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THE SYNTHESIS OF α,ω-BIS-(SILYL)POLYFLUOROALKANE DERIVATIVES

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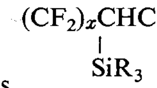
SUMMARY

Fluorosilicones of the type, $R_3SiCH_2CH_2(CF_2)_xCH_2CH_2SiR_3$ where R equals $CF_3CH_2CH_2$, CH_3, Cl, and/or H and where x ranges from 1 to 10, were prepared either by the chloroplatinic acid or peroxide-catalyzed addition of appropriate silanes to $CH_2{=}CH(CF_2)_xCH{=}CH_2$. The addition of $CH_2{=}CH_2$ to $Y(CF_2)_xY$, $Y = Br$ or I, followed by dehydrohalogenation of the resulting $YCH_2CH_2(CF_2)_xCH_2CH_2Y$ provided the required dienes.

While the free-radical induced addition of $CH_2{=}CH_2$ to $Br(CF_2)_6Br$ and $BrCH_2CH_2(CF_2)_6Br$ gave a high yield of $BrCH_2CH_2(CF_2)_6CH_2CH_2Br$, the addition of $CH_2{=}CH_2$ to $BrCF_2CF_2Br$ and $BrCH_2CH_2CF_2CF_2Br$ under identical conditions resulted in the formation of no more than a trace amount of $BrCH_2CH_2CF_2CF_2CH_2CH_2Br$. A similar unsuccessful result was obtained in an attempted addition of $CH_2{=}CH_2$ to $BrCF_2Br$ and $BrCF_2CH_2CH_2Br$, indicating the importance of the chain length of $Br(CF_2)_xBr$ for the formation of α,ω-diethylene addition products.

Although no complication was encountered in the peroxide-catalyzed addition of silane to $CH_2{=}CH(CF_2)_xCH{=}CH_2$, the chloroplatinic acid induced addition of silane to the dienes yielded the corresponding rearranged mono-addition products, $R_3SiCH_2CH_2(CF_2)_{x-1}CF{=}CHCH_3$ in addition to the diadducts, $R_3SiCH_2CH_2(CF_2)_xCH_2CH_2SiR_3$. The decomposition of a reversely oriented platinum–olefin or platinum–diene complex without actual formation of the reverse adduct,  $-(CF_2)_x\underset{\displaystyle SiR_3}{\underset{|}{C}}HCH_3$, is thought to account for the rearranged mono-addition products.

INTRODUCTION

As part of our synthetic program, it was necessary to prepare α,ω-bis-(silyl)polyfluoroalkane derivatives, $\equiv SiCH_2CH_2(CF_2)_xCH_2CH_2Si\equiv$. A careful consideration of the design of the synthesis of the silylpolyfluoroalkane suggests the synthetic route shown in Scheme 1.

$$\begin{tikzcd}
\mathrm{Y(CF_2)_xY + CH_2{=}CH_2} \arrow[r] & \mathrm{YCH_2CH_2(CF_2)_xCH_2CH_2Y} \arrow[d, "-\mathrm{HY}"] \\
\mathrm{{\equiv}SiCH_2CH_2(CF_2)_xCH_2CH_2Si{\equiv}} & \mathrm{CH_2{=}CH(CF_2)_xCH{=}CH_2} \arrow[l, "\mathrm{{\equiv}SiH}"']
\end{tikzcd}$$

Scheme 1

It has been shown[1] that telomerization of $CH_2=CH_2$ with $Br(CF_2)_xBr$, $x=2$, 4, and 6, will occur, but the formation of $BrCH_2CH_2(CF_2)_xCH_2CH_2Br$, $x=2$ and 6, was not mentioned. The author, however, did report the formation of $BrCH_2CH_2(CF_2)_4CH_2CH_2Br$ from the free-radical catalyzed addition of $CH_2=CH_2$ to $BrCH_2CH_2(CF_2)_4Br$. Recently Tarrant and Tandon[2] reported the addition of $CH_2=CH_2$ to $BrCF_2CF_2Br$ to give rise to a 32% yield of a 1:1 adduct, $BrCF_2CF_2CH_2CH_2Br$, and a 2:1 adduct, which was shown to be $BrCF_2CF_2(CH_2)_4Br$ rather than $BrCH_2CH_2CF_2CF_2CH_2CH_2Br$.

RESULTS AND DISCUSSION

The investigation of the addition of $CH_2=CH_2$ to $Y(CF_2)_xY$ to form $YCH_2CH_2(CF_2)_xCH_2CH_2Y$ was initiated with commercially-available $BrCF_2CF_2Br$ (I). Although seemingly a straightforward reaction, the free-radical catalyzed addition of $CH_2=CH_2$ to dibromide (I) resulted in the formation of 1:1 adduct, $BrCH_2CH_2CF_2CF_2Br$ (II), in high yield and no more than a trace amount of the desired 1:1:1 diadduct, $BrCH_2CH_2CF_2CF_2CH_2CH_2Br$ (IV) (Scheme 2).

$$\begin{array}{llll}
\underset{\text{(I)}}{\mathrm{BrCF_2CF_2Br}} + \mathrm{CH_2{=}CH_2} & \xrightarrow[\text{conv.}]{\sim 67\%} & \underset{\text{(II)}}{\mathrm{BrCF_2CF_2CH_2CH_2Br}} & (\sim 65\%) \\
 & & \underset{\text{(III)}}{\mathrm{BrCF_2CF_2(CH_2)_4Br}} & (\sim 15\%) \\
 & & \underset{\text{(IV)}}{\mathrm{BrCH_2CH_2CF_2CF_2CH_2CH_2Br}} & (\sim 8\%)
\end{array}$$

Scheme 2

The results of several examples of this addition reaction are shown in Table 1. After several unsuccessful attempts to prepare the desired diadduct (IV) in quantity directly from dibromide (I), the addition reaction of $CH_2=CH_2$ to adduct (II) was investigated. The reaction of $CH_2=CH_2$ with adduct (II) should occur preferentially at the $BrCF_2$– group rather than at the $BrCH_2$– end[1,3]. Therefore, if the reaction of $CH_2=CH_2$ with adduct (II) occurs, the predominant product would be the desired diadduct (IV).

