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ScienceDirect
Journal of Fluorine Chemistry 129 (2008) 435–442
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Coupling routes to hexafluoro-1,3-butadiene, substituted-1, 3-fluorine-containing butadienes and fluorinated polyenes

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Received 26 September 2007; received in revised form 2 November 2007; accepted 5 November 2007
Available online 13 November 2007

Abstract

Hexafluoro-1,3-butadiene was readily prepared *via* a variety of self-coupling processes, such as Cu(0) mediated self-coupling of iodotrifluoroethene, Pd(0) catalyzed coupling of iodotrifluoroethene with the trifluorovinylzinc reagent, and $CuBr_2$ mediated coupling of the trifluorovinylzinc reagent. Perfluoro-2,3-dimethyl-1,3-butadiene was readily synthesized by the reaction of pentafluoropropenyl-2-zinc reagent with either $CuBr_2$ or $FeCl_3$. Alternatively, perfluoro-2,3-dimethyl-1,3-butadiene was prepared by oxidation of the pentafluoropropenyl-2-copper reagent with dioxygen. Cu(0) mediated coupling of an (*E*)-substituted α,β-difluoro-β-iodostyrene provided the first useful route to a (*Z*)(*Z*)-1,4-diaryl-1,3-tetrafluorobutadiene. Extension of the Cu(0) mediated coupling methodology to a perfluorodienyl iodide demonstrated a useful stereospecific route to perfluoropolyenes.

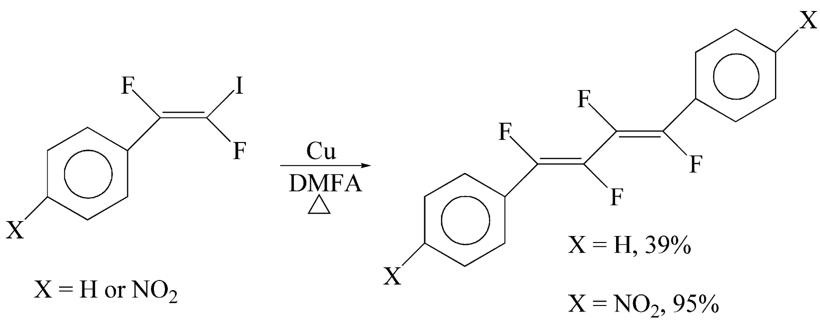
Keywords: Hexafluoro-1,3-butadiene; Perfluoro-2,3-dimethyl-1,3-butadiene; (*Z*)(*Z*)-1,4-aryl-1,3-tetafluorobutadiene; (2*E*)(4*E*)(6*E*)(8*E*)-perfluorodecatetraene; Trifluorovinylzinc reagent; Pentafluoropropenyl-2-zinc reagent; Pentafluoropropenyl-2-copper reagent

1. Introduction

Self-coupling of polyfluorinated vinyl iodides with copper–bronze was first reported by Tatlow and co-workers in 1966 [1] (Eq. (1).

$$FClC = CFI \underset{145\,^{\circ}C\ 24\,h}{\xrightarrow{Cu}} \underset{\text{mixture of three isomers}}{FClC = CFCF = CFCl} \qquad (1)$$

Two perfluorocyclic vinyl bromides, 2-bromononafluorocyclohexene and 1-bromoheptafluorocyclopentene also were reported to undergo reductive coupling with copper–bronze. Subsequently in 1978, Yagupol'skii and co-workers demonstrated that substituted (*Z*)-1-iodo-α,β-difluorostyrenes could be prepared stereospecifically by heating the vinyl iodide with copper in anhydrous DMFA [2] (Eq. (2)). Reiss and co-workers prepared a series of 1,2,3,4-tetrakis (perfluoroalkyl)-1,3-butadienes *via* copper coupling of bis 1,2(perfluoroalkyl)-iodoethenes [3] (Eq. (3)).



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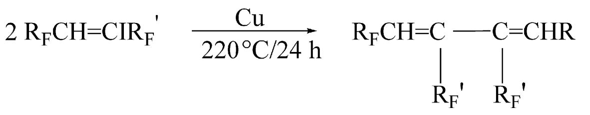
doi:10.1016/j.jfluchem.2007.11.004

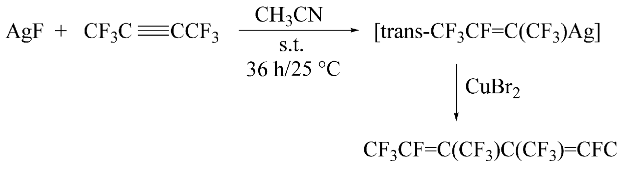


$$2\,R_FCH{=}CIR_F' \xrightarrow[220\,°C/24\,h]{Cu} R_FCH{=}\underset{R_F'}{C}-\underset{R_F'}{C}{=}CHR \quad (3)$$

