Journal of Fluorine Chemistry, 35 (1987) 415–420
Received: October 3, 1986; accepted: October 20, 1986

PRELIMINARY NOTE

The Stereospecific Preparation of Fluorinated Vinyl Zinc Reagents From Polyfluorinated Vinyl Iodides or Bromides and Zinc Metal

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SUMMARY

Fluorinated vinyl zinc reagents can be prepared readily via the direct reaction of polyfluorinated vinyl iodides or bromides with zinc metal in a variety of solvents, such as DMF, DMAc, THF, glymes, and acetonitrile. The formation of symmetrical dienes via coupling of the vinyl halide is not observed. With *E* and *Z*-vinyl substrates total retention of configuration is observed in the formation of the zinc reagents, and in subsequent functionalization reactions. The excellent thermal stability of these zinc reagents at or above room temperature, and the possibility of employing a variety of solvents allow subsequent reactions to be easily tailored to meet experimental requirements. Therefore, this approach provides a facile, easily scaled up, stereospecific, one-pot procedure to these stable vinyl organometallic reagents.

The limited thermal stability of fluorinated vinyl lithium and vinyl Grignard reagents has greatly restricted their synthetic utility. 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 [1,2,3] and others [4,5] have demonstrated some success with *F*-alkyl and/or *F*-aryl reagents. However, except for recent reports with Pd^0 catalyzed coupling of *F*-vinyl zinc reagents [6,7,8,9], the *F*-vinyl analogs, thus far, have received only limited attention. Consequently, our attention has focused on a general direct route to *stable* *F*-vinyl organometallic compounds that would satisfy several critical criteria [10].

0022-1139/87/$3.50

We are pleased to report herein a preparation of vinyl zinc reagents which meets all of our criteria. Fluorinated vinyl iodides react smoothly with zinc metal at room temperature in a variety of solvents, including DMF, DMAc, THF, glymes, and acetonitrile. *E*-vinyl bromides also readily react with zinc metal at room temperature in DMF. The induction periods for these reactions vary from a few seconds to several minutes. The zinc reagents are formed as a mono/bis mixture, and this ratio varied with the structure of the vinylic halide and the solvent (cf. Table I).

$$\underset{X=I,Br}{R_FCF{=}CFX} + Zn \xrightarrow[RT]{solvent} \underset{mono}{R_FCF{=}CFZnX} + \underset{bis}{(R_FCF{=}CF)_2Zn} + ZnX_2$$

The mono and bis zinc reagents were distinguished by ^{19}F NMR, by enhancement of the signal for the mono reagent on addition of the appropriate zinc halide at the expense of the signal for the bis reagent, as expected from the following equilibrium:

$$(R_FCF{=}CF)_2Zn + ZnX_2 \rightleftharpoons 2\ R_FCF{=}CFZnX$$

The vinyl zinc reagents exhibit exceptional thermal stability. A sample of *Z*-$CF_3CF{=}CFZnX$ in TG showed no loss of activity after 3 days at room temperature, and a loss of only 10% activity after 36 days at room temperature. Similarly, *Z*-$CF_3CF{=}CFZnX$ showed only a 5% loss of activity after 3 days at 65°C, and 25% loss of activity after 36 days at 65°C. A sample of $CF_3C(Ph){=}CFZnX$ in DMF lost only 1% activity after 16 hours at 70°C. This excellent stability permits these reagents to be formed on a large scale and utilized over an extended period in a variety of synthetic reactions without any significant change in activity of the stock reagent.[+]

The stereochemical integrity of the *E,Z*-vinyl halides is preserved at all times. The stereochemistry is conveniently monitored by ^{19}F NMR. *Cis* and *trans* vinyl fluorines in the zinc reagent are readily distinguished by the large coupling between *trans* vinyl fluorines (typically 100-113 Hz *vs.*

[+] Stock reagents of [$CF_2{=}CFZnX$] are routinely prepared on a 0.5 M scale. The resulting solution can be stored at room temperature or in a refrigerator under nitrogen for several days to several weeks.

TABLE I

Preparation of Vinyl Zinc Reagents from *E*-vinyl Halides and Zinc Metal

$$R_FCF{=}CFX + Zn \xrightarrow{\text{solvent/RT}} R_FCF{=}CFZnX + (R_FCF{=}CF)_2Zn + ZnX_2$$

