

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

Kunio Okuhara

Contribution from the Government Industrial Research Institute,
Nagoya, Hirate Machi, Kita-ku, Nagoya, Japan. Received April 12, 1979

Abstract: Reaction of $\text{CF}_2=\text{CCl}_2$ (**1**) with alkyl Grignard reagents (RMgX ; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, i\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, s\text{-C}_4\text{H}_9, t\text{-C}_4\text{H}_9, t\text{-C}_4\text{H}_9, n\text{-C}_8\text{H}_{17}, \text{C}_6\text{H}_5\text{CH}_2$) in ether afforded complex mixtures containing $\text{RCF}_2\text{CCl}_2\text{H}$ (**3**), $\text{RCF}=\text{CCl}_2$, $\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)\text{CF}_2\text{CCl}_2\text{H}$, and $\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)\text{CF}=\text{CCl}_2$, among which **3** was the most abundant except for the reactions with CH_3MgBr and with $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$. From $n\text{-C}_3\text{H}_7\text{MgBr}$, $n\text{-C}_4\text{H}_9\text{MgBr}$, and from $n\text{-C}_8\text{H}_{17}\text{MgBr}$, compounds $\text{R}'\text{CF}=\text{CCl}_2$ ($\text{R}' = i\text{-C}_3\text{H}_7, s\text{-C}_4\text{H}_9$, and $n\text{-C}_6\text{H}_{13}\text{CH}(\text{CH}_3)$, respectively) were formed in preference to $\text{RCF}=\text{CCl}_2$. Also identified are compounds of the types $\text{CCl}_2=\text{CFCR}_1\text{R}_2\text{CR}_3\text{R}_4\text{CF}_2\text{CCl}_2\text{H}$ (**7**), $\text{CR}_1\text{R}_2\text{CR}_3\text{R}_4\text{CF}_2\text{CCl}_2\text{CFCCl}_2\text{H}$ (**8**), $\text{CR}_1\text{R}_2\text{CR}_3\text{R}_4\text{CF}_2\text{CCl}_2\text{CFCCl}_2\text{H}$ (**9**), and $\text{CR}_1\text{R}_2\text{CR}_3\text{R}_4\text{CF}_2\text{CCl}=\text{CCCl}_2\text{H}$ (**10**) ($\text{RMgX} \equiv \text{HCR}_1\text{R}_2\text{CR}_3\text{R}_4\text{MgX}$ or $\text{HCR}_3\text{R}_4\text{CR}_1\text{R}_2\text{MgX}$). Use of deuterium-labeled Grignard reagents ($\text{C}_2\text{D}_5\text{MgBr}$ and $\text{CH}_3\text{CD}_2\text{MgBr}$) revealed that the hydrogen of the CCl_2H group originates mainly from β hydrogen of the Grignard reagents: $\text{RMgBr} \rightarrow \text{R}\cdot \rightarrow \text{RCF}_2\text{CCl}_2\cdot$; $\text{RCF}_2\text{CCl}_2\cdot + \text{HCR}_1\text{R}_2\text{CR}_3\text{R}_4\text{MgBr} (\equiv \text{RMgBr}) \rightarrow \text{RCF}_2\text{CCl}_2\text{H} + \cdot\text{CR}_1\text{R}_2\text{CR}_3\text{R}_4\text{MgBr}$. The formation of $\text{R}'\text{CF}=\text{CCl}_2$, **7**, and five-membered ring compounds (**8**, **9**, and **10**) is taken as evidence for the formation of radicals of the type $\cdot\text{CR}_1\text{R}_2\text{CR}_3\text{R}_4\text{MgBr} \rightleftharpoons$ (or \leftrightarrow) $\text{BrMgCR}_1\text{R}_2\text{CR}_3\text{R}_4$. For example, the formation of $i\text{-C}_3\text{H}_7\text{CF}=\text{CCl}_2$, **7**, and **8** from $n\text{-C}_3\text{H}_7\text{MgBr}$ and from $i\text{-C}_3\text{H}_7\text{MgBr}$ is explained as follows: $\text{CH}_3\text{CH}(\text{MgBr})\text{CH}_2\cdot \rightleftharpoons \text{CH}_3\text{CHCH}_2\text{MgBr} \rightarrow \text{CH}_3\text{CH}(\text{CF}_2\text{CCl}_2)\text{CH}_2\text{MgBr} \rightarrow \text{CH}_3\text{CH}(\text{CF}_2\text{CCl}_2)\text{CH}_2\cdot \rightarrow \text{CH}_3\text{CH}(\text{CF}=\text{CCl}_2)\text{CH}_2\cdot \rightarrow i\text{-C}_3\text{H}_7\text{CF}=\text{CCl}_2$; $\text{CH}_3\text{CH}(\text{CF}=\text{CCl}_2)\text{CH}_2\cdot \rightarrow \text{CH}_3\text{CH}(\text{CF}=\text{CCl}_2)\text{CH}_2\text{CF}_2\text{CCl}_2\cdot \rightarrow \text{CH}_3\text{CH}(\text{CF}=\text{CCl}_2)\text{CH}_2\text{CF}_2\text{CCl}_2\text{H}$; $\text{CH}_3\text{CH}(\text{CF}=\text{CCl}_2)\text{CH}_2\text{CF}_2\text{CCl}_2\cdot \rightarrow \text{CH}_3\text{CHCH}_2\text{CF}_2\text{CCl}_2\text{CFCCl}_2\cdot \rightarrow \text{CH}_3\text{CHCH}_2\text{CF}_2\text{CCl}_2\text{CFCCl}_2\text{H}$. Products from $\text{CH}_3\text{CD}_2\text{MgBr}$ are also satisfactorily explained in terms of $\cdot\text{CH}_2\text{CD}_2\text{MgBr} \rightleftharpoons \text{BrMgCH}_2\text{CD}_2\cdot$. Products from $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{MgBr}$ indicate the formation of $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{MgBr} [\rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}(\text{MgBr})\text{CH}_2\cdot]$ as well as $\text{CH}_3\text{CHCH}(\text{CH}_3)\text{MgBr}$. The present results, where reduction is also observed, suggest that the reduction of hindered ketones by alkyl Grignard reagents would involve β -hydrogen atom abstraction from Grignard reagents by ketyls if ketyls are involved as intermediate.

