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A FACILE, GENERAL ROUTE TO PERFLUOROALKYL ALLENES

Donald J. Burton*, Greg A. Hartgraves and Jeffrey Hsu
Department of Chemistry, The University of Iowa
Iowa City, Iowa 52242, U.S.A.

Abstract: Perfluoroalkyl copper reagents react with propargyl halides or tosylates in DMF or DMSO at 0°C-RT to afford perfluoroalkyl allenes regiospecifically in good yield.

Organomagnesium, zinc, and copper reagents have been widely utilized to prepare substituted allenes from propargylic halides, esters, tosylates or ethers.[1] However, only one example of a similar route to perfluoroalkyl allenes has been reported by Coe and Milner,[2] who attempted to react perfluoro-n-heptyl copper with propargyl bromide. These authors report that "minor explosions" were observed during workup and <10% of 1-(perfluoro-n-heptyl)-1,2-propadiene was isolated. Further investigation of this route to perfluoroalkyl allenes was inhibited by the apparently hazardous nature of the reaction.

In an earlier report, we had demonstrated that difluoromethyl cadmium and copper reagents reacted readily (and safely) with propargyl halides and tosylates to afford the difluoromethyl allenes in good yield.[3]

$$CF_2HCu + HC{\equiv}CC(CH_3)_2Cl \xrightarrow[-55°C]{DMF} \underset{78\%}{CF_2HCH{=}C{=}C(CH_3)_2}$$

We now wish to report that perfluoroalkyl copper reagents[4,5] also react readily with propargyl halides and tosylates to afford the corresponding perfluoroalkyl allenes in good yields.

$$R_FCu + \underset{X = Cl \text{ or } OTs}{HC{\equiv}CCR^1R^2X} \xrightarrow[\substack{\text{or DMSO}\\ 0°C\text{-RT}}]{DMF} R_FCH{=}C{=}CR^1R^2 + CuX$$

The reaction is applicable to primary, secondary, and tertiary propargylic halides or tosylates, and exhibits excellent regioselectivity.[6]

The choice of leaving group in the propargyl substrate is important. For example, when R_F is CF_3, C_2F_5 or n-C_3F_7, the tosylate analog gives better yields and simplifies the isolation procedure.[7] But the chloride analog works well when R_F is n-C_6F_{13} or n-C_8F_{17}, and is easily separated from the allene product.[8] Table I summarizes these results.

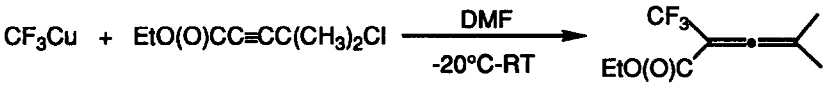
Table I: Preparation of Perfluoroalkyl Substituted Allenes[a]

$$F(CF_2)_nCu + HC\equiv CCR^1R^2X \xrightarrow[\text{DMSO} \atop \text{0°C-RT}]{\text{DMF} \atop \text{or}} F(CF_2)_nCH{=}C{=}CR^1R^2 + CuX$$

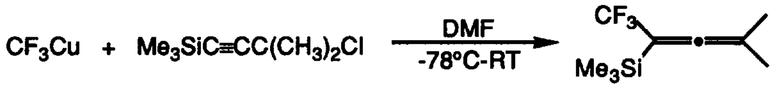
				Yields %[b]			
R^1	R^2	X	n=	1[c]	3[d]	6[d]	8[d]
H	H	OTs		68	41	49	30
H	CH_3	OTs		65	67	58	55
CH_3	CH_3	Cl		73	68	66	60
$-(CH_2)_5-$		Cl		66	64	54	54

a) All products gave satisfactory ^{19}F, ^{1}H, ^{13}C NMR, FT-IR and MS data
b) isolated yields
c) DMF solvent
d) DMSO solvent

This methodology is also applicable to the preparation of functionalized perfluoroalkyl substituted allenes. For example:



