Journal of Fluorine Chemistry, *50* (1990) 257–263

Received June 28, 1990; accepted August 6, 1990

PRELIMINARY NOTE

The Preparation and Allylation of Perfluoroallyl Cadmium and Copper Reagents

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SUMMARY

Perfluoroallyl iodide reacts readily with acid-washed cadmium powder in DMF at 0° C to give the F-allylcadmium reagent. Metathesis of F-allylcadmium with Cu(I)Br at -35° C in DMF gives the F-allylcopper reagent. With zinc powder, perfluoroallyl iodide affords mainly F-1,5-hexadiene. Only a low yield of F-allylzinc was detected. Both F-allylcadmium and F-allylcopper react with allyl bromide to yield 1,1,2,3,3-pentafluoro-1,5-hexadiene.

Recent reports from our laboratory have demonstrated the facile preparation of *stable* F-alkyl[2,3], difluoromethyl[4], F-vinyl[5-7], and F-acetylenic[8] cadmium and zinc reagents as well as functionalized analogs containing these metals[9-11]. We have also reported that trifluoromethylcopper[12-14], F-vinyl copper[7,15] and F-acetylenic copper[16] reagents could be readily obtained via a copper (I) halide metathesis reaction of the corresponding cadmium or zinc reagent. These reagents have found extensive utility in preparative organofluorine chemistry[17-26]. Notable, however, is the complete absence of any F-allyl reagent from the list of known cadmium, zinc and copper species, although such moieties could be invaluable in the construction of monomers of fluoropolymers and precursors of fluoroepoxides or β-sultones.

0022-1139/90/$3.50

Consequently, we have addressed the preparation of a *stable* F-allyl organometallic reagent, and in this report we summarize the recent results of our work in this area.

Since the F-zinc reagents[2,6,8] have demonstrated exceptional stability, we initially attempted to prepare the F-allylzinc species from F-allyl iodide, **I**. However, mainly F-1,5-hexadiene, **II**, was detected under a variety of reaction conditions (48-77%). Spectroscopic evidence indicated that the F-allylzinc reagent was present in only 7-14% ^{19}F NMR yield in solvents such as THF,

$$\underset{\textbf{I}}{F_2C{=}CFCF_2I} + Zn \xrightarrow{\text{DMF}} \underset{\textbf{II}}{CF_2{=}CF(CF_2)_2CF{=}CF_2} + ZnI_2$$

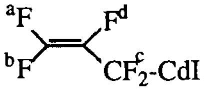
DMSO, DMF or DMAC.

However, the analogous F-allylcadmium reagent, **III**, could be prepared by the dropwise addition of **I** to a suspension of acid-washed cadmium powder in DMF at 0°C. The overall ^{19}F NMR yield of the cadmium reagents, existing as a mixture of mono and bis reagents in an initial ratio of 63:37, was 71%. A small amount (11%) of **II** was also formed, but this by-product could be effectively removed from the reaction mixture under reduced pressure.

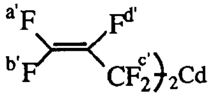
$$F_2C{=}CFCF_2I + Cd \xrightarrow[\substack{1\text{ hr}\\ 2)\text{ RT, 1 hr}}]{1)\text{ DMF, }0^\circ\text{ C}} \underset{\textbf{III}}{CF_2{=}CFCF_2CdI + (CF_2{=}CFCF_2)_2Cd} + \textbf{II}$$

The formation of the F-allylcadmium reagents was confirmed via analysis of the ^{19}F NMR spectrum of the reaction mixture. The ^{19}F NMR spectrum showed distinct resonances for three vinyl fluorines and one difluoromethylene group. Fluorine atoms in the positions α and β to cadmium exhibited the expected satellite peaks due to coupling with the ^{111}Cd/^{113}Cd isotopes. Although it was difficult in the ^{19}F NMR spectrum to distinguish between the mono and bis cadmium reagents, addition of cadmium iodide shifted the Schlenk equilibrium in favor of the mono reagent and the spectroscopic assignments (shown below) of both reagents could be made.

$$(CF_2{=}CFCF_2)_2Cd + CdI_2 \rightleftharpoons 2CF_2{=}CFCF_2CdI$$



^{19}F NMR (DMF): F^a: -102.9 ppm (1F, ddt); F^b: -114.3 ppm (1F, ddt); F^c: -105.6 ppm (2F, dd with ^{111}Cd/^{113}Cd satellites); F^d: -181.8 ppm (1F, dd with ^{111}Cd/^{113}Cd satellites); $J_{ab} = 74$ Hz; $J_{ac} = 11$ Hz; $J_{ad} = 30$ Hz; $J_{bc} = 21$ Hz; $J_{bd} = 114$ Hz; $J_{F^c\,^{111/113}Cd} \cong 240$ Hz; $J_{F^d\,^{111/113}Cd} \cong 68$ Hz.



