Reaction of 1,1-Dichloro-2,2-difluoroethylene with Alkyl Grignard Reagents. Evidence for Radical Reaction Involving  $\beta$ -Hydrogen Atom Abstraction from Grignard Reagents. Implication Regarding the Mechanism of Reduction by Grignard Reagents

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Abstract: Reaction of CF<sub>2</sub>=CCl<sub>2</sub> (1) with alkyl Grignard reagents (RMgX: R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>4</sub>H<sub>9</sub>, *s*-C<sub>4</sub>H<sub>9</sub>, *i*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>6</sub>H<sub>17</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>) in ether afforded complex mixtures containing RCF<sub>2</sub>CCl<sub>2</sub>H (3), RCF=CCl<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>OCH(CH<sub>3</sub>)CF<sub>2</sub>CCl<sub>2</sub>H, and CH<sub>3</sub>CH<sub>2</sub>OCH(CH<sub>3</sub>)CF=CCl<sub>2</sub>, among which 3 was the most abundant except for the reactions with CH<sub>3</sub>MgBr and with C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>MgCl. From *n*-C<sub>3</sub>H<sub>7</sub>MgBr, *n*-C<sub>4</sub>H<sub>9</sub>MgBr, and from *n*-C<sub>8</sub>H<sub>17</sub>MgBr, compounds R'CF=CCl<sub>2</sub> (R' = *i*-C<sub>3</sub>H<sub>7</sub>, *s*-C<sub>4</sub>H<sub>9</sub>, and *n*-C<sub>6</sub>H<sub>13</sub>CH(CH<sub>3</sub>), respectively) were formed in preference to RCF=CCl<sub>2</sub>. Also identified are compounds of the types CCl<sub>2</sub>=CFCR<sub>2</sub>R<sub>3</sub>CR<sub>3</sub>R<sub>4</sub>CF<sub>2</sub>CCl=CCl<sub>2</sub>H (7), <u>CR<sub>1</sub>R<sub>2</sub>CR<sub>3</sub>R<sub>4</sub>CF<sub>2</sub>CCl<sub>2</sub>CFCCl<sub>2</sub>H (8), <u>CR<sub>1</sub>R<sub>2</sub>CR<sub>3</sub>R<sub>4</sub>CF<sub>2</sub>CClH</u>CFCCl<sub>2</sub>H (9), and <u>CR<sub>1</sub>R<sub>2</sub>CR<sub>3</sub>R<sub>4</sub>CF<sub>2</sub>CCl=</u>CCl<sub>2</sub>H (7), <u>CR<sub>1</sub>R<sub>2</sub>CR<sub>3</sub>R<sub>4</sub>CF<sub>2</sub>CCl<sub>2</sub>CFCCl<sub>2</sub>H (8), CR<sub>1</sub>R<sub>2</sub>CR<sub>3</sub>R<sub>4</sub>CF<sub>1</sub>CR<sub>1</sub>R<sub>2</sub>MgX). Use of deuterium-labeled Grignard reagents (C<sub>2</sub>D<sub>5</sub>MgBr and CH<sub>3</sub>CD<sub>2</sub>MgBr) revealed that the hydrogen of the Cl<sub>2</sub>H group originates mainly from  $\beta$  hydrogen of the Grignard reagents: RMgBr  $\rightarrow$  R· $\rightarrow$  RCF<sub>2</sub>CCl<sub>2</sub>, 7, and five-membered ring compounds ( $\hat{8}$ , 9, and 10) is taken as evidence for the formation of radicals of the type ·CR<sub>1</sub>R<sub>2</sub>CR<sub>3</sub>R<sub>4</sub>MgBr = (or  $\rightarrow$ ) BrMgCR<sub>1</sub>R<sub>2</sub>CR<sub>3</sub>R<sub>4</sub>. For example, the formation of *i*-C<sub>3</sub>H<sub>7</sub>CH<sub>2</sub>MgBr  $\rightarrow$  CH<sub>3</sub>CH(CF=CCl<sub>2</sub>)CH<sub>2</sub>CFCCl<sub>2</sub>H. 7, and 8 from *n*-C<sub>3</sub>H<sub>7</sub>CH<sub>3</sub>CH(CF=CCl<sub>2</sub>)CH<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>C+CCl<sub>2</sub>CFCCl<sub>2</sub>H. CH<sub>3</sub>CH(CF=CCl<sub>2</sub>)CH<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>C+Cl<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>CFCCl<sub>2</sub>H. 7, and 8 from *n*-C<sub>3</sub>H<sub>7</sub>MgBr and from *i*-C<sub>3</sub>H<sub>7</sub>CR<sub>3</sub>R<sub>4</sub>MgBr  $\rightarrow$  CH<sub>3</sub>CH(CF=CCl<sub>2</sub>)CH<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>CFCCl<sub>2</sub>H. Products from C<sub>3</sub>H<sub>7</sub>MgBr are also satisfactorily explained as follows: CH<sub>3</sub>CH(MgBr)CH<sub>2</sub>· $\rightarrow$  *i*-C<sub>3</sub>H<sub>7</sub>CF=CCl<sub>2</sub>, CH<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>CFCCl<sub>2</sub>H. Products from CH<sub>3</sub>CHC<sub>2</sub>CH<sub>3</sub>MgBr are also satisfactorily explained in terms of -CH<sub>2</sub>CD<sub>2</sub>MgBr  $\neq$  BrMgCH<sub>2</sub>CD<sub>2</sub>. Products from CH<sub>3</sub>CHC(CH<sub>3</sub>)MgBr indicate the formation of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>MgBr (= CH<sub>3</sub>CH<sub></u></u></sub>

Although  $CF_2 = CCl_2$  (1) affords compounds of the type RCF=CCl<sub>2</sub> in good yield upon treatment with aryl Grignard reagents,<sup>1-3</sup> the reaction of 1 with alkyl Grignard reagents results in complex mixtures, in each of which a compound of the type RCF<sub>2</sub>CCl<sub>2</sub>H is a main component as mentioned before.<sup>2</sup> The possibility that the hydrogen is introduced during hydrolysis of the possible intermediates RCF<sub>2</sub>CCl<sub>2</sub>MgX<sup>4,5</sup> was quickly eliminated by hydrolysis with D2O followed by examination of the products. In identifying other products and pursuing the origin of the hydrogen of the CCl<sub>2</sub>H group of such compounds, the author was lead to a surprising conclusion that the hydrogen atom not only originates from  $\beta$  hydrogen of the Grignard reagent but also becomes abstracted directly from the Grignard reagent. This appears to be a previously unrecognized (or not well known) mode of reaction of Grignard reagents, yet having a considerable potential importance. Here we present our results and interpretation leading to the conclusion together with relevant discussions.

#### Results

The reaction of  $CF_2$ =CCl<sub>2</sub> (1) with alkylmagnesium halides (2) in ether proceeded with more or less heat generation upon addition of 1 to a solution of 2 or upon inverse addition and was nearly complete after refluxing the resulting mixture for a few hours by external heating, though longer reaction times were sometimes used particularly in earlier experiments. The reaction with methylmagnesium bromide was markedly slower and was discontinued at an appropriate stage. Each reaction mixture became heterogeneous as the reaction proceeded.

The reaction mixtures were complex, containing a number of products, among which the following compounds (3-10)

have been identified.

$$CF_{2} = CCl_{2} + RMgX \xrightarrow{ether} RCF_{2}CCl_{2}H \quad RCF = CCl_{2}$$
**1 2 3 4 a**, R = CH\_{3} **e**, R = n-C\_{4}H\_{9} **i**, R = n-C\_{8}H\_{17}
**b**, R = C\_{2}H\_{5} **f**, R = s-C\_{4}H\_{9} **j**, R = C\_{6}H\_{5}CH\_{2}
**c**, R = n-C\_{3}H\_{7} **g**, R = i-C\_{4}H\_{9} **[k**, R = n-C\_{6}H\_{13}CH(CH\_{3}) for 4 only]

The product distributions are summarized in Table I. Physical data of products are given in Table II.