vinyl halide	solvent[a]	Zinc reagent[b]	mono:bis	Yield[c]
$CF_2{=}CFI$	DMF	$CF_2{=}CFZnX$	80:20	79%
	DMAc		84:16	97%
	MG			60%
	TG		68:32	95%
	TetG		67:33	85%
$CF_2{=}CFBr$	DMF	$CF_2{=}CFZnX$	95:5	72%
$CF_2{=}CBr_2$	DMF	$CF_2{=}CBrZnX$	68:32	97%
Z-$CF_3CF{=}CFI$	THF	*Z*-$CF_3CF{=}CFZnX$	68:32	98%
	TG		65:36	96%
	DMF		74:26	100%
	CH_3CN		81:19	90%
E-$CF_3CF{=}CFI$	TG	*E*-$CF_3CF{=}CFZnX$	59:41	100%
Z-$CF_3CF_2CF{=}CFI$	TG	*Z*-$CF_3CF_2CF{=}CFZnX$		90%
Z-$CF_3(CF_2)_4CF{=}CFBr$	DMF	*Z*-$CF_3(CF_2)_4CF{=}CFZnX$		77%
Z-$CF_3(CF_2)_4CF{=}CFI$	TG	*Z*-$CF_3(CF_2)_4CF{=}CFZnX$		74%
$CF_3C(Ph){=}CFBr$[d]	DMF	$CF_3C(Ph){=}CFZnX$[d]		94%
$CF_3C(Ph){=}CBr_2$	DMF	$CF_3C(Ph){=}CBrZnX$[e]		95%
E-$CF_3C(Ph){=}CFI$	THF	*E*-$CF_3C(Ph){=}CFZnX$	67:33	78%
Z-$CF_3(C_6F_5)C{=}CFI$	THF	*Z*-$CF_3(C_6F_5)C{=}CFZnX$	57:43	86%
$CF_3CF{=}C(Ph)CF{=}CFBr$[f]	DMF	$CF_3CF{=}C(Ph)CF{=}CFZnX$[f]		71%
E-$CF_3CH{=}CFI$	TG	*E*-$CF_3CH{=}CFZnX$	67:33	89%
E-$CF_3CF{=}C(CF_3)I$	TG	*E*-$CF_3CF{=}C(CF_3)ZnX$	80:20	75%

[a] MG = monoglyme, TG = triglyme, TetG = tetraglyme.

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

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

[d] *E*/*Z* mixture; *E*/*Z* = 59/41

[e] *E*/*Z* = 67/33

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

0-32 Hz for *cis* vinyl fluorines). While not as dramatic, the coupling between a vinyl fluorine and a vinyl CF_3 (typically 10-12 Hz for *trans vs.* 19-22 Hz for *cis*) in the zinc reagent may also be used to monitor stereochemistry. The stereochemistry of the zinc reagents prepared from 1,1-dibromoolefins was determined from the hydrolysis product using the proton / fluorine coupling constants (typically 0 Hz for *trans vs.* 2 Hz for *cis* coupling between a vinyl H and a vinyl CF_3).

The zinc reagents are moisture sensitve and are readily hydrolyzed to $R_fCF{=}CFH$. The zinc reagents also react rapidly with I_2 to yield the corresponding iodides. This reaction allows the more accessible *E*-vinyl bromides [11] to be conveniently converted to the *E*-iodides. Perhaps the most significant reaction of these zinc reagents is the metathesis reaction with copper bromide. The *E*-vinyl copper reagents have been prepared from the zinc reagents in DMF at room temperature by reaction with CuBr [12]. The copper reagents are formed stereospecifically and possess excellent functionalization capability.

It is important to note that while the copper reagents have been observed only in DMF solvent, the zinc reagents participate in similar functionalization reactions, under CuBr mediation, in a variety of solvents. In solvents like glymes or THF the addition of CuBr to the zinc reagent does not yield an NMR observable copper species. However, in the presence of CuBr the reactivity of the zinc reagent is greatly enhanced. This property has proven to be very valuable in the preparation of trifluorovinyl ketones. Acylation of the trifluorovinyl copper reagent in DMF results in decomposition [13], presumably due to reaction of the highly reactive product with DMF. However, if the trifluorovinyl zinc reagent is formed in a glyme solvent, the acylation reaction produces high yields of the trifluorovinyl ketones with CuBr catalysis [14].

Vinyl cadmium reagents have been formed via an analogous reaction [10]. While the cadmium reagents also meet our criteria, the zinc reagents have some superior qualities. The zinc reagents may be prepared at room temperature from the often more accessible *E*-vinyl bromides as well as the *E*-iodides. There is also less concern over toxicity and cost with zinc. Finally, perhaps the most important advantage is the possibility for functionalization in solvents other than DMF.

The operational details of a typical experimental procedure are outlined for the preparation of *E*-$CF_3CF{=}CFZnX$:

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 zinc powder (9.8 g, 150 mmoles) and 50 ml of dry TG, and the apparatus maintained under a nitrogen atmosphere. To this mixture was added *E*-1-iodo-*E*-propene (12.9 g, 50 mmoles). The reaction was stirred until the mild exotherm subsided and the mixture had cooled to room temperature. Then, the excess zinc was removed by pressure filtration (under dry nitrogen) of the reaction mixture through a medium fritted glass filter (Schlenk funnel). ^{19}F NMR analysis of the resultant solution indicated a 100% yield (*vs.* $PhCF_3$) of the *E*-$CF_3{}^aCF^c{=}CF^bZnX$ reagent (mono/bis = 59/41). ^{19}F NMR (TG) exhibits resonances for the mono reagent at -69.3 ppm (dd) CF_3, -135.3 ppm (q) F^b, -152.4 ppm (q) F^c, J_{ab} 7.3 Hz, J_{ac} 17.1 Hz; for the bis reagent at -70.6 ppm (m) CF_3, -137.2 ppm (m) F^b, -153.6 ppm (q) F^c, J_{ac} 14.6 Hz.

In conclusion, a simple, mild, high yield, stereospecific preparation of fluorinated vinyl zinc reagents is described. These organometallic compounds meet and even surpass the criteria designed for the preparation of stable fluorinated vinyl organometallic reagents [10], 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 National Science Foundation and the Air Force Office of Scientific Research for support of our work. TDS also acknowledges the Graduate College of the University of Iowa for a Teaching-Research Fellowship.

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