187 (34), 185 (100), 169 (62), 136 (100), 101 (66), 69 (30); HRMS calc for $C_9H_5F_3{}^{79}Br^{35}Cl$ 283.9215, obs 283.9215; ^{1}H NMR δ 7.4 (m, 3 H), 7.2 (m, 2 H); ^{19}F NMR δ −59.2 (s) for (*Z*)-**13**, −59.1 (s) for (*E*)-**13**.

General Procedure for the Preparation of α-Halovinyl Zinc Reagents. A two-neck 50-mL flask equipped with a Teflon-coated stir bar, N_2 tee,

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and septa was charged with zinc, a catalytic amount (1–5 mg) of $HgCl_2$, and DMF. For volatile dibromoalkenes **5** and **8**, a tap water condenser was also employed. The dibromoalkene was then added *via* syringe: all at once for <10 mmol scale reactions or slowly for >10 mmol scale reactions, in order to moderate the exothermic reaction. Initiation times varied with dibromoalkene substrates and were realized when the mixture turned light green and then black in color and an exothermic reaction occurred. The zinc reagents were hydrolyzed with 10–50% HCl/H_2O, and the products were analyzed by NMR techniques and GC–MS in some instances. See Table II for ratios of zinc reagent isomers.

(*E*)- and (*Z*)-$CF_3(C_6H_5)C{=}CBrZnX$ (37, 38).[16] Zn (3.72 g, 56.9 mmol) and **1** (10.43 g, 31.6 mmol) in 25 mL of DMF were stirred overnight at room temperature: ^{19}F NMR (DMF) δ –55.9 (s, bis **38**), –56.4 (s, mono **38**), –60.2 (s, bis **37**), –60.4 (mono **37**). Data for (*E*)-$CF_3(C_6H_5)C{=}CHBr$: ^1H NMR (acetone-d_6) δ 7.74 (q, $^4J_{H\text{-}F}$ = 1.8 Hz, 1 H), 7.3–7.5 (m, 5 H); ^{19}F NMR (acetone-d_6) δ –64.6 (d, $^4J_{H\text{-}F}$ = 1.7 Hz). Data for (*Z*)-$CF_3(C_6H_5)C{=}CHBr$: ^1H NMR (acetone-d_6) δ 7.3–7.5 (m); ^{19}F NMR (acetone-d_6) δ –59.0 (s).

(*E*)- and (*Z*)-$CF_3CF_2(C_6H_5)C{=}CBrZnX$. Zn (3.2 g, 49 mmol) and **2** (12.8 g, 33.7 mmol) in 30 mL of DMF were stirred overnight at room temperature: ^{19}F NMR (DMF) δ –80.6 (s, 3 F, 19%), –80.8 (s, 3 F, 64%), –81.1 (s, 3 F, 13%), –81.9 (s, 3 F, 4%), –104.5 (s, 2 F, 4%), –105.1 (s, 2 F, 13%), –107.5 (s, 2 F, 64%), –107.8 (s, 2 F, 19%).

(*E*)- and (*Z*)-$CF_3CF_2CF_2(C_6H_5)C{=}CBrZnX$. Zn (0.96 g, 14.7 mmol) and **3** (4.06 g, 9.45 mmol) in 10 mL of DMF were stirred for 4 h at room temperature: ^{19}F NMR (DMF) δ –80.0 (m, 3 F), –101.8 (m, 2 F, 25%), –104.3 (m, 2 F, 75%), –122.1 (m, 2 F).

(*E*)- and (*Z*)-$CF_3(C_6F_5)C{=}CBrZnX$. Zn (1.40 g, 21.4 mmol) and **4** (6.25 g, 14.9 mmol) in 30 mL of DMF were stirred for 2 h at room temperature: ^{19}F NMR (DMF) δ –58.2 to –61.5 (m, 3 F, 100%), –140.0 (m, 2 F), –154.1 (m, 1 F), –162.8 (m, 2 F, 100%).

$(CF_3)_2C{=}CBrZnX$. Zn (0.14 g, 2.1 mmol) and **5** (0.62 g, 1.9 mmol) in 2 mL of DMF were stirred for 1 h at room temperature: ^{19}F NMR (DMF) δ –59.6 (q, J = 7 Hz, 1 F), –58.0 (q, J = 7 Hz, 1 F).

$(CF_3)_2C{=}C(ZnX)_2$ (14). Zn (0.52 g, 8.0 mmol) and **5** (0.65 g, 2.0 mmol) in 4 mL of DMF were stirred for 1 h at room temperature and then for 20 h/75 °C: ^{19}F NMR (DMF) δ –61.0 (s), 61% ^{19}F NMR yield *vs* $PhCF_3$ internal standard.