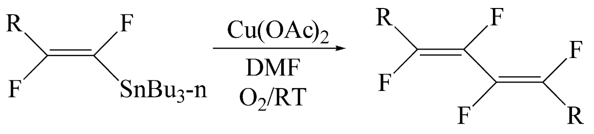
Organometallic reagents have also been employed in a variety of self-coupling processes. For example, Norris and Finnegan prepared 1,1,1,6,6,6-hexafluorohexa-2,4-diyne *via* oxidative coupling of the 3,3,3-trifluoropropyne derivative, $CF_3C{\equiv}CZnX$, with cupric chloride [4] (Eq. (4)). Similarly, Cairncross and Sheppard, in their pioneering work on the preparation of pentafluorophenylcopper (I), reported that C_6F_5Cu is oxidized cleanly at 0 °C with $CuBr_2$ to perfluoro biphenyl [5] (Eq. (5)). Similarly, Miller reported that perfluoro-1-methylpropenylsilver reacted with cupric bromide in CH_3CN to produce the corresponding diene [6] (Eq. (6)). More recently work from our laboratory by Blumenthal has shown that substituted 1,2-difluorovinylstannanes with anhydrous $Cu(OAc)_2$ in DMF, under an oxygen atmosphere, at room temperature stereospecifically give the corresponding symmetrical 1,3-dienes in good to excellent yield [7] (Eq. (7)). The corresponding *cis*-vinyl stannane gave the *cis*, *cis*-diene. This reaction was proposed to proceed mechanistically *via* organocopper intermediates.

$$CF_3CCl=CCl_2 \xrightarrow[DMF]{Zn} [CF_3C{\equiv}CZnX] \xrightarrow[DMF]{CuCl_2} \underset{46\%}{CF_3C{\equiv}C-C{\equiv}CCF_3} \quad (4)$$

$$C_6F_5Cu + CuBr_2 \xrightarrow{0\,°C} C_6F_5-C_6F_5 \quad (5)$$



$$\begin{tikzcd} AgF + CF_3C{\equiv}CCF_3 \arrow[r, "CH_3CN", "\text{s.t.}\ 36\,h/25\,°C"'] & {[trans\text{-}CF_3CF{=}C(CF_3)Ag]} \arrow[d, "CuBr_2"] \\ & CF_3CF{=}C(CF_3)C(CF_3){=}CFCF_3 \end{tikzcd} \quad (6)$$



(7)

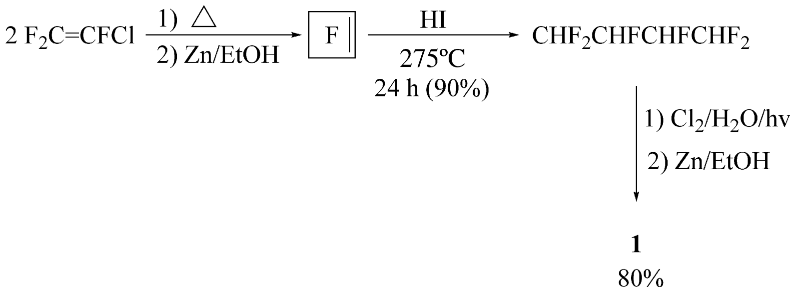
R = n-Bu, sec-Bu, t-Bu, Et_3Si, C_6H_5

2. Results and discussion

2.1. Preparation of hexafluoro-1,3-butadiene

Hexafluoro-1,3-butadiene (**1**) is an important industrial gas and has been of interest to fluorine chemists for several decades. One of the principal synthetic routes to **1** is *via* the dehalogenation of 1,2,3,4-tetrahalohexafluorobutanes. The classical route to the butane precursor was initially reported by Haszeldine, starting from chlorotrifluoroethene, as outlined below [8] (Eq. (8)). Similar coupling and dehalogenation were also reported by Henne and Postelneck [9]. The low cost of the alkene precursor is an attractive feature of this method. Other workers have approached the requisite precursor in other ways. For example, Dedek and Chvatal prepared 1,4-dibromo-2,3-dichlorohexafluorobutane *via* photochemical addition of 1,2-dibromo-1-chlorotrifluoroethane to chlorotrifluoroethene [9]; dehalogenation gave **1** [10]. However, the photochemical addition process gave the butane precursor in only modest yield (38%), thus the overall yield of **1** is not high. Haszeldine also prepared the requisite tetrahalohexafluorobutane *via* a multi-step route from chlorotrifluoroethene *via* a cyclobutene intermediate [11] (Eq. (9)).

$$F_2C=CFCl \xrightarrow[97\%]{ICl} CF_2ClCFClI \xrightarrow[\text{hv sealed tube}]{Hg} \underset{71\text{–}82\%}{CF_2ClCFClCFClCF_2Cl} \xrightarrow[EtOH\ 98\%]{Zn} \underset{\mathbf{1}}{F_2C=CFCF=CF_2} \quad (8)$$



(9)

Thermal decomposition of sodium perfluoroadipate has also been utilized as a route to **1** [12]. However, the low yield (30%) has limited the application of this process.

In our initial work to prepare trifluorovinylcopper from iodotrifluoroethene (**2**), Hansen discovered that direct insertion of Cu(0) into the carbon–iodine bond did not produce a stable trifluorovinylcopper reagent [13]. Instead, as found by Tatlow and Yagupol'skii (see above) copper mediated coupling of the vinyl iodide occurred to give the symmetrical diene [13–17], **1** (Eq. (10)).

$$2\underset{\mathbf{2}}{F_2C=CFI} + Cu(0) \xrightarrow[DMF]{\Delta} \mathbf{1} + 2CuI \quad (10)$$

Similarly (*Z*)-$CF_3CF{=}CFI$ gave only the (*E*)(*E*)-homodimer on reaction with copper–bronze in DMF [13]. Hansen speculated that the trifluorovinylcopper reagent was most likely formed but reacted rapidly with **2** to give **1** (Eq. (11)). Indeed, when trifluorovinylcopper

$$\mathbf{2} + 2\mathrm{Cu}(0) \xrightarrow[\Delta]{\mathrm{DMF}} \mathrm{CuI} + [\mathrm{F_2C = CFCu}] \xrightarrow{\mathbf{2}} \mathbf{1} \qquad (11)$$

