

SYNTHESIS AND CO-TELOMERIZATION OF
4-BROMO- AND 4-CHLOROHEPTAFLUORO-1,2-EPOXYBUTANES

T. I. ITO, J. KAUFMAN, R. H. KRATZER, J. H. NAKAHARA,
and K. J. L. PACIOREK

Ultrasystems, Inc., 2400 Michelson Drive
Irvine, California 92715 (U.S.A.)

SUMMARY

4-Bromo- and 4-chloroheptafluoro-1,2-epoxybutanes were synthesized and successfully copolymerized with hexafluoropropene oxide derived acid fluorides. Transformation of the bromine-containing acid fluorides to hydrogen terminated compounds was accompanied by substitution of bromine by hydrogen; this interference was absent in the copolymers of 4-chloroheptafluoro-1,2-epoxybutane. Ultraviolet irradiation in the presence of mercury was found effective in coupling the bromo-substituted perfluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$, without any side reactions.

INTRODUCTION

Perfluoroalkylether systems as represented by poly(hexafluoropropene oxide) are not amenable to crosslinking. Introduction into a perfluoroalkylether polymer of a bromine-group containing side chain would be expected to provide on curing the thermally, oxidatively, and chemically stable $CF_2 - CF_2$ linkages. The current study was thus undertaken to determine the feasibility of synthesizing 4-bromoheptafluoro-1,2-epoxybutane and to evaluate its ability to undergo co-telomerizations with acid fluorides. The investigation of the coupling behavior of the bromine-containing perfluoroalkylether as well as the effect of the end-groups upon this process constituted additional aspects of this work.

RESULTS AND DISCUSSION

To optimize the epoxide synthesis and the subsequent telomerization and transformation processes, due to the relative difficulty in obtaining large quantities of the starting material, 1,1,1-trichloro-5-bromoperfluoropentane, the closely related 1,1,1,5-tetrachloroperfluoropentane [1] was utilized. Following the established procedures [2,3], the olefins 4-chloroperfluorobutene-1 and 4-bromoperfluorobutene-1 were obtained in overall 71 and 61% yields from the respective pentane-precursors. Difficulties were experienced in the preparation of the chloro-epoxide due to the material's volatility and the facile reaction of the initially formed oxide with methanol to give a methyl-ester, most likely of the form $\text{ClCF}_2\text{CF}_2\text{CF}(\text{OCH}_3)\text{CO}_2\text{CH}_3$, in analogy with the hexafluoropropene oxide studies of Sianesi et al [4]. Zapevalov [5] reported a yield of 65% for the chloro-epoxide; it is believed that using larger quantities of starting material would lead to yields higher than the realized 35%. Employing the optimized procedure for the preparation of the bromo-analogue, in most instances olefin-free product was obtained which eliminated the bromination step usually necessary for olefin removal.

Coupling of bromo-compounds by ultraviolet irradiation in the presence of mercury is a well known procedure. Unfortunately, the telomers obtained from cesium fluoride catalyzed epoxide additions are acid fluoride terminated. These can be readily transformed into methyl esters; however, it has been reported [6] that esters when subjected to ultraviolet irradiation undergo dimerization accompanied by carbon dioxide, ethane and perfluoroacetyl fluoride evolution. To determine what kind of end-groups would not interfere with the coupling reaction and to assess the telomerization characteristics of the epoxybutanes, both of the epoxides were telomerized with acid fluorides. These tests are summarized in Table 1 whereas the product distribution is given in Table 2. It would appear from these compilations that changing the catalyst: acid fluoride ratio and the cesium alkoxide formation conditions had no effect on the yield of $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_2\text{CF}_2\text{Cl})\text{COF}$, which stayed constant at $\sim 40\%$. On the other hand, utilizing the shorter chain acid fluoride and a 1:1 proportion of cesium fluoride to acid fluoride resulted in significantly lower quantities of the desired telomer than the 1:2 ratio

TABLE 1

Summary of Telomerization Reactions^a

Run No.	Reagents		Recovered				Conditions ^c				CsF mole % of A	ml tg/mg CsF		
	A		B		A	B	(I)		(II)					
	Type ^b	g	mmol	Type	g	mmol	wt %	wt %	Temp °C	Time hr			Temp °C	Time hr
1	HHHCOF	1.00	2.01	C ₄ F ₇ ClO	0.47	2.02	29	-	-23	2	-20	16	52	0.002
2 ^d	HHHCOF	1.20	2.42	C ₄ F ₇ ClO	0.57	2.46	34	-	-23	2	-20	17	90	0.002
3	HHHCOF	1.00	2.01	C ₄ F ₇ ClO	0.