THE REACTION OF PERFLUOROALKYLCOPPER COMPOUNDS WITH 1-BROMO-1-PERFLUOROALKYLETHYLENES

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Abstract—Perfluoroalkylcopper compounds [F_FCu], when they react with 1-bromo-1-perfluoroalkyl-ethylenes **1**, do not give the expected *gem*-disubstituted compounds **3**, but the *vic*-disubstituted products **2** in 60–70% yields. These results show that the reaction does not proceed through a simple vinylic substitution. ^{1}H and ^{19}F NMR data are given for the new compounds.
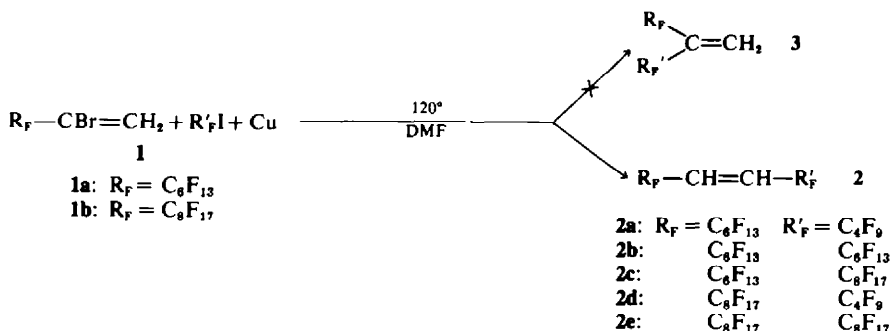
The reaction of perfluoroalkyl iodides with vinyl halides in the presence of copper has always result-ed in the selective replacement of the halogen atom (Br or I) by a perfluoroalkyl group.[1] Although the formation of an intermediate perfluoroalkylcopper compound is generally admitted,[2] the mechanism of this type of reaction has never been fully establish-ed.

We undertook a study of the copper-induced reaction of various perfluoroalkyl iodides with 1-bromo-1-perfluoroalkylethylenes **1** in order to syn-thesize the 1,1-bis(perfluoroalkyl)ethylenes **3**. However, the reaction gave the unexpected 1,2-bis-(perfluoroalkyl) ethylenes **2**, as summarized in the following scheme:

samples prepared by an alternate route, as well as by chemical identification.

Spectral identification included ^{1}H and ^{19}F NMR (Tables 1 and 2). In the proton spectra, all the bis-(perfluoroalkyl)ethylenes **2** exhibit the characteris-tic symmetric $X_2AA'X'_2$ pattern which is shown on Fig 1.* A *trans*-structure for **2** is indicated by the absence of detectable absorption in the IR near 1620 cm^{-1}, where the C=C stretching frequencies are found for the vinylic bromides **1**. Mass spectro-metry gives the usual fragmentations for the per-fluorinated aliphatic chains and the characteristic fragments corresponding to the allylic cleavage of these compounds.[4]
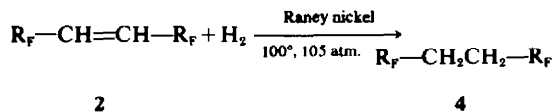
Catalytic hydrogenation of compound **2b** ($R_F =$

$$R_F—CBr=CH_2 + R'_FI + Cu \xrightarrow[\text{DMF}]{120°} \begin{cases} \begin{array}{c} R_F \\ R_F' \end{array}\!\!>C=CH_2 \quad \textbf{3} \\[2ex] R_F—CH=CH—R'_F \quad \textbf{2} \end{cases}$$

1

1a: $R_F = C_6F_{13}$
1b: $R_F = C_8F_{17}$

2a:	$R_F = C_6F_{13}$	$R'_F = C_4F_9$
2b:	C_6F_{13}	C_6F_{13}
2c:	C_6F_{13}	C_8F_{17}
2d:	C_8F_{17}	C_4F_9
2e:	C_8F_{17}	C_8F_{17}

The *vic*-disubstituted compounds **2** were obtained in 60–70% yields. The formation of the expected *gem*-disubstituted compounds **3** was never detected.