(prepared by metathesis of $\mathrm{F_2C{=}CFZnBr}$ with Cu(I)Br) was treated with **2** at room temperature, **1** was formed in 63% yield [18]. For this route to be a useful approach to **1**, a practical method to **2** must be available. The literature method for the preparation of **2** was first reported by Park et al. [19], as outlined below (Eq. (12)). Hansen demonstrated that **2** could be more

$$\mathrm{F_2C = CFH} \xrightarrow[\text{autogenous pressure}]{\mathrm{ICl}} \underset{72\%\ \text{conversion}}{\mathrm{CF_2ClCFHI}} \xrightarrow[\text{KOH mineral oil } 95\,^\circ\mathrm{C}]{\text{powdered}} \underset{76\%\ \text{conversion}}{\mathbf{2}} \qquad (12)$$

readily prepared *via* quenching of the trifluorovinylzinc reagent [20–25] with iodine [20].

Raghavenpillai also discovered that quenching the trifluorovinylzinc reagent (prepared *via* metallation of $\mathrm{CF_3CH_2F}$) with iodine also gave **2** in 61% yield [26]. A large-scale procedure for the preparation of **2** from $\mathrm{F_2C{=}CFBr}$ has recently been published [27] (Eq. (13)).

$$\begin{tikzcd}
\mathrm{F_2C{=}CFBr} \arrow[r, "\mathrm{Zn}", "\mathrm{DMF}"'] & {[\mathrm{F_2C{=}CFZnX}]} \arrow[d, "\mathrm{I_2}"] & \mathrm{CF_3CFH_2} \arrow[l, "\mathrm{LDA}"', "\substack{\mathrm{ZnCl_2}\\ \mathrm{THF/RT}}"] \\
 & \substack{\mathrm{F_2C{=}CFI},\ 69\%\ \text{from}\ \mathrm{F_2C{=}CFBr}\ [27] \\ 61\%\ \text{from}\ \mathrm{CF_3CH_2F}\ [26]} &
\end{tikzcd} \qquad (13)$$

An alternative, mild pathway to **1** mimics the route that we developed for the preparation of (*E*)- and (*Z*)-perfluoro-1,3-pentadienes [28–30]. Thus, the palladium catalyzed coupling of the trifluorovinylzinc reagent with **2** readily provides **1** [31] (Eq. (14)).

$$[\mathrm{F_2C = CFZnX}] + \mathrm{F_2C = CFI} \xrightarrow[\mathrm{Pd(PPh_3)_4}\ \mathrm{RT\ to\ 40\,^\circ C} \sim 1\,\mathrm{h}\ 66\%]{\text{Triglyme}} \mathbf{1} \qquad (14)$$

In both the Cu(0) mediated coupling and Pd(0) catalyzed coupling processes, **2** is required as a reagent. Since **2** is prepared most conveniently from $[\mathrm{F_2C{=}CFZnX}]$, a more simple procedure would involve the preparation of **1** directly from the vinylzinc reagent. In the introduction section, it was noted that Norris and Finnegan [4] were successful in coupling $[\mathrm{CF_3C{\equiv}CZnCl}]$ to the diyne with $\mathrm{CuCl_2}$. Thus Hansen attempted to couple $[\mathrm{F_2C{=}CFZnX}]$ with $\mathrm{CuBr_2}$ as a direct route to **1** [32]. This reaction was extremely exothermic, and although **1** was obtained in low yield, the procedure was not easily scaled up. Later, Morken modified his $\mathrm{CuBr_2}$ procedure for the coupling of the pentafluoropropenyl-2-zinc reagent [33] to the coupling of the trifluorovinylzinc reagent with $\mathrm{CuBr_2}$. Success was achieved by simultaneous addition of the

$$[\mathrm{F_2C{=}CFZnBr}] + \mathrm{CuBr_2} \xrightarrow[\substack{\mathrm{DMF} \\ 0.5\ \text{to}\ 1\ \mathrm{mm\ Hg} \\ -25\,^\circ\mathrm{C}\ \text{to}\ -15\,^\circ\mathrm{C} \\ 97\%}]{\text{simultaneous addn.}} \underset{97\ :\ 3}{\mathbf{1} + \mathrm{F_2C{=}CFBr}} \qquad (15)$$

vinylzinc reagent and $\mathrm{CuBr_2}$ at lower temperature (−25 °C) (Eq. (15)). This simultaneous addition permitted better temperature control and condensation of **1** [34] (Eq. (15)). The small amount of $\mathrm{F_2C{=}CFBr}$ formed could be due to some residual olefin that was not removed by degassing of the trifluorovinylzinc reagent solution, but more likely is due to the known halogenation ability of Cu(I) halides [36,37].