Compound 3 was the main product in each case except for the reactions with  $CH_3MgBr$  (2a) and with  $C_6H_5CH_2MgCl$ (2j). A clear indication of the structure is seen in the doublet splitting in the <sup>19</sup>F NMR signal due to the coupling with the  $CCl_2H$  proton in addition to the splitting due to the coupling with the  $\alpha$  proton of the alkyl group. In mass spectroscopy compound 3 easily loses  $CCl_2H$  to give  $RCF_2^+$ , generally showing no parent peak. However, the peaks due to  $CF_2=CHCl$  and  $CF_2=CDCl$  were found to be usable for estimation of the relative amount of  $RCF_2CCl_2H$  and  $RCF_2CCl_2D$  in deuterium-labeling experiments. (Most of the  $CCl_2H$ -containing compounds other than 3 show parent peaks.)

Though compound 4 was generally a minor product, it is of particular interest to note that, from some Grignard reagents, compounds of the type  $R'CF=CCl_2$  were formed, where R' is an alkyl group isomeric to that of the Grignard reagent. Thus from  $n-C_3H_7MgBr$  (2c),  $n-C_4H_9MgBr$  (2e), and from  $n-C_8H_{17}MgBr$  (2i), there were formed  $i-C_3H_7CF=CCl_2$  (4d),  $C_2H_5CH(CH_3)CF=CCl_2$  (4f), and  $n-C_6H_{13}CH(CH_3)$ -

Table I. Reaction of CF<sub>2</sub>==CCl<sub>2</sub> (1) with Alkyl Grignard Reagents (2);<sup>a</sup> Product Yields in Terms of GC Peak Area<sup>b</sup>

	reflux	GC peak area, % <sup>b</sup>									
RMgX (RX) <sup>c</sup>	time, h <sup>d</sup>	3	4 <sup>e</sup>	4/	5	6	7	8	9	10	$R_{1-4}g$
2a (methyl bromide)	58 <sup>h</sup>	21	$11^{i}$		2	4					
<b>2b</b> (ethyl bromide)	16	13 <i>j</i>	4 <i>j</i>		1	0.5	17	0.3	2	0.4	b
<b>2b</b> (ethyl bromide)	5 <sup>k</sup>	$8^{j}$	17		1	0.4	20	1	3	1	b
<b>2c</b> ( <i>n</i> -propyl bromide)	4.5	9	т	1.1 ( <b>d</b> )	1		4	2	16	1	c
2d (isopropyl bromide)	3	14	4		0.7		3	0.3	2	0.4	с
2e (n-butyl bromide)	10	17	п	0.8 ( <b>f</b> )	1		0.6	0.5	6	1	е
<b>2e</b> ( <i>n</i> -butyl bromide) <sup>o</sup>	3 <i>P</i>	17	п	1.4 ( <b>f</b> )	1		0.7	0.5	6	1	e
<b>2f</b> ( <i>sec</i> -butyl bromide) <sup>o</sup>	2.5 <sup>p</sup>	16	1.5	n	(1)		1.5		2		e
· •							0.6		1	0.3	ſ
<b>2g</b> (isobutyl bromide)	5	104	0.4 <i>i</i>	0.2 <sup><i>i</i></sup> ( <b>h</b> )	+			2	11	3	g
<b>2h</b> ( <i>tert</i> -butyl chloride)	4	12	<3	. ,	1			0.5	0.9	0.8	g
<b>2h</b> ( <i>tert</i> -butyl bromide) <sup>o</sup>	$2^{p,r}$	4	0.5					1.4	1	3	g
<b>2i</b> ( <i>n</i> -octyl bromide)	35,1	24	и	0.9 ( <b>k</b> )	1	0.5					0
2j (benzyl chloride)	7 <i>s</i>	$11^{i}$	14 <sup>i</sup>		1	0.6					

" Small portions of the total mixtures obtained after workup from reactions of preparative scale (0.5 mol) had been reserved and were subjected to the GC peak area determination all under the same continuously operated conditions. Retention times obtained during this determination are given in Table II. <sup>b</sup> The percentages of the peak areas relative to the peak area of *n*-decane of an ether solution containing an equal molar amount of n-decane to that of the initial RX per the volume of the total mixture from which the sample solution had been withdrawn. Experimentally, 20 µL volumes of sample solutions and solutions of n-decane of one-fifth of the above concentration were injected at 200 °C, and the peak areas of *n*-decane taken as 20% each. CUnless otherwise stated, Grignard grade magnesium was used. d Unless otherwise stated, the total refluxing times of the following procedure: 1 (ca. 30% excess) was added to a solution of 2 with cooling (internal temperature: 3-27 °C) generally over a period of 1-5 min. The resulting mixture was allowed to warm to reflux (for up to 1.5 h) and externally heated after the reaction subsided. Where considerable heat generation was apparent during the first period of the addition, the addition was conducted under mildly refluxing conditions over a relatively long period (17-21 min) in order to decrease the extent of accumulation of reactants. e Compounds having the same alkyl group as that of 2. <sup>f</sup> Compounds having an alkyl group isomeric to that of 2. <sup>g</sup> The notation for the set of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R4 for the compounds 7-10. <sup>h</sup> The total refluxing time over a period of 1 week. <sup>i</sup> Mutually unseparated under the GC conditions used. The total area divided into two according to the  $^{19}$ F NMR intensity ratio. <sup>j</sup> The total area divided into two according to the ratio of the GC peak areas obtained at lower column temperature. k Inverse addition to 100% excess 1 during the first 2.5 h of this period. m A small amount of 4c detected by GC-mass ( $\sim 1/10$  of 4d). " A small amount of 4e detected by GC-mass and/or <sup>19</sup>F NMR. " Ventron magnesium (99.99%) was used. P Inverse addition over a period of 10-23 min. Other conditions are similar to those described in footnote d. 4 Small amounts of 3e, 3f, and 3h were also detected. Their main origins were suspected to be n-, sec-, and tert-butyl bromides probably present as impurities in the commercial sample of isobutyl bromide (reagent grade). In the gas chromatogram, the compounds 3e, 3f, 3h, and 5 form a broad peak having 1.3% peak area. r Low product yields reflect the low yield (~50% as judged from recovered magnesium) of the formation of 2h from tert-butyl bromide. 8 As in other cases, the reaction mixture was heterogeneous. In this case, however, the upper and the lower layers were mutually separated by decantation, and only the mixture obtained from the upper layer was subjected to GC peak area determination. ' The products obtained by fractional distillation of the major portion of the mixture include 1-octene (<17% yield) contaminated with n-octane. " A small amount of 4i detected by GC-mass.



CF=CCl<sub>2</sub> (4k), respectively, in preference to n-C<sub>3</sub>H<sub>7</sub>CF=CCl<sub>2</sub> (4c), n-C<sub>4</sub>H<sub>9</sub>CF=CCl<sub>2</sub> (4e), and n-C<sub>8</sub>H<sub>17</sub>CF=CCl<sub>2</sub> (4i). This finding was confirmed in the case of the reaction of n-C<sub>3</sub>H<sub>7</sub>MgBr (2c), using a purified (preci-

sion distillation) sample of n-C<sub>3</sub>H<sub>7</sub>Br, in which i-C<sub>3</sub>H<sub>7</sub>Br was undetected.

The identities of compounds  $5^6$  and  $6^7$  were confirmed by the infrared spectra indistinguishable from those of authentic samples obtained by Muramatsu et al. of our institute. When  $n-C_4H_9MgBr$  was prepared in ether and the reaction with 1 was conducted in tetrahydrofuran after removal of most of the ether, as well as when tetrahydrofuran was used for the preparation and reaction of the Grignard reagent, compounds 11<sup>6</sup> and 12<sup>7</sup> were formed instead of 5 and 6. This experiment was



thought necessary as the formation of  $CH_3CH_2OCH(CH_3)$ -MgBr, which could be the precursor of 5, seemed possible.<sup>8b</sup> The above results indicate that such a course, if any, is not important and that 5 was derived from the solvent during the reaction of 1 with 2.

The <sup>19</sup>F NMR spectra of compounds 7 show the presence of both the  $-CF=CCl_2$  and  $-CF_2CCl_2H$  groups. Although the  $CF_2$  portions of the <sup>19</sup>F NMR spectra of 7c and 7f show signals much more complex than expected, all other available spectroscopic data (Table II), including the CF portion of the <sup>19</sup>F NMR spectra of 7c and 7f as well as the whole <sup>19</sup>F NMR spectra of 7b and 7e, point to the assigned structure.