(*E*)-$CF_2Cl(C_6H_5)C{=}CBrZnX{\cdot}TMEDA$ (16). Zn (0.53 g, 8.1 mmol), TMEDA (1.06 g, 9.12 mmol), and **6** (1.62 g, 4.85 mmol) in 5 mL of DMF were stirred for 1 h at room temperature: ^{19}F NMR (DMF) δ –45.9 (s, bis **16**), –47.1 (s, mono **16**).

(*Z*)-$CF_2Cl(C_6H_5)C{=}CBrI$ (23). Zinc reagent **16** (24 mmol) was filtered through a medium frit Schlenk funnel under positive Ar pressure, cooled to 0 °C, and then quenched with 7.0 g (28 mmol) of I_2. The reaction mixture was poured into 75 mL of 10% HCl and extracted with CH_2Cl_2 (4 × 50 mL). The organic extracts were combined and washed with 10% HCl (2 × 50 mL), 5% $Na_2S_2O_3$ (3 × 50 mL), and H_2O (1 × 50 mL), dried over Na_2SO_4, and filtered, and the solvent was removed by rotary evaporation. The residue was distilled to give 4.36 g (46% yield) of **23**, bp 117–119 °C/1.7 mmHg, 100% GLPC purity: GC–MS 396 ($M^{\bullet+}$, 8), 394 ($M^{\bullet+}$, 30), 392 ($M^{\bullet+}$, 23), 359 (18), 357 (17), 267 (9), 265 (7), 186 (22), 151 (100), 127 (31), 101 (32), 75 (52), 74 (30), 51 (33), 50 (21); FTIR 3063.4 (w), 1949.2 (vw), 1686.9 (w), 1577.3 (w), 1261.3 (m), 1141.8 (vs), 1002.9 (m); HRMS calc for $C_9H_5F_2{}^{35}Cl^{79}BrI$ 391.8276, obs 391.8272; calc for $C_9H_5F_2{}^{37}Cl^{79}BrI$ 393.8247, obs 393.8252; calc for $C_9H_5F_2{}^{37}Cl^{81}BrI$ 395.8226, obs 395.8225; ^{19}F NMR δ –45.3 (s); ^1H NMR δ 7.38 (m, 3 H), 7.23 (m, 2 H); ^{13}C NMR δ 147.0 (t, J = 27 Hz), 136.1, 129.1, 128.63, 128.59, 124.4 (t, J = 294 Hz), 60.5 (bs).

***E*-$CF_2Cl(C_6H_5)C{=}CHBr$ (24).** Zinc reagent **16** (4.85 mmol) was poured into 20 mL of 10% HCl, and then extracted with hexane (3 × 20 mL). The organic extracts were washed with 10% HCl (2 × 20 mL) and H_2O (1 × 20 mL), dried over Na_2SO_4, and filtered, and the solvent was removed by rotary evaporation. The residue was distilled to give 0.41 g (31% yield) of **24**, bp 88–89 °C/5.0 mmHg, 98% GLPC pure: FTIR 3092.2 (w), 3062.6 (w), 1950.2 (vw), 1626.0 (m), 1494.3 (m), 1323.4 (m), 1213.6 (m), 1156.3 (s), 1121.4 (s); GC–MS 270 ($M^{\bullet+}$, 20), 268 ($M^{\bullet+}$, 78), 266 ($M^{\bullet+}$, 60), 233 (91), 231 (92), 189 (25), 187 (76), 152 (77), 151 (84), 102 (100); HRMS calc for $C_9H_6F_2{}^{35}Cl^{79}Br$ 265.9310, obs 265.9301; calc for $C_9H_6F_2{}^{37}Cl^{79}Br$ 267.9280, obs 267.9286; calc for $C_9H_6F_2{}^{37}Cl^{81}Br$ 269.9259, obs 269.9260; ^{19}F NMR (acetone-d_6) δ –51.0 (m): ^1H NMR (acetone-d_6) δ 7.60 (t, $^4J_{H\text{-}F}$ = 1.5 Hz, 1 H), 7.46 (m, 3 H); 7.34 (m, 2 H); ^{13}C NMR (acetone-d_6) δ 141.7 (t, J = 24 Hz), 132.8, 130.3, 130.1, 129.3, 125.9 (t, J = 291 Hz), 117.2 (bs).

$CF_2H(C_6H_5)C{=}CBrZnX$ (17). Zn (0.09 g, 1 mmol) and **7** (0.30 g, 0.96 mmol) in 1 mL of DMF were stirred for 1 h at room temperature. See Scheme I for ^{19}F NMR data of **17**, **20**, and **21**. ^1H NMR for **20**: 7.47–7.31 (m, 5 H), 7.01 (t, $^4J_{H\text{-}F}$ = 2.7 Hz, 1 H), 6.22 (t, $^2J_{H\text{-}F}$ = 55.3 Hz, 1 H). ^1H NMR for **21**: 7.47–7.31 (m, 5 H), 6.91 (t, J = 54.4 Hz, 1 H), 6.73 (s, 1 H).