The results of several examples of the free-radical catalyzed addition of $CH_2=CH_2$ to adduct (II) are summarized in Table 2. As these data show, only

TABLE 1

REACTION OF $CH_2=CH_2$ WITH $BrCF_2CF_2Br$

Run	Mole of $BrCF_2CF_2Br$	Reaction press. $CH_2=CH_2$ psi	Catalyst	Reaction time (h)	Reaction temp. (°C)	% Conv. of $BrCF_2CF_2Br$, GLC (isolation)	% Yield, GLC (isolation)		
							(II)[a]	(III)[b]	(IV)[c]
1	1.42	85	DTBP	25	120	16	57		
2	1.42	150	DTBP	27	120	67 (73)	51 (59)	28 (18)	8 (6)
3	1.42	120	DTBP	25	120	68	64	19	8
4	1.42	80	DTBP	72	120	75 (89)	68 (46)	9	9 (6)
5	0.62	120	None	25	120	no reaction			
6[d]	7.04	115	DTBP	17	135	58	87	4	5

[a] $BrCH_2CH_2CF_2CF_2Br$

[b] $Br(CH_2)_4CF_2CF_2Br$

[c] $BrCH_2CH_2CF_2CF_2CH_2CH_2Br$

[d] About 5 mole% catalyst and a 2 l stainless-steel stirring pressure reactor were used.

TABLE 2

REACTION OF $CH_2=CH_2$ WITH $BrCF_2CF_2CH_2CH_2Br$

Run	Mole of $BrCF_2CF_2CH_2CH_2Br$	Reaction press. $CH_2=CH_2$ psi	Catalyst[a]	Reaction time (h)	Reaction temp. (°C)	% Conv. of $BrCF_2CF_2CH_2CH_2Br$ GLC (isolation)	% Yield, GLC (isolation)		
							(IV)[b]	(III)[c, d]	(V)[e]
1	0.694	110	Bz_2O_2	20	70	14 (26)	20 (1)	18	40 (16)
2	0.694	180	DTBP	44	110	23	19	8	33
3	0.347	120	DTBP	25	110	23	38	7	4
4	0.347	100	DTBP	13	140	15	13	Trace	
5[f]	0.246	60	DTBP	46	120	9	5	Trace	5
6[g]	0.4			85	65	no reaction			

[a] About 3 mole%.

[b] $BrCH_2CH_2CF_2CF_2CH_2CH_2Br$

[c] $Br(CH_2)_4CF_2CF_2Br$

[d] Since this was identified by GLC retention time only, the identification is not considered to be positive.

[e] $Br(CH_2)_4CF_2CF_2CH_2CH_2Br$

[f] 0.8 g of $NaHCO_3$ added.

[g] UV induced reaction bubbling $CH_2=CH_2$ into the telogen.

an average of about 17% conversion of adduct (II) was realized, and approximately 19% of this was the desired diadduct (IV). The remainder of the product consisted of about 10% of diadduct (III), $BrCH_2CH_2CF_2CF_2(CH_2)_4Br$ (V) and several unidentified products. All of the above experimental results clearly indicate that the addition reaction of $CH_2{=}CH_2$ to dibromide (I) or adduct (II) cannot be employed as a practical method for the production of diadduct (IV). Similar low conversion was obtained in the addition of $CH_2{=}CH_2$ to CF_2Br_2 (VI) and $BrCF_2CH_2CH_2Br$ (VII). The free-radical catalyzed addition of $CH_2{=}CH_2$ to dibromide (VI) gave adduct (VII) in high yield, but the addition of $CH_2{=}CH_2$ to adduct (VII) under free-radical catalysis resulted in only about a 5% conversion of adduct (VII), in which $BrCH_2CH_2CF_2CH_2CH_2Br$ (VIII) amounted to about 46%.

After unsuccessful attempts to obtain diadduct (IV) and (VIII) in quantity from the addition of $CH_2{=}CH_2$ to adducts (II) and (VII), respectively, our effort was directed toward the investigation of the addition of $CH_2{=}CH_2$ to $Br(CF_2)_6Br$ (IX). The addition of $CH_2{=}CH_2$ to dibromide (IX) was conducted under 50–60 psi of constant $CH_2{=}CH_2$ pressure at 130–140°. The results (average and isolated yield) of this addition reaction are shown in Scheme 3.

$$\begin{array}{lll}
\underset{\text{(IX)}}{Br(CF_2)_6Br} + CH_2{=}CH_2 \xrightarrow[73\%\ \text{conv.}]{\text{DTBP}} & \underset{\text{(X)}}{Br(CF_2)_6CH_2CH_2Br} & (63\%) \\
& \underset{\text{(XI)}}{BrCH_2CH_2(CF_2)_6CH_2CH_2Br} & (18\%) \\
& \text{Other Telomers} & \\
& \text{(XI)} & (60\%) \\
\text{(X)} + CH_2{=}CH_2 \xrightarrow[69\%\ \text{conv.}]{\text{DTBP}} & \underset{\text{(XII) (presumed)}}{BrCH_2CH_2(CF_2)_6(CH_2)_4Br} & (18\%)
\end{array}$$