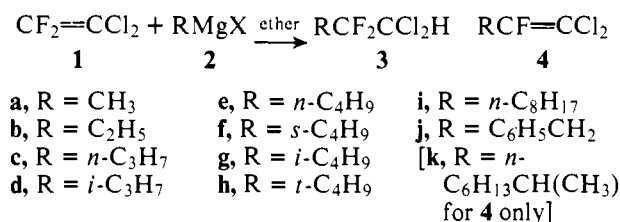
Although $\text{CF}_2=\text{CCl}_2$ (**1**) affords compounds of the type $\text{RCF}=\text{CCl}_2$ in good yield upon treatment with aryl Grignard reagents,¹⁻³ the reaction of **1** with alkyl Grignard reagents results in complex mixtures, in each of which a compound of the type $\text{RCF}_2\text{CCl}_2\text{H}$ is a main component as mentioned before.² The possibility that the hydrogen is introduced during hydrolysis of the possible intermediates $\text{RCF}_2\text{CCl}_2\text{MgX}$ ^{4,5} was quickly eliminated by hydrolysis with D_2O followed by examination of the products. In identifying other products and pursuing the origin of the hydrogen of the CCl_2H group of such compounds, the author was lead to a surprising conclusion that the hydrogen atom not only originates from β 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 $\text{CF}_2=\text{CCl}_2$ (**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.



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

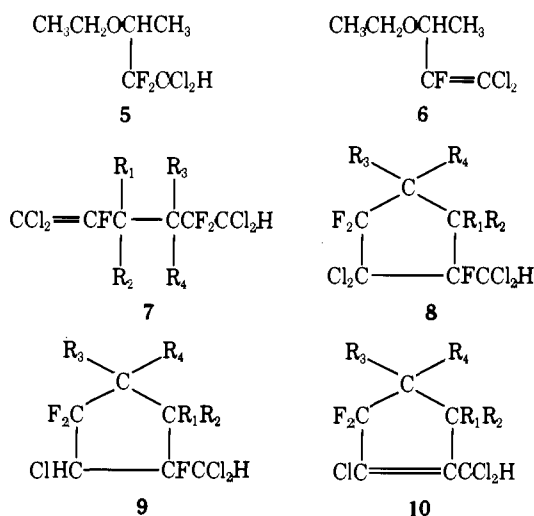
Compound **3** was the main product in each case except for the reactions with CH_3MgBr (**2a**) and with $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$ (**2j**). A clear indication of the structure is seen in the doublet splitting in the ^{19}F NMR signal due to the coupling with the CCl_2H proton in addition to the splitting due to the coupling with the α 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 $\text{CF}_2=\text{CHCl}$ and $\text{CF}_2=\text{CDCl}$ were found to be usable for estimation of the relative amount of $\text{RCF}_2\text{CCl}_2\text{H}$ and $\text{RCF}_2\text{CCl}_2\text{D}$ 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 $\text{R}'\text{CF}=\text{CCl}_2$ were formed, where R' is an alkyl group isomeric to that of the Grignard reagent. Thus from $n\text{-C}_3\text{H}_7\text{MgBr}$ (**2c**), $n\text{-C}_4\text{H}_9\text{MgBr}$ (**2e**), and from $n\text{-C}_8\text{H}_{17}\text{MgBr}$ (**2i**), there were formed $i\text{-C}_3\text{H}_7\text{CF}=\text{CCl}_2$ (**4d**), $\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{CF}=\text{CCl}_2$ (**4f**), and $n\text{-C}_6\text{H}_{13}\text{CH}(\text{CH}_3)\text{CF}=\text{CCl}_2$ (**4k**).

Table I. Reaction of CF₂=CCl₂ (**1**) with Alkyl Grignard Reagents (**2**):^a Product Yields in Terms of GC Peak Area^b

RMgX (RX) ^c	reflux time, h ^d	GC peak area, % ^b								R ₁₋₄ ^g		
		3	4 ^e	4 ^f	5	6	7	8	9		10	
2a (methyl bromide)	58 ^h	2 ⁱ	11 ⁱ		2	4						
2b (ethyl bromide)	16	13 ^j	4 ^j		1	0.5	17	0.3	2	0.4		b
2b (ethyl bromide)	5 ^k	8 ^j	1 ^j		1	0.4	20	1	3	1		b
2c (<i>n</i> -propyl bromide)	4.5	9	<i>m</i>	1.1 (d)	1		4	2	16	1		c
2d (isopropyl bromide)	3	14	4		0.7		3	0.3	2	0.4		c
2e (<i>n</i> -butyl bromide)	10	17	<i>n</i>	0.8 (f)	1		0.6	0.5	6	1		e
2e (<i>n</i> -butyl bromide) ^o	3 ^p	17	<i>n</i>	1.4 (f)	1		0.7	0.5	6	1		e
2f (<i>sec</i> -butyl bromide) ^o	2.5 ^p	16	1.5	<i>n</i>	(1)		1.5		2			e
							0.6		1	0.3		f
2g (isobutyl bromide)	5	10 ^q	0.4 ⁱ	0.2 ⁱ (h)	+			2	11	3		g
2h (<i>tert</i> -butyl chloride)	4	12	<3		1			0.5	0.9	0.8		g
2h (<i>tert</i> -butyl bromide) ^o	2 ^{p,r}	4	0.5					1.4	1	3		g
2i (<i>n</i> -octyl bromide)	3 ^{s,t}	24	<i>u</i>	0.9 (k)	1	0.5						
2j (benzyl chloride)	7 ^s	11 ⁱ	14 ⁱ		1	0.6						

^a 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. ^b 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 μ L 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. ^c Unless 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**. ^f Compounds having an alkyl group isomeric to that of **2**. ^g The notation for the set of R₁, R₂, R₃, and R₄ for the compounds **7**–**10**. ^h The total refluxing time over a period of 1 week. ⁱ Mutually unseparated under the GC conditions used. The total area divided into two according to the ¹⁹F NMR intensity ratio. ^j 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. ^l A small amount of **4c** detected by GC-mass ($\sim 1/10$ of **4d**). ^m A small amount of **4e** detected by GC-mass and/or ¹⁹F NMR. ⁿ Ventron magnesium (99.99%) was used. ^o Inverse addition over a period of 10–23 min. Other conditions are similar to those described in footnote *d*. ^p 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. ^q Low product yields reflect the low yield ($\sim 50\%$ as judged from recovered magnesium) of the formation of **2h** from *tert*-butyl bromide. ^r 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. ^s The products obtained by fractional distillation of the major portion of the mixture include 1-octene ($<1\%$ yield) contaminated with *n*-octane. ^t A small amount of **4i** detected by GC-mass.