2.2. *Preparation of perfluoro-2,3-dimethyl-1,3-butadiene*

Perfluoro-2,3-dimethyl-1,3-butadiene (**3**) has been prepared by pyrolysis (300–350 °C) of perfluoro-2-enylsilver in 56% yield [38], by pyrolysis (300 °C) of 1,3-bis-(trifluoromethyl)-2,2,4,4-tetrafluorobicyclobutane [39] and by fragmentation of $\mathrm{C_2F_5(CF_3)C{=}C(CF_3)C_2F_5}$ (Pt/530°–700 °C) [40]. Low yields, cyclization by-products and the use of toxic or expensive reagents plagued these previous reports. In a preliminary report, Morken described the preparation of 2,2-dibromohexafluoropropane and its facile conversion to the perfluoropropenyl-2-zinc reagent (**4**) [33,41]. He found that **4** could be readily converted to **3** *via* reaction with either $\mathrm{CuBr_2}$ or $\mathrm{FeCl_3}$

$$\begin{tikzcd}
\mathrm{CF_3CBr_2CF_3} \arrow[r, "\mathrm{Zn}", "\mathrm{DMF}"'] & \underset{\mathbf{4}}{\mathrm{CF_3C(ZnX){=}CF_2}} \arrow[r, "\mathrm{CuBr_2}", "\mathrm{DMF}"'] \arrow[d, "\mathrm{FeCl_3/DMF}"] & \underset{80\%}{\mathbf{3}} \\
 & \mathbf{3},\ 68\% &
\end{tikzcd} \qquad (16)$$

[33] (Eq. (16)). This route provides a convenient useful entry to this reactive diene under mild conditions [42]. Other workers have also described the oxidation of organocopper reagents [5] or copper (I) ate complexes with dioxygen [43]. Similarly, pyrolysis of organocopper reagents readily yield homodimers [5,44]. Thus, we investigated the reaction of the pentafluoropropenyl-2-copper reagent with dioxygen at room temperature [45,46] (Eq. (17)). Note (cf. experimental)

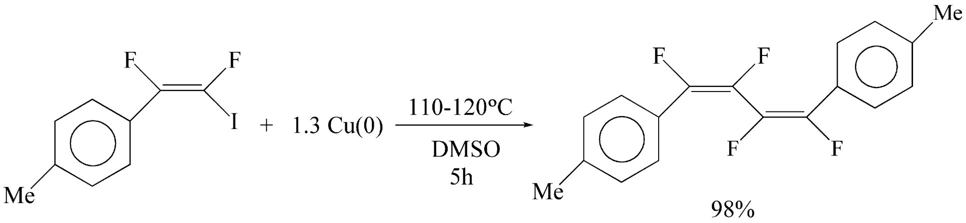
$$\underset{\mathbf{4}}{\mathrm{CF_3C(ZnX) = CF_2}} \xrightarrow[\mathrm{DMF\,RT}]{\mathrm{CuBr}} [\mathrm{CF_3C(Cu) = CF_2}] \xrightarrow[\mathrm{RT}]{\mathrm{O_2}} \underset{62\%}{\mathbf{3}} \qquad (17)$$

that **4** does not react with dioxygen. Morken also found that an (*E*),(*Z*) mixture of $\mathrm{CF_3(C_6H_5)C{=}CFCu}$ (prepared from a (*E*),(*Z*)- mixture of $\mathrm{CF_3(C_6H_5)C{=}CFZnBr}$) gave a mixture of the three isomers of $[\mathrm{CF_3(C_6H_5)C{=}CF}]_2$ on treatment with dioxygen at room temperature [47]. The three isomers could not be separated; the isomers were found in a 1:1.1:1.9 ratio [(*E*)(*E*)/(*Z*)(*Z*)/(*E*)(*Z*)]- as determined by ^{19}F NMR analysis of the reaction mixture [48]. The GC/MS of the mixture was in agreement with the molecular formula of the homodimers. Similarly, a degassed sample of (*E*)(*Z*)-$\mathrm{CF_3C(C_6H_5)C{=}CFCu}$

was heated in an NMR tube at 50–60 °C for 9 days and monitored by ^{19}F NMR. The major products (as determined by ^{19}F NMR) were the (*E*)(*E*), (*Z*)(*Z*) and (*E*)(*Z*)-homodimers. Thus, dioxygen oxidation or pyrolysis of fluorinated vinylcopper reagents appears to be an alternative entry to fluorinated symmetrical dienes [49]. Fluorinated vinylzinc and/or copper reagents are not the only precursors that can be dimerized by Cu(II) salts. For example, Muller and Dressler have reported that $K_2[F_2C{=}CFSiF_5]$ reacts with $Cu(II)SO_4$ to give **1** (14%) [50].

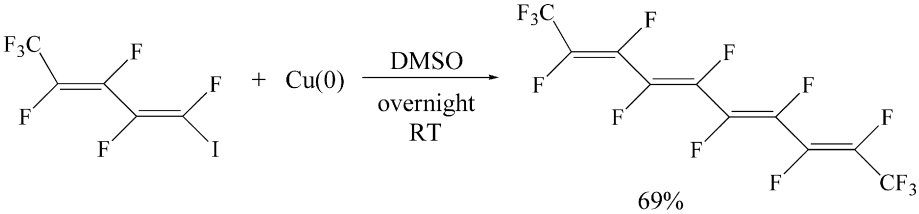
2.3. Other Cu(0) mediated symmetrical coupling reactions

Yagupol'skii and co-workers reported that (*Z*)-1-iodo-2-aryl-α,β-difluorostyrenes couples with Cu(0) in DMFA to give the (*E*)(*E*)-1,4-diaryl-1,3-tetrafluorobutadienes [2,51–53]. The corresponding (*Z*)(*Z*)-1,4-diaryl-1,3-tetrafluorobutadiene has only been reported by photoisomerization of the (*E*)(*E*)-analog [56]. Recently, we have reported a stereospecific route to (*E*)-α,β-difluoro-β-iodostyrenes [57]. To demonstrate that the corresponding (*Z*)(*Z*)-1,4-diaryl-1,3-tetrafluorobutadienes could be prepared stereospecifically by Cu(0) mediated coupling, Davis reacted (*E*)-p-$MeC_6H_4CF{=}CFI$ with activated copper in DMSO [58] (Eq. (18)).