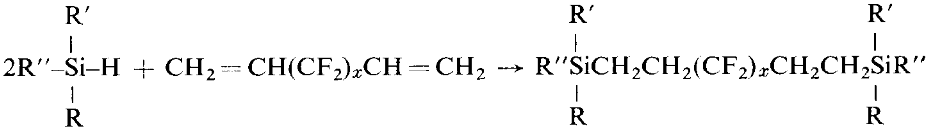
Scheme 3

The addition of $CH_2{=}CH_2$ to dibromide (IX) was found to proceed smoothly giving rise to 1:1 adduct (X), 1:1:1 adduct (XI) and other telomers. The further addition of $CH_2{=}CH_2$ to adduct (X) gave the desired diadduct (XI) without difficulty. Dehydrobromination of diadduct (XI) yielded $CH_2{=}CH(CF_2)_6CH{=}CH_2$ (XIII) in high yield. Although the exact nature of the failure to form a reasonable yield of diadducts (IV) and (VIII) is not clear at present, the successful formation of diadduct (XI) from the addition of $CH_2{=}CH_2$ to dibromide (IX) or adduct (X) indicates the importance of the chain length of α,ω-dibromoperfluoroalkanes for the formation of α,ω-diethylene addition products.

In contrast to the results of the addition of $CH_2{=}CH_2$ to dibromide (I), Brace[4a] and Knunyants *et al.*[4b] reported that thermal addition of $CH_2{=}CH_2$ to ICF_2CF_2I (XIV) gave rise to 1:1:1 adduct, $ICH_2CH_2CF_2CF_2CH_2CH_2I$ (XV), in high yield. However, the free-radical catalyzed addition of $CH_2{=}CH_2$ to di-iodide (XIV) gives no adduct and generally results in almost quantitative recovery of starting material[4a]. The required α,ω-divinylperfluoroalkanes (XVI) were therefore prepared from α,ω-di-iodoperfluoroalkanes following the reported method[4, 5] with the exception of (XVI)(a) which was obtained according to the method of Henne and DeWitt[6].

$CH_2{=}CH(CF_2)_xCH{=}CH_2$
(XVI) (a); $x = 1$
(b); $x = 2$
(c); $x = 4$
(d); $x = 8$
(e); $x = 10$

The addition of $\equiv$SiH to the dienes (XVI)(a)–(e) and (XIII) was successfully effected either by chloroplatinic acid or di-t-butyl peroxide catalysis (Scheme 4). However, the chloroplatinic acid-catalyzed addition of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b) to the dienes (XVI)(b)–(d) and (XIII) gives rise to the corresponding rearranged mono-addition products (XXIV)(a)–(d) in addition to the diadducts (XIX)(b)–(XXII)(b), respectively (Scheme 5).

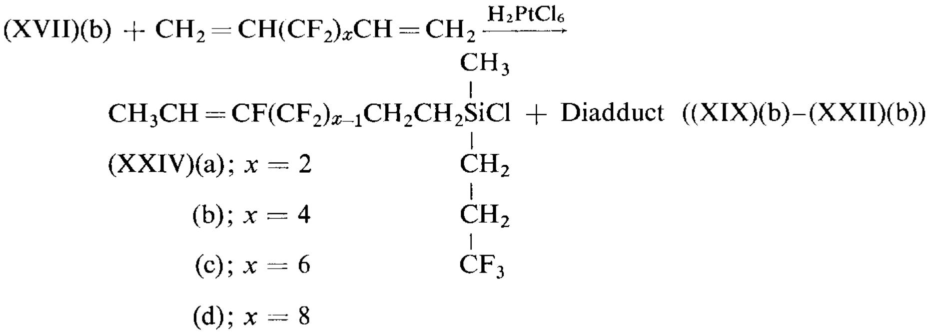


$$2R''\!-\!\underset{R}{\overset{R'}{|}}\!\!\!\!Si\!-\!H + CH_2{=}CH(CF_2)_xCH{=}CH_2 \rightarrow R''\underset{R}{\overset{R'}{Si}}CH_2CH_2(CF_2)_xCH_2CH_2\underset{R}{\overset{R'}{Si}}R''$$

(XVII) (a); $R = R' = CH_3, R'' = Cl$
(b); $R = CH_3\text{–}, R' = CF_3CH_2CH_2\text{–}, R'' = Cl$
(c); $R = R' = CF_3CH_2CH_2\text{–}, R'' = Cl$
(d); $R = CH_3\text{–}, R' = C_4F_9CH_2CH_2\text{–}, R'' = Cl$
(e); $R = CH_3\text{–}, R' = R'' = Cl$
(f); $R = R' = R'' = Cl$
(g); $R = CH_3\text{–}, R' = CF_3CH_2CH_2\text{–}, R'' = H$
(h); $R = CF_3CH_2CH_2\text{–}, R' = R'' = H$

(XVIII) (b); $x = 1$
(XIX) (b); $x = 2$
(XX) (b); $x = 4$
(XXI)(a)–(h); $x = 6$
(XXII) (b); $x = 8$
(XXIII) (b); $x = 10$

Scheme 4



$$(XVII)(b) + CH_2{=}CH(CF_2)_xCH{=}CH_2 \xrightarrow{H_2PtCl_6} CH_3CH{=}CF(CF_2)_{x-1}CH_2CH_2\underset{\substack{|\\CH_2\\|\\CH_2\\|\\CF_3}}{\overset{\substack{CH_3\\|}}{Si}}Cl + \text{Diadduct } ((XIX)(b)\text{–}(XXII)(b))$$

(XXIV)(a); $x = 2$
(b); $x = 4$
(c); $x = 6$
(d); $x = 8$

Scheme 5

The yield of the rearranged monoadduct (XXIV) and the diadduct ((XIX)(b)–(XXII)(b)), and the ratio of the diadduct to the rearranged monoadduct (XXIV) are summarized in Table 3.