$CF_3CH{=}CBrZnX$ (18). Zn (0.36 g, 5.5 mmol) and **8** (0.74 g, 2.9 mmol) in 4 mL of DMF were stirred for 3 h at room temperature: ^{19}F NMR (DMF) δ –57.6 (d, J = 7.3 Hz, bis (*Z*)-**18**), –57.9 (d, J = 7.3 Hz, mono (*Z*)-**18**), –59.8 (d, J = 7.3 Hz, bis (*E*)-**18**), –60.0 (d, J = 7.3 Hz, mono (*E*)-**18**). Data for (*E*)-$CF_3CH{=}CHBr$: ^{19}F NMR (DMF) δ –64.6 (dd, J = 7.3, 2.1 Hz); ^1H NMR δ 7.14 (dq, J = 14, 7 Hz, 1 H), 6.30 (m, 1 H). Data for (*Z*)-$CF_3CH{=}CHBr$: ^{19}F NMR δ –60.9 (d, J = 7.3 Hz); ^1H NMR δ 6.88 (d, J = 8.6 Hz, 1 H), 6.45 (dq, J = 8.6, 7 Hz, 1 H).

(*Z*)-$C_6H_5CF{=}CBrZnX$ (19). Zn (0.05 g, 0.8 mmol) and **12** (0.14 g, 0.5 mmol) in 1 mL of DMF were stirred for 2 h at room temperature. ^{19}F NMR analysis indicated the formation of (*Z*)-**19** and (*Z*)-$C_6H_5CF{=}CHBr$ in an 80:20 ratio. ^{19}F NMR (DMF) for (*Z*)-**19**: δ –72.0 (bs). ^{19}F NMR (DMF) for (*Z*)-$C_6H_5CF{=}CHBr$: δ –105.8 (d, J = 29 Hz).

$CF_3(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_3$ (25, 26). A solution of **37** and **38** (31.6 mmol) in DMF was cooled with a –40 °C dry ice/isopropyl alcohol bath, then CuBr (0.36 g, 2.5 mmol) was added to the mixture, and the solution was warmed to room temperature over a 4-h period. The DMF was removed by distillation at low pressure (0.5 mmHg/50 °C), the residue and 3 g of silica gel were dissolved in hexane, and the hexane was removed by rotary evaporation. The remaining solid was sprinkled onto a silica gel (700 g) column and eluted with hexane. Two broad yellow bands were collected, and the solvent was removed by rotary evaporation to afford 0.83 g of **26** (100% isomeric ^{19}F NMR purity, R_f = 0.64) and 3.06 g of **25** (93% isomeric ^{19}F NMR purity, R_f = 0.52), combined yield = 72%. The *Z* isomer could be obtained isomerically pure by recrystallization from hexane or by collecting a later fraction from the second yellow band during the silica gel column isolation. Injection of pure (*E*)- or (*Z*)-$CF_3(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_3$ of a mixture of isomers always resulted in one peak in the GC–MS spectrum: GC-MS 340 ($M^{\bullet+}$, 100), 321 (9.7), 251 (54), 202 (90), 69 (7.3); HRMS calc for $C_{18}H_{10}F_6$ 340.0687, obs 340.0677. Data for **26**: mp 140–141 °C; FTIR 3063.9 (vw), 2363.4 (vw), 2360.2 (vw), 1447.2 (w), 1187.3 (s), 1175.2 (s), 1139.4 (s); ^{19}F NMR (hexane) δ –59.9 (s); ^1H NMR δ 7.70 (m, 2 H), 7.44 (m, 3 H); ^{13}C NMR δ 156.9, 131.1, 130.4, 129.1, 127.9, 121.9 (q, J = 275 Hz), 115.7 (q, J = 34.9 Hz). Data for **25**:[19] mp 104–107 °C; FTIR 3057.4 (vw), 2358.7 (vw), 2349.6 (w), 1564.0 (vw), 1175.9 (s), 1133.6 (s); ^1H NMR δ 7.45 (m, 3 H), 7.67 (m, 2 H); ^{19}F NMR (hexane) δ –60.4 (s); ^{13}C NMR δ 157.7, 131.5, 130.3, 129.2, 128.2, 121.7 (q, J = 275 Hz), 116.0 (q, J = 35.3 Hz). UV data are presented in Table III.