Compounds **2** were characterized through spec-tral analysis and identification with authentic

$R_F = C_6F_{13}$) was achieved, according to:

$$R_F—CH=CH—R_F + H_2 \xrightarrow[\text{100°, 105 atm.}]{\text{Raney nickel}} R_F—CH_2CH_2—R_F$$

2   **4**

^{1}H NMR, IR and CPV analysis were used to iden-tify the saturated compound **4** with an authentic sample of 1,2-bis(perfluoroalkyl)ethane.[5]

Further chemical identification of **2b** was attempt-ed through alkaline permanganate oxidation. It

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*Compounds **2** were recently prepared for $R_F = R'_F = C_3F_7$ or C_7F_{15} by copper-induced reactions of R_FI on 1,2-diiodoethylene;[3] comparable ^{1}H NMR patterns were obtained, which were assimilated to a triplet in first approximation.

Table 1. ^1H chemical shifts[a] and coupling constants[b]

Compound	δH_A	δH_B	^3H_A—H_B	^3H_A—F_C	^3H_B—F_C	Solvent[c]
C_5F_{11}—CF_2—$CHBr$—CH_2Br C A B	4·47	3·77	d	d	d	CCl_4
C_7F_{15}—CF_2—$CHBr$—CH_2Br C A B	4·44	3·75	d	d	d	CCl_4
C_5F_{11}—CF_2 \\ C=C / H $_A$ / Br \\ H $_B$	6·57	6·27	2·3	0·6	1·1	CCl_4
C_7F_{15}—CF_2 \\ C=C / H $_A$ / Br \\ H $_B$	6·59	6·29	2·3	0·6	1·1	CCl_4

[a]In ppm. from TMS, taken positively with decreasing fields.
[b]In Hz.
[c]ca 0·3 M solutions.
[d]Not directly measurable on the spectrum.

Table 2. ^{19}F chemical shifts[a]

Compound	$^\alpha CF_2$[b]	$^\beta CF_2$	$^\gamma CF_2$	$^\delta CF_2$	$^\varepsilon CF_2$	$^\zeta CF_2$	$^\eta CF_2$	CF_3	Solvent[c]
$C_6F_{13}CHBrCH_2Br$	111·2	118·7	121·6–122·4[d]	126·2				81·6	CCl_4
$C_8F_{17}CHBrCH_2Br$	111·2	118·7	————121·6[e]————				126·0	81·8	CCl_4
$C_6F_{13}CBr=CH_2$	108·7	120·4	121·6–122·9[d]	126·6				81·8	CCl_4
$C_8F_{17}CBr=CH_2$	108·5	120·1	————121·6[e]————				126·2	81·6	CCl_4
C_6F_{13} \\ C=C / H / H \\ C_4F_9	114·1 114·1	122·9 124·4	122·0–122·9[d] 126·2	126·2				81·2 81·2	CCl_3F
C_6F_{13} \\ C=C / H / H \\ C_6F_{13}	114·1	122·9	121·6–122·9[d]	126·2				81·6	CCl_3F
C_6F_{13} \\ C=C / H / H \\ C_8F_{17}	114·5 114·5	123·3 123·3	——122[e]—— ————122·0[e]————	126·6			126·6	81·8 81·8	CCl_3F
C_8F_{17} \\ C=C / H / H \\ C_4F_9	114·1 114·1	123·3 124·9	126·2	122·0[e]			126·6	82·0 82·0	CCl_3F
C_8F_{17} \\ C=C / H / H \\ C_8F_{17}	114·5	123·7	————122·0[e]————				126·6	81·6	CCl_3F

[a]In ppm from CCl_3F as an internal reference, taken positively with increasing fields.
[b]First CF_2 adjacent to $CHBr$ (or $CBr=$, or $CH=$) is α, second is β, third is γ, etc. . . .
[c]ca. 0·3 M solutions.
[d]These signals could not be specifically attributed to γ or δCF_2.
[e]Broad signal.

required rather drastic conditions to convert ca 20% of the starting material into the 1-hydroper-fluoroalkane 5, which results from the easy decar-boxylation[6] of the oxidation product:

$$R_F—CH=CH—R_F \xrightarrow[150°, 3\ days]{KMnO_4,\ KOH} [R_FCOOK] \rightarrow$$
$$R_FH\ 5\ (20\%)$$

2b   (+ 80% unreacted **2b**)

The formation of the ketone R_F—C(=O)—R_F was not observed.

