Journal of Fluorine Chemistry, 31 (1986) 461–465

Received: February 25, 1986; accepted: March 10, 1986

PRELIMINARY NOTE

The Stereospecific Preparation of *E*-Alkenyl Cadmium Reagents Directly From *E*-Alkenyl Iodides and Bromides and Cadmium Metal[+]

DONALD J. BURTON[*] and STEVEN W. HANSEN

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242 (U.S.A.)

SUMMARY

E-Alkenyl cadmium reagents can be readily prepared via the direct reaction of *E*-alkenyl iodides or bromides with cadmium powder in DMF at room temperature to 60°C. The reactions proceed with total retention of configuration, and subsequent functionalization processes also proceed with stereochemical control. The thermal stability of the cadmium reagents is excellent, and the *bis* reagent (Z-$CF_3CF{=}CF)_2Cd$ was isolated (via distillation) as a DMF or triglyme solvate. This approach provides a facile, easily scaled up, stereospecific, one-pot procedure to these stable alkenyl synthetic reagents.

The synthetic utility of fluorinated vinyl lithium and vinyl Grignard reagents has been impeded by the restricted thermal stability of these organometallic compounds. Current work in our laboratory has therefore been directed toward the preparation and synthetic applications of thermally stable fluorinated organometallic reagents, and recent reports from our laboratory [1,2] and others [3,4] have demonstrated some success with *E*-alkyl and/or *E*-aryl reagents. However, except for recent reports with Pd^0 catalyzed coupling of *E*-vinyl zinc reagents [5,6,7], the *E*-alkenyl analogs, thus far, have received only limited attention.

Consequently, our attention has focused on a general route to *stable* *E*-vinyl organometallic compounds that would satisfy the following

---

[+] Presented in part at the 11th International Symposium on Fluorine Chemistry, East Berlin, G.D.R., August 1985, Abstracts B-4

0022-1139/86/$3.50

criteria: (1) the reagents must possess thermal stability at room temperature or above, so that reactions could be readily scaled up and pregeneration of the organometallic compound could be accomplished with minimal experimental difficulty in standard glassware apparatus; (2) stereochemical integrity with *E,Z*-precursors should be retained in formation of the organometallic reagent, so that stereochemical control could potentially be accomplished in further elaboration of these intermediates; (3) the reagents must possess functionalization (or exchange) capability, so that they could be utilized in preparative synthetic transformations to yield polyfunctionalized materials; and (4) formation of these reagents be achievable in a one step (or one-pot) from accessible precursors.

Our initial focus concentrated on the direct preparation of *F*-alkenyl copper reagents. However, all attempts to pregenerate *F*-vinylic copper reagents directly via reaction of *F*-vinylic halides and activated copper were unsuccessful; only the coupled product (symmetrical diene) was obtained. Apparently, the vinyl copper intermediate reacts rapidly with

$$2\ CF_2{=}CFI \ + \ 2\ Cu \longrightarrow CF_2{=}CF{-}CF{=}CF_2 \ + \ 2\ CuI$$

additional vinyl halide to give the symmetrical diene. Consequently, an additional prerequisite in our approach was the selection of an organometallic compound that not only met the previously noted criteria, but one that would not readily couple with the vinyl halide precursor.

Thus, we selected organocadmium reagents for our initial model studies. Analogous hydrocarbon analogs exhibited stability and gave no indication of coupling with vinyl halides. Additionally, the ^{111}Cd and ^{113}Cd NMR active isotopes in the organometallic compound would allow us to monitor formation of the organometallic reagent and assist in mono or bis structural assignments. Also, in the formation of *F*-aryl cadmium reagents from bromopentafluorobenzene and cadmium metal, no biphenyl (coupled) product was observed [1].

We are pleased to report herein that these expectations were realized and that alkenyl cadmium reagents can be easily prepared via direct reaction of *F*-vinyl iodides or bromides in DMF under mild conditions. The vinyl iodides react readily (short induction period) at room temperature,

$$\underset{X\ =\ I,\ Br}{R_FCF{=}CFX} \ + \ Cd \xrightarrow[\text{RT-60}^{\circ}\text{C}]{\text{DMF}} R_FCF{=}CFCdX \ + \ (R_FCF{=}CF)_2Cd \ + \ CdX_2$$

and the vinyl bromides require mild heating (60°C). The cadmium reagents were formed as a mono/bis mixture and this ratio varied with structure of the vinylic halide. However, no significant difference in mono/bis rates of reaction was detected in functionalization of these reagents. Table I summarizes these preliminary results.

TABLE I

Preparation of Alkenyl Cadmium Reagents from *E*-Vinyl Halides and Cadmium

$$R_FCF{=}CFX + Cd \xrightarrow[RT-60^{o}C]{DMF} R_FCF{=}CFCdX + (R_FCF{=}CF)_2Cd + CdX_2$$

Olefin	Cadmium Reagent[a]	Yield[b]
$CF_2{=}CFI$	$CF_2{=}CFCdX$	99
Z-$CF_3CF{=}CFI$	*Z*-$CF_3CF{=}CFCdX$	96
E-$CF_3CF{=}CFI$	*E*-$CF_3CF{=}CFCdX$	92
Z-$CF_3(CF_2)_4CF{=}CFI$	*Z*-$CF_3(CF_2)_4CF{=}CFCdX$	95
$CF_3CF{=}CICF_3$[c]	$CF_3CF{=}C(CF_3)CdX$[d]	91
$CF_3CF{=}C(Ph)CF{=}CFBr$[e]	$CF_3CF{=}C(Ph)CF{=}CFCdX$[f]	61
E-$CF_3C(Ph){=}CFI$	*E*-$CF_3C(Ph){=}CFCdX$	77

[a] Mixture of mono and bis reagent; X = halogen or another *E*-alkenyl group.