Table II. Physical Data of Compounds Obtained from the Reaction of CF2=CCl2 (1) with Alkyl Grignard Reagents (2)<sup>a,b</sup>

14.0			20	<sup>19</sup> F N.M	R, ppm <sup>e,f</sup>		<sup>1</sup> H NMR, ppm <sup>e.g</sup>	<u>cult</u>		
compd <sup><i>u</i>-c</sup>	ьр, «С	RT, min <sup>a</sup>	<i>n</i> <sup>20</sup> D	CF <sub>2</sub>	CF	CH <sub>3</sub>	CH <sub>2</sub>	CH*	MS'	
3a <sup>3, k</sup>		1.53		19.4 (q 18) (d 6)		1.82 (t 18)		5.72 (t 6)		
36 <sup>7</sup>	110-111	1.96	1.3994	30.1 (t 17) (d 7)		1.09 (t 7)	2.17 (t 17) (q 7)	<b>5.75</b> (t 7)	$79 M - CHCl_2$ (100)	
3c	60 (60)	2.4	1.4060	27.9 (t 17) (d 7)		1.01 (17)	1.4-1.9 (2 H) 1.9-2.4 (2 H)	<b>5.71</b> (t 7)	93 M – CHCl <sub>2</sub> (100)	
3d)	52 (60)	2.5	1.4095	38.2 (d 15) (d 9)		1.09 (d 7)		2.53 (t 15) (sep 7) 5 82 (t 9)	93 M – $CHCl_2$ (100)	
Зе	67 (50)	3.3	1.4138	28.1 (t 17) (d 7)		0.94 (t 7)	1.1-1.8 (4 H) 1.8-2.4 (2 H)	5.73 (1 7)	107 M – CHCl <sub>2</sub> (40) 87 M – (CHCl <sub>2</sub> ,	
3f	77 (50)	3.4	1.4191	36.4 (d 14) <sup>1</sup>		0.97 (t 7)	1.2-1.5 (1 H)	2.0-2.6	HF) (100) 107 M – CHCl <sub>2</sub>	
3g	56-58 (35)	2.8	1.4125	(d 9.5) <sup>7</sup> 26.2 (t 19)		1.07 (d 7) 1.02 (d 6)	1.6-2.0 (1 H) 1.7-2.3 (3 H) <sup>m</sup>	<b>5.84</b> (t 9) <i>m</i>	(100) 139 M – (CH <sub>3</sub> ,	
				(d 7)				<b>5.70</b> (t 7)	HCl) (7) 107 M $-$ CHCl <sub>2</sub> (100)	
3h	71-71.5 (50)	3.3	1.4204	33.1 (d 9)		1.19'(t 1.2)		<b>5.90</b> (t 9)	139 M – (CH <sub>3</sub> , HCl) (2) 107 M – CHCl <sub>2</sub> (100)	
3i	78 (5)	14.9	1.4302	27.9 (t 17) (d 7)		0.89 (t 5.5)	1.3 br (12 H) 1.8-2.4 (2 H)	<b>5.70</b> (t 7)	246 M (2) $163 M - CHCl_2$ (27) 121 (100)	
3j <sup><i>j</i>,<i>n</i></sup>	~85 (8)	15.3		26.7 (t 16) (d 8)			3.43 (t 16)	<b>5.55</b> (t 8) 7.36 phenyl	$\begin{array}{c} 224 \text{ M} (17) \\ 141 \text{ M} - \text{CHCl}_2 \\ (15) \\ 91 \text{ C}_6\text{H}_5\text{CH}_2 \\ (100) \end{array}$	
4a <sup>j.k</sup> 4b <sup>j</sup>	104-105	1.53 1.96	1.4294		15.6 (q 16) 24 4 (t 22)	2.09 (d 16) 1.14 (t 8)	2.50 (d 22) (q 8)		142 M (59) 127 M – CH <sub>3</sub>	
4c°	64-65 (100)	2.4	1.4335		22.4 (t 22)	0.97 (t 7)	1.61 (t 7, q 7, 2 H) 2.44 (d 22, t 7, 2		(100) 156 M (46) 127 M $- C_2 H_5$ (100)	
4d <i>°</i>	~49 (60)	2.1	1.4309		36.2 (d 29)	1.14 (d 7)	H)	3.07 (d 29) (sep 7)	(100) 156 M (37) 141 M - CH <sub>3</sub>	
<b>4e</b> <sup>o</sup>	83 (100)	3.25	1.4388		22.3 (t 22)	0.93 (t 7)	1.1-1.7 (4 H) 2.50 (d 22, t 7, 2		(100) 170 M (100) 127 M $- C_3 H_7$ (29)	
4f	~57 (50)	2.7	1.4367		35.8 (d 30)	0.92 (t 7) 1.11 (d 7)	1.3-1.7	2.85 (d 30) (sex 7)	(29) 170 M (29) 141 M - C <sub>2</sub> H <sub>5</sub> (100)	
4g <i>°</i>	~78 (98)	2.8	1.4367		20.1 (t 23)	0. <b>99 (d</b> 7)	2.36 (d 22)	1.99 (no 6.5)	170 M (100)	
4h°	72-73 (100)	2.8	1.4421		15.7 (2.0%)	1.31 (d 2.0)	(a /)		$155 \text{ M} = \text{CH}_3(16)$ 170 M (25)	
4i*°	105-106 (10)	13.7	1.4492		22.4 (t 22)	0.89 (t, 5.5)	1.3 br 1.5-1.8 (12 H) 2.50 (d 22, t, 7, 2		$\begin{array}{l} 155 \text{ M} = \text{CH}_3(98) \\ 226 \text{ M}(6) \\ 91 \text{ M} = (\text{C}_7\text{H}_{15}, \\ \text{HCl})(100) \end{array}$	
4k**	~74 (5)	13.7	1.4370		35.9 (d 29)	0.88 (t 5.5) 1.12 (d 7)	H) 1.3 br (10 H)	2.97 (d 31) (m 7)	226 M (46) 141 M $- C_6 H_{13}$ (57)	
<b>4j</b> <i>°</i>	96-97.5 (9)	15.3	1.5303		21.0 (t 22)		3.78 (d 22)	7.32 phenyl	57 C <sub>4</sub> H <sub>9</sub> (100) 204 M (58) 133 M – (Cl, HCl)	
7b	86-90 (10)	11.8	1.4588	28.6 (t 17) (d 7)	24.2 (t 19)		2.1-3.0	<b>5.77</b> (t, 6)	(100) 274 M (12) 140 CH <sub>2</sub> =CHCF=CCl <sub>2</sub> (19) 127 CH <sub>2</sub> CF=CCl <sub>2</sub>	
7c*	~76 (3)	12.7	1.4585	27.3 (c)	36.7 (d 29) (t 2.7)9	1.27 (d 7)	1.9-2.8	3.43 (d 29) (m 7) <b>5.72</b> (t 7)	(100) 288 M (8) 273 M - CH <sub>3</sub> (3) 141 CH <sub>3</sub> CHCF=CCl <sub>2</sub>	
7e***	~80 (3)	17.0	(1.4592)	27.5 (t, 17) (d 7)	36.2 (d 29)	1.07 (t 7)	1.62 (m 7) 2.1–2.7	2.8-3.6 <b>5.72</b> (t 7)	(100) 302  M (21) $273 \text{ M} - C_2 H_5 (55)$ 155 $C_2 H_2 CHCE = CC$	
7f*	~89 (3)	20.4	1.4682	33.8 (c)	31.0 (d 28)	1.14 (d 6.5) 1.22 (d 6.5)		2.4-3.0 3.40 (d 28) (m 7) <b>5.82</b> (d 11, d, 7)	(100) 302 M (7) 141 CH <sub>3</sub> CHCF=CCl <sub>2</sub> 7) (100)	
									105 CH <sub>2</sub> =CHCF=CCI (14)	

Table II. (Continued)