$CF_3CF_2(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_2CF_3$ (27, 28). A solution of $CF_3CF_2(C_6H_5)C{=}CBrZnX$ (33.7 mmol) in DMF was filtered under positive N_2 pressure through a medium frit Schlenk funnel and cooled in an ice water bath, and then a catalytic amount of CuBr (20–30 mg) was added to the stirring mixture, and the solution was warmed to room temperature over a 4-h period. The DMF was removed by distillation at low pressure (0.5 mmHg/50 °C), then the residue was dissolved in hexane, and the solvent was removed by rotary evaporation with 3 g of silica gel. The remaining solid was sprinkled onto a silica gel (700 g) column and eluted with hexane. As the solvent eluted, two broad yellow bands with a light yellow region between them were observed. These three fractions were collected, and the solvent was removed by rotary evaporation to afford 2.14 g of **28** (first band, 100% isomeric ^{19}F NMR purity, R_f = 0.53), 0.38 g of the tailing portion of the first yellow band and the beginning of the second yellow band (55:45 **28**:**27**), and 2.32 g of **27** (second band, 99% isomeric ^{19}F NMR purity, R_f = 0.38), combined yield = 65%. Injection of pure **27** or **28** or a mixture of isomers always resulted in one peak in the GC–MS spectrum. GC–MS of the mixture, 1 peak observed: 440 ($M^{\bullet+}$, 100), 371 (75.9), 251 (60.7), 202 (88.4), 151 (13.6), 101 (17.9); HRMS calc for $C_{20}H_{10}F_{10}$ 440.0623, obs 440.0603. Data for **28**: mp 92–93 °C; FTIR 1148.6 (s), 1164.1 (vs), 1254.4 (vs), 1324.4 (vs), 1445.8 (w), 1902.7 (vw), 3064.2 (vw); ^1H NMR δ 7.58 (m, 2 H), 7.33 (m, 3 H); ^{19}F NMR δ –83.0 (s, 3 F), –107.6 (s, 2 F); ^{13}C NMR δ 160.9 (t, J = 6.6 Hz), 132.8, 130.6, 129.3, 129.2, 119.4 (qt, J = 287, 37.6 Hz), 116.0 (t, J = 27 Hz), 112.8 (tq, J = 257, 38.9 Hz). Data for **27**: mp 74–76 °C; FTIR 1153.5 (vs), 1209.6 (vs), 1253.8 (s), 1325.6 (s), 1445.3 (w), 1952.1 (vw), 3063.7 (vw); ^1H NMR δ 7.58 (m, 2 H), 7.33 (m, 3 H); ^{19}F NMR δ –82.6 (s, 3 F), –107.2 (s, 2 F); ^{13}C NMR δ 160.1 (t, J = 6.8 Hz), 132.2, 130.5, 129.1, 128.8, 119.2 (qt, J = 287, 37.7 Hz), 115.7 (t, J = 25.0 Hz), 112.7 (tq, J = 257, 38.6 Hz). UV data are presented in Table III.

$CF_3CF_2CF_2(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_2CF_2CF_3$ (29, 30). A solution of n-$C_3F_7(C_6H_5)C{=}CBrZnX$ (9.45 mmol) in DMF was filtered under positive N_2 pressure through a medium frit Schlenk funnel and cooled in an ice water bath, then a catalytic amount of CuBr (20–30 mg) was added to the stirred mixture, and the solution was warmed to room temperature over a 1-h period. The DMF was removed by distillation at low pressure (0.5 mmHg/50 °C), then the residue was dissolved in hexane, and the solvent was removed by rotary evaporation with 3 g of silica gel. The remaining solid was sprinkled onto a silica gel (700 g) column and eluted with hexane. Two bright yellow bands with an intermediate faint yellow band were observed to elute. These three bands were collected, and the solvent was removed by rotary evaporation to afford 1.0 g of **30** (first bright band, 99% isomeric ^{19}F NMR purity, R_f = 0.64) and 0.8 g of **29** (intermediate faint band, 92% isomeric ^{19}F NMR purity, R_f = 0.44), combined yield = 70%. Isomer **29** could be further purified by recrystallization from hexane. GC–MS of the mixture, 1 signal observed: 540 ($M^{\bullet+}$, 42), 521 (2), 421 (100), 302 (64), 251 (82), 202 (66), 151 (33), 101 (24), 77 (15), 69 (13). Data for **30**: mp 95–96 °C; FTIR 3064.2 (vw), 1494.5 (vw), 1445.4 (w), 1341.4 (m), 1231.6 (vs), 1212.8 (vs), 1186.8 (s), 1117.0 (s); ^1H NMR δ 7.6 (m, 2 H), 7.4 (m, 3 H); ^{19}F NMR δ –80.2 (t, J = 9.8 Hz, 3 F), –104.2 (q, J = 9.8 hz, 2 F), –124.7 (s, 2 F); ^{13}C NMR δ 160.6 (t, J = 7.5 Hz), 132.3, 130.5, 129.1, 128.1, 118.1 (qt, J = 288, 34 Hz), 116.2 (t, J = 27 Hz), 114.4 (tt, J = 258, 32 Hz), 109.4 (t of sextets, J = 267, 38 Hz). Data for **29**: mp 66–73 °C; FTIR 3064.0 (vw), 1493.7 (w), 1445.1 (w), 1345.1 (m), 1231.2 (vs), 1212.1 (vs), 1186.3 (s), 1117.3 (s); ^1H NMR δ 7.7 (m, 2 H), 7.4 (m, 3 H); ^{19}F NMR δ –80.7 (t, J = 9.8 Hz, 3 F), –104.4 (q, J = 9.8 Hz, 2 F), –125.1 (s, 2 F); ^{13}C NMR δ 161.6 (t, J = 7.1 Hz), 132.8, 130.5, 129.2 (overlapping carbons), 118.5 (qt, J = 288, 34 Hz), 116.5 (t, J = 25 Hz), 114.3 (tt, J = 258, 32 Hz), 109.5 (t of sextets, J = 267, 38 Hz). HRMS: calc for $C_{22}H_{10}F_{14}$ 540.0556. obs 540.0570. UV data are presented in Table III.