An alternate route was used to prepare compounds 2, which consists of a thermal addition of the perfluoroalkyl iodides onto the perfluoroalkyl-ethylenes,[7, 5] according to:

$$R_F\text{—}CH\text{=}CH_2 + R_F'I \xrightarrow{180\text{–}200°} R_F\text{—}CH\text{—}CH_2\text{—}R_F'$$
$$\downarrow I$$
$$\xrightarrow{KOH/EtOH} \mathbf{2}$$

Compounds **1** were prepared from 1-perfluoroalkylethylenes $R_FCH\text{=}CH_2$ by thermal bromination and subsequent debromhydratation. The thermal bromination gave comparable or better yields than those previously reported for the photochemical[8] or catalytic[9] bromination of shorter-chain homologs. Debromhydratation[10] afforded only the 1-bromo-1-perfluoroalkylethylene **1** in 80–90% yields.

excess Br_2 were evaporated *in vacuo*. The residue was distilled off to give the pure dibromide in nearly quantitative yield, $C_6F_{13}CHBrCH_2Br$; b.p. 75° (12 mm); (Found: C, 19·21; H, 0·57; F, 48·59; Br, 31·43. Calc. for $C_8H_3F_{13}$-Br_2: C, 18·97; H, 0·59; F, 48·81; Br, 31·62%). C_8F_{17}-$CHBrCH_2Br$; b.p. 108° (17 mm); (Found: C, 19·82; H, 0·55; F, 53·32; Br, 26·13. Calc. for $C_{10}H_3F_{17}Br_2$: C, 19·80; H, 0·50; F, 53·30; Br, 26·40%).

Debromhydratation of the dibromides. A 10% alcoholic KOH (*ca* 20% excess) was added dropwise at 0° under agitation to the dibromide, dissolved in a minimum of absolute alcohol. The mixture was stirred for 2 more hr at room temp after complete addition and poured into *ca* two volumes of water. The lower phase, consisting of almost pure vinylic bromide **1**, was decanted, dried over molecular sieves and distilled off. $C_6F_{13}CBr\text{=}CH_2$ **1a**;
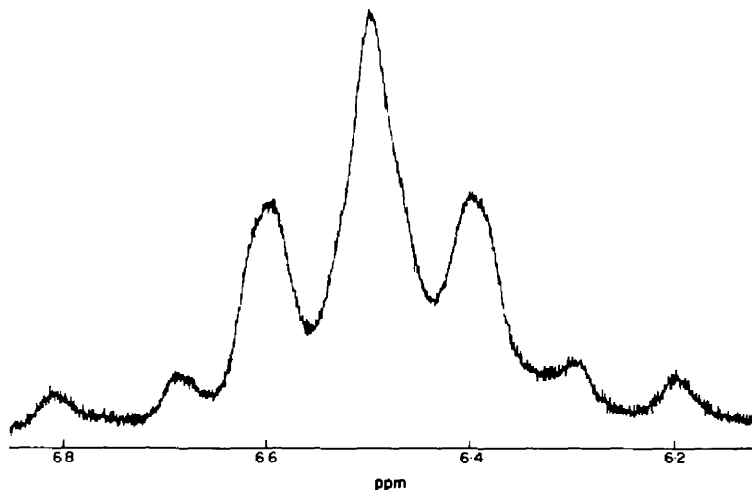
Fig 1. ^1H NMR spectrum of $C_6F_{13}\text{—}CH\text{=}CH\text{—}C_4F_9$ (**2a**) (0·3 M solution in CCl_3F + TMS).

EXPERIMENTAL

General. The ^1H and ^{19}F NMR spectra were run on a JEOL C-60 HL spectrometer, the IR spectra on a LEITZ Model IIIG, and the mass spectra on a CEC 21-130 spectrometer. The VPC analysis were performed on a GIRDEL 3000 chromatograph, with a $10' \times 1/8''$ column, packed with 20% QF1 on Chromosorb PAW 60–80 mesh.

