Butatriene Formation *via* CuBr-induced Self Coupling of an α-Bromo Vinyl Zinc Reagent: Synthesis and X-Ray Structure of *Z*-1,1,1,6,6,6-Hexafluoro-2,5-diphenylhexa-2,3,4-triene

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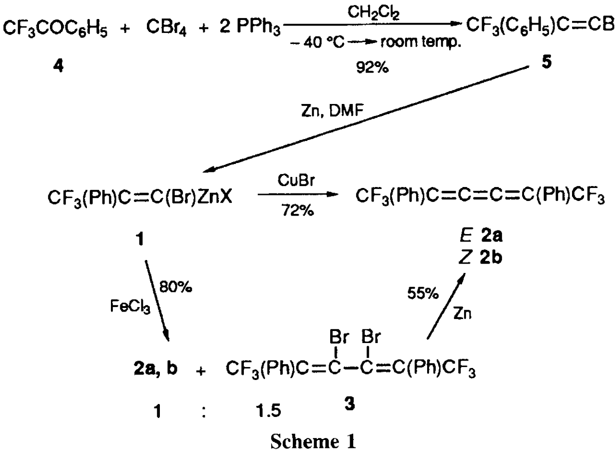
Title cumulenes **2a** and **2b** were prepared by reaction of $CF_3(Ph)C{=}C(Br)ZnX$ [X = Br, $CF_3(Ph)C{=}CBr{-}$] **1** with CuBr, or by oxidative coupling of **1** with $FeCl_3$ to form **2a,b** and $[CF_3(Ph)C{=}CBr{-}]_2$ **3**, which can be dehalogenated with zinc to afford **2a,b**; the cumulene isomers are readily separated by silica-gel chromatography, and may be prepared in good yield on a multi-gram scale.

Reports of fluorinated butatrienes are rare and only four examples have been reported in the literature. Of these, only one, $(CF_3)_2C{=}C{=}C{=}C(C_6H_5)_2$,[1] has been prepared on a scale amenable to further study.[2] $F_2C{=}C{=}C{=}CF_2$[3] proved to be explosive while $(CF_3)_2C{=}C{=}C{=}C(CF_3)_2$[4] and $[(Me_3C)_2C{=}C{=}C{=}C(CF_3){-}]_2$[5] have not been studied, perhaps owing to the complexity of their synthesis. Herein we report that the *E*-and *Z*-isomers of $CF_3(Ph)C{=}C{=}C{=}C(Ph)CF_3$ can be prepared and separated in high yield on a multi-gram scale and that the stereochemical assignment of these isomers has been demonstrated unequivocally by an X-ray crystal structure determination.

Recent work in our laboratory has demonstrated the preparation and synthetic utility of polyfluorinated vinyl organozinc,[6] cadmium[7] and copper[8] reagents. In contrast to the labile fluorinated vinyl lithium and magnesium reagents, the Zn, Cd and Cu reagents exhibit remarkable thermal stability. We have, however, noted one conspicuous dissimilarity between the vinylic copper reagent and the vinyl zinc or cadmium reagent. The vinyl zinc and cadmium reagents manifest excellent stability regardless of the type of α-halogen (F, Cl, Br, I); however, the vinyl copper reagents exhibit stability *only* when the α-halogen is fluorine. We have been unable to detect a vinyl copper reagent when the α-halogen is Cl, Br, I: only decomposition products of the organometallic compound were observed.



Scheme 1

The dibromo-styrene **5** was chosen as a model substrate and is readily prepared from trifluoroacetophenone and CBr_4–PPh_3 (Scheme 1). Treatment of **5** with acid-washed zinc in dimethylformamide (DMF) solvent yields a 1 : 3 mixture of mono- and bis-*E*- and *Z*-**1** in 90% yield, as determined by ^{19}F NMR integration *vs.* hexafluorobenzene internal standard. Reaction of **1** with a stoichiometric or catalytic amount of CuBr affords **2a, b** in 72% yield† (Scheme 1). Compounds **2a** and **2b** are readily separated by silica gel chromatography with hexane eluent (R_f values 0.64 and 0.52, respectively). Alternatively, oxidative coupling of **1** with $FeCl_3$ produces diene **3** as a

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† Satisfactory analytical data were obtained. *Selected spectroscopic data* for **2a, b**: mass spectrum, *m/z* 340 (100%), 321 (9.7%), 251 (54.1%), 202 (89.9%), 69 (7.3%); high resolution MS, calculated 340.0687, observed 340.0677; satisfactory elemental analysis; **2b**, m.p. 104–107 °C; ^{19}F NMR (90 MHz, $CDCl_3$) δ −60.41 (s); ^1H NMR (300 MHz, $CDCl_3$) δ 7.4 (m) and 7.7 (m); ^{13}C NMR (300 MHz, $CDCl_3$) δ C-9 157.7 (s), C-7 116.0 (q, J_{CF} 35.3 Hz) and C-8 121.7 (q, J_{CF} 275 Hz); UV (MeCN), λ_{max} 376.0 nm (ε 27000 l mol^{-1} cm^{-1}); **2a**, m.p. 140–141 °C; ^{19}F NMR (90 MHz, $CDCl_3$) δ −59.94 (s); ^1H NMR (300 MHz, $CDCl_3$) δ 7.5 (m) and 7.7 (m); ^{13}C NMR (300 MHz, $CDCl_3$) δ 156.9 (s), 115.7 (q, J_{CF} 34.9 Hz) and 121.9 (q, J_{CF} 275 Hz); UV (MeCN), λ_{max} 387.5 nm (ε 32000 l mol^{-1} cm^{-1}).