$CF_3(C_6F_5)C{=}C{=}C{=}C(C_6F_5)CF_3$ (31, 32). A solution of $CF_3(C_6F_5)C{=}CBrZnX$ (14.9 mmol) in DMF was allowed to settle, and then the supernatant was removed from the excess Zn by syringe and added to a 100-mL flask equipped with a Teflon-coated stir bar and N_2 tee. A catalytic amount of CuBr was added, and a mild exotherm was immediately observed. After stirring at room temperature for 2 h, the DMF was removed by distillation at 60 °C/2 mmHg. The residue was extracted with hexane and CH_2Cl_2 and then dry-loaded onto a silica gel column. Elution with pentane afforded 2.63 g (68% yield) of a mixture of ~1:1 **31**:**32** (R_f = 0.46). The isomers also sublimed (0.5 mmHg, 80 °C) simultaneously. The isomers could be separated by fractional recrystallization from hexane, and a single recrystallization of a 50:50 mixture of isomers gave crystals that had a 97:3 **32**:**31** composition. A second recrystallization gave **32** in 100% ^{19}F NMR purity. Five successive recrystallizations of the mother liquors gave crystals and mother liquor that were 89% and 86% **31**, respectively. Further recrystallizations did not increase the ratio of **31** in either the mother liquor or the crystals, so 89% was the isomeric purity limit for **31** by recrystallization from hexane. Attempted recrystallization from commercial grade or freshly distilled diethyl ether resulted in decomposition, as evidenced by the appearance of several new peaks in the ^{19}F NMR spectrum. Compounds **31** and **32** both isomerized during GC–MS analysis. Injection (250 °C GC injector) of 100% **32** or 89% **31** afforded two peaks in the chromatogram at 6.09 and 6.14 min (~40:60 for each trial), both with identical mass chromatograms: GC–MS 520 ($M^{\bullet+}$, 42), 501 (10), 451 (63), 382 (100), 313 (21), 69 (40); HRMS calc for $C_{18}F_{16}$ 519.9745, obs 519.9763. Data for **32**: FTIR 1649.9 (m), 1521.9 (vs), 1501.0 (vs), 1457.4 (w), 1426.9 (s), 1257.9 (vs), 1166.6 (vs), 1141.6 (vs); mp 105 °C; ^{19}F NMR δ –62.9 (t, J = 9.8 Hz, 3 F), –137.3 (m, 2 F), –148.7 (tt, J = 21, 4 Hz, 1 F), –160.2 (m, 2 F); ^{13}C NMR δ 167.9 (bs), 145.3 (dm, J = 255 Hz), 143.3 (dtt, J = 260, 13.3, 4.6 Hz), 138.3 (dm, J = 255 Hz), 120.0 (q, J = 276 Hz), 107.1 (q, J = 41.3 Hz), 106.0 (m, J = 17.0 Hz). Data for **31**: FTIR 1650.5 (m), 1522.3 (vs), 1501.9 (vs), 1428.7 (m), 1291.2 (s), 1257.5 (s), 1165.6 (vs), 1147.4 (vs), 1086.3 (s); mp 45–51 °C; ^{19}F NMR δ –62.2 (t, J = 9.8 Hz, 3 F), –137.3 (m, 2 F), –148.5 (tt, J = 21, 4 Hz, 1 F), –160.2 (m, 2 F); ^{13}C NMR δ 167.4 (bs), 145.2 (dm, J = 256 Hz), 143.3 (dtt, J = 261, 13.3, 4.7 Hz), 138.3 (dm, J = 252 Hz), 120.0 (q, J = 276 Hz), 107.2 (q, J = 42 Hz), 106.2 (tm, J = 17 Hz). UV data are presented in Table III.