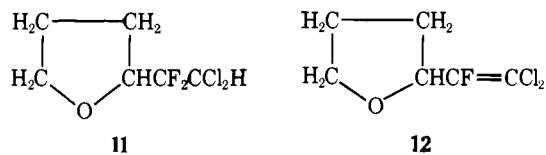


- b**, R₁ = R₂ = R₃ = R₄ = H (from **2b**)
c, R₁ = CH₃; R₂ = R₃ = R₄ = H (from **2c** and **2d**)
e, R₁ = C₂H₅; R₂ = R₃ = R₄ = H (from **2e** and **2f**)
f, R₁ = R₃ = CH₃; R₂ = R₄ = H (from **2f**)
g, R₁ = R₂ = CH₃; R₃ = R₄ = H (from **2g** and **2h**)

CF=CCl₂ (**4k**), respectively, in preference to *n*-C₃H₇CF=CCl₂ (**4c**), *n*-C₄H₉CF=CCl₂ (**4e**), and *n*-C₈H₁₇CF=CCl₂ (**4i**). This finding was confirmed in the case of the reaction of *n*-C₃H₇MgBr (**2c**), using a purified (precipi-

tion distillation) sample of *n*-C₃H₇Br, in which *i*-C₃H₇Br 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*-C₄H₉MgBr 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**⁶ and **12**⁷ were formed instead of **5** and **6**. This experiment was



thought necessary as the formation of CH₃CH₂OCH(CH₃)-MgBr, which could be the precursor of **5**, seemed possible.^{8b} 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 ¹⁹F NMR spectra of compounds **7** show the presence of both the -CF=CCl₂ and -CF₂CCl₂H groups. Although the CF₂ portions of the ¹⁹F 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 ¹⁹F NMR spectra of **7c** and **7f** as well as the whole ¹⁹F 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)^{a,b}

compd ^{a-c}	bp, °C	RT, min ^d	n _D ²⁰	¹⁹ F NMR, ppm ^{e,f}		¹ H NMR, ppm ^{e,g}			MS ⁱ
				CF ₂	CF	CH ₃	CH ₂	CH ^h	
3a ^{j,k}		1.53		19.4 (q 18)		1.82 (t 18)		5.72 (t 6)	
3b ^l	110-111	1.96	1.3994	30.1 (t 17)		1.09 (t 7)	2.17 (t 17)	5.75 (t 7)	79 M - CHCl ₂ (100)
3c	60 (60)	2.4	1.4060	27.9 (t 17)		1.01 (t 7)	1.4-1.9 (2 H)	5.71 (t 7)	93 M - CHCl ₂ (100)
3d ^l	52 (60)	2.5	1.4095	38.2 (d 15)		1.09 (d 7)	1.9-2.4 (2 H)	2.53 (t 15)	93 M - CHCl ₂ (100)
				(d 9)				5.82 (t 9)	
3e	67 (50)	3.3	1.4138	28.1 (t 17)		0.94 (t 7)	1.1-1.8 (4 H)	5.73 (t 7)	107 M - CHCl ₂ (40)
				(d 7)			1.8-2.4 (2 H)		87 M - (CHCl ₂ , HF) (100)
3f	77 (50)	3.4	1.4191	36.4 (d 14) ^l		0.97 (t 7)	1.2-1.5 (1 H)	2.0-2.6	107 M - CHCl ₂ (100)
				(d 9.5) ^l		1.07 (d 7)	1.6-2.0 (1 H)	5.84 (t 9)	
3g	56-58 (35)	2.8	1.4125	26.2 (t 19)		1.02 (d 6)	1.7-2.3 (3 H) ^m	^m	139 M - (CH ₃ , HCl) (7)
				(d 7)				5.70 (t 7)	107 M - CHCl ₂ (100)
3h	71-71.5 (50)	3.3	1.4204	33.1 (d 9)		1.19 (t 1.2)		5.90 (t 9)	139 M - (CH ₃ , HCl) (2)
									107 M - CHCl ₂ (100)
3i	78 (5)	14.9	1.4302	27.9 (t 17)		0.89 (t 5.5)	1.3 br (12 H)	5.70 (t 7)	246 M (2)
				(d 7)			1.8-2.4 (2 H)		163 M - CHCl ₂ (27)
3j ^{i,n}	~85 (8)	15.3		26.7 (t 16)			3.43 (t 16)	5.55 (t 8)	121 (100)
				(d 8)				7.36 phenyl	224 M (17)
									141 M - CHCl ₂ (15)
									91 C ₆ H ₅ CH ₂ (100)
4a ^{j,k}		1.53			15.6 (q 16)	2.09 (d 16)			
4b ^l	104-105	1.96	1.4294		24.4 (t 22)	1.14 (t 8)	2.50 (d 22)		142 M (59)
							(q 8)		127 M - CH ₃ (100)
4c ^o	64-65 (100)	2.4	1.4335		22.4 (t 22)	0.97 (t 7)	1.61 (t 7, q 7, 2 H)		156 M (46)
							2.44 (d 22, t 7, 2 H)		127 M - C ₂ H ₅ (100)
4d ^o	~49 (60)	2.1	1.4309		36.2 (d 29)	1.14 (d 7)		3.07 (d 29)	156 M (37)
								(sep 7)	141 M - CH ₃ (100)
4e ^o	83 (100)	3.25	1.4388		22.3 (t 22)	0.93 (t 7)	1.1-1.7 (4 H)		170 M (100)
							2.50 (d 22, t 7, 2 H)		127 M - C ₃ H ₇ (29)
4f	~57 (50)	2.7	1.4367		35.8 (d 30)	0.92 (t 7)	1.3-1.7	2.85 (d 30)	170 M (29)
						1.11 (d 7)		(sex 7)	141 M - C ₂ H ₅ (100)
4g ^o	~78 (98)	2.8	1.4367		20.1 (t 23)	0.99 (d 7)	2.36 (d 22)	1.99 (no 6.5)	170 M (100)
							(d 7)		155 M - CH ₃ (16)
4h ^o	72-73 (100)	2.8	1.4421		15.7 (2.0) ^o	1.31 (d 2.0)			170 M (25)
									155 M - CH ₃ (98)
4i ^o	105-106 (10)	13.7	1.4492		22.4 (t 22)	0.89 (t, 5.5)	1.3 br (12 H)		226 M (6)
							1.5-1.8 (12 H)		91 M - (C ₇ H ₁₅ , HCl) (100)
							2.50 (d 22, t, 7, 2 H)		
4k ^{**}	~74 (5)	13.7	1.4370		35.9 (d 29)	0.88 (t 5.5)	1.3 br (10 H)	2.97 (d 31)	226 M (46)
						1.12 (d 7)		(m 7)	141 M - C ₆ H ₁₃ (57)
									57 C ₄ H ₉ (100)
4j ^o	96-97.5 (9)	15.3	1.5303		21.0 (t 22)		3.78 (d 22)	7.32 phenyl	204 M (58)
									133 M - (Cl, HCl) (100)
7b	86-90 (10)	11.8	1.4588	28.6 (t 17)	24.2 (t 19)		2.1-3.0	5.77 (t, 6)	274 M (12)
				(d 7)					140
									CH ₂ =CHCF=CCl ₂ (19)
									127 CH ₂ CF=CCl ₂ (100)
7c [*]	~76 (3)	12.7	1.4585	27.3 (c)	36.7 (d 29)	1.27 (d 7)	1.9-2.8	3.43 (d 29)	288 M (8)
					(t 2.7) ^q			(m 7)	273 M - CH ₃ (3)
								5.72 (t 7)	141
									CH ₃ CHCF=CCl ₂ (100)
7e ^{***}	~80 (3)	17.0	(1.4592)	27.5 (t, 17)	36.2 (d 29)	1.07 (t 7)	1.62 (m 7)	2.8-3.6	302 M (21)
				(d 7)			2.1-2.7	5.72 (t 7)	273 M - C ₂ H ₅ (55)
									155
									C ₂ H ₅ CHCF=CCl ₂ (100)
7f [*]	~89 (3)	20.4	1.4682	33.8 (c)	31.0 (d 28)	1.14 (d 6.5)		2.4-3.0	302 M (7)
						1.22 (d 6.5)		3.40 (d 28)	141
								(m 7)	CH ₃ CHCF=CCl ₂ (100)
								5.82 (d 11, d, 7)	105
									CH ₂ =CHCF=CCl ₂ (14)