				<sup>19</sup> F NMR, ppm <sup>e,f</sup>					
compd <sup>a-c</sup>	bp, °C	RT, min <sup>d</sup>	n <sup>20</sup> D	CF <sub>2</sub>	CF	CH3	CH <sub>2</sub>	CH <sup>h</sup>	MS <sup>i</sup>
8b	~91 (3)	20.8	mp 54-56	13.4 + 29 4 (227)	78.4		2.2-2.8	6.27 (d 20)	274 M (13)
8c	~92 (3)	23.1	1.4729	2.6 + 32.9 (227)	84.3	1.25 (d 7)	2.4-3.1	1.6-2.3	239 M – CI (100) 288 M (5)
8g	~94 (3)	28.0	1.4767	12.7 + 33.4 (229)	84.8	(d 2) 1.28 (d 5) 1.33 (d 3)	1.9-2.6	6.28 (d 20) 6.27 (d 20)	$253 \text{ M} - \text{Cl} (100)  287 \text{ M} - \text{CH}_3 (2)  267 \text{ M} - \text{Cl} (76)  191 \text{Cr} \text{H}_3 \text{Cl} (100) $
9b	~80 (8)	9.0	1.4538	10.2 + 20.6	80.37		2.1-2.9	4.2-4.9	240 M (1)
				19.5 br/.w	78.0*			<b>5.91</b> (d 5) <i>r</i> <b>6.07</b> (d 19) <i>r</i>	$205 \text{ M} - \text{Cl}(15) \\ 157 \text{ M} - \text{CHCl}_2 \\ (100)$
9c <i>s</i>	64-75 (3)	10.7× 11.3×	1.4520	13.5 + 32.7 (231) 17.5 + 28.8 (232) 15.3 + 24.7 (239)	74.9 80.7 86.4	1.1-1.4	(2.3)-3.1	1.7-(2.3) 4.2-4.9 6.04 (d 17) <sup>7</sup>	254 M (1) 219 M – Cl (9) 171 M – CHCl <sub>2</sub>
				31.3 + 42.6 (221)	67.0			<b>5.94</b> (d 6) <sup>u</sup> <b>6.09</b> (d 16) <sup>v</sup>	(100)
9e <i>s</i>	~84 (3)	15.5	1.4557	10.2 + 32.0 (238) 13.6 + 27.9 (228) 15.9 + 24.7 (232) 27.8 + 41.6 (233)	75.2 81.8 83.2 67.7	0.9-1.2	1.3-(2.2) (3 H) <sup>m</sup> (2.2)-3.0 (2 H)	4.2-4.9 6.04 (d 17) <sup>t</sup> 6.08 (d 15) <sup>v</sup>	233 M - Cl (9) 185 M - CHCl <sub>2</sub> (44) 149 M - (CHCl <sub>2</sub> ,
9f	~70 (3)	14.1	1.4565	25.4 + 39.8 (228)	73.2	1.21 (t 6.5) 1.22 (t 7.5)		1.9-2.8 4.52 (d 22) (d 12, d, 8) <b>5.96</b> (d 9)	HCl) (100) 197 M - (Cl, HCl) (3) 185 M - CHCl <sub>2</sub> (22)
9g <i>s</i>	90-93 (8)	13.0	1.4540	28.5 + 32.8 (232) 34.3 + 36.6 (224)	66.9 71.7	1.1-1.3	2.1-2.7	<i>4.4–5.0</i> <b>5.96</b> (d 14) <sup>1</sup>	$149 \text{ M} - (CHCl_2, HCl) (100)$ 233  M - Cl (5) 217  M - (HCl, Cl, Cl)
								<b>5.88</b> (d 5) <sup>u</sup>	(100)
10e*	~70 (3)	11.7	1,4672	14.9 + 26.6 (249)		1.04 (t 7)	1.3-2.0 (2 H) 2.2-2.7 (2 H) 2.8-3.2 (1 H)	<i>m</i> <b>6.63</b> s, br	248 M (8) 213 M – Cl (100)
10f**	~61 (3)	10.3	(1.4704)	16.7 + 28.7 (247)		1.19 (d 7) (d 2.4) 1.43 (d 7)	210 <i>3.2</i> (1 11)	1.7-2.4 <b>6.65</b> s, br	248 M (9) 233 M $-$ CH <sub>3</sub> (3) 165 M $-$ CHCl <sub>2</sub> (100)
10g*	~74 (9)	8.4	1.4666	28.9 s, br		1.20 (t 1.6)	2.58 (t 4)	<b>6.63</b> s, br	284 M (9) 213 M - Cl (100)

<sup>a</sup> Satisfactory analytical data (±0.4% for C and H) were obtained for all new compounds unmarked by \*. The increasing proportion of impurity is roughly represented by the increasing number of \*. The analytical data for the samples having one \* mark each are as follows: Calcd for 4i: C, 52.87; H, 7.55. Found: C, 53.62; H, 7.73. Calcd for 7c: C, 28.99; H, 2.43. Found: C, 29.61; H, 2.50. Calcd for 7f: C, 31.61; H, 2.98. Found: C, 32.97; H, 3.20. Calcd for 10e C, 38.51; H, 3.64. Found: C, 39.15; H, 4.04. Calcd For 10g: C, 38.51; H, 3.64. Found: C, 39.72; H, 4.00. <sup>b</sup> Compounds 4, 7, and 10 show  $\nu_{C=C}$  at 1660–1673 cm<sup>-1</sup>. However, 4h has an unusual value of 1638 cm<sup>-1</sup>. <sup>c</sup> Generally purified by preparative GC. Unless otherwise stated, isolated from the mixtures resulting from the reaction of 1 with 2. d GC retention times obtained when peak area determination for Table I was performed. See footnotes a and b of Table I. GC retention times not listed in the table are as follows: n-decane, 3.3; 8e, 32.8; 10b, 7.0; 10c, 7.9. e 20% solution in CDCl<sub>3</sub> (50% solution for 9c and 9e). Splitting pattern and coupling constants (Hz) are indicated in parentheses (m for multiplet; c for complex). f Upfield relative to external CF<sub>3</sub>CO<sub>2</sub>H. Data for AB pattern are presented as follows: chemical shift of A + chemical shift of B (J<sub>F-F</sub>). g Downfield relative to internal tetramethylsilane. h CHCl<sub>2</sub> signals indicated by boldface. -CHClsignals indicated by italics. i m/e, assignment, and relative intensity (in parentheses) are given. See ref 28. Known compound. Compound. only as a mixture of 3a and 4a. Mutual separation not attempted. <sup>1</sup> Three apparent coupling constants (3.5, 9.5, and 14 Hz; doublet splitting each) are seen. Probably the value 3.5 Hz corresponds to the difference between the chemical shifts of the two nonequivalent fluorine nuclei. " CH2 signals and CH signals could not be distinguished. " Obtained only as a mixture of 3j and 4j. The spectroscopic data, obtained from the data of the mixture by subtraction of the data of 4j, essentially agree with those reported: H. Kimoto, H. Muramatsu, and K. Inukai, Nippon Kagaku Kaishi, 684 (1977). <sup>o</sup> Prepared from RCF<sub>2</sub>CCl<sub>2</sub>H by treatment with 1 equiv plus of *n*-butyllithium in ether at low temperatures. <sup>*p*</sup> Ten lines with relative intensities consistent with the structure. <sup>*q*</sup> Probably  $J_{F-F}$ , <sup>*r*</sup> Assignment to isomer I or II was not possible as only ~1.1 isomeric mixtures were obtained. 5 The isomers are designated as I, II, III, and IV according to their increasing GC retention time, as judged from their relative amounts in GC divided fractions. <sup>19</sup>F NMR data arranged in this order. Assignment of <sup>1</sup>H NMR signals to individual isomers was difficult except for the signals due to the CHCl<sub>2</sub> group. ' For isomer I. " For isomer II. " For isomer III. " Interpreted as a special case of an AB pattern where the difference between the chemical shifts of A and B is very small. \* Partially separated two peaks are observed on the analytical column. On the GC-mass column under appropriate conditions, the peaks were completely separated from each other and gave almost indistinguishable mass spectra.