$CF_3(C_6H_5)C{=}CClZnX$ (35, 36). Zn (0.09 g, 1 mmol) and **13** (0.15 g, 0.53 mmol) in 2 mL of DMF were stirred 2 h at room temperature. See eq 4 for ^{19}F NMR data of **35** and **36**. Data for (Z)-$CF_3(C_6H_5)C{=}CHCl$; ^{19}F NMR (DMF) δ –58.4 (s). Data for (E)-$CF_3(C_6H_5)C{=}CHCl$: ^{19}F NMR (DMF) δ –63.9 (s).

$CF_3(C_6H_5)C{=}CFZnX$ (33, 34).[18] Zn (2.07 g, 31.7 mmol) and $CF_3(C_6H_5)C{=}CFBr$ (5.58 g, 20.8 mmol) in 20 mL of DMF were stirred for 18 h at room temperature. ^{19}F NMR (DMF) for **33**: δ –55.5 (d, J = 22 Hz, 3 F), –75.2 (q, J = 22 Hz, 1 F). For **34**: δ –58.6 (d, J = 12 Hz, 3 F), –84.5 (q, J = 12 Hz, 1 F).

$CF_3(C_6H_5)C{=}CFCu$ (39, 40).[18] $CF_3(C_6H_5)C{=}CFZnX$ (9.5 mmol) and CuBr (1.43 g, 10 mmol) were stirred for 30 min at room temperature. ^{19}F NMR (DMF) for **39**: δ –53.6 (d, J = 22 Hz, 3 F), –59.0 (q, J = 22 Hz, 1 F). For **40**: δ –56.2 (d, J = 15 Hz, 3 F), –70.6 (q, J = 15 Hz, 1 F).

Thermal decomposition of **39** and **40** was carried out in an NMR tube with a J. Young valve. The tube was charged with **39** and **40** prepared under O_2-scrubbed Ar, degassed, sealed, and then heated at 50–60 °C/9 days with periodic monitoring by ^{19}F NMR. The minor decomposition product was $CF_3(C_6H_5)C{=}CHF$ and the major product was **45**.

The assignment of **45** was confirmed by the preparation of an authentic sample of dimer **45** by oxidation of **39** and **40** with dioxygen. After passage of a stream of O_2 through a solution of **39** and **40** (0.53 mmol) and purification by silica gel chromatography (hexane), 48.0 mg (49% yield) of **45** was isolated as a clear liquid (R_f = 0.3–0.6). ^{19}F NMR analysis revealed 16% (E)-$CF_3(Ph)C{=}CFBr$ impurity. The remaining 84% of the solution was found to be three isomers of $[CF_3(Ph)C{=}CF]_2$ (**45**) in a 1:1.1:1.9 ratio, assigned to the E,E,Z,Z, and E,Z isomers respectively. ^{19}F NMR for (E,E)-**45**: δ –61.3 (t, J = 7–8 Hz, 3 F), –95.4 (m, 1 F). For (Z,Z)-**45**: δ –60.3 (dm, J = 20–25 Hz, 3 F), –99.6 (m, 1 F). For (E,Z)-**45**: δ –60.7 (dm, J = 22 Hz, 3 F), –62.0 (m, 3 F), –94.3 (dq, J = 40, 10 Hz, 1 F), –96.9 (m, 1 F). Typical GC–MS spectrum for **45**: 378 ($M^{\bullet+}$, 9), 339 (8), 309 (100), 300 (42), 289 (37), 269 (32), 240 (83), 220 (46), 78 (16), 69 (5).

Low-Temperature ^{19}F NMR Study of $CF_3(C_6H_5)C{=}CClCu$ (41, 42). CuBr (25 mg, 0.17 mmol) was added to a cooled (–45 °C) 0.25 M solution of **41** and **42** (0.5 mL, 0.13 mmol). The tube was shaken, quickly placed in a cooled (–45 °C) NMR probe, and then warmed to 0 °C over a 30-min period. The sample was then cooled to –30 °C, and several drops of 1:1 HCl:Et_2O were added by pipet. The solution was allowed to warm to room temperature overnight. The ^{19}F NMR spectrum of this sample was too complex to interpret. The mixture was extracted with pentane (4 × 1 mL), and the pentane extracts were washed with H_2O (3 × 2 mL). GC–MS analysis indicated small quantities of (E)- and (Z)-$CF_3(C_6H_5)C{=}CHCl$ and a major and minor isomer of **47**: typical GC–MS 378 ($M^{\bullet+}$, 0.44), 376 ($M^{\bullet+}$, 1.8), 341 (M – Cl, 13), 340 (M – HCl, 4.4), 307 (M – CF_3, 16), 301 (25), 298 (44), 272 (38), 251 (44), 203 (56), 202 (100), 193 (87), 159 (32), 126 (85), 101 (60), 77 (38), 69 (11), 51 (40); HRMS of mixture calc for $C_{18}H_{11}{}^{35}ClF_6$ 376.0453, obs 376.0455; calc for $C_{18}H_{11}{}^{37}ClF_6$ 378.0424, obs 378.0431. In a separate experiment, $CF_3(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_3$ was determined to be unreactive with HCl/Et_2O under the reaction conditions.