(18)

The (*Z*)(*Z*)-diene was produced in excellent yield. This Cu(0) mediated coupling of fluorinated vinyl iodides was extended by MacNeil to the coupling of perfluorodienyl iodides [59]. Thus, when 1-iodo-1(*Z*)(3*E*)-heptafluoro-1,3-pentadiene was reacted with Cu(0), a good yield of (2*E*)(4*E*)(6*E*)(8*E*)-perfluoro-2,4,6,8-decatetraene was formed (Eq. (19)), as outlined below. As expected, the increase in the number of fluorines in the precursor enhanced the reactivity of the vinyl iodide precursor.



(19)

3. Conclusions

Hexafluoro-1,3-butadiene can be readily prepared *via* a variety of self-coupling processes, such as Cu(0) mediated coupling of iodotrifluoroethene, Pd(0) catalyzed coupling of iodotrifluoroethene with the trifluorovinylzinc reagent, and $CuBr_2$ mediated coupling of the trifluorovinylzinc reagent. Perfluoro-2,3-dimethyl-1,3-butadiene can be readily formed by treatment of the pentafluoropropenyl-2-zinc reagent with either $CuBr_2$ or $FeCl_3$. Alternatively, this substituted butadiene can be prepared by oxidation of the pentafluoropropenyl-2-copper reagent with dioxygen. Cu(0) mediated coupling of a (*E*)-substituted α,β-difluoro-β-iodostyrene provided the first useful route to (*Z*)(*Z*)-1,4-diaryl-1,3-tetrafluorobutadienes. Extension of the Cu(0) mediated coupling methodology to a perfluorodienyliodide demonstrated a useful process for the stereospecific preparation of perfluoropolyenes.

4. Experimental

4.1. General experimental procedures

The ^{19}F NMR spectra were recorded on a JEOL FX90Q Spectrometer or a Bruker AC-300 Spectrometer. Chemical shifts have been reported in ppm upfield from $CFCl_3$ and were generally determined in $CDCl_3$ solvent or d_6-acetone (10% by volume solutions) unless otherwise noted. ^{19}F NMR yields were determined by integration relative to internal benzotrifluoride. Routine ^{1}H NMR spectra were recorded on a JEOL FX90Q Spectrometer. High field ^{1}H NMR spectra were recorded on a Bruker WM 360X or a Bruker AC-300 Spectrometer using $CDCl_3$ as the internal lock solvent. Chemical shifts are reported in ppm downfield from internal TMS. The ^{13}C NMR spectra were obtained on a Brucker AC-300 Spectrometer with $CDCl_3$ as the internal lock solvent. Chemical shifts are reported in ppm downfield from internal TMS. Infrared absorbance spectra were obtained using a Mattson Cygnus 100 FTIR Spectrophotometer from solutions in CCl_4. The sample solutions were prepared from 10 μl of sample in 1 ml of CCl_4. All IR values have been reported in units of reciprocal centimeters. Low-resolution spectra

(LRMS) were obtained using a TRIO-1 GC Mass spectrometer operated at 70 eV in the electron impact mode, using a DB-1 column (0.25 mm ID × 15 m). High-resolution mass spectra (HRMS) were performed by the University of Iowa High Resolution Mass Spectroscopy Facility. The data were collected on a VG Analytical ZAB-HF mass spectrometer operated at 70 eV in the electron impact mode. Analytical GLPC were performed on a Hewlett-Packard Model 5890 equipped with a TCD detector and 3393A integrator. The column was packed with 5% OV101 on Chromosorb B. Capillary GLPC were performed using a FID. All boiling points were determined during fractional distillation and are uncorrected. Melting points were determined in a Thomas-Hoover Unimelt apparatus and are uncorrected. Starting materials were obtained from commercial vendors and/or prepared by literature procedures. DMSO was dried over CaH_2 overnight and distilled at ~70 °C/0.5 mm Hg prior to use. THF was distilled from sodium benzephenone ketyl at atmospheric pressure. DMF was dried by stirring overnight over CaH_2, then distilled at reduced pressure (bp ~ 65 °C/5 mmHg) prior to use. Copper–bronze powder was obtained from Aldrich and activated as described below. $FeCl_3$ (Aldrich, anhydrous, 98%) was dried in a Kugelrohr oven apparatus at 80 °C/5 mm Hg for 30 h. P_2O_5 was used in the cold receptacle of the apparatus. $CuBr_2$ (Aldrich) was used as received.

4.2. Activation of copper–bronze

Copper–bronze powder (Aldrich) was activated by the addition of 100 g to a solution made up of 200 ml CCl_4 and 30 g I_2. The mixture was stirred until the iodine color was no longer evident. The metal was filtered, washed with a solution of 20 ml conc. HCl in 200 ml acetone, followed by a washing with acetone. The copper metal was dried under full vacuum overnight.