A notable feature of cyclic compounds 8 and 9 (together with some of compounds 10) is that the <sup>19</sup>F NMR signals of CF<sub>2</sub> appear as a gross AB pattern having  $J_{F-F}$  of 221–249 Hz. (Compounds 5 and 11 also show <sup>19</sup>F NMR signals of CF<sub>2</sub> as an AB pattern.) Compounds 8 and 9 show additional signals of somewhat unusually high <sup>19</sup>F NMR chemical shift, indicative of fluorine attached to tertiary carbon. These features together with the existence (and even the numbers in some cases, as described below) of isomers are consistent with the assigned structures. Although the possibility of alternative





data of the present study seems difficult and since the possibility of different structures for different sets of  $R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  requires a detailed examination for individual cases.<sup>9</sup>

For compounds 9, the number of isomers detected by <sup>19</sup>F NMR was four in the cases where  $R_1 = CH_3$ ,  $R_2 = R_3 = R_4$ = H and where  $R_1 = C_2H_5$ ,  $R_2 = R_3 = R_4 = H$  and two in the cases where  $R_1 = R_2 = R_3 = R_4 = H$  and where  $R_1 = R_2 =$  $CH_3$ ,  $R_3 = R_4 = H$ . For compounds 8, only one isomer each was found in the cases where  $R_1 = R_2 = R_3 = R_4 = H$  and where  $R_1 = R_2 = CH_3$ ,  $R_3 = R_4 = H$ . In these cases the numbers agree with the numbers of possible stereoisomers for these structures. On the other hand, only one isomer was clearly seen for compound 8c, whereas two isomers are possible.

Consistent with the structure 10, where one isomer each is possible for compounds under consideration, the two fluorine atoms of the CF<sub>2</sub> group are shown to be equivalent (a singlet in <sup>19</sup>F NMR, though somewhat broad) in the case where R<sub>1</sub> = R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = R<sub>4</sub> = H and nonequivalent (an AB pattern in <sup>19</sup>F NMR) in the cases where R<sub>1</sub> = C<sub>2</sub>H<sub>5</sub>, R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = H and where R<sub>1</sub> = R<sub>3</sub> = CH<sub>3</sub>, R<sub>2</sub> = R<sub>4</sub> = H.

In order to see whether or not a Grignard reagent converts 3 into 4 under the reaction conditions, 3b was treated with



ethylmagnesium bromide. Slow reduction to 16, instead of dehydrofluorination to 4b, of 3b was found to occur. When 7b was treated with ethylmagnesium bromide, a complex mixture resulted, in which 9b has been found.

Conversion of 3 to 4 was effected by treatment with *n*-butyllithium in ether. This method was used to prepare most of 3 since isolation of pure samples of 3 from the mixtures of the reaction of 1 with 2 was generally difficult.

$$\begin{array}{c} \operatorname{RCF}_{2}\operatorname{CCl}_{2}\operatorname{H} \xrightarrow{n-\operatorname{C}_{4}\operatorname{H}_{9}\operatorname{Li}} \operatorname{RCF}_{2}\operatorname{CCl}_{2} \\ 3 & 4 \end{array}$$

Deuterium-labeling experiments using  $C_2D_5MgBr$  and  $CH_3CD_2MgBr$  were conducted in order to answer questions such as the following: (1) From where is the  $CHCl_2$  hydrogen of  $RCF_2Cl_2H$  formed? (2) On which carbon atom of 7 does the original  $\alpha$  hydrogen of  $C_2H_5MgBr$  reside? The following distributions of isotopic species were found.<sup>10</sup> From  $1 + C_2D_5MgBr$ :



## From $1 + CH_3CD_2MgBr$ :

- 1. CH<sub>3</sub>CD<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>H (**3b**-*d*<sub>2</sub>) 92% CH<sub>3</sub>CD<sub>2</sub>CF<sub>2</sub>CCl<sub>2</sub>D (**3b**-*d*<sub>3</sub>) 8%
- 2.  $CH_3CD_2CF=CCl_2(4b-d_2)60\%$
- + CHD<sub>2</sub>CH<sub>2</sub>CF=CCl<sub>2</sub> (**4b**- $d_{2'}$ ) 40%
- 3. 5,~100%
- 4. 6, 100%
- 5.  $CH_2CF_2CCl_2H$   $| (7b-d_2) 50\%^{10C} + | (7b-d_2') 50\%^{10C}$   $CD_2CF=CCl_2$   $CD_2CF=CCl_2$  $CD_2CF=CCl_2$



#### Discussion

In some cases of reactions with Grignard reagents, participation of radical mechanisms has been reported.<sup>11-15</sup> It appears that alkyl Grignard reagents have an intrinsic tendency to produce the corresponding alkyl radicals according to one or more schemes such as the following<sup>16</sup> and the tendency is often overshadowed by more rapidly proceeding ionic (polar) reactions.

$$RMgBr \rightarrow R \cdot + \cdot MgBr \tag{1}$$

$$RMgBr + A \rightarrow R \cdot + MgBr^{+} + A^{-} \cdot$$
(2)

$$RMgBr + YX \rightarrow R \cdot + MgBrX + Y \cdot$$
(3)

The present results are explicable throughout by radical mechanism. Probably  $CF_2$ = $CCl_2$  (1) does not possess sufficient ionic reactivity toward alkyl Grignard reagents, which is polarized only to a small extent due to the relative instability of alkyl anions, but possesses sufficient reactivity toward radicals formed under the reaction conditions.

From comparison of the results of the reactions of 1 with  $C_2H_5MgBr$  (2b),  $CH_3CD_2MgBr$ , and  $C_2D_5MgBr$ , it is evident that the hydrogen of the  $CCl_2H$  group in compound 3b originates from the  $\beta$  hydrogen of the Grignard reagent (2b). It seems reasonable to consider that the  $\beta$  hydrogens of other Grignard reagents also serve as the source of hydrogen of the  $CCl_2H$  group of compounds 3. This view is consistent with the fact that the amount of 3 relative to that of 4 is quite low in the cases as seen in Table I.

$$R \cdot + CF_2 = CCl_2 \rightarrow RCF_2CCl_2 \cdot$$

$$I$$

$$RCF_2CCl_2 \cdot + HCR_1R_2CR_3R_4MgX (\equiv RMgX)$$

$$\rightarrow RCF_2CCl_2H + \cdot CR_1R_2CR_3R_4MgX$$

$$3$$

$$RCF_{2}CCl_{2} + CH_{3}CH_{2}OCH_{2}CH_{3} \rightarrow 3$$
  
+ CH\_{3}CH\_{2}OCHCH\_{3}  
CH\_{3}CH\_{2}OCHCH\_{3} + 1 \rightarrow CH\_{3}CH\_{2}OCH(CH\_{3})CF\_{2}CCl\_{2}.  
17

#### $17 + H \cdot donor \rightarrow 5$

Although the above point alone does not require it, only a radical mechanism seems to offer a simple and consistent explanation for the experimental results. In particular, the formation of R'CF=CCl<sub>2</sub> and compounds of the types **7**, **8**, **9**, and **10** is difficult to explain unless radicals to be derived from the Grignard reagents by abstraction of  $\beta$  hydrogen are assumed as intermediates.<sup>17</sup>

Initially, the formation of 4 having a (seemingly) rearranged alkyl group (R'CF=CCl<sub>2</sub>) was quite puzzling. Since secondary alkyl radicals are considerably more stable than primary radicals, the compounds might be considered as resulting from the rearranged alkyl radicals. However, radical rearrangement of this type is generally difficult,<sup>18,19</sup> and it is not understood why R'CF<sub>2</sub>CCl<sub>2</sub>H is not formed if R'CF=CCl<sub>2</sub> is formed by such a route. These difficulties are resolved in the proposed reaction sequence shown in Scheme I. (For the cyclic compounds, the alternative structures **13**, **14**, and **15** result if the reaction sequence outlined in Scheme II is followed.)