$CF_2H(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_2H$ (54) and $[CF_2H(C_6H_5)C{=}C]_4$ (55). A –20 °C solution of **17** (4.94 mmol) was treated with a catalytic amount of CuBr (0.1 g, ~15 mol %) and warmed to room temperature over a 1-h period. The DMF was removed by vacuum distillation (1 mmHg/40 °C), the residue was dry-loaded onto a 150-g silica gel column and eluted with hexane, then 8:2 hexane:CH_2Cl_2, and 200-mL fractions were collected. Fractions were analyzed by TLC, and those fractions with similar spots were combined and the solvent was removed by rotary evaporation and brief exposure to vacuum (1 mmHg/room temperature/1 min). A minute amount (<0.01 g) of $CF_2H(Ph)C{=}CHBr$ (R_f = 0.50, hexane) isomers was isolated and identified by ^{19}F NMR. A later fraction (R_f = 0.22, hexane) contained 0.03 g (4%) of a 70:30 isomeric mixture of **54**: GC–MS (1 peak) 304 ($M^{\bullet+}$, 53), 253 (21), 233 (76), 202 (100), 152 (29), 151 (32), 127 (70), 51 (31); ^1H NMR δ 7.68 (m, 3 H), 7.40 (m, 3 H); ^{19}F NMR δ –111.4 (d, J = 56.2 Hz, 30%), –111.8 (d, J = 56.2 Hz, 70%); ^{13}C NMR δ 157.3 (m, 30%), 156.7 (m, 70%), 132.7–127.5 (Ar carbons), 117.6 (m), 113.3 (t, J = 244 Hz, 30%), 112.7 (t, J = 243 Hz, 70%). A broad fraction (R_f = 0.21–0.36, 8:2 hexane:CH_2Cl_2) contained 0.48 g (64%) of a mixture of isomers of **55**. The ^{19}F NMR spectrum was complex, suggesting that more than one isomer was present. Fractional recrystallization techniques were unsuccessful: DIP-MS 609 (M + 1, 14), 608 ($M^{\bullet+}$, 40), 557 (M – CF_2H, 11), 537 (11), 506 (11), 486 (13), 479 (17), 466 (10), 435 (17), 416 (26), 365 (30), 357 (28), 251 (18), 215 (26), 202 ($C_{16}H_{25}{}^{\bullet+}$, 100), 179 (31), 151 (23), 141 (26), 127 (66), 109 (39), 91 (26), 77 (29), 57 (30), 51 (29); HRMS calc for $C_{36}H_{24}F_8$ 608.1750, obs 608.1723.

General Procedure for the Thermal Isomerization of Butatrienes. A triglyme solution of each butatriene isomer in an NMR tube was heated

in a 100–115 °C oil bath. The thermal equilibrium reaction was judged complete when ^{19}F NMR analysis of each solution revealed similar ratios of isomers.

Reaction of (*Z*)-$CF_3(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_3$ (25) with Cyclopentadiene. A mixture of **25** (87.8 mg, 0.258 mmol), cyclopentadiene (1 mL), and toluene (0.5 mL) was stirred for 2 h at 45–50 °C, then additional cyclopentadiene (1 mL) was added, and the mixture was stirred for another 3 h at 45–55 °C. The solvent and excess mono- and dicyclopentadiene were removed at low pressure (30 °C/0.5 mmHg) to afford 66.9 mg of (64%) white oil/solid. Silica gel chromatography did not resolve the product isomers (R_f = 0.2–0.35 in hexane). The isomers were separated by preparative HPLC (83:17 MeOH:H_2O), and 10.5 mg of the first isomer to elute (^{19}F NMR δ –61.0 (s, 1 F), –67.9 (s, 1 F)) and 8.4 mg of the second isomer to elute (^{19}F NMR δ –61.2 (s, 1 F), –66.5 (s, 1 F)) were obtained. Typical GC–MS: 406 ($M^{\bullet+}$, 2.2), 340 (100), 321 (10), 271 (20), 251 (85), 202 (100), 126 (15), 77 (22), 66 (80), 51 (20). Data for first isomer of **48**: HRMS calc for $C_{23}H_{16}F_6$ 406.1156, obs 406.1161; FTIR 2961.2 (w), 1965.2 (vw), 1497.8 (m), 1304.8 (s), 1238.2 (s), 1174.7 (vs), 1130.8 (s); ^1H NMR δ 7.08–7.48 (m, 10 H), 6.20 (dd, J = 5.4, 3.0 Hz, 1 H), 6.01 (dd, J = 5.4, 3.1 Hz, 1 H), 3.72 (bs, 1 H), 3.78 (bs, 1 H), 2.47 (d, J = 9.4 Hz, 1 H), 1.83 (d, J = 9.4 Hz, 1 H); ^{13}C NMR δ 199.8 (q, J = 4.3 Hz), 139.7, 134.9, 137.1, 129.9, 128.8, 128.5, 127.9, 127.8, 127.2, 126.2 (q, J = 283 Hz), 123.4 (q, J = 274 Hz), 110.8, 104.7 (q, J = 34.5 Hz), 63.3 (q, J = 25 Hz), 50.6, 49.1, 47.9. Data for second isomer: FTIR 3063.9 (w), 1965.4 (vw), 1304.1 (s), 1164.4 (vs), 1130.0 (vs); ^1H NMR δ 7.19–7.54 (m, 10 H), 6.49–6.41 (m, 2 H), 3.71 (m, 2 H), 1.67 (d, J = 8.7 Hz, 1 H), 1.58 (d, J = 8.7 Hz, 1 H); ^{13}C NMR δ 200.2 (q, J = 3.8 Hz), 137.0, 135.7, 136.8, 130.1, 128.8, 128.5, 128.4, 128.2, 127.7, 126.0 (q, J = 282 Hz), 123.4 (q, J = 275 Hz), 111.1, 105.1 (q, J = 34.7 Hz), 63.9 (q, J = 25 Hz), 51.3, 50.2, 48.8 (bs).