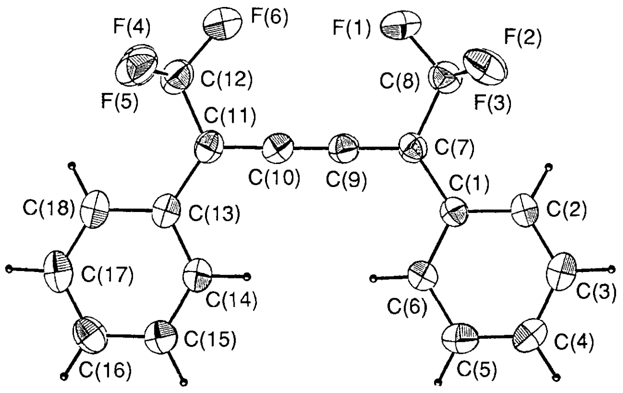

Fig. 1 ORTEP diagram for **2b**. Bond distances (Å) and bond angles (°) with estimated standard deviations in parentheses: F(1)–C(8) 1.316(3), F(2)–C(8) 1.323(3), F(3)–C(8) 1.330(3), F(4)–C(12) 1.336(3), F(5)–C(12) 1.333(3), F(6)–C(12) 1.334(3), C(1)–C(7) 1.472(3), C(7)–C(8) 1.497(3), C(7)–C(9) 1.333(3), C(9)–C(10) 1.253(3), C(10)–C(11) 1.322(3), C(11)–C(12) 1.485(3), C(11)–C(13) 1.479(3); C(7)–C(9)–C(10) 178.7(2), C(9)–C(10)–C(11) 179.0(2).

mixture of isomers as well as a significant quantity of the cumulene. Substituted diene **3** can be dehalogenated with Zn to afford **2a, b**.

X-Ray analysis‡ (Fig. 1) of **2b** provided unequivocal evidence for the stereochemical assignment. The C(7)–C(9) and C(9)–C(10) bond lengths of 1.33 and 1.25 Å are in agreement with reported values for butatrienes.[9] The two phenyl groups are nearly coplanar, as the dihedral angle between the two phenyl ring planes is 2 ± 1.5°. The *ortho* hydrogens have then forced the CF_3 groups to adopt a staggered conformation, with the two nearest fluorine atoms being equal distances above and below the ring.

Vinyl α-fluoro copper reagents are stable at room temperature and are observable by ^{19}F NMR spectroscopy.[8] However, the methathesis of zinc reagent **1** with CuBr does not generate an observable α-bromo copper reagent. Instead, only **2a, b** are detected spectroscopically. A possible route from $CF_3(Ph)C{=}CBrCu$ to **2a, b** could involve α-elimination of CuBr to generate an alkylidene carbene, which dimerizes to form **2a, b**. However, attempts to trap a carbene with butyl vinyl ether or tetrahydrothiophene have thus far been unsuccessful. Decomposition of $CF_3(C_6H_5)C{=}CBrLi$ in Et_2O also afforded only **2a, b** and no $CF_3{-}C{\equiv}C{-}C_6H_5$ was detected. This behaviour is in contrast with that of the non-fluorinated analogue, $CH_3(C_6H_5)C{=}CBrLi$, which was reported to rearrange to $CH_3C{\equiv}C{-}C_6H_5$ in ether solvent.[10] Perhaps the inductive effect of the trifluoromethyl group strengthens the C(1)–C(7) bond, thus inhibiting migration of the aryl group.

^{19}F NMR analysis of the reaction mixture of **1** and CuBr reveals an 8.5 : 1 ratio of **2b** to **2a**. However, the ratio after work-up and isolation is 4 : 1, indicative of isomerization of **2b** to **2a**. Indeed, heating a solution of **2b** in triglyme for 6 h at 115 °C produces a 3 : 2 ratio of **2a** to **2b**. Further heating at this temperature did not significantly alter this ratio.

In summary, the reaction of vinyl zinc reagent **1** with CuBr provides a facile, high-yield route to the novel and separable butatriene isomers **2a, b**. Fluorinated α-bromo vinyl zinc reagents have been determined to be stable at ambient temperature while the corresponding Cu reagent immediately decomposes to the title butatrienes. Easily accessible butatrienes with well-defined stereochemistry such as **2a** and **2b** will find application in studies assessing stereochemical influences in cycloaddition reactions.

We thank the National Science Foundation for support of this work and for a Graduate Fellowship (P.M.).

Received, 21st January 1991; Com. 1/00268F

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‡ *Crystal data* for **2b**: $C_{18}H_{10}F_6$, M = 340.27, orthorhombic, space group *Pbca*, a = 11.027(11), b = 16.524(4), c = 17.271(3) Å, U = 3147(4) Å^3, Z = 8, D_c = 1.44 g cm^{-3}, λ(Cu-Kα) = 1.5418 Å, μ(Cu-Kα) = 11.5 cm^{-1}. A half-sphere of diffraction intensity data from a single yellow needle crystal was collected at 295 K on an Enraf-Nonius CAD-4 diffractometer for 2θ from 2° to 140°. The 10008 measurements yielded 7077 observed reflections which averaged to 3383 unique reflections (internal agreement = 2.8% on F), of which 2094 had values greater than 3σ. The data were corrected for Lorentz, polarization and absorption (empirical absorption method) effects and the structure was solved by direct methods using the Enraf-Nonius SDP-VAX program package. Anisotropic least-squares refinement on all atoms except the hydrogen atoms (which were placed in fixed idealized positions and not refined) gave an agreement factor of R = 0.057 and R_w = 0.084. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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