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PRELIMINARY NOTE

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The Preparation and Allylation of Difluoromethylcadmium

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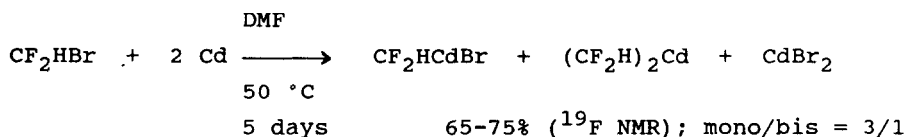
SUMMARY

The reaction of iodo- and bromodifluoromethane with cadmium powder in DMF at room temperature provides a useful route to difluoromethylcadmium. This partially fluorinated cadmium reagent exhibits excellent thermal stability to temperatures of 65-75 °C, and rapid decomposition does not occur until 105 °C. This reagent reacts readily with allylic halides and shows promise as a new difluoromethylation reagent.

The preparation of F-alkyl and F-vinylcadmium reagents has recently received considerable attention [1-13]. These F-cadmium compounds display excellent thermal stability and have been utilized as difluorocarbene, F-alkyl and F-vinyl transfer reagents.

The ease of reaction of F-alkyl iodides and bromopentafluorobenzene with cadmium metal [7] prompted us to examine this approach as a method for the preparation of a partially fluorinated cadmium reagent. Our initial interest focused on: (a) the ease of formation of a partially fluorinated cadmium reagent vs. the F-alkyl analog; (b) the stability of this reagent vs. the F-analog; and (c) the reactivity of this reagent vs. the F-analog.

Iododifluoromethane reacted with acid-washed cadmium powder in DMF in less than one hour to give a 91% ( $^{19}\text{F}$  NMR) yield of difluoromethylcadmium. Bromodifluoromethane reacted similarly albeit more slowly. After five days at 50 °C, the reaction with bromodifluoromethane was >90% complete. The difluoromethylcadmium reagents were identified via their characteristic  $^{19}\text{F}$  NMR spectrum, which showed the expected doublets at -117.7 ppm and -119.2 ppm, respectively, for the



difluoromethyl groups with the distinctive  $^{111}\text{Cd}/^{113}\text{Cd}$  satellites (cf. Fig. 1). The mono and bis reagents were unequivocally identified from the  $^{113}\text{Cd}$  NMR spectrum of the mixture, which shows a triplet of doublets at 253.3 ppm for the mono species and a pentet of triplets for the bis reagent (cf. Fig. 2) at 228.6 ppm. Hydrolysis of the reaction mixture with  $\text{D}_2\text{O}$  gave a 65% isolated yield of  $\text{CF}_2\text{HD}^*$ , and treatment of the reaction mixture with iodine gave a 96% isolated yield of  $\text{CF}_2\text{HI}^{**}$  consistent with the spectroscopic assignments.

The difluoromethylcadmium reagent is thermally stable at room temperature with loss of only 31% activity after two months. When a DMF solution of this reagent is heated, little decomposition occurs until 65-75 °C. At temperatures >105 °C, decomposition is rapid. The main decomposition product detected is  $\text{CF}_2\text{H}_2$ . Thus, the thermal stability of difluoromethylcadmium in DMF is similar to trifluoromethylcadmium in DMF [8].

\*  $^{19}\text{F}$  NMR ( $\text{CCl}_4$ ):  $\phi^*$  -143.2 ppm (dt);  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  5.62 (t);  $^2\text{D}$  NMR ( $\text{CCl}_4$ ):  $\delta$  3.60 (t) rel. to  $\text{d}_6$  acetone;  $J_{\text{FD}}$  7.8 Hz,  $J_{\text{FH}}$  50.8 Hz; GC/MS: m/e 50 (5.4), 51 (43.1), 52 (100), 53 (12.1).

\*\*  $^{19}\text{F}$  NMR ( $\text{d}_6$  acetone):  $\phi^*$  -67.5 ppm (d);  $^1\text{H}$  NMR ( $\text{d}_6$  acetone):  $\delta$  8.16 (t);  $J_{\text{HF}}$  56.2 Hz; GC/MS: m/e 51 (33.7), 127 (100), 159 (21.9), 178 (60.6).

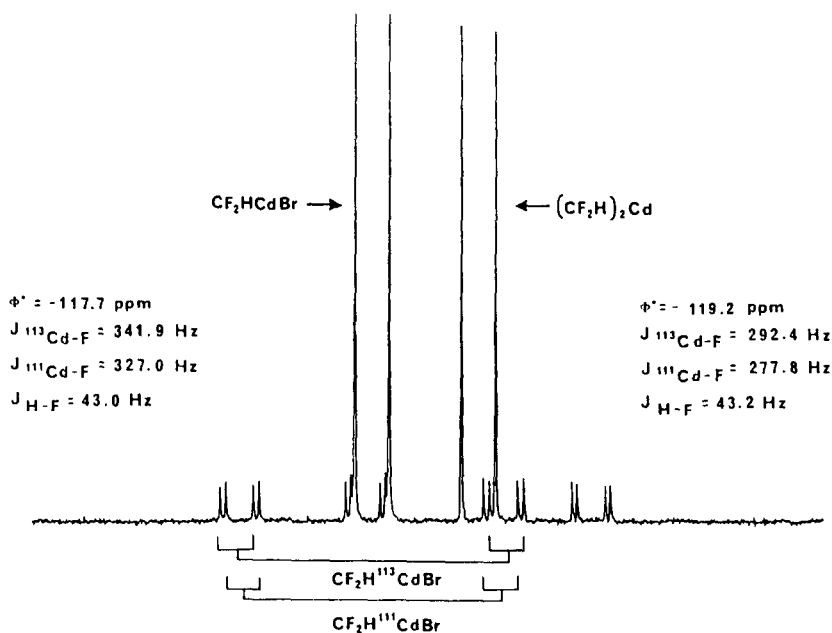


Fig. 1.  $^{19}\text{F}$  NMR Spectrum of  $\text{CF}_2\text{HCdBr}$  and  $(\text{CF}_2\text{H})_2\text{Cd}$  in DMF.