The formation of  $i-C_3H_7CF=CCl_2$ , 7c, and cyclic compounds 8c, 9c, and 10c from  $n-C_3H_7MgBr$  (2c) and from *i*- $C_3H_7MgBr$  (2d) is rationalized in terms of the interconversion specifically shown in eq 4, where the equilibrium point lies far left. Likewise, the distribution of deuterium in the products obtained from the reaction of CH<sub>3</sub>CD<sub>2</sub>MgBr is explicable in terms of eq 5. The reaction of s-C<sub>4</sub>H<sub>9</sub>MgBr (2f) constitutes the most complex case as two directions of  $\beta$ -hydrogen atom abstraction are possible, leading to the radicals shown in eq 7 in addition to the ones shown in eq 6. The experimental results indicate that the  $\beta$ -hydrogen atom abstraction from this Grignard reagent (2f) occurs indeed into the two directions. Such radicals believed to be formed in the reactions with isobutylmagnesium bromide as well as tert-butylmagnesium halides (eq 8) and with *n*-octylmagnesium bromide (eq 9) are also shown.

$$CH_{3}\dot{C}HCH_{2}MgBr \leftrightarrows CH_{3}CH(MgBr)CH_{2}$$
(4)

$$\cdot CH_2 CD_2 MgBr \leftrightarrows BrMgCH_2 CD_2 \cdot (5)$$

$$CH_{3}\dot{C}HCH(MgBr)CH_{3} = CH_{3}CH(MgBr)\dot{C}HCH_{3} \qquad (6)$$
19 20

$$CH_{3}CH_{2}CH(MgBr)CH_{2} \rightleftharpoons CH_{3}CH_{2}CHCH_{2}MgBr \quad (7)$$
21
22

$$CH_3C(CH_3)CH_2MgBr \Leftrightarrow CH_3C(CH_3)(MgBr)CH_2$$
 (8)

$$n - C_6 H_{13} CHCH_2 MgBr \leftarrow n - C_6 H_{13} CH(MgBr) CH_2$$
(9)

The radical species resulting from  $\beta$ -hydrogen atom abstraction from a Grignard reagent is expected to be relatively stable and to be formed easily because the corresponding anion is the resonance stabilized radical anion of an olefin.<sup>20</sup>



The interconversion of the type shown in eq 4-9, that is, 1,2-shift of MgBr in the radical, is also expected to occur easily because of the partial ionic character of carbon-magnesium bond coupled with the existence of a significant partial negative charge at the radical center in contrast to the difficult 1,2-shift of hydrogen at the conventional radical<sup>18,19</sup> as well as carbanion center.

The alternative possibility is that only an intermediate state

Scheme I



could represent an energy minimum, and this possibility seems to be favored by the results of the reaction of *s*-butylmagnesium bromide.<sup>21</sup> However, the structure of equilibrating radicals is tentatively adopted for convenience in view of difficulty in making an unequivocal choice in such a structural problem.

CL

ĊFCCl₀∙

A considerable difference between the isotopic ratios of  $3b-d_6/3b-d_5$  and  $5-d_1/5$  indicates some difference in nature between the process of formation of 3 and that of 5. This may be attributed to the properties of a Grignard reagent. Thus due to the oligomeric nature of Grignard reagents,<sup>22</sup> RCF<sub>2</sub>CCl<sub>2</sub>. should have greater chance than CH<sub>3</sub>CH<sub>2</sub>OC(CH<sub>3</sub>)H· in finding RMgX to react with since RCF<sub>2</sub>CCl<sub>2</sub>. is formed most probably in or near the region where the R· radical has been generated, while CH<sub>3</sub>CH<sub>2</sub>OC(CH<sub>3</sub>)H· is formed by radicals which have escaped distant from the region. However, the possibility that the above difference in isotopic ratio reflects more fundamental differences between the course of the formation of 3 and that of 5 is not completely eliminated.

Radical 17 seems to be an obvious intermediate of 6. How-

ever, it is well known that a conversion of the type  $17 \rightarrow 6 + F$ . is energetically unfavorable. The probable course is given below:

 $17 + RMgX \rightarrow CH_{3}CH_{2}OCH(CH_{3})CF_{2}CCl_{2}MgX + R \cdot \downarrow \\ 6 + MgFX$ 

Since a similar radical course is also possible for the formation of 4, it is not known whether 4 (having the same alkyl group to that of 2) results mainly from a direct ionic reaction between 1 and 2 or from such a radical course as above.

Reducing Action of Grignard Reagents. Reduction of 3b to 16 and reductive cyclization of 7b to 9b can also be explained by a radical mechanism in a way consistent with the mechanism of the formation of compounds 3-10 from the reaction of 1 with 2. The essential step of the reduction is elimination of the chlorine radical, and its course is apparently interrelated with the formation of the alkyl radical from the Grignard reagents. If the alkyl radical is formed from the Grignard reagent according to eq 1, there is a good chance of elimination of chlorine by  $\cdot$ MgX. ( $\cdot$ CR<sub>1</sub>R<sub>2</sub>CR<sub>3</sub>R<sub>4</sub>MgX is also expected to be capable of forming  $\cdot$ MgX as well as R<sub>1</sub>R<sub>2</sub>C==CR<sub>3</sub>R<sub>4</sub>.) Alternatively, the decomposition of the Grignard reagent to form the alkyl radical and the chlorine elimination may occur in a coordinated way according to eq 3, YX (X = CI) being ultimately converted into YH. At any rate, the chlorine abstraction is likely to involve the formation of the Mg-Cl bond (or, alternatively, electron transfer followed by release of the chloride ion) since the abstraction of hydrogen from the -CCl<sub>2</sub>H group is expected as preferred to the chlorine abstraction if an alkyl radical is the abstracting agent.



The compounds 9 found in the products of the reaction of 1 with 2 are considered as derived mainly from 8 rather than from 7 in view of the relatively low rate of conversion of 7b to 9b as well as the expected greater stability of 18 as compared with that of 23. These reductions are to be completed by abstraction of hydrogen by the intermediate radicals from the  $\beta$  position of Grignard reagents and from the  $\alpha$  position of diethyl ether, generally the former being superior as hydrogen atom donor according to the present interpretation. Significantly, not only the CCl<sub>2</sub>H hydrogen of 3b but also the hydrogen introduced into 9b by reduction is deuterated (as shown by the formation of **9b**- $d_6$ ), where the  $\beta$  hydrogen of the Grignard reagent is deuterated ( $C_2D_5MgBr$ ). In view of primary isotope effects in hydrogen atom abstraction reactions,<sup>23</sup> Grignard reagents having ordinary hydrogen (protium) at the  $\beta$  position are considered even more efficient as a hydrogen atom donor than indicated by the results of the reaction with C<sub>2</sub>D<sub>5</sub>MgBr.

The above mechanism of reduction is consistent with a previous observation that the reduction of a *gem*-dibromocyclopropane (7,7-dibromonorcarane) to the corresponding monobromocyclopropane with methylmagnesium bromide in tetrahydrofuran leads to an isomer ratio characteristic of that of the radical reduction of this compound.<sup>24</sup> It is also understandable that in this system tetrahydrofuran acts as the hydrogen atom donor<sup>24</sup> because methylmagnesium bromide has no significant ability (in a kinetic sense) to donate the hydrogen atom in the present results.

The course of the reduction of halogeno compounds by Grignard reagents seems to have a considerable bearing on the



mechanism of the reduction of hindered ketones by Grignard reagents. A hydride transfer process via a cyclic transition state  $A^{25}$  has long been accepted for the reduction of ketones. Recently, a two-step radical process  $B^{26}$  has also been reconsidered<sup>27</sup> apparently in the upsurge of the concept of single electron transfer. The conclusion of the present study suggests a mechanism involving  $\beta$ -hydrogen atom abstraction from the Grignard reagents. The suggested mechanism C is similar to the mechanism  $B^{27}$  but differs from it in that the magnesium ketyl abstracts the hydrogen atom from the Grignard reagent instead of the alkyl radical. The participation of a cyclic coordination complex such as **24** is conceivable.



### **Experimental Section**

All temperature readings were uncorrected. <sup>1</sup>H NMR and <sup>19</sup>F NMR spectra were recorded on a Hitachi R-20BK operated at 56.451 MHz and on a Hitachi R-22 operated at 90 MHz, respectively. <sup>1</sup>H and <sup>19</sup>F chemical shifts (in 20% solution in CDCl<sub>3</sub>) are measured downfield relative to internal tetramethylsilane and upfield relative to external CF<sub>3</sub>CO<sub>2</sub>H, respectively. IR spectra were recorded on a Hitachi EP1-G3. GC-mass spectra<sup>28</sup> (including spectra of pure samples) were obtained on a Shimazu GCMS-7000 by using a 3-m column of OV-17. GC works were performed by using a 4-m column of Silicon-DC 550. For the preparative column (4 m), Silicon-DC 550 was also used. GC peak area ratios were obtained by weighing papers under curves. All reactions with Grignard reagents as well as n-butyllithium were conducted under an atmosphere of nitrogen by using sodium-dried ether. Grignard grade magnesium (turning, >99%), used in the C<sub>2</sub>D<sub>5</sub>MgBr and CH<sub>3</sub>CD<sub>2</sub>MgBr reactions and most of the other experiments, was obtained from Wako Pure Chemical Industries, Ltd. Ventron magnesium (chips, 99.99%) was also used in the later stages of the study.