TABLE 3

H_2PtCl_6 CATALYZED ADDITION OF SILANE (XVII)(b) TO DIENES[a]

	Yield (%)					
Diene	Rearranged Monoadduct (XXIV)		Diadduct		Diadduct/Rearranged Monoadduct	
	A	*B*	*A*	*B*	*A*	*B*
(XVI)(b)	9	9	74	86	8.2	9.6
(XVI)(c)	19	29	75	43	4.0	1.5
(XIII)	20		71		3.6	
	33		51		1.5	
(XVI)(d)	11		78		7.1	2.8
	22	24	72	63	3.3	

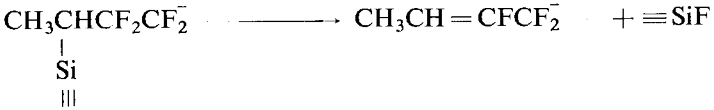
[a] Gas chromatographic analysis.

A. Diene was added to silane containing catalyst (H_2PtCl_6) at 100–110°.

B. Silane was introduced to diene containing catalyst (H_2PtCl_6) at 100–110° except (XVI)(b), (~ 70°).

These results are unexpected and quite interesting. Although the addition of $\equiv$SiH to a variety of olefins including dienes, functional olefins, and polyfluoroolefins, such as $CF_2=CF_2$ and $CH_2=CF_2$ has been abundantly documented[7], little work on the addition of $\equiv$SiH to vinylperfluoroalkanes, especially α,ω-di(vinyl)-perfluoroalkanes, has been reported. As the data in the Table 3 show, the formation of the rearranged monoadduct (XXIV) is quite significant, and the ratio of the diadduct to the rearranged monoadduct (XXIV) could not always be reproduced. These non-reproducible results appear to suggest that the reaction is heterogeneous in most cases. The ratio of the diadduct to the rearranged monoadduct (XXIV) was found to be unaffected by subjecting the reaction mixture, that already completed, to the conditions of its formation. Similarly, the chloroplatinic acid-catalyzed addition of silane (XVII)(a) to diene (XIII) gave a 29% yield of $CH_3CH=CF(CF_2)_5CH_2CH_2Si(CH_3)_2Cl$ (XXV) and a 51% yield of diadduct (XXI)(a).

Although the rearranged monoadduct (XXIV) may possibly be formed by a reverse addition followed by decomposition of the adduct (XXVI) as shown in Scheme 6, it is difficult to conceive that such an $\equiv$SiF elimination would occur

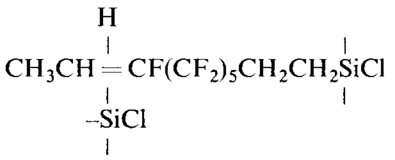


$$CH_3\underset{\underset{|||}{\overset{|}{Si}}}{C}HCF_2CF_2^- \longrightarrow CH_3CH=CFCF_2^- + \equiv SiF$$

(XXVI)

Scheme 6

under relatively mild conditions of the reaction (100–110°) or during the isolation of the rearranged monoadduct (XXIV) (< 100°). In fact, polyfluoroalkylsilicon compounds similar to adduct (XXVI) are reported to be reasonably stable[7e,8]. On the basis of the mechanism advanced for the chloroplatinic acid-catalyzed addition of organosilicon hydrides to hydrocarbon olefins[7b,7c], the rearranged monoadduct (XXIV) appears to have been formed by the decomposition of a reversely oriented Pt–olefin or Pt–diene complex without actual formation of the reverse adduct (XXVI). No attempt has been made to detect the rearranged diene, $CH_3CH{=}CF(CF_2)_yCF{=}CHCH_3$ (XXVII) which might have been formed to some extent. Although exact mechanistic aspects of the formation of the rearranged monoadduct (XXIV) are uncertain at the present time, platinum or its derivative indeed causes the formation of the rearranged monoadduct (XXIV). This conclusion is based on the observation that the peroxide-catalyzed addition of the silane (XVII)(b) to the dienes (XIII), (XVI)(b), (XVI)(d) and (XVI)(e) yielded the desired diadducts (XXI)(b), (XIX)(b), (XXII)(b) and (XXIII)(b), respectively, in high yield without the formation of the rearranged monoadduct (XXIV) in an appreciable quantity (less than 3% if any). Since no reaction was observed between the silane (XVII)(b) and the rearranged monoadduct (XXIV)(c) under the conditions of free-radical reaction, the possibility of the formation of a non-separable rearranged diadduct of the type (XXVIII) under the free-radical conditions was ruled out. The similar free-radical catalyzed addition of the silanes (XVII)(d)–(h) to the diene (XIII), respectively, offered the



$$\mathrm{CH_3CH\overset{\displaystyle H\atop |}{\underset{|\atop {-SiCl}\atop |}{=}}CF(CF_2)_5CH_2CH_2\overset{|}{\underset{|}{Si}}Cl}$$

(XXVIII)

diadducts (XXI)(d)–(h) in high yield without any complication.

EXPERIMENTAL

All melting points and boiling points are uncorrected. All melting points were taken on a Thomas–Hoover capillary melting point apparatus. Infrared absorption spectra were determined on a Perkin–Elmer Model 521 Grating Infrared Spectrophotometer. The ^{19}F reasonance spectra were measured on a Varian high-resolution NMR spectrometer operating at 56.4 Mcps. Chemical shifts were determined in parts per million using CCl_3F as an internal standard (δ 0 ppm). The proton resonance spectra were obtained on a Varian A-60 NMR spectrometer using tetramethylsilane as an internal standard (δ 0 ppm). Gas chromatography was carried out on a Hewlett–Packard Model 5750 using a 3.05 m × 6.35 mm column containing 20% Dow Corning® FS 1265 Fluid (10,000 cSt.) on Anakrom 90–100 mesh ABS.