Table II. (Continued)

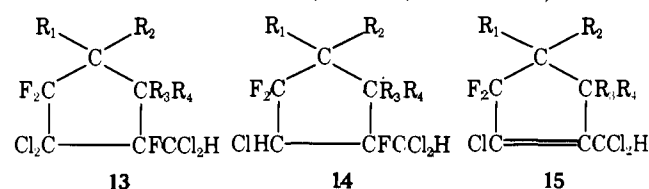
compd ^{a-c}	bp, °C	RT, min ^d	<i>n</i> ²⁰ _D	¹⁹ F NMR, ppm ^{e,f}		H NMR, ppm ^{e,g}			MS ⁱ
				CF ₂	CF	CH ₃	CH ₂	CH ^h	
8b	~91 (3)	20.8	mp 54-56	13.4 + 29.4 (227)	78.4		2.2-2.8	6.27 (d 20)	274 M (13) 239 M - Cl (100)
8c	~92 (3)	23.1	1.4729	2.6 + 32.9 (227)	84.3	1.25 (d 7) (d 2)	2.4-3.1	1.6-2.3 6.28 (d 20)	288 M (5) 253 M - Cl (100)
8g	~94 (3)	28.0	1.4767	12.7 + 33.4 (229)	84.8	1.28 (d 5) 1.33 (d 3)	1.9-2.6	6.27 (d 20)	287 M - CH ₃ (2) 267 M - Cl (76) 191 C ₄ H ₃ Cl ₄ (100) 240 M (1)
9b	~80 (8)	9.0	1.4538	10.2 + 20.6 (235) ^r 19.5 br ^{r,w}	80.3 ^r 78.0 ^r		2.1-2.9	4.2-4.9 5.91 (d 5) ^r 6.07 (d 19) ^r	205 M - Cl (15) 157 M - CHCl ₂ (100)
9c^s	64-75 (3)	10.7 ^x 11.3 ^x	1.4520	13.5 + 32.7 (231) 17.5 + 28.8 (232) 15.3 + 24.7 (239) 31.3 + 42.6 (221)	74.9 80.7 86.4 67.0	1.1-1.4	(2.3)-3.1	1.7-(2.3) 4.2-4.9 6.04 (d 17) ⁱ 5.94 (d 6) ^u 6.09 (d 16) ^c	254 M (1) 219 M - Cl (9) 171 M - CHCl ₂ (100)
9e^s	~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) ^m (2.2)-3.0 (2 H)	4.2-4.9 6.04 (d 17) ⁱ 6.08 (d 15) ^v	233 M - Cl (9) 185 M - CHCl ₂ (44) 149 M - (CHCl ₂ , HCl) (100)
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) 5.96 (d 9)	197 M - (Cl, HCl) (3) 185 M - CHCl ₂ (22) 149 M - (CHCl ₂ , HCl) (100)
9g^s	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	4.4-5.0 5.96 (d 14) ^c 5.88 (d 5) ^u	233 M - Cl (5) 217 M - (HCl, CH ₃) (1) 185 M - CHCl ₂ (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> 6.63 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)		1.7-2.4 6.65 s, br	248 M (9) 233 M - CH ₃ (3) 165 M - CHCl ₂ (100)
10g*	~74 (9)	8.4	1.4666	28.9 s, br		1.20 (t 1.6)	2.58 (t 4)	6.63 s, br	284 M (9) 213 M - Cl (100)

^a Satisfactory analytical data ($\pm 0.4\%$ 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.

^b Compounds **4**, **7**, and **10** show $\nu_{C=C}$ at 1660-1673 cm^{-1} . However, **4h** has an unusual value of 1638 cm^{-1} . ^c 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 CDCl₃ (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 CF₃CO₂H. Data for AB pattern are presented as follows: chemical shift of A + chemical shift of B (*J*_{F-F}). ^g Downfield relative to internal tetramethylsilane. ^h CHCl₂ signals indicated by boldface. -CHCl- signals indicated by italics. ⁱ *m/e*, assignment, and relative intensity (in parentheses) are given. See ref 28. ^j Known compound. ^k Obtained only as a mixture of **3a** and **4a**. Mutual separation not attempted. ^l 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. ^m CH₂ signals and CH signals could not be distinguished. ⁿ 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). ^o Prepared from RCF₂CCl₂H by treatment with 1 equiv plus of *n*-butyllithium in ether at low temperatures. ^p Ten lines with relative intensities consistent with the structure. ^q Probably *J*_{F-F}. ^r Assignment to isomer I or II was not possible as only ~1:1 isomeric mixtures were obtained. ^s 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. ^t ¹⁹F NMR data arranged in this order. Assignment of ¹H NMR signals to individual isomers was difficult except for the signals due to the CHCl₂ group. ^u For isomer I. ^v For isomer II. ^w For isomer III. ^x Interpreted as a special case of an AB pattern where the difference between the chemical shifts of A and B is very small. ^y 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 ¹⁹F NMR signals of CF₂ appear as a gross AB pattern having *J*_{F-F} of 221-249 Hz. (Compounds **5** and **11** also show ¹⁹F NMR signals of CF₂ as an AB pattern.) Compounds **8** and **9** show additional signals of somewhat unusually high ¹⁹F 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

structures **13**, **14**, and **15** for these compounds is not eliminated, the structures **8**, **9**, and **10** are tentatively assigned since clear distinction between **8** and **13** (**9** and **14**, or **10** and **15**) from the

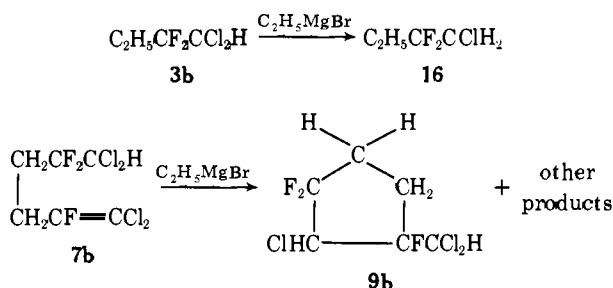


data of the present study seems difficult and since the possibility of different structures for different sets of R_1 , R_2 , R_3 , and R_4 requires a detailed examination for individual cases.⁹

For compounds **9**, the number of isomers detected by ¹⁹F NMR was four in the cases where $R_1 = \text{CH}_3$, $R_2 = R_3 = R_4 = \text{H}$ and where $R_1 = \text{C}_2\text{H}_5$, $R_2 = R_3 = R_4 = \text{H}$ and two in the cases where $R_1 = R_2 = R_3 = R_4 = \text{H}$ and where $R_1 = R_2 = \text{CH}_3$, $R_3 = R_4 = \text{H}$. For compounds **8**, only one isomer each was found in the cases where $R_1 = R_2 = R_3 = R_4 = \text{H}$ and where $R_1 = R_2 = \text{CH}_3$, $R_3 = R_4 = \text{H}$. 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.