Reaction of 1 with sec-ButyImagnesium Bromide (2f). To an icecooled solution of 1 (90 g, 0.68 mol) in ether (50 mL) was added over a 23-min period a solution of the Grignard reagent (2f) prepared from 0.50 mol (68.5 g) of sec-butyl bromide and magnesium (Ventron, 13 g, excess removed) in ether (320 mL). During the addition, the internal temperature was kept at 20-28 °C with cooling. The resulting mixture was allowed to warm to refluxing conditions, which lasted for 0.5 h, and hydrolyzed with aqueous hydrochloric acid after additional 2 h of external heating. From 92% of the ether solution obtained after washing with aqueous sodium bicarbonate followed by drying with sodium sulfate, most of the solvent was removed by distillation, and the residual liquid was fractionally distilled. The compositions of individual fractions were roughly estimated by inspection of the gas chromatograms and <sup>19</sup>F NMR spectra; fr 1, 8.02 g, the cold-trap condensate while fr 2-4 came out; fr 2, 0.56 g, bp 32-57 °C (50 mm), 4f 20%; fr 3, 3.06 g, bp 57-77 °C (50 mm), 4f 30%, 3f 40%; fr 4, 10.73 g, bp 77 °C (50 mm), 3f ~100%; fr 5, 2.72 g, the cold-trap condensate while fr 6-11 came out, 3f 80%, 5, 15%; fr 6, 4.23 g, bp up to 52 °C (3 mm), **3f** 80%, **5**, 15%; fr 7, 2.51 g, bp 59-67 °C (3 mm), **10f** 30%, 9f 40%; fr 8, 3.04 g, bp 67-75 °C (3 mm), 9f 40%, 9e 20%, 7e 10%; fr 9, 4.12 g, bp 75-83 °C (3 mm), 9e 20%, 7e 40%, 7f 10%; fr 10, 2.92 g, bp 83-104 °C (3 mm), 7e 15%, 7f 30%; fr 11, 1.79 g, bp 104-123 °C (3 mm); residue, 7.34 g. The estimated yields for individual compounds calculated from the above estimation are as follows: 4f, 1.0 g (1.3%); **3f**, 17.5 g (20%); **5**, 1.0 g (1.1%); **10f**, 0.75 g (0.7%); **9f**, 2.2 g (1.8%); 9e, 1.4 g (1.2%); 7e, 2.4 g (1.8%); 7f, 1.3 g (1.0%). The product yields in terms of GC peak area for the total mixture of this run are included in Table I.

Reaction of 1 with C<sub>2</sub>D<sub>5</sub>MgBr. A solution of C<sub>2</sub>D<sub>5</sub>MgBr in ether was prepared from C<sub>2</sub>D<sub>5</sub>Br (Merck Sharp & Dohme; 8.0 g, 0.070 mol) and magnesium (2.1 g) and transferred through a glass woolplugged tube to the reaction flask, a total 65 mL of ether being used. To the solution with stirring and ice cooling, 1 (18 g) was added in one portion, causing a rather vigorous boiling. The resulting mixture was kept under refluxing conditions for a total of 13 h, hydrolyzed, and worked up. Fractional distillation of the liquid remaining after evaporation of most of the ether afforded the following fractions: fr 1, 3.54 g, the cold-trap condensate while fr 2 came out, ether,  $3b-d_6$ , **3b**-*d*<sub>5</sub>, **4b**-*d*<sub>5</sub>, **4b**-*d*<sub>4</sub>, **5**, **5**-*d*<sub>1</sub>, **6**, **10**-*d*<sub>5</sub>; fr 2, 1.71 g, bp 85–91 °C (10 mm), 9b-d<sub>6</sub> 20%, 7b-d<sub>5</sub> 80%; fr 3, 0.42 g, bp lower than 162 °C (3 mm), 8b-d<sub>5</sub> 90%; residue, 0.56 g. A sample (ca. 0.5 g) of 3b-d<sub>6</sub> (<sup>19</sup>F NMR: 30.6 ppm, s, br) was obtained by preparative GC of fr 1. The presence of a small small amount of  $3b-d_5$  in the sample was indicated by weak <sup>1</sup>H NMR signals of CCl<sub>2</sub>H (5.74 ppm, t, J = 7 Hz). The <sup>19</sup>F NMR data (24.5 ppm, s, br, 1 F; 28.8 ppm, s, br, 2 F) for the main component of fr 2 is consistent with the structure 7b- $d_5$ . The <sup>19</sup>F NMR data of fr 3 [14.2 ppm + 30.1 ppm, AB pattern,  $J_{F-F} = 223$  Hz; 79.6 ppm, d,  $J_{F-F} = 18$  Hz (coupling with the 14.2 ppm signals)] is consistent with the structure  $8b-d_5$ .

The GC-mass spectrum of deuterated analogues of 4 in fr 1 (as well as in the total mixture) shows peaks at m/e 146 (C<sub>2</sub>HD<sub>4</sub>CF=CCl<sub>2</sub>), m/e 147 (C2D5CF=CCl2), m/e 129 (CD2CF=CCl2), m/e 111 (C<sub>2</sub>HD<sub>4</sub>CF=CCl), and at *m/e* 112 (C<sub>2</sub>D<sub>5</sub>CF=Cl) but no significant peak at m/e 128 (CHDCF=CCl<sub>2</sub>), indicating the presence of  $C_2D_5CF = CCl_2$  (4b-d<sub>5</sub>) and CHD<sub>2</sub>CD<sub>2</sub>CF = CCl<sub>2</sub> (4b-d<sub>4</sub>). No deuterated analogue of 6 was found by GC-mass spectroscopic examination of fr 1. The GC-mass spectrum of  $5 (m/e \ 163, 141, 125)$ showed the presence of a monodeuterated analogue  $(m/e \ 164, 142,$ 126), but no peak of monodeuterated ions corresponding to m/e 45 (CH<sub>3</sub>CHOH) and m/e 73 (CH<sub>3</sub>CH<sub>3</sub>OCHCH<sub>3</sub>) was observed, the fact indicating the presence of  $5 - d_1$  as well as 5.

Reaction of 1 with CH<sub>3</sub>CD<sub>2</sub>MgBr. CH<sub>3</sub>CD<sub>2</sub>Br was prepared according to a reported method<sup>8</sup> starting from *n*-butyl acetate and lithium aluminum deuteride (Merck Sharp & Dohme). From a reaction of 1 with CH<sub>3</sub>CD<sub>2</sub>MgBr prepared from 7.0 g (0.063 mol) of CH<sub>3</sub>CD<sub>2</sub>Br, the following fractions were obtained as above: fr 1, 2.90 g, the cold-trap condensate while fr 2 came out, ether,  $3b-d_2$ ,  $4b-d_2$ , **4b**- $d_{2'}$ , **5**, **6**, **10b**- $d_2$ , **10b**- $d_{2'}$ ; fr 2, 1.26 g, bp 86–90 °C (9 mm), (**9b**- $d_2$ + 9b- $d_{2'}$ ) 40%, (7b- $d_2$  + 7b- $d_{2'}$ ) 55%; fr 3, 1.11 g, bp 71-76 °C (3 mm),  $(7\mathbf{b} \cdot d_2 + 7\mathbf{b} \cdot d_{2'}) \sim 100\%$ ; fr 4, 0.47 g, bp 85–123 °C (3 mm),  $(7\mathbf{b} \cdot d_2 + 7\mathbf{b} \cdot d_{2'})$  35%,  $(8\mathbf{b} \cdot d_2 + 8\mathbf{b} \cdot d_{2'})$  60%. A sample (ca. 0.5 g) of **3b**- $d_2$  obtained by preparative GC of fr 1 showed consistent <sup>1</sup>H NMR (1.09 ppm, singlet with fine structure, 3 H; 5.76 ppm, t, J = 7 Hz, 1 H) and <sup>19</sup>F NMR (30.3 ppm, eight lines having relative intensities 251