[b] ^{19}F NMR yield *vs.* $PhCF_3$.

[c] E/Z mixture; E/Z = 39/61

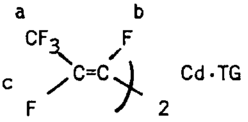
[d] E/Z = 37/63

[e] E,Z:Z,Z = 90/10

[f] E,Z:Z,Z = 90/10

The reactions proceed with total retention of configuration, as determined from ^{19}F NMR or ^{113}Cd NMR analysis of the cadmium compound or ^{19}F NMR analysis of the resultant hydrolysis product, $R_FCF{=}CFH$. The thermal stability of these organometallic compounds is remarkable. A solution of *Z*-$CF_3CF{=}CFCdX$ in dry DMF at room temperature lost only 3% activity in one day, 12% activity in 8 days, and 15% activity in 35 days.

Even at 123°C this solution lost only 25% activity in 1.5 hours. Indeed, a short-path distillation of such a reaction mixture followed by recrystallization from CH_2Cl_2/pentane (1:5) gave white crystals of the ($\underset{\sim}{Z}$-$CF_3CF{=}CF)_2Cd{\cdot}DMF$ solvate, mp 77-80°C. Distillation of the reaction mixture from triglyme, followed by recrystallization of the distillate from CH_2Cl_2/pentane (1:7) gave an analogous triglyme solvate, ($\underset{\sim}{Z}$-$CF_3CF{=}CF)_2Cd{\cdot}TG$, mp 64-65°C with the following spectroscopic properties:



^{19}F NMR ($CDCl_3$) :	a	-67.2 ppm (dd)	J_{ab} = 22.3 Hz
	b	-145.8 ppm (ddq)	J_{ac} = 12.8 Hz
	c	-177.5 ppm (dq)	J_{bc} = 103.8 Hz
^{113}Cd NMR ($CDCl_3$)	:	236.4 ppm (tt)*	$J_{b,}{}^{111}Cd$ = 306 Hz
			$J_{b,}{}^{113}Cd$ = 320 Hz
			$J_{c,}{}^{111}Cd,{}^{113}Cd$ = 48 Hz

All the cadmium reagents are extremely moisture sensitive and are rapidly hydrolyzed to $R_FCF{=}CFH$. Functionalization with $CH_2{=}CHCH_2Br$, $(EtO)_2PCl$, and Ph_2PCl occurred readily. Acylation with acyl halides or acid anhydrides, however, failed to give the α,β -unsaturated ketone; but instead gave $(CH_3)_2NCH(R_F)_2$ via a solvent participation reaction.

The operational details of a typical experimental procedure are outlined for the preparation of $\underset{\sim}{Z}$-$CF_3CF{=}CFCdX$ from $\underset{\sim}{Z}$-1-iodo-$\underset{\sim}{E}$-propene and cadmium powder.

A two-necked, 50 ml, round bottom flask fitted with thermometer, septum port, magnetic stir bar, and condenser connected to a nitrogen source was charged with acid-washed cadmium powder (1.70 grams, 15 mmoles) and 11 ml of dry DMF, and the apparatus maintained under a nitrogen atmosphere. To this mixture was added $\underset{\sim}{Z}$-1-iodo-$\underset{\sim}{E}$-propene (3.1 grams, 12 mmoles). The reaction mixture was stirred until the mild exotherm sub-

---

*Under extreme high resolution the spectrum appears as a triplet of triplets of septets. However with normal resolution the coupling of ^{113}Cd-CF_3, J = 4 Hz, is normally not observed.

sided and the mixture had cooled to room temperature. Then, the excess cadmium was removed by pressure filtration (under dry nitrogen) of the reaction mixture through a fine fritted glass filter (Schlenk funnel). ^{19}F NMR analysis of the resultant solution indicated a 96% yield (vs. $PhCF_3$) of the Z-$CF_3{}^aCF^c{=}CF^bCdX$ reagent (mono/bis = 67/33); ^{19}F NMR (DMF) exhibits resonances at -65.9 ppm (dd)CF_3; -141.5 ppm (bd.m)F^b; -177.8 ppm (bd.dq) F^c; J_{ab} 23 Hz; J_{ac} 12 Hz; J_{bc} 102 Hz. Functionalization reactions were carried out utilizing this solution.

In conclusion, a simple, mild, high yield, stereospecific preparation of E-alkenyl cadmium reagents is described. These organometallic compounds adequately meet the criteria designed for the preparation of stable E-alkenyl organometallic reagents, and we anticipate they will find extensive utilization in preparative chemistry as well as applicability for the synthesis of other organometallic compounds (not available via direct synthesis) via metathesis processes. Our work continues to explore these interesting reagents and future reports will detail applications of these organometallic reagents.

We wish to thank the Air Force Office of Scientific Research and the National Science Foundation for support of our work.

1 P.L. Heinze and D.J. Burton, J. Fluorine Chem., 29 (1985) 359.
2 D.J. Burton and D.M. Wiemers, J. Am. Chem. Soc., 107 (1985) 5014.
3 L.J. Krause and J.A. Morrison, J. Chem. Soc. Chem. Commun., (1980) 671.
4 H. Lange and D. Naumann, J. Fluorine Chem., 26 (1984) 1; 26 (1984) 93.
5 P.L. Heinze and D.J. Burton, J. Fluorine Chem., 31 (1986) 115.
6 J.P. Gillet, R. Sauvetre, and J.F. Normant, Tetrahedron Letters, (1985) 3999.
7 F. Tellier, R. Sauvetre, and J.F. Normant, J. Organometallic Chemistry, 292 (1985) 19.