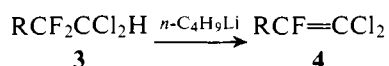
Consistent with the structure **10**, where one isomer each is possible for compounds under consideration, the two fluorine atoms of the CF_2 group are shown to be equivalent (a singlet in ¹⁹F NMR, though somewhat broad) in the case where $R_1 = R_2 = \text{CH}_3$, $R_3 = R_4 = \text{H}$ and nonequivalent (an AB pattern in ¹⁹F NMR) in the cases where $R_1 = \text{C}_2\text{H}_5$, $R_2 = R_3 = R_4 = \text{H}$ and where $R_1 = R_3 = \text{CH}_3$, $R_2 = R_4 = \text{H}$.

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.

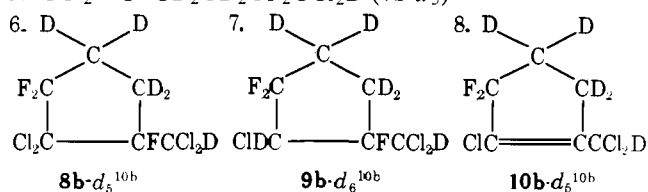
Conversion of **3** to **4** was effected by treatment with *n*-butyllithium in ether. This method was used to prepare most of **3** since isolation of pure samples of **3** from the mixtures of the reaction of **1** with **2** was generally difficult.



Deuterium-labeling experiments using $\text{C}_2\text{D}_5\text{MgBr}$ and $\text{CH}_3\text{CD}_2\text{MgBr}$ were conducted in order to answer questions such as the following: (1) From where is the CHCl_2 hydrogen of $\text{RCF}_2\text{CCl}_2\text{H}$ formed? (2) On which carbon atom of **7** does the original α hydrogen of $\text{C}_2\text{H}_5\text{MgBr}$ reside? The following distributions of isotopic species were found.¹⁰

From **1** + $\text{C}_2\text{D}_5\text{MgBr}$:

- $\text{C}_2\text{D}_5\text{CF}_2\text{CCl}_2\text{D}$ (**3b-d₆**) 85%
+ $\text{C}_2\text{D}_5\text{CF}_2\text{CCl}_2\text{H}$ (**3b-d₅**) 15%
- $\text{C}_2\text{D}_5\text{CF}=\text{CCl}_2$ (**4b-d₅**) 40%
+ $\text{CHD}_2\text{CD}_2\text{CF}=\text{CCl}_2$ (**4b-d₄**) 60%^{10a}
- $\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)\text{CF}_2\text{CCl}_2\text{D}$ (**5-d₁**) 54% + **5**, 46%
- 6**, 100%
- $\text{CCl}_2=\text{CFCD}_2\text{CD}_2\text{CF}_2\text{CCl}_2\text{D}$ (**7b-d₅**)^{10b}

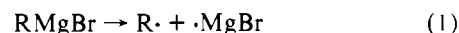


From **1** + $\text{CH}_3\text{CD}_2\text{MgBr}$:

- $\text{CH}_3\text{CD}_2\text{CF}_2\text{CCl}_2\text{H}$ (**3b-d₂**) 92%
 $\text{CH}_3\text{CD}_2\text{CF}_2\text{CCl}_2\text{D}$ (**3b-d₃**) 8%
- $\text{CH}_3\text{CD}_2\text{CF}=\text{CCl}_2$ (**4b-d₂**) 60%
+ $\text{CHD}_2\text{CH}_2\text{CF}=\text{CCl}_2$ (**4b-d_{2'}**) 40%
- 5**, ~100%
- 6**, 100%
- $\begin{array}{c} \text{CH}_2\text{CF}_2\text{CCl}_2\text{H} \\ | \\ \text{CD}_2\text{CF}=\text{CCl}_2 \end{array}$ (**7b-d₂**) 50%^{10c} + $\begin{array}{c} \text{CD}_2\text{CF}_2\text{CCl}_2\text{H} \\ | \\ \text{CH}_2\text{CF}=\text{CCl}_2 \end{array}$ (**7b-d_{2'}**) 50%^{10c}
- $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{F}_2\text{C} \quad \text{CD}_2 \\ | \quad | \\ \text{Cl}_2\text{C} \quad \text{CFCCl}_2\text{H} \end{array}$ (**8b-d₂**) 50%^{10c} + $\begin{array}{c} \text{D} \quad \text{D} \\ \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{F}_2\text{C} \quad \text{CH}_2 \\ | \quad | \\ \text{Cl}_2\text{C} \quad \text{CFCCl}_2\text{H} \end{array}$ (**8b-d_{2'}**) 50%^{10c}
- $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{F}_2\text{C} \quad \text{CD}_2 \\ | \quad | \\ \text{ClHC} \quad \text{CFCCl}_2\text{H} \end{array}$ (**9b-d₂**) 50%^{10c} + $\begin{array}{c} \text{D} \quad \text{D} \\ \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{F}_2\text{C} \quad \text{CH}_2 \\ | \quad | \\ \text{ClHC} \quad \text{CFCCl}_2\text{H} \end{array}$ (**9b-d_{2'}**) 50%^{10c}
- $\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{F}_2\text{C} \quad \text{CD}_2 \\ | \quad | \\ \text{ClC}=\text{CCCl}_2\text{H} \end{array}$ (**10b-d₂**)^{10d} + $\begin{array}{c} \text{D} \quad \text{D} \\ \diagdown \quad / \\ \text{C} \\ / \quad \backslash \\ \text{F}_2\text{C} \quad \text{CH}_2 \\ | \quad | \\ \text{ClC}=\text{CCCl}_2\text{H} \end{array}$ (**10b-d_{2'}**)^{10d}

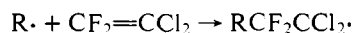
Discussion

In some cases of reactions with Grignard reagents, participation of radical mechanisms has been reported.¹¹⁻¹⁵ 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 following¹⁶ and the tendency is often overshadowed by more rapidly proceeding ionic (polar) reactions.