4.3. Preparation of hexafluoro-1,3-butadiene via the reaction of $F_2C{=}CFCu$ and $F_2C{=}CFI$

The olefin, $F_2C{=}CFI$ (30 μl), was added to an NMR tube containing $F_2C{=}CFCu$ in DMF (0.6 ml of a 0.7 M solution—prepared from $F_2C{=}CFZnBr + CuBr$). ^{19}F NMR analysis showed no reaction after 5 min, but after 24 h at RT, $F_2C{=}CFCu$ had completely disappeared and hexafluorobutadiene was present in 63% ^{19}F NMR yield. The mixture was flash distilled and the distillate analyzed by GC–MS and ^{19}F NMR. GC-MS, *m/z* (relative intensity): 162 (42.5, M^+), 93 (100, M-CF_3). ^{19}F NMR (triglyme) (ppm): $\delta -93.1$ (dm, $^2J_{FF} = 48$ Hz, 1F), −107.1 (ddm, $^3J_{FF} = 105$ Hz, $^2J_{FF} = 48$ Hz), −180.4 (ddm, $^3J_{FF} = 105$ Hz, $^3J_{FF} = 27$ Hz), in good agreement with literature data [60–63].

4.4. Preparation of hexafluoro-1,3-butadiene via palladium coupling of the trifluorovinylzinc reagent and iodotrifluoroethene

A 100 ml flask was fitted with a dry ice/isopropyl alcohol condenser (with a nitrogen inlet, stir bar, septum and N_2 tee. The flask was charged with 50 ml of dry triglyme (*via* syringe) followed by the addition of 5.0 g (0.070 mol) of acid-washed zinc and 10.4 g (0.050 mol) of iodotrifluoroethene. After stirring for ~30 min, the flask became warm and the reaction mixture turned green. After the contents of the flask returned to room temperature, the stirring was stopped and the excess zinc allowed to settle. The supernatant solution was transferred (*via* syringe) into another 100 ml flask, which was connected to a trap cooled in a dry ice/isopropyl alcohol bath. Then, 3.00 g (0.0025 mol) $Pd(PPh_3)_4$ and 9.7 g (0.0467 mol) of $F_2C{=}CFI$ were added to the trifluorovinylzinc reagent solution, and the reaction mixture heated to 40 °C for 40 h. The contents of the reaction mixture were dark-brown and 2–3 ml of colorless liquid had collected in the trap. The reaction mixture was flash distilled at 40 mm/Hg, the volatiles transferred to Rotoflo tube to obtain 5.3 g (66%) of hexafluoro-1,3-butadiene. The ^{19}F NMR spectrum was identical to the reported literature [61–63] and to the butadiene prepared by alternative routes by co-workers (cf. above).

4.5. Preparation of hexafluoro-1,3-butadiene via oxidation of the trifluorovinylziinc reagent with cupric bromide

Trifluorovinylzinc reagent was prepared in 72% ^{19}F NMR yield from $F_2C{=}CFBr$ (34.2 g, 0.213 mol) and activated zinc (10.7 g, 0.164 mol) in DMF *via* the literature procedure [21,22]. Then, a 3-necked 250 ml flask, equipped with a stir bar, rubber septum, and a solids addition tube containing $CuBr_2$ (40.1 g, 0.157 mol) was connected to two −196 °C traps linked to a vacuum manifold. The flask was charged with 10 ml of dry DMF, cooled to −25 °C, and degassed at 0.5–1.0 mm Hg for several minutes. The previously prepared trifluorovinylzinc reagent (76 ml, 0.119 mol) was then syringed (slowly) into the flask with concomitant slow addition of $CuBr_2$ from the solids addition tube. Immediate boiling of hexafluoro-1,3-butadiene was observed in the flask. After complete addition of the zinc reagent and $CuBr_2$, the reaction mixture was stirred for 1.5 h with slow warming to −15 °C. At this time, trap #1 contained the bulk of the product and a small amount of DMF, while trap #2 contained small amounts of product—but no DMF. The volatile contents of trap #1 were allowed to distill into trap #2 by slowly warming trap #1 to room temperature. After 30 min, 9.32 g (0.0575 mol, 97% based on the amount of zinc reagent used) of product was isolated in trap #2. ^{19}F NMR analysis of the contents of trap #2 indicated a ratio of $C_4F_6{:}F_2C{=}CFBr$ of 97:3. The ^1H NMR of this mixture was silent. No $F_2C{=}CFH$ was observed by either ^{19}F or ^1H NMR or FTIR. The ^{19}F NMR data was in good agreement with literature values [61–63].

4.6. Preparation of pentafluoropropenyl-2-zinc reagent

A 4-neck 2 l flask was equipped with a pressure equalizing dropping funnel, immersion thermometer, stir bar, and a dry ice/isopropyl alcohol condenser attached to a nitrogen source. The apparatus was purged with N_2 then charged with activated zinc (155 g, 2.37 mol) and 600 ml of dry DMF. A solution of $CF_3CBr_2CF_3$ [41] (300 g, 0.968 mol) in DMF (300 ml) was then added dropwise to the well-stirred reaction mixture over a 3–4 h period at a rate that maintained the internal temperature at 70–80 °C. After completion of the reaction, the excess zinc was removed by filtration through a medium frit Schlenk funnel under positive N_2 pressure. The yield of the pentafluoropropenyl-2-zinc reagent was determined by ^{19}F NMR integration *vs.* internal hexafluorobenzene; yields ranged from 90 to 95%. ^{19}F NMR (DMF) (ppm): δ-49.0 (dd, $^4J_{FF} = 18$ Hz, $^4J_{FF} = 13$ Hz, 3F), −60.9 (dq, $^2J_{FF} = 37$ Hz, $^4J_{FF} = 18$ Hz, 1F), −72.5 (dq, $^2J_{FF} = 37$ Hz, $^4J_{FF} = 13$ Hz, 1F).