^{19}F NMR (DMF): $F^{a'}$: -103.2 ppm (1F, ddt); $F^{b'}$: -115.1 ppm (1F, ddt); $F^{c'}$: -106.1 ppm (2F, dd-->t with ^{111}Cd/^{113}Cd satellites); $F^{d'}$: -182.7ppm (1F, dd with ^{111}Cd/^{113}Cd satellites); $J_{a'b'} = 75$ Hz; $J_{a'c'} = 12$ Hz; $J_{a'd'} = 31$ Hz; $J_{b'c'} = 18$ Hz; $J_{b'd'} = 115$ Hz; $J_{F^{c'}\,^{111/113}Cd} \cong 203$ Hz; $J_{F^{d'}\,^{111/113}Cd} \cong 86$ Hz.

The ^{113}Cd NMR spectrum of the mono reagent exhibited a triplet of doublets at 264 ppm (rel. to $CdSO_4$) with $^2J_{Cd,F} = 247$ Hz and $^3J_{Cd,F} = 70$ Hz in agreement with the values obtained from the ^{19}F NMR spectrum.

Consistent with the formation of the F-allylcadmium reagents, hydrolysis of the reaction mixture with dilute HCl gave a 97% isolated yield of 3-hydropentafluoropropene, **IV**, and treatment of the reaction mixture of the F-allylcadmium reagents with iodine gave a 64% isolated yield of **I**.

$$F_2C{=}CFCF_2CdX + HCl \xrightarrow{DMF} F_2C{=}CFCF_2H$$

IV

The F-allylcadmium reagent was thermally stable at -20°C without any significant change in concentration after 40 days, whereas 58% of the reagent decomposed at room temperature after 7 days. When a DMF solution of this reagent was heated, decomposition became rapid at 50°C. The main decomposition product observed was **IV**.

Like difluoromethylcadmium[4], the F-allylcadmium reagent also reacted with allyl bromide at room temperature to give 1,1,2,3,3-pentafluoro-1,5-hexadiene, **V**, in 78% isolated yield.

$$F_2C{=}CFCF_2CdX + CH_2{=}CHCH_2Br \xrightarrow[RT]{DMF} F_2C{=}CFCF_2CH_2CH{=}CH_2$$

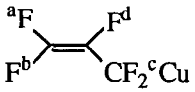
V

The corresponding F-allylcopper reagent, **VI**, can be obtained in 61% ^{19}F NMR yield via metathesis of the F-allylcadmium reagent with Cu(I)Br at -35°C.

$$F_2C{=}CFCF_2CdX + CuBr \xrightarrow[-35°C]{DMF} F_2C{=}CFCF_2Cu$$

VI

The resonances for **VI** in the ^{19}F NMR spectrum of **VI** were not well resolved. The resonance for vinyl fluorine, F^a, partially overlapped with one of the CF_2Cu peaks, and those for F^b and F^d were severely broadened. The CF_2Cu signals appeared at -98.8 ppm and -102.2 ppm (in a 29:71 ratio), indicative of two different copper species -- previously observed in many F-alkylcopper species in our laboratory[14]. As expected, the $^{111/113}Cd$ satellite couplings had disappeared.



^{19}F NMR (DMF): F^a: -103.1 ppm (1F, d overlapped with F^c); F^b: -114.3 ppm (1F, dm); F^c: -98.8 ppm and -102.2 ppm (2F, bm); F^d: -184.8 ppm (1F, bd); $J_{ab} = 60$ Hz; $J_{bd} = 110$ Hz.

VI was less thermally stable than the cadmium counterpart. A DMF solution of **VI** was cooled at -50°C and then allowed to warm gradually; at -30°C a mixture of decomposition products was detected and decomposition was rapid at temperatures > -20°C. Thus, this reagent must be formed and utilized at temperatures ≤ -30°C.

Hydrolysis of **VI** with dilute HCl did not give **IV**; only thermal decomposition was detected on warming. However, treatment of **VI** with iodine gave a 46% isolated yield of **I**.

VI also undergoes allylation readily at low temperatures. The problem of thermal lability can be overcome by utilizing catalytic amounts of CuBr in reactions of **VI**.

$$F_2C{=}CFCF_2Cu + CH_2{=}CHCH_2Br \xrightarrow[\text{-40°C-->RT}]{\substack{\text{cat. CuBr}\\ \text{DMF}}} \text{V}$$

86% isolated yield

In summary, *stable* F-allylcadmium and copper reagents have been prepared, and both exhibit high reactivity with allyl bromide. Further applications of these novel reagents are in progress, and detailed results will be reported in the near future.

We wish to thank the National Science Foundation and the Air Force Office of Scientific Research for support of this work. YT wishes to thank Shin-Etsu Chemical Co., Ltd. for the release time to pursue this research.

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