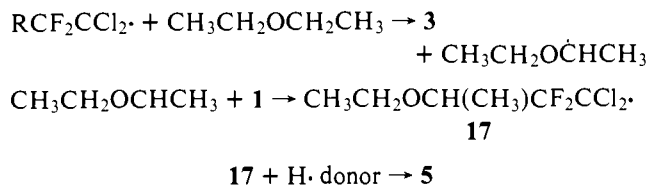
The present results are explicable throughout by radical mechanism. Probably $\text{CF}_2=\text{CCl}_2$ (**1**) does not possess sufficient ionic reactivity toward alkyl Grignard reagents, which is polarized only to a small extent due to the relative instability of alkyl anions, but possesses sufficient reactivity toward radicals formed under the reaction conditions.

From comparison of the results of the reactions of **1** with $\text{C}_2\text{H}_5\text{MgBr}$ (**2b**), $\text{CH}_3\text{CD}_2\text{MgBr}$, and $\text{C}_2\text{D}_5\text{MgBr}$, it is evident that the hydrogen of the CCl_2H group in compound **3b** originates from the β hydrogen of the Grignard reagent (**2b**). It seems reasonable to consider that the β 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 case of the reaction with CH_3MgBr (**2a**) in contrast with other cases as seen in Table I.



1

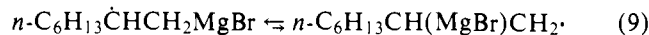
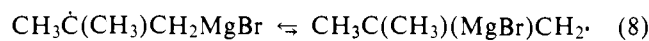
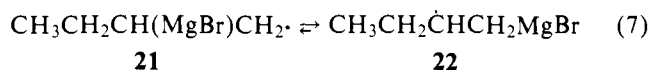
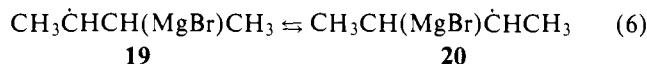
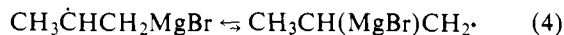




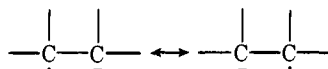
Although the above point alone does not require it, only a radical mechanism seems to offer a simple and consistent explanation for the experimental results. In particular, the formation of $\text{R}'\text{CF}=\text{CCl}_2$ and compounds of the types **7**, **8**, **9**, and **10** is difficult to explain unless radicals to be derived from the Grignard reagents by abstraction of β hydrogen are assumed as intermediates.¹⁷

Initially, the formation of **4** having a (seemingly) rearranged alkyl group ($\text{R}'\text{CF}=\text{CCl}_2$) 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,^{18,19} and it is not understood why $\text{R}'\text{CF}_2\text{CCl}_2\text{H}$ is not formed if $\text{R}'\text{CF}=\text{CCl}_2$ 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*- $\text{C}_3\text{H}_7\text{CF}=\text{CCl}_2$, **7c**, and cyclic compounds **8c**, **9c**, and **10c** from *n*- $\text{C}_3\text{H}_7\text{MgBr}$ (**2c**) and from *i*- $\text{C}_3\text{H}_7\text{MgBr}$ (**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 $\text{CH}_3\text{CD}_2\text{MgBr}$ is explicable in terms of eq 5. The reaction of *s*- $\text{C}_4\text{H}_9\text{MgBr}$ (**2f**) constitutes the most complex case as two directions of β -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 β -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.



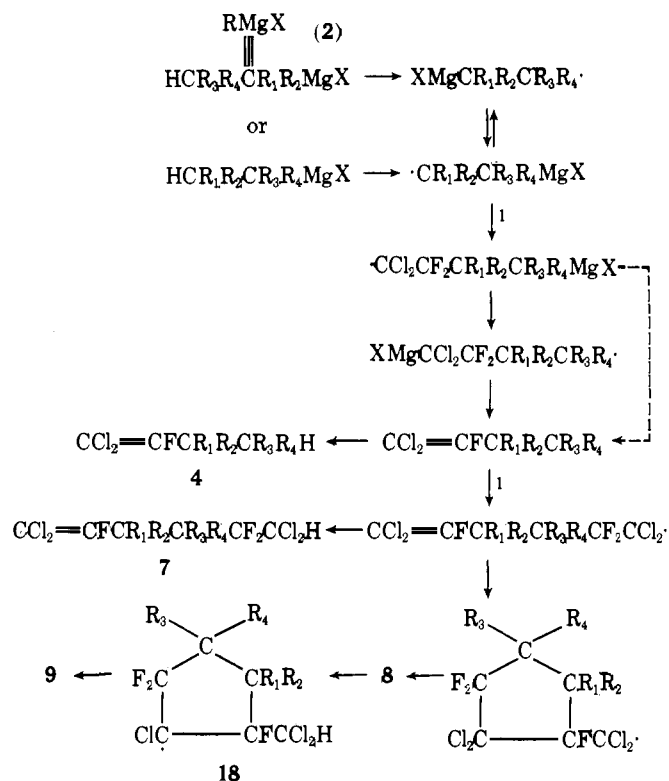
The radical species resulting from β -hydrogen atom abstraction from a Grignard reagent is expected to be relatively stable and to be formed easily because the corresponding anion is the resonance stabilized radical anion of an olefin.²⁰



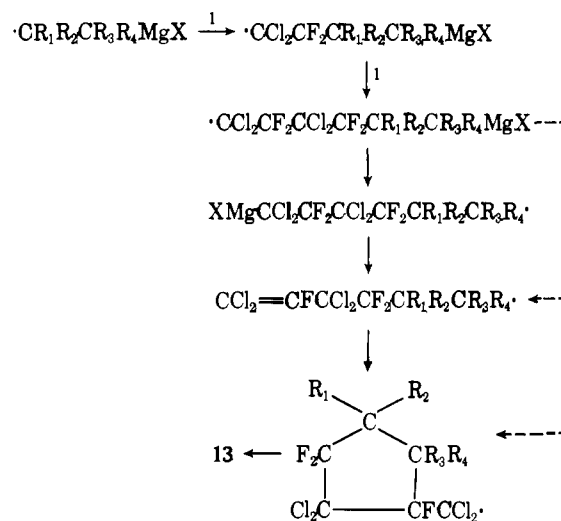
The interconversion of the type shown in eq 4-9, that is, 1,2-shift of MgBr in the radical, is also expected to occur easily because of the partial ionic character of carbon-magnesium bond coupled with the existence of a significant partial negative charge at the radical center in contrast to the difficult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

The alternative possibility is that only an intermediate state

Scheme I



Scheme II



could represent an energy minimum, and this possibility seems to be favored by the results of the reaction of *s*-butylmagnesium bromide.²¹ 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.