4.7. Preparation of perfluoro-2,3-dimethyl-1,3-butadiene via cupric bromide oxidation of pentafluoropropenyl-2-zinc reagent

A 100 ml flask was equipped with a Teflon coated stir bar and a solids addition tube containing 11.6 g (0.052 mol) of $CuBr_2$. The flask was cooled to 0 °C and charged with 0.042 mol of the pentafluoropropenyl-2-zinc reagent (prepared as described above). A −196 °C trap was connected to the apparatus and to a vacuum source (0.5–1 mm Hg). Then, with stirring, the $CuBr_2$ was added slowly *via* the solids addition tube at a rate to keep the reaction mixture from foaming into the trap. The lower layer of the distillate was removed by pipette to afford 4.41 g (80% yield) of perfluoro-2,3-dimethyl-1,3-butadiene, GLPC purity, 100%. ^{19}F NMR ($CDCl_3$) (ppm): δ −61.2 (dd, $^4J_{FF} = 20$ Hz, $^4J_{FF} = 14$ Hz, 3F); −67.8 (qd, $^4J_{FF} = 20$ Hz, $^2J_{FF} = 8$ Hz, 1F); −69.6 (m, 1F).

4.8. Preparation of perfluoro-2,3-dimethyl-1,3-butadiene via ferric chloride oxidation of pentafluoropropenyl-2-zinc reagent

A 100 ml flask equipped with a septum, solids addition tube containing anhydrous $FeCl_3$ (4.36 g, 0.0269 mol) and stir bar was charged with 10 ml of dry DMF. The flask was cooled to −15 °C, then the $FeCl_3$ was added slowly to control the exothermic reaction between the Lewis acid ($FeCl_3$) and the Lewis base (DMF). The apparatus was connected to a −196 °C trap linked to a vacuum system (0.5–1 mm Hg) and the $FeCl_3$/DMF solution degassed at −15 °C for several minutes. Then, 0.020 mol of a pentafluoropropenyl-2-zinc reagent was slowly added (*via* syringe) to the $FeCl_3$/DMF solution at a rate to keep the reaction mixture from foaming into the trap. The lower layer of the distillate was removed by pipette to afford 1.79 g (68%) perfluoro-2,3-dimethyl-1,3-butadiene, GLPC purity 100%. The ^{19}F NMR spectrum was identical to that reported above.

4.9. Preparation of perfluoro-2,3-dimethyl-1,3-butadiene via dioxygen oxidation of pentafluoropropenyl-2-copper reagent

A 2-necked 25 ml flask equipped with a septum and a glass stopcock was connected to a −78 °C trap, which was vented to a N_2 source. A 6 in. needle attached to the N_2 source was inserted into the septum and the apparatus purged with N_2. The flask was charged with 10 ml of a 0.57 M pentafluoropropenyl-2-zinc reagent solution (0.0057 mol); then an O_2 source was attached to the needle and dioxygen bubbled into the mixture at a rate sufficient to insure agitation and to keep the −78 °C trap under positive pressure. No reaction or distillate was observed after 1 h and ^{19}F NMR analysis of the reaction mixture indicated only $CF_3(ZnX)C{=}CF_2$. Then CuBr (1.34 g, 0.00934 mol) was added to the reaction mixture and the dioxygen flow resumed. After 15 min, the flask was warm to the touch and liquid had condensed in the trap. After an additional 30 min stirring, the −78 °C trap was found to contain 0.42 g (62% yield) of perfluoro-2,3-dimethyl-1,3-butadiene and a trace of DMF, as determined by ^{19}F and ^{1}H NMR, respectively.

4.10. Copper (0)-mediated-coupling of (Z)-p-nitro-β-iodo-α,β-difluorostyrene

A 25 ml flask equipped with a nitrogen tee, stir bar, septum port and condenser was charged with 0.05 g (0.00079 mol) of activated copper metal, 0.12 g (0.00038 mol) of (*Z*)-*p*-nitro-β-iodo-α,β-difluorostyrene and 5 ml of dry DMSO. The reaction mixture was stirred at 120 °C overnight. ^{19}F NMR analysis of the reaction mixture indicted total consumption of the starting material. After cooling, the reaction mixture was separated by flash column chromatography on silica gel using hexane/CH_2Cl_2 as eluant to give 0.05 g (71%) of a mixture of (1*E*), (3*E*)-1,4-di(*p*-nitrophenyl)-1,3-tetrafluorobutadiene and (1*E*), (3*Z*)-1,4-di(*p*-nitrophenyl)-1,3-tetrafluoro-butadiene in a ratio of 10:3. ^{19}F NMR ($CDCl_3$) (ppm): (1*E*), 3(*E*) isomer: δ −141.6 (d, $^3J_{FF} = 130$ Hz, 2F), −151.6 (d, $^3J_{FF} = 130$ Hz, 2F); ^{1}H NMR ($CDCl_3$) (ppm): δ 8.35 (d, $^3J_{HH} = 9.0$ Hz, 4H), 8.00 (d, $^3J_{HH} = 9.0$ Hz, 4H): For the (1*E*), (3*Z*) isomer: ^{19}F NMR ($CDCl_3$) (ppm): δ −120.6 (ddd, $^3J_{FF} = 13.6$ Hz, $^5J_{FF} = 7.9$ Hz, $^4J_{FF} = 5.7$ Hz, 1F), −138.3 (ddd, $^3J_{FF} = 40.7$ Hz, $^4J_{FF} = 15.3$ Hz, $^3J_{FF} = 14.0$ Hz), −141.5 (ddd, $^3J_{FF} = 131.6$ Hz, $^4J_{FF} = 15.9$ Hz, $^5J_{FF} = 8.2$ Hz, 1F), −151.2 (ddd, $^3J_{FF} = 131.6$ Hz, $^3J_{FF} = 40.7$ Hz, $^4J_{FF} = 5.7$ Hz, 1F); ^{1}H NMR ($CDCl_3$) (ppm): δ 8.31 (d, $^3J_{HH} = 8.7$ Hz, 2H), 8.26 (d, $^3J_{HH} = 8.5$ Hz, 2H), 7.82 (d, $^3J_{HH} = 8.8$ Hz, 2H), 7.72 (d, $^3J_{HH} = 8.9$ Hz, 2H).