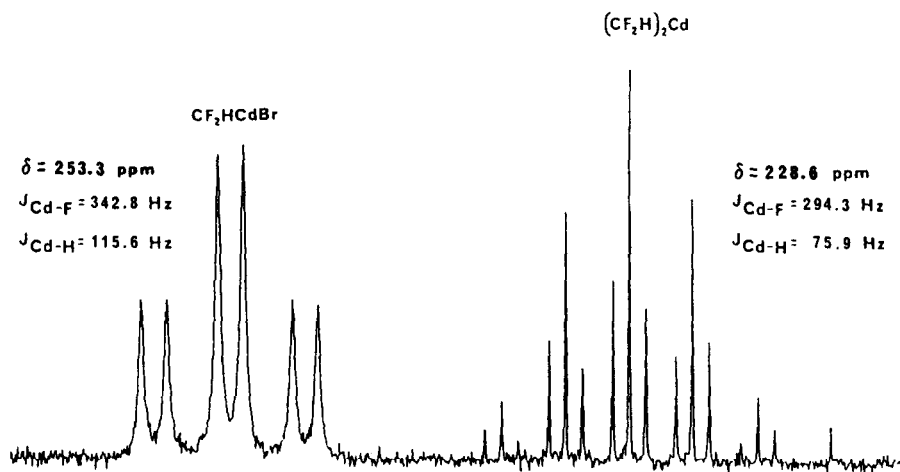


Fig. 2.  $^{113}\text{Cd}$  NMR Spectrum of  $\text{CF}_2\text{HCdBr}$  and  $(\text{CF}_2\text{H})_2\text{Cd}$  in DMF.

TABLE I

Reaction of difluoromethylcadmium with allyl halides

$$\text{CF}_2\text{HcdX} + \begin{array}{c} \text{R}^4 \text{ hal} \\ \diagup \quad \diagdown \\ \text{C} - \text{R}^5 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \end{array} \xrightarrow[\text{RT}]{\text{DMF}} \begin{array}{c} \text{R}^4 \text{ CF}_2\text{H} \\ \diagup \quad \diagdown \\ \text{C} - \text{R}^5 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \end{array} + \begin{array}{c} \text{CF}_2\text{H} \text{ R}^2 \\ \diagup \quad \diagdown \\ \text{C} - \text{R}^4 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R}^1 \quad \text{R}^3 \quad \text{R}^5 \end{array}$$

$\alpha$ -product
 $\gamma$ -product

R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	halogen	yield <sup>a</sup>	$\alpha$	$\gamma$
H	H	H	H	H	Br	85		
H	H	CH <sub>3</sub>	H	H	Cl	68		
CH <sub>3</sub> <sup>b</sup>	H	H	H	H	Cl	62	41	59
H	H	H	H	CH <sub>3</sub>	Cl	45	7	93
CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	Cl <sup>c</sup>	68	89	8
H	H	H	CH <sub>3</sub>	CH <sub>3</sub>	Cl <sup>d</sup>	63	15	80
C <sub>6</sub> H <sub>5</sub> <sup>e</sup>	H	H	H	H	Br	87	52	48
C <sub>6</sub> H <sub>5</sub> <sup>f</sup>	H	H	H	H	Cl	62	45	55

a isolated yields

b trans isomer

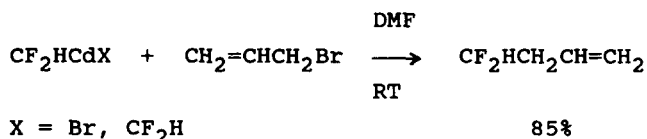
c 3% CH<sub>2</sub>=C(CH<sub>3</sub>)CH=CH<sub>2</sub>d 5% CH<sub>2</sub>=C(CH<sub>3</sub>)CH=CH<sub>2</sub>

e trans isomer

f trans isomer

There have been only a few reports of the reaction of organocadmium reagents with allylic halides. Cason and Fessenden found no significant reaction between an alkylcadmium reagent with allyl bromide [14]; however, Jones and Costanzo reported that phenylcadmium reacted with allyl bromide and 3-bromocyclohexene [15]. In our earlier work with the trifluoromethylcadmium reagent [8], we found that this F-

alkyl reagent reacted only sluggishly with allylic halides consistent with the report of Cason and Fessenden. However, the difluoromethylcadmium reagent reacted readily (within



several hours at room temperature) with allyl bromide. With substituted allylic halides, products of both  $\alpha$ - and  $\gamma$ -attack are observed (cf. Table I).

In summary, difluoromethylcadmium is readily prepared from iodo- or bromodifluoromethane and cadmium metal. This reagent is thermally stable and is capable of direct functionalization. With allylic halides, difluoromethylcadmium exhibits enhanced reactivity compared to trifluoromethylcadmium. This new reagent holds promise as a difluoromethylation reagent and future work will focus on application of this reagent and analogs.

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