Bromination of the perfluoroethylenes. A mixture of the olefin (0·2 mole), Br_2 (0·3 mole), and CCl_4 (50 ml) was heated in a sealed tube for 5 hr at 120°. The solvent and

b.p. 38° (15 mm); (Found: C, 23·08; H, 0·48; F, 57·70; Br, 18·36. Calc. for $C_8H_2F_{13}Br$: C, 22·58; H, 0·47; F, 58·11; Br, 18·28%); IR: ν C=C = 1620 cm^{-1}. $C_8F_{17}CBr\text{=}CH_2$ **1b**; b.p. 63°C (12 mm); (Found: C, 22·96; H, 0·31; F, 61·67; Br, 15·04. Calc. for $C_{10}H_2F_{17}Br$: C, 22·85; H, 0·38; F, 61·52; Br, 15·24%); IR: ν C=C = 1620 cm^{-1}.

Preparation of the bis(perfluoroalkyl)ethylenes **2**. A mixture of **1** (0·1 mole), perfluoroalkyl iodide (0·125 mole), precipitated Cu (20 g)[11] and N,N-dimethylformamide (80 ml) was heated during 20 hr at 120–140° in a sealed tube. The resultant mixture was filtered. The filtrate was

Table 3. Some physical constants and analysis of the bis(perfluoroalkyl)ethylenes prepared via perfluoroalkylcopper compounds.

Compound	m.p. (°C)	b.p. (°C/mm Hg)	Yield %	Found % C	H	F	Calculated % C	H	F
2a $C_6F_{13}CH\text{=}CHC_4F_9$		74/30	66	25·89	0·40	73·39	25·53	0·35	74·11
2b $C_6F_{13}CH\text{=}CHC_6F_{13}$		56/0·4	70	25·33	0·39	74·46	25·30	0·30	74·40
2c $C_6F_{13}CH\text{=}CHC_8F_{17}$		62/0·3	60	25·59	0·21	74·38	25·13	0·26	74·61
2d $C_8F_{17}CH\text{=}CHC_4F_9$		45/0·15	70	25·35	0·31	74·09	25·30	0·30	74·40
2e $C_8F_{17}CH\text{=}CHC_8F_{17}$	56		60	25·48	0·32	74·25	25·00	0·23	74·77

poured into 500 ml water and the aqueous phase was extracted 3 times with 50 ml ether. The ppt was washed twice by 50 ml ether. The combined ethereal solns were dried over $MgSO_4$ and evaporated. The residue was distilled to give 2, yields and analytical results are given in Table 3.

Hydrogenation of 2b. Compound 2b (28·6 g) was hydrogenated in the presence of Raney Ni (0·1 g) in a 250 ml rocking autoclave. Since no absorption was noticed after 1h30 at 25° under 95 bar hydrogen pressure, the autoclave was heated at 100°, and the pressure raised to 105 bar. Hydrogen absorption started after a few min. Pressure stabilized after 3 hr. Hydrogen was then evacuated, the autoclave was purged 3 times with N_2, cooled and opened. The solid residue was identified as a mixture of 2b (40%) and $C_6F_{13}CH_2CH_2C_6F_{13}$ (60%), which was characterized by comparison with an authentic sample (VPC, ^1H and ^{19}F NMR spectroscopy).

Permanganate oxidation of 2b. Compound 2b (21 g), $KMnO_4$ (35 g), KOH (17 g) and water (150 ml) were heated under reflux during 3 days. The mixture was then acidified to pH 1 with conc HCl and filtered. The aqueous soln was treated by ferrous sulfate until complete decoloration and filtered again. The filtrate was extracted by 3 times 30 ml ether, the ppts were washed by twice 15 ml ether. The combined ether solns were dried over $MgSO_4$ and evaporated. The residue (5 g), as analysed by ^1H and ^{19}F NMR, was composed of compound $C_6F_{13}H$ (20%) and unchanged 2b (80%).

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