4.11. Preparation of (Z,Z)-1.4-bis(p-tolyl)-1,3-tetrafluorobutadiene

A 25 ml flask equipped with a stir bar, N_2 tee, condenser, and septum port was charged with 0.25 g (0.004 mol) of activated Cu(0) powder, 8–10 ml of dry DMSO, and 0.95 g (0.0034 mol) of (*E*)-*p*-$MeC_6H_4CF{=}CFI$ [57]. The mixture was heated in an oil bath with stirring for 5 h at 110–120 °C. After cooling, the mixture was poured into 50 ml H_2O and extracted with Et_2O (3 ml × 75 ml). The ether layer was dried ($MgSO_4$) filtered, and the solvent removed by rotary evaporation. The product, 1.67 g (98%) was purified by column chromatography (R_f 0.3, hexane) to obtain a white solid: mp 71–72 °C. ^{19}F NMR ($CDCl_3$)(ppm): δ −119.1 (d, $^3J_{FF} = 9.5$ Hz, 1F), −139.3 (d, $^3J_{FF} = 9.5$ Hz, 1F); ^{13}C NMR ($CDCl_3$) (ppm): 136.4 (dddd, vinyl carbon, $^1J_{CF} = 252.7$ Hz, $^2J_{CF} = 32.1$ Hz, $^3J_{CF} = 24.4$ Hz, $^4J_{CF} = 6.1$ Hz), 151.5 (dm, vinyl carbon, $^1J_{CF} = 257.6$ Hz), 125.2 (dd, ${}^2J_{CF}$ = 24.4 Hz, ${}^3J_{CF}$ = 1.8 Hz, quaternary ring carbon), 126.8 (m, ring carbon), 129.0 (m, ring carbon), 140.7 (quaternary ring carbon), 21.9 (CH_3 carbon); ^{1}H NMR ($CDCl_3$) (ppm): 2.30 (s, 3H), 7.03 (d, ${}^3J_{HH}$ = 8.3 Hz, 2H), 7.08 (d, ${}^3J_{HH}$ = 8.3 Hz, 2H): FTIR (CCl_4): 3038 (w), 2925 (w), 1680 (m), 1613 (w), 1515 (w), 1284 (s), 1125 (m), 1018 (s), 956 (m), 862 (m). HRMS: calculated for $C_{18}H_{14}F_4$; 306.1032, observed 306.1028.

4.12. Preparation of (2E,4E,6E,8E)-perfluoro-2,4,6,8-decatetraene

A 25 ml flask with a septum port was fitted with a stir bar and N_2 tee. Then 5 ml of dry DMSO was syringed into the flask followed by the addition of activated copper metal (1.0 g, 0.015 mol) and 1.45 g (0.0045 mol) of 1-iodo-1(*E*),3(*E*)-heptafluoropentadiene. The mixture was stirred overnight at room temperature; then the contents of the flask were flash distilled. The distillate contained the product as a small bottom layer, which was pipetted from the distillate to give 0.6 g (69%) of the tetraene: GLPC purity, 98%; bp 42–43 °C (15 mm/Hg). ^{19}F NMR ($CDCl_3$) (ppm): δ −68.0 (dd, CF_3, ${}^3J_{FF}$ = 8 Hz, ${}^4J_{FF}$ = 20 Hz); −155.0 (bd, vinyl F, ${}^3J_{FF}$ = 136 Hz), −155.9 (dq, vinyl F, ${}^3J_{FF}$ = 136 Hz, ${}^4J_{FF}$ = 20 Hz), −150.9 (AB pattern, middle vinyl F's); ^{13}C NMR ($CDCl_3$) (ppm): 118.3 (qdd, CF_3, ${}^1J_{CF}$ = 270 Hz, ${}^3J_{CF}$ = 35 Hz, ${}^4J_{CF}$ = 4 Hz), vinyl F's 139.4–144.6. GCMS; *m*/*z* (relative intensity): 386 (M^+, 11.8), 317 (85.2), 267 (86.8), 248 (41.1), 229 (28.3), 217 (100.0), 205 (21.0), 198 (20.9), 186 (24.2), 181 (22.6), 179 (51.4), 155 (33.0), 131 (45.6), 117 (34.9), 93 (35.0), 69 (87.8). HRMS: calculated for $C_{10}F_{14}$ 385.9776, observed 385.9748. FTIR (CCl_4): 700 (m), 912 (m), 920 (m), 1012 (w), 1026 (w), 1146 (s), 1161 (s), 1169 (s), 1180 (s), 1186 (s), 1190 (s), 1201 (s), 1213 (s), 1226 (s), 1234 (s), 1290 (s), 1298 (s), 1304 (s), 1329 (m), 1337 (m), 1362 (s), 1380 (s), 1392 (s), 1425 (w), 1688 (w), 1715 (w).

Acknowledgement

We gratefully appreciate the financial support from the Air Force Office of Scientific Research and the National Science Foundation.

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