Reaction of $CH_2=CH_2$ *with* $BrCF_2CF_2Br$ *(I)*

Run No. 2 in Table 1 is described as a typical example of the procedures. The results of several experiments are summarized in Table 1, and elemental analyses and physical properties are tabulated in Table 4.

Into an evacuated 300 ml stainless steel autoclave were charged, in the absence of air, 1.42 moles of dibromide (I) and approximately 2 mole% of di-t-butyl peroxide. The autoclave was heated while rocking end to end. When the reaction temperature reached 110°, the autogeneous pressure was about 30 psi. Then, $CH_2=CH_2$ was charged to a total pressure of 150 psi and maintained for 27 h at 120°. The autoclave was cooled to room temperature and excess $CH_2=CH_2$ was released. The crude reaction product (410 g) was an amber colored liquid.

The proton resonance spectrum of the 1:1:1 adduct, $BrCH_2CH_2CF_2CF_2CH_2CH_2Br$ (IV), comprised signals centered at δ 2.63 (CF_2CH_2) and at δ 3.50 (CH_2Br), and an integrated area ratio was 1:1. The spectral data are consistent with diadduct (IV) and inconsistent with the 2:1 adduct, $BrCF_2CF_2(CH_2)_4Br$ (III).

Reaction of $CH_2=CH_2$ *with* $BrCF_2CF_2CH_2CH_2Br$ *(II)*

The procedure used was identical to that described above for the reaction of $CH_2=CH_2$ with dibromide (I). The reaction conditions and product analyses are summarized in Table 2. Physical properties and analytical data are shown in Table 4.

The proton resonance spectrum of $BrCH_2CH_2CF_2CF_2CH_2(CH_2)_3Br$ (V) showed signals centered at δ ~3.42 (CH_2Br, two triplets), δ ~2.6 (CF_2CH_2, multiplet), and δ ~1.83 (CH_2CH_2, multiplet), with an area ratio of 1:1:1. This is consistent with the telomer (V) and inconsistent with the isomer $BrCF_2CF_2(CH_2)_6Br$.

Reaction of $CH_2=CH_2$ *with* $BrCF_2CH_2CH_2Br$ *(VII)*

A 1 l stainless-steel stirred reactor was charged with 770 g (3.1 moles) of adduct (VII) and 22 g (5 mole%) of di-t-butyl peroxide. The system was flushed with $CH_2=CH_2$, heated to 130°, and maintained at 130–140° under 75 psi of $CH_2=CH_2$ pressure for 21 h. Gas chromatographic analysis of the crude product (780 g) indicated that the desired $BrCH_2CH_2CF_2CH_2CH_2Br$ (VIII) was formed in a 46% yield based on starting material, (VII), consumed (5%). Unreacted (VII) was recovered by distillation, and the product (VIII) was isolated from the pot residue by preparative gas chromatography.

The ^{19}F and ^{1}H resonance spectra were completely in agreement with structure (VIII). The ^{19}F resonance spectrum showed a quintet ($J(HF) \simeq 13$ Hz) centered at δ +99.3. The ^{1}H resonance spectrum consisted of signals centered at δ 2.47 and δ 3.48 with an area ratio of 1:1.

Reaction of $CH_2=CH_2$ with $Br(CF_2)_6Br$ (IX)

Into a 2 l stainless-steel stirred reactor were charged 1480 g (3.3 moles) of dibromide (IX) and 17.5 g (0.12 mole) of di-t-butyl peroxide. After flushing the system with $CH_2=CH_2$, the reaction mixture was heated while stirring. When the reaction temperature reached 90°, $CH_2=CH_2$ was charged into the system to a total pressure of 50 psi and heating was continued while stirring. The reaction temperature was then allowed to rise to 130–140°, and the pressure of $CH_2=CH_2$ was maintained at *ca.* 50–60 psi for 18 h. The reactor was cooled, and the contents were removed to yield 1539 g of crude product. Four additional runs were similarly made so that a total of 6850 g (14.9 moles) of dibromide (IX) were reacted. The combined crude products (7284 g) were distilled through a bubble-cap column (0.915 m) to yield, after forecuts and intercuts, 1836 g (27% recovery) of (IX), 2702 g (51% yield) of $Br(CF_2)_6CH_2CH_2Br$ (X), and 2376 g of still residue. The still residue was then distilled through a short Vigreaux column (*ca.* 15 cm) to give the following fractions:

(a) 1747 g, b.p. 91°/7 mm -140°/3 mm,
(b) 325 g, b.p. 159–180°/3 mm,
(c) 212 g, still residue.

Fraction (a) was filtered to give an additional 665 g (12% yield) of slightly impure adduct (X) (filtrate) and 1057 g (18% yield) of reasonably pure solid $BrCH_2CH_2(CF_2)_6CH_2CH_2Br$ (XI). The diadduct (XI) was washed with cold ethanol in which it was found to be sparingly soluble, and dried *in vacuo* at room temperature to give an analytical sample. The fractions (b) and (c) were not characterized. However, gas chromatographic analysis of the fraction (b) showed the presence of one major component which is presumed to be $BrCH_2CH_2(CF_2)_6(CH_2)_4Br$. Physical properties and analytical data are summarized in Table 4.

It was found that the other telomers, $Br(CH_2CH_2)_{\geqslant 0}(CF_2)_6(CH_2CH_2)_{\geqslant 2}Br$, are very soluble in cold ethanol while diadduct (XI) is not. Therefore, the desired (XI) could be separated from other telomers without much difficulty by washing the mixture with cold ethanol. The spectral properties were consistent with the assigned structures.