57%



52%

In a typical experimental procedure, a 100 mL three-necked round-bottomed flask fitted with a septum, magnetic stir bar and a nitrogen inlet was charged with 58 mL of a 0.82 M *n*-perfluorohexyl copper reagent (48 mmol) in DMSO.[5] The solution was cooled in an ice bath and 4.6 g (45 mmol) of 3-chloro-3-methyl-1-butyne was added dropwise *via* syringe. After the addition was completed, the reaction mixture was warmed to room temperature and stirred overnight. The nitrogen inlet was replaced with a vacuum distillation head which was fitted with a 100 mL receiving flask (cooled by liquid nitrogen). The volatile components were removed under vacuum, washed with 2 x 100 mL of water and dried over 4 Å molecular sieves. Distillation through a short path distillation apparatus gave 11.4 g (66%) of $CF_3{}^aCF_2{}^bCF_2{}^cCF_2{}^dCF_2{}^eCF_2{}^fCH=C=C(CH_3)_2$, 100% GLPC purity, bp 75-78°C/41 mm Hg. ^{19}F NMR (Jeol, 90 MHz)(*vs.* $CFCl_3$)($CDCl_3$): δ^a -81.4 ppm (t, J_{ac}=9.8 Hz), δ^b -126.8 ppm (m), $\delta^{c,d}$ -124.1 ppm (m), δ^e -122.1 ppm (m), δ^f -108.6 ppm (m); ^1H NMR (360 MHz)(*vs.* TMS)($CDCl_3$):δ 1.79 ppm (d, J =2.9 Hz, 6H), δ 5.22 ppm (thept, J =10.7 Hz, 1 H); ^{13}C NMR (*vs.* TMS)($CDCl_3$) $CF_3CF_2CF_2CF_2CF_2CF_2{}^fCH^g=C^h=C^i(CH_3)_2{}^j$: δ^g 81.5 ppm (t, J_{gFf} = 29.9 Hz), δ^h 204.7 ppm (t, J_{hFf} =7.8 Hz), δ^i 102.9 ppm (s), δ^j 17.6 ppm (s). FT-IR: 2991 (m), 2951 (m), 2915 (m), 1980 (C=C=C,m), 1447 (m), 1408 (m), 1364 (m), 1314 (m), 1289 (vs), 1241 (vs), 1205 (s), 1168 (m), 1146 (s), 1112 (m), 1067 (m), 1010 (m), 646 (m) cm^{-1}. High Resolution Mass Spectrum: Calc'd.: 386.0340; Found: 386.0313.

The ready availability of a wide variety of perfluoroalkyl copper reagents and propargyl precursors, the ease and safety of the experimental procedure, and the mild reaction conditions make this preparation an alternative route to perfluoroalkyl allenes, a class of useful partially fluorinated building blocks.

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5. CF_3Cu was prepared in DMF *via* the reported procedure; Wiemers, D.M., Burton, D.J. *J. Am. Chem. Soc.*, **1986**, *108*, 882. Perfluoroalkyl copper reagents ($>C_2$) were prepared from activated copper bronze powder (150 mmol), 50 mL of dry DMSO and 50 mmol of the appropriate *n*-perfluoroalkyl iodide. The reaction mixture was heated at 120°C for 2 hours and stirred at RT for 2 hours. Typical yields of the *n*-perfluoroalkyl copper reagents were 90-95%. Aliquots of the desired quantity of the *n*-perfluoroalkyl copper reagents were syringed from the supernatant liquid.

6. **Only** the perfluoroalkylallene was observed in the examples reported in Table I. In the case of $CH_3C{\equiv}CCH_2Br$ and *n*-C_3F_7Cu in DMSO, a 94/6 ratio of allene to alkyne (56% overall yield) was detected.[4]

7. The high molecular weight and lower volatility of the propargylic tosylate permitted easier separation of the allene from any unreacted propargylic substrate.

8. The higher-boiling allenes were easier to separate from any unreacted propargyl chloride than from the less volatile propargyl tosylate.

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