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,²² $\text{RCF}_2\text{CCl}_2\cdot$ should have greater chance than $\text{CH}_3\text{CH}_2\text{OC}(\text{CH}_3)\text{H}\cdot$ in finding RMgX to react with since $\text{RCF}_2\text{CCl}_2\cdot$ is formed most probably in or near the region where the $\text{R}\cdot$ radical has been generated, while $\text{CH}_3\text{CH}_2\text{OC}(\text{CH}_3)\text{H}\cdot$ 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-

tries, Ltd. Ventron magnesium (chips, 99.99%) was also used in the later stages of the study.

Reaction of 1 with *sec*-Butylmagnesium Bromide (2f). To an ice-cooled 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 ¹⁹F 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 1.

Reaction of 1 with C₂D₅MgBr. A solution of C₂D₅MgBr in ether was prepared from C₂D₅Br (Merck Sharp & Dohme; 8.0 g, 0.070 mol) and magnesium (2.1 g) and transferred through a glass wool-plugged 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-d₆**, **3b-d₅**, **4b-d₅**, **4b-d₄**, **5**, **5-d₁**, **6**, **10-d₅**; fr 2, 1.71 g, bp 85–91 °C (10 mm), **9b-d₆** 20%, **7b-d₅** 80%; fr 3, 0.42 g, bp lower than 162 °C (3 mm), **8b-d₅** 90%; residue, 0.56 g. A sample (ca. 0.5 g) of **3b-d₆** (¹⁹F NMR: 30.6 ppm, s, br) was obtained by preparative GC of fr 1. The presence of a small amount of **3b-d₅** in the sample was indicated by weak ¹H NMR signals of CCl₂H (5.74 ppm, t, *J* = 7 Hz). The ¹⁹F 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-d₅**. The ¹⁹F 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-d₅**.

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 (C₂HD₄CF=CCl₂), *m/e* 147 (C₂D₅CF=CCl₂), *m/e* 129 (CD₂CF=CCl₂), *m/e* 111 (C₂HD₄CF=CCl), and at *m/e* 112 (C₂D₅CF=CCl) but no significant peak at *m/e* 128 (CHDCF=CCl₂), indicating the presence of C₂D₅CF=CCl₂ (**4b-d₅**) and CHD₂CD₂CF=CCl₂ (**4b-d₄**). 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 (CH₃CHOH) and *m/e* 73 (CH₃CH₃OCHCH₃) was observed, the fact indicating the presence of **5-d₁** as well as **5**.

Reaction of 1 with CH₃CD₂MgBr. CH₃CD₂Br was prepared according to a reported method⁸ starting from *n*-butyl acetate and lithium aluminum deuteride (Merck Sharp & Dohme). From a reaction of **1** with CH₃CD₂MgBr prepared from 7.0 g (0.063 mol) of CH₃CD₂Br, the following fractions were obtained as above: fr 1, 2.90 g, the cold-trap condensate while fr 2 came out, ether, **3b-d₂**, **4b-d₂**, **4b-d₂**, **5**, **6**, **10b-d₂**, **10b-d₂**; fr 2, 1.26 g, bp 86–90 °C (9 mm), (**9b-d₂** + **9b-d₂**) 40%, (**7b-d₂** + **7b-d₂**) 55%; fr 3, 1.11 g, bp 71–76 °C (3 mm), (**7b-d₂** + **7b-d₂**) ~100%; fr 4, 0.47 g, bp 85–123 °C (3 mm), (**7b-d₂** + **7b-d₂**) 35%, (**8b-d₂** + **8b-d₂**) 60%. A sample (ca. 0.5 g) of **3b-d₂** obtained by preparative GC of fr 1 showed consistent ¹H NMR (1.09 ppm, singlet with fine structure, 3 H; 5.76 ppm, t, *J* = 7 Hz, 1 H) and ¹⁹F NMR (30.3 ppm, eight lines having relative intensities

of approximately 1:2:3:3:3:2:1 with spacings of 2.4 Hz) spectra. The fine structure of the CH₃ 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 Hz as compared with 1.1 Hz calculated from *J*_{HH} = 7 Hz of **3b** by dividing by 2 μH/μD = 2 × 2.7927/0.85738 = 6.5) with two D nuclei, while the above described fine structure of ¹⁹F is a composite (*J*_{FD} = 7.2 Hz) of two such patterns (*J*_{FD} = 2.4 Hz as compared with 2.6 Hz calculated from *J*_{FD} = 17 Hz of **3b** by dividing by 2 μH/μD). Fraction 3 was shown to be a very nearly 1:1 mixture of **7b-d₂** and **7b-d₂** by its ¹H 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 ¹⁹F 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 (CD₂CF=CCl₂) and *m/e* 129 (CH₂CF=CCl₂) was used for estimation of the relative amount of **4b-d₂** and **4b-d₂** and the relative amounts of **7b-d₂** and **7b-d₂**, a necessary correction for contribution of CH₂CF=C³⁷Cl³⁵Cl to the intensity of the peak at *m/e* 129 being made. Similarly, the relative intensity of the peaks at *m/e* 93 (CH₂CF=CHCl) and at *m/e* 95 (CD₂CF=CHCl) was used for estimation of the relative amount of **8b-d₂** and **8b-d₂** and the relative amount of **9b-d₂** and **9b-d₂**.

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 ¹⁹F 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-2,2-difluorobutane (**16**) was obtained by preparative GC directly from the worked-up mixture. ¹H 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); ¹⁹F NMR: 25.1 ppm (t, *J* = 16 Hz; t, *J* = 12 Hz). *n*²⁰_D 1.3812.

Anal. Calcd for C₄H₇ClF₂: 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 HCCl₂CF₂CH₂CH₂C(C₂H₅)=CCl₂ (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**.

References and Notes

- P. Tarrant and D. A. Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1954).
- K. Okuhara, *J. Org. Chem.*, **41**, 1487 (1976).
- A compound of this type was also obtained from the reaction with allyl magnesium bromide: P. Tarrant and J. Heyes, *J. Org. Chem.*, **30**, 1485 (1965).
- (a) Perfluoroalkyl Grignard reagents are obtainable but unstable at room temperature: C. F. Smith, E. J. Soloski, and C. Tamborski, *J. Fluorine Chem.*, **4**, 35 (1974), and literature cited therein. (b) Polyfluoroalkyl Grignard reagents are less unstable: R. Sullivan, J. R. Lacher, and J. D. Park, *J. Org. Chem.*, **29**, 3664 (1964).
- The formation of RC(CN)₂C(CN)₂MgBr from tetracyanoethylene and RMgBr is reported: H. C. Gardner and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 558 (1976).
- H. Muramatsu, K. Inukai, and T. Ueda, *J. Org. Chem.*, **29**, 2220 (1964).
- H. Muramatsu, K. Inukai, Y. Iwata, and S. Murakami, *Bull. Chem. Soc. Jpn.*, **40**, 1284 (1967).
- (a) E. C. Ashby, J. D. Buhler, I. G. Lopp, T. L. Wisemann, J. S. Bower, Jr., and J. T. Laemmle, *J. Am. Chem. Soc.*, **98**, 6561 (1976). (b) Equation 12 of this paper suggested this possibility to the present author.
- The compound assigned the structure **8g** has mass spectroscopic peaks at *m/e* 191, 193, 195, 197, and 199 in relative intensities consistent with four chlorine atoms. If this agreement in relative intensities is not fortuitous, there should exist a fragment C₄H₃Cl₄, which is more easily accommodated by the structure **13g** than by the structure **8g**. The relative intensities of the peaks beginning with *m/e* 191 are also in agreement with those expected for C₄H₃Cl₄ in the case of **8c**, considerably different in the case of **8e**, and clearly different in the case of **8b**.
- 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-d₂** and **7c-d₂** 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 of **4b-d₄** (75%). (b) The ratio of the intensities of the M⁺ peak (where all chlorine atoms are ³⁵Cl) of the indicated species and the peak at the (M – 1)⁺ 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.