Reaction of $CH_2=CH_2$ with $Br(CF_2)_6CH_2CH_2Br$ (X)

Following the procedure outlined above for the reaction of $CH_2=CH_2$ with dibromide (IX), the reaction of adduct (X) (1990 g, 4.1 moles) with $CH_2=CH_2$ in the presence of di-t-butyl peroxide gave 613 g (31% recovery) of (X), 866 g (60% yield) of diadduct (XI) and 274 g (18% yield) of presumed $BrCH_2CH_2(CF_2)_6(CH_2)_4Br$ (XII).

Preparation of $CH_2=CH(CF_2)_6CH=CH_2$ (XIII)

Into a stirred slurry of 764 g (1.5 moles) of diadduct (XI) in 500 ml of ethanol was added drop-wise over a period of 1h a solution of 230 g (3.5 moles) of potassium

TABLE 4

PHYSICAL PROPERTIES AND ANALYTICAL DATA[a]

Compd.	b.p. (°C)(mm)	m.p. (°C)	n_D^{25}	Formula	Calc'd. (%)						Found (%)					
					C	H	Br	Cl	F	Si	C	H	Br	Cl	F	Si
(II)	135–6 (732)		1.4145	$C_4H_4Br_2F_4$	16.7	1.40	55.5		26.4		17.0	1.51	55.2		25.8	
(III)	115–7 (36)		1.4320	$C_6H_8Br_2F_4$	22.8	2.56	50.6		24.0		22.9	2.55	51.0		24.1	
(IV)	113–5 (25)	58–9[b]		$C_6H_8Br_2F_4$	22.8	2.56	50.6				22.9	2.66	50.6			
(V)		37–9[b]		$C_8H_{12}Br_2F_4$	27.9	3.52					28.6[c]	3.56				
(VIII)			1.4697	$C_5H_8Br_2F_2$	22.7	3.03					22.9	3.01				
(X)	91 (7)		1.3706	$C_8H_4Br_2F_{12}$	19.6	0.82			46.6		19.8	0.98			46.9	
(XI)		43–4		$C_{10}H_8Br_2F_{12}$	23.5	1.56	31.0		44.2		23.2	1.64	30.7		44.2	
(XIII)	77 (25)		1.3297	$C_{10}H_6F_{12}$	33.9	1.71			64.5		34.1	1.73			64.7	
(XVI)(d)	100 (25)		1.3270[d]	$C_{12}H_6F_{16}$	31.7	1.32			66.9		31.5	1.44			66.3	
(XVI)(e)	130 (29)		1.3295	$C_{14}H_6F_{20}$	30.3	1.09					30.6	1.20				
(XVIII)(b)	84 (0.25)	32–4		$C_{13}H_{22}Cl_2F_8Si_2$	34.2	4.83					34.4	4.99				
(XIX)(b)	100 (0.2)	36–8		$C_{14}H_{22}Cl_2F_{10}Si_2$	33.2	4.35					33.6	4.64				
(XX)(b)	123 (0.3)	38–9		$C_{16}H_{22}Cl_2F_{14}Si_2$	31.6	3.65		11.7			32.0	3.71		11.2		
(XXI)(a)	130 (1.0)	47–50		$C_{14}H_{20}Cl_2F_{12}Si_2$	30.9	3.68			42.0	10.3	31.3	3.77			42.3	10.9
(XXI)(b)	140–1 (0.07)	41–2		$C_{18}H_{22}Cl_2F_{18}Si_2$	30.6	3.13		10.0		7.94	30.7	3.39		9.22		7.36
(XXI)(c)	192–3 (0.3)	81–2		$C_{22}H_{24}Cl_2F_{24}Si_2$	30.3	2.78		8.12	52.3	6.44	30.5	3.03		8.14	51.9	6.45
(XXI)(d)	182 (0.3)	61		$C_{24}H_{22}Cl_2F_{30}Si_2$	28.6	2.20					28.7	2.18				
(XXI)(e)	131 (0.7)	51–2		$C_{12}H_{14}Cl_4F_{12}Si_2$	24.7	2.42					24.9	2.34				
(XXI)(f)	150–2 (0.3)	62		$C_{10}H_8Cl_6F_{12}Si_2$	19.2	1.29			36.5		19.2	1.34			36.6	
(XXI)(g)	116 (0.3)	38–9		$C_{18}H_{24}F_{18}Si_2$	33.9	3.79					33.7	3.94				
(XXI)(h)	118 (0.4)	30–1		$C_{16}H_{20}F_{18}Si_2$					56.0						56.6	
(XXII)(b)	165 (0.15)	38–9		$C_{20}H_{22}Cl_2F_{22}Si_2$					51.8						52.3	
(XXIII)(b)	178 (0.25)	64		$C_{22}H_{22}Cl_2F_{26}Si_2$					54.4						54.4	
(XXIV)(a)			1.3995	$C_{10}H_{15}ClF_6Si$	38.4	4.80					38.7	5.00				
(XXIV)(b)[e]	64–5 (0.3)		1.3810	$C_{12}H_{15}ClF_{10}Si$	34.9	3.66		8.59			35.2	3.66		8.74		
(XXIV)(c)	85 (0.4)		1.3741	$C_{14}H_{15}ClF_{14}Si$	32.8	2.95					32.8	3.10				
(XXV)	120 (12)			$C_{12}H_{14}ClF_{11}Si$	33.4	3.25				6.50	33.6	3.39				6.34

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[a] All compounds reported are new except (II)[2], (III)[2], (X)[1], (XI)[2] and (XIII)[4b].

[b] Recrystallized from n-hexane.

[c] Although the carbon value is high, it is felt that spectral and physical data support the proposed structure (V).

[d] Taken at 29°.

[e] Slightly impure.

hydroxide in 600 ml of ethanol. The reaction temperature was kept reasonably close to room temperature by means of a water bath. After overnight stirring, water (800 ml) was added until the potassium bromide formed during the reaction was dissolved. The organic layer (bottom) was separated, washed twice with an equal volume of water and dried over Drierite. Distillation gave 463 g (87% yield) of analytically pure diene (XIII). For physical properties and analytical data see Table 4. The spectral properties were in agreement with those expected for diene (XIII).