Reaction of (*E*)-$CF_3(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_3$ (26) with Cyclopentadiene. A mixture of **26** (37.8 mg, 0.111 mmol), cyclopentadiene (1 mL), and toluene (0.5 mL) was stirred for 3 h at 50–55 °C. The solvent and excess mono- and dicyclopentadiene were removed at low pressure (50 °C/0.5 mmHg) to afford 33.7 mg (75%) of yellow oil/solid **49**, **49′**. The mixture was analyzed by NMR, FTIR, and GC–MS and found to have similar characteristics to **48** and **48′**: FTIR of the mixture of isomers 3066.4 (w), 2962.8 (m), 1964.1 (vw), 1950.1 (vw), 1728.2 (w), 1497.9 (w), 1301.5 (m), 1261.6 (s), 1171.4 (vs), 1130.1 (vs), 1015.4 (s), 908.7 (m); ^{19}F NMR (DMSO-d_6) δ –59.7 (s, 1.3 F), –60.1 (s, 1 F), –65.6 (s, 1.3 F), –66.9 (s, 1 F); ^{13}C NMR (DMSO-d_6) δ 199.5 (q, J = 4–4.5 Hz), 199.3 (q, J = 4–4.5 Hz), + others.

Reaction of (*E*)- and (*Z*)-$CF_3(C_6H_5)C{=}C{=}C{=}C(C_6H_5)CF_3$ (25, 26) with Bromine. A –40 °C solution of **25** (0.3776 g, 1.11 mmol) in 20 mL of CH_2Cl_2 was treated with Br_2 (0.18 g, 1.1 mmol). The orange Br_2 color did not disappear quickly at –40 °C; however, after the dry ice/isopropyl alcohol bath was allowed to warm to room temperature over a 1.5-h period, the solution was colorless. The solvent was removed by rotary evaporation and exposure to vacuum (2 mmHg, 25 °C, 2 min), leaving yellow, oil/solid **50** (0.50 g, 91%).

Isomer **26** was brominated in a similar fashion, although the bath temperature was raised to –25 °C for the less soluble *E* isomer. Treatment of **26** (0.3177 g, 0.934 mmol) with Br_2 (0.15 g, 0.94 mmol) in 25 mL of CH_2Cl_2 at –25 °C gave 0.46 g (99%) of yellow oil **50** after similar workup.

The NMR, GC–MS, and FTIR spectra of the two reaction mixtures were identical within the experimental error of the instruments. The product ratio was found to be 70:30 by GC–MS integration. ^{19}F NMR was not useful for product identification as some of the singlets overlapped, although the reaction mixtures had identical patterns (small impurities including starting butatriene were also present): FTIR 3066.2 (w), 1969.6 (vw), 1953.1 (vw), 1898.3 (vw), 1880.4 (vw), 1495.3 (m), 1299.9 (vs), 1239.5 (vs), 1173.5 (vs), 698.0 (vs); GC–MS 500 ($M^{\bullet+}$, 0.3), 421 (18), 419 (17), 340 (100), 339 (43), 271 (45), 270 (54), 251 (47), 202 (80); ^1H NMR δ 7.23–7.79 (m); ^{13}C NMR δ 201.5 (q, J = 4 Hz, 30%), 200.4 (q, J = 3.6 Hz, 70%), + others.

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