- (11) T. E. Stevens, *J. Org. Chem.*, **32**, 1641 (1967).
- (12) (a) R. C. Lamb, P. W. Ayers, M. K. Toney, and J. F. Garst, *J. Am. Chem. Soc.*, **88**, 4261 (1966). (b) C. Walling and A. Cloffari, *ibid.*, **92**, 6609 (1970).
- (13) R. G. Gough and J. A. Dixon, *J. Org. Chem.*, **33**, 2148 (1968).
- (14) C. Blomberg and H. S. Mosher, *J. Organomet. Chem.*, **13**, 519 (1968).
- (15) T. Holm and I. Crossland, *Acta Chem. Scand.*, **25**, 59 (1971).
- (16) Some courses of the formation of the alkyl radicals from Grignard reagents may be catalyzed by transition metal impurity in view of known catalytic activity of such metals in closely related reactions: M. S. Kharasch, S. C. Kleiger, J. A. Martin, and F. R. Mayo, *J. Am. Chem. Soc.*, **63**, 2305 (1941), and ref 8.
- (17) The cyclization of 5-hexenyl to cyclopentylmethyl radicals is considered a probe for alkyl radical reaction intermediates: J. F. Garst, J. A. Pacifici, C. C. Felix, and A. Nigam, *J. Am. Chem. Soc.*, **100**, 5974 (1978), and literature cited therein.

- (18) J. W. Wilt, "Free Radicals", J. K. Kochl, Ed., Wiley, New York, 1973, p 378.
- (19) W. A. Pryor "Free Radicals", McGraw-Hill, New York, 1966, p 273.
- (20) Replacement of the nitro group by hydrogen upon treatment with sodium thiomethoxide has recently been explained in terms of abstraction of hydrogen from the methylmercaptide ion: N. Kornblum, S. C. Carlson, and R. G. Smith, *J. Am. Chem. Soc.*, **101**, 647 (1979); N. Kornblum, J. Widmer, and S. C. Carlson, *ibid.*, **101**, 658 (1979).
- (21) The expected decreasing stability of the radicals is **22** > **19** (&b>20) > **21**, and definite stability differences seem to exist among them. If this is the case, the formation of comparable amounts of **19** and **22** is not understood unless one of the following conditions is satisfied: (1) Conversion of **2f** to **19** is reversible. (2) Direct conversion of **2f** to **22** occurs. (3) **21** and **22** (thus, **19** and **20**, too) are canonical forms of a resonance hybrid rather than equilibrating species. Condition 3 seems most probable.
- (22) (a) F. W. Walker and E. C. Ashby, *J. Am. Chem. Soc.*, **91**, 3845 (1969). (b) J. Toney and G. D. Stucky, *Chem. Commun.*, 1168 (1967).
- (23) For a simple model, a primary isotope effect (k_H/k_D) of approximately 7 is expected: G. A. Russell, ref 18, pp 311–312.
- (24) D. Seyferth and B. Prokal, *J. Org. Chem.*, **31**, 1702 (1966).
- (25) F. C. Whitmore (1943) as cited in *J. Am. Chem. Soc.*, **72**, 3994 (1950).
- (26) F. F. Blicke and L. D. Powers, *J. Am. Chem. Soc.*, **51**, 3378 (1929).
- (27) T. Holm, *J. Organomet. Chem.*, **29**, C45 (1971); T. Holm, *Acta Chem. Scand.*, **27**, 1552 (1973).
- (28) Where a structure containing chlorine is assigned, the existence of isotopic peaks in the relative intensities consistent with the number of chlorine atoms has been confirmed. In such cases, only the intensities of fragment (or parent) peaks where the chlorine atoms are all ³⁵Cl are indicated.

Studies on Organic Fluorine Compounds. 28.¹ Synthesis and Some Reactions of Tetrakis(trifluoromethyl)-1,4-diphospha-benzene

Yoshiro Kobayashi,* Hiroshi Hamana, Shomi Fujino, Akio Ohsawa,
and Itsumaro Kumadaki

Contribution from Tokyo College of Pharmacy, Horinouchi,
Hachioji, Tokyo 192-03, Japan. Received February 28, 1979

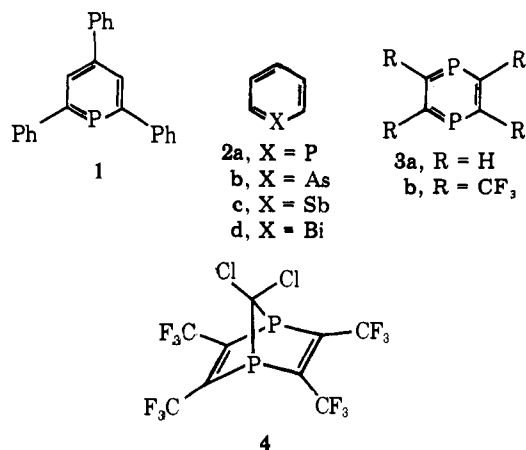
Abstract: Tetrakis(trifluoromethyl)-1,4-diphospha-benzene (**3b**), the first example of diphospha-benzenes, was synthesized by the thermolysis of 2,3,5,6,7,8-hexakis(trifluoromethyl)-7-methoxy-1,4-diphospha-bicyclo[2.2.2]octa-2,5-diene (**6**), which was obtained by addition of methanol to hexakis(trifluoromethyl)-1,4-diphospha-barrelene (**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 diphospha-barrelene 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.² 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**).³ Further, he succeeded in the synthesis of arsabenzene³ (**2b**), stibabenzene⁴ (**2c**), and bismabenzene⁵ (**2d**) and reported the reactions and structural studies of these compounds.^{5,6} But the diphospha-benzene derivatives, which contain two phosphorus atoms in one ring, have not been synthesized yet. Particularly, unsubstituted diphospha-benzene (**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-

Chart 1



duction of perfluoroalkyl groups into the diphospha-benzene might allow the isolation of this new type of compound. From