Chloroplatinic acid-catalyzed addition of $\equiv SiH$ *to* $CH_2=CH(CF_2)_xCH=CH_2$

Physical properties and analytical data are shown in Table 4.

For x = *1*

A stirred solution of 50 g (0.28 mole) of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b) containing six drops of a 0.1 *M* solution of chloroplatinic acid in isopropanol was heated at 90° and treated drop-wise with 7 g (0.067 mole) of $CH_2=CHCF_2CH=CH_2$ (XVI)(a) over a period of 30 min. Gas chromatographic analysis after complete addition showed essentially 90% conversion of the diene (XVI)(a) had occurred. After refluxing the mixture for 48 h, the mixture was distilled to yield 15 g (49% yield) of $Cl(CF_3CH_2CH_2)(CH_3)SiCH_2CH_2CF_2CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XVIII)(b).

The ^{19}F resonance spectrum of this compound displayed signals centered at δ +69.0 ($-CF_3$, triplet) and δ +103.4 (CF_2, quintet) in an integrated ratio of 3:1, respectively. The proton resonance spectrum consisted of signals centered at δ 0.48 ($SiCH_3$, 3H), δ 1.05 ($SiCH_2$, 4H), and δ 2.05 (CF_2CH_2, 4H).

For x = *2*

Following the procedure described above for $x = 1$, about 40 g (0.26 mole) of $CH_2=CHCF_2CF_2CH=CH_2$ (XVI)(b) was reacted with 175 g (1.0 mole) of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b). Distillation of the reaction mixture gave 88 g (67% yield) of $Cl(CF_3CH_2CH_2)(CH_3)SiCH_2CH_2CF_2CF_2CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XIX)(b). The rearranged monoadduct $CH_3CH=CFCF_2CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XXIV)(a) was isolated from a forecut by preparative gas chromatography. The similar results were obtained with a reverse addition.

The spectral properties were in agreement with the assigned structures, (XIX)(b) and (XXIV)(a), respectively.

For x = *4*

Following the procedure outlined above for $x = 1$ with an exception that silane was added to a mixture of diene and catalyst, a reaction of 39 g (0.15 mole) of $CH_2=CH(CF_2)_4CH=CH_2$ (XVI)(c) and 65 g (0.37 mole) of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b) yielded 19 g (30% yield) of slightly impure $CH_3CH=CF$-

$(CF_2)_3CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XXIV)(b) and 37 g (40% yield) of $Cl(CF_3CH_2CH_2)(CH_3)SiCH_2CH_2(CF_2)_4CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XX)(b).

The spectral properties were completely in agreement with the assigned structures (XXIV)(b) and (XX)(b). On the basis of spectral and gas chromatographic analyses, the major impurity in the rearranged monoadduct (XXIV)(b) appeared to be $CH_2{=}CH(CF_2)_4CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$.

When the reaction was conducted by adding diene to a mixture of silane and catalyst, the ratio of the rearranged monoadduct (XXIV)(b) to diadduct (XX)(b) was about 1:4, respectively.

For x = *6*

Following the procedure described above for $x = 1$ with an exception that silane was added to a mixture of diene and catalyst, a reaction of 44 g (0.25 mole) of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b) and 35 g (0.1 mole) of $CH_2{=}CH(CF_2)_6CH{=}CH_2$ (XVIII) gave 15 g (28% yield) of $CH_3CH{=}CF(CF_2)_5CH_2CH_2Si(CF_3CH_2CH_2)(CH_3)Cl$ (XXIV)(c) and 38 g (54% yield) of $Cl(CH_3)(CF_3CH_2CH_2)SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CF_3CH_2CH_2)(CH_3)Cl$ (XXI)(b). Similarly, $CH_3CH{=}CF(CF_2)_5CH_2CH_2Si(CH_3)_2Cl$ (XXV) (76 g, 29% yield) and $Cl(CH_3)_2SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CH_3)_2Cl$ (XXI)(a) (164 g, 51% yield) were obtained from a reaction of 210 g (0.595 mole) of the diene (XIII) and 118 g (1.24 moles) of $(CH_3)_2SiHCl$ (XVII)(a).

The spectral properties are consistent with the assigned structures respectively. When the reaction was repeated, the ratio of the rearranged monoadduct (XXIV)(c) to diadduct (XXI)(b) was approximately 1:3.6, respectively.

For x = *8*

Following the procedure outlined above for $x = 1$, about 53 g (0.3 mole) of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b) was reacted with 45 g (0.1 mole) of $CH_2{=}CH(CF_2)_8CH{=}CH_2$ (XVI)(d). Gas chromatographic analysis of the reaction mixture showed the presence of $CH_3CH{=}CF(CF_2)_7CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XXIV)(d) and $ClSi(CF_3CH_2CH_2)(CH_3)CH_2CH_2(CF_2)_8CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XXII)(b) in a ratio of approximately 1:7, respectively. The rearranged monoadduct (XXIV)(d) was strip-distilled and isolated by preparative gas chromatography; however, an analytical gas chromatogram of the isolated rearranged monoadduct (XXIV)(d) shows the presence of an unidentified component as a shoulder. When the reaction was repeated, the ratio of the rearranged monoadduct (XXIV)(d) to diadduct (XXII)(b) was about 1:3.3, respectively, and the ratio remained unchanged with additional heating. A similar ratio (1:2.8) of (XXIV)(d) to (XXII)(b) was obtained even though the addition was reversed. The spectral properties were consistent with the assigned structure (XXIV)(d) containing some impurity.