fine structure of the CH<sub>3</sub> peak (five partially resolved peaks having relative heights of 1:1.9:2.5:1.9:1 with spacings of 1.0 Hz) is approximately a pattern (1:2:3:2:1 relative intensities) expected for the case of coupling  $(J_{HD} = 1.0 \text{ Hz as compared with } 1.1 \text{ Hz calculated})$ from  $J_{\rm HH}$  = 7 Hz of 3b by dividing by 2  $\mu$ H/ $\mu$ D = 2 × 2.7927/ 0.85738 = 6.5) with two D nuclei, while the above described fine structure of <sup>19</sup>F is a composite ( $J_{FH} = 7.2 \text{ Hz}$ ) of two such patterns  $(J_{\rm FD} = 2.4 \text{ Hz} \text{ as compared with } 2.6 \text{ Hz} \text{ calculated from } J_{\rm FH} = 17$ Hz of **3b** by dividing by  $2\mu H/\mu D$ ). Fraction 3 was shown to be a very nearly 1:1 mixture of 7b- $d_2$  and 7b- $d_{2'}$  by its <sup>1</sup>H NMR spectrum (2.43 ppm, t, J = 17 Hz, 1 H; 2.77 ppm, d, J = 19 Hz, 1 H; 5.77 ppm, t, J = 7 Hz, 1 H) and by its <sup>19</sup>F NMR spectrum (24.3 ppm, t, J = 19 Hz; t,  $J_{F-F} = 1.4$  Hz; superimposed with a broad signal at 24.5 ppm; total 1 F) (28.5 ppm, t, J = 17 Hz; d, J = 7 Hz; d,  $J_{F-F} = 1.4$  Hz; superimposed with a broad signal at 28.8 ppm; total 2 F).

GC-mass spectra of fr 1 (as well as the total mixture) showed the presence of 5 and 6 but none of their deuterated analogues. The relative intensity of the peaks at m/e 129 (CD<sub>2</sub>CF=CCl<sub>2</sub>) and m/e 129  $(CH_2CF=CCl_2)$  was used for estimation of the relative amount of 4b- $d_2$  and 4b- $d_{2'}$  and the relative amounts of 7b- $d_2$  and 7b- $d_{2'}$ , a necessary correction for contribution of CH<sub>2</sub>CF=C<sup>37</sup>Cl<sup>35</sup>Cl to the intensity of the peak at m/e 129 being made. Similarly, the relative intensity of the peaks at m/e 93 (CH<sub>2</sub>CF=CHCl) and at m/e 95 (CD<sub>2</sub>CF=CHCl) was used for estimation of the relative amount of **8b**- $d_2$  and **8b**- $d_{2'}$  and the relative amount of **9b**- $d_2$  and **9b**- $d_{2'}$ .

Treatment of 1,1-Dichloro-2,2-difluorobutane (3b) with Ethylmagnesium Bromide (2b). An ethereal solution (25 mL) containing 3b (2.09 g, 0.013 mol) and 2b (0.036 mol) was refluxed for a total of 23 h in 4 days with occasional monitoring. The gas chromatogram and <sup>19</sup>F NMR spectrum indicated the presence of 3b and reduction product 16 in an approximate ratio of 3:2. The GC-mass spectrum of 16, which is similar to that of 3b, was as follows: m/e (rel intensity), 79 (100), 59 (17), 51 (24). The analytical sample of 1-chloro-2,2difluorobutane (16) was obtained by preparative GC directly from the worked-up mixture. <sup>1</sup>H NMR: 1.04 ppm (t, J = 7 Hz, 3 H), 2.02 ppm (t, J = 16 Hz; quad, J = 7 Hz; 2 H), 3.66 ppm (t, J = 12 Hz, 2 H); <sup>19</sup>F NMR: 25.1 ppm (t, J = 16 Hz; t, J = 12 Hz).  $n^{20}$ <sub>D</sub> 1.3812

Anal. Calcd for C<sub>4</sub>H<sub>7</sub>ClF<sub>2</sub>: C, 37.37; H, 5.49. Found: C, 37.65; H, 5.70

Treatment of 1,1,6,6-Tetrachloro-2,5,5-trifluorohexene-1 (7b) with Ethylmagnesium Bromide (2b). An ethereal solution (25 mL) containing 7b (1.55 g, 0.0056 mol) and 2b (0.036 mol) was refluxed for a total of 11 h. A complex mixture resulted, in which the GC peak areas of 9b, unchanged 7b, and the compound suspected to be  $HCCl_2CF_2CH_2CH_2C(C_2H_5) = CCl_2$  (from the GC-mass spectrum) constituted roughly 20, 50, and 10%, respectively, of the total area. The GC-mass spectrum of 9b found in this mixture completely agrees with the spectrum of this compound obtained from the reaction of 1 with 2b.

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- (10) The proportions of isotopic species were estimated from the GC-mass

spectrum obtained from the mass spectroscopic scan at nearly the center of each gas chromatographic peak for the total mixture. The following observation indicated the necessity of such a consideration (center of the peak), but the accuracy attained by this method is unknown for some compounds. When the gas chromatographic peak of deuterated 7b was covered by three consecutive mass spectrometric scans, the first, the second, and the last spectra indicated the presence of  $7c-d_2$  and  $7c-d_2'$ in 60-40, 47-53, and 40-60%, respectively. (a) A portion withdrawn for monitoring at an earlier reaction time (2 h) indicated a higher proportion for **4b**- $d_4$  (75%). (b) The ratio of the intensities of the M<sup>+</sup> peak (where all chlorine atoms are <sup>35</sup>Cl) of the indicated species and the peak at the (M - 1)<sup>+</sup> position is approximately 92:8. (c) Values of 47–53%, subject to deviation from GC-mass run to run, obtained. (d) The spectrum is consistent with the structures. However, no peak apparently enables one to distinguish the two species.

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# Studies on Organic Fluorine Compounds. 28.<sup>1</sup> Synthesis and Some Reactions of Tetrakis(trifluoromethyl)-1,4-diphosphabenzene

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Abstract: Tetrakis(trifluoromethyl)-1,4-diphosphabenzene (3b), the first example of diphosphabenzenes, was synthesized by the thermolysis of 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphosphabicyclo[2.2.2]octa-2,5-diene (6), which was obtained by addition of methanol to hexakis(trifluoromethyl)-1,4-diphosphabarrelene (5) in the presence of rhodium trichloride or some other catalysts. The compound 3b seems to have some aromaticity since it shows a large absorption maximum at 282 nm. It is sensitive to air, but thermally stable and reacts with acetylenic compounds to give diphosphabarrelene compounds. Further, 3b reacts with carbon tetrachloride to give a diphosphanorbornadiene compound (4). The air sensitivity and the formation of 4 suggests that the phosphorus atom of 3b has some character of a trivalent phosphorus atom, while that of 5 hardly does.

#### Introduction

One of the heteroaromatic compounds containing group 5 elements, phosphabenzene, has been of much interest from the standpoints of its theoretical implication, structural property, and chemical reaction, since it is the first member of the series of compounds having an empty d orbital. The first synthesis of this type of compounds was achieved in 1967 by G. Märkl.<sup>2</sup> He synthesized 2,4,6-triphenylphosphabenzene (1) and reported that it was fairly stable. In 1971, A. J. Ashe reported the synthesis of unsubstituted phosphabenzene (2a).<sup>3</sup> Further, he succeeded in the synthesis of arsabenzene<sup>3</sup> (2b), stibabenzene<sup>4</sup> (2c), and bismabenzene<sup>5</sup> (2d) and reported the reactions and structural studies of these compounds.<sup>5,6</sup> But the diphosphabenzene derivatives, which contain two phosphorus atoms in one ring, have not been synthesized yet. Particularly, unsubstituted diphosphabenzene (3a) is predicted to be very unstable because it has two trivalent phosphorus atoms.

On the other hand, the perfluoroalkyl group is known to stabilize strained or labile compounds. This effect is often called "perfluoroalkyl effect".7 We expected that the intro-





duction of perfluoroalkyl groups into the diphosphabenzene might allow the isolation of this new type of compound. From