Di-t-butyl Peroxide-Catalyzed Addition of $\equiv SiH$ *to* $CH_2=CH(CF_2)_xCH=CH_2$

Physical properties and analytical data are summarized in Table 4.

For x = *2*

A solution of 5 g (0.0325 mole) of $CH_2=CHCF_2CF_2CH=CH_2$ (XVI)(b), 50 g (0.284 mole) of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b), and 1.3 g (*ca.* 3% to (XVII)(b)) of di-t-butyl peroxide was placed in an evacuated sealed glass ampule and heated at 120° with shaking for 72 h. Gas chromatographic analysis of the reaction mixture indicated the presence of $ClSi(CH_3)(CF_3CH_2CH_2)CH_2CH_2CF_2CF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiCl$ (XIX)(b) in 82% yield and no appreciable amount (< 2% if any) of $CH_3CH=CFCF_2CH_2CH_2(CF_3CH_2CH_2)(CH_3)SiCl$ (XXIV)(a).

For x = *6*

A solution of 106 g (0.3 mole) of $CH_2=CH(CF_2)_6CH=CH_2$ (XIII), 528 g (3.0 moles) of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b), and 3 g (0.02 mole) of di-t-butyl peroxide was heated under reflux. As the reaction proceeded, the reaction (reflux) temperature rose from *ca.* 105° to *ca.* 110°. Gas chromatographic analysis of the reaction mixture at the end of 24 h indicated about 90% completion of the reaction. At the end of 72 h, gas chromatographic analysis of the reaction mixture showed the presence of $Cl(CF_3CH_2CH_2)(CH_3)SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XXI)(b) as a major component and no appreciable amount (< 3% if any) of $CH_3CH=CF(CF_2)_5CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)Cl$ (XXIV)(c). Distillation of the reaction mixture gave, after recovery of excess silane (XVII)(b), 192 g (85% yield) of analytically pure diadduct (XXI)(b) and 29 g of still residue.

The spectral properties were identical in every detail with those of diadduct (XXI)(b) obtained by chloroplatinic acid catalysis. Similarly, $Cl(CF_3CH_2CH_2)_2SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CF_3CH_2CH_2)_2Cl$ ((XXI)(c), 78% isolated yield) from the diene (XIII) and $(CF_3CH_2CH_2)_2SiHCl$ (XVII)(c) and $Cl(CF_3CF_2CF_2CF_2CH_2CH_2)(CH_3)SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CH_3)(CF_3CF_2CF_2CF_2CH_2CH_2)Cl$ ((XXI)(d), 81% isolated yield) from the diene (XIII) and $CF_3CF_2CF_2CF_2CH_2CH_2(CH_3)SiHCl$ (XVII)(d) were prepared. The spectral properties were consistent with the assigned structures, (XXI)(c) and (XXI)(d), respectively.

Following the procedure outlined above for the addition of the silane (XVII)(b) to the diene (XVI)(b), $H_2(CF_3CH_2CH_2)SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CF_3CH_2CH_2)H_2$ ((XXI)(h), 65% isolated yield), $H(CF_3CH_2CH_2)(CH_3)SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CH_3)(CF_3CH_2CH_2)H$ ((XXI)(g), 81% isolated yield), $Cl_2(CH_3)SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CH_3)Cl_2$ ((XXI)(e), 81% isolated yield), and $Cl_3SiCH_2CH_2(CF_2)_6CH_2CH_2SiCl_3$ ((XXI)(f), 71% isolated yield) were prepared from the diene (XIII) and silane (XVII)(e)–(h). The spectral properties were in agreement with the assigned structures, respectively.

For x = *8*

Following the procedure outlined above for the addition of the silane (XVII)(b) to the diene (XIII), about 199 g (0.45 mole) of $CH_2{=}CH(CF_2)_8CH{=}CH_2$ (XVI)(d) was reacted with $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b) to yield 228 g (66% yield) of $Cl(CF_3CH_2CH_2)(CH_3)SiCH_2CH_2(CF_2)_8CH_2CH_2Si(CH_3)$-$(CF_3CH_2CH_2)Cl$ (XXII)(b).

The spectral properties were completely in agreement with the assigned structure (XXII)(b).

For x = *10*

Following the procedure described above for the addition of the silane (XVII)(b) to the diene (XIII), a reaction of 41 g (0.074 mole) of $CH_2{=}CH(CF_2)_{10}$-$CH{=}CH_2$ (XVI)(e) and 144 g (0.83 mole) of $CF_3CH_2CH_2(CH_3)SiHCl$ (XVII)(b) gave 39 g (60% yield) of $ClSi(CH_3)(CF_3CH_2CH_2)SiCH_2CH_2(CF_2)_{10}CH_2CH_2Si$-$(CF_3CH_2CH_2)(CH_3)Cl$ (XXIII)(b).

The spectral properties were consistent with the assigned structure (XXIII)(b).

Reaction of $CF_3CH_2CH_2(CH_3)SiHCl$ *(XVII)(b) with* $CH_3CH{=}CF(CF_2)_5$-$CH_2CH_2(CH_3)(CF_3CH_2CH_2)SiCl$ *(XXIV)(c)*

A solution of 1.2 g (0.0025 mole) of the silane (XXIV)(c), 1.3 g (0.0075 mole) of the silane (XVII)(b) and 20 mg of di-t-butyl peroxide was placed in an evacuated sealed glass ampule and heated at 115° for 24 h while shaking. Gas chromatographic analysis of the reaction mixture revealed about 96% recovery of the silane (XXIV)(c) and the absence of a component having the same retention time as that of $Cl(CH_3)(CF_3CH_2CH_2)SiCH_2CH_2(CF_2)_6CH_2CH_2Si(CF_3CH_2CH_2)(CH_3)Cl$ (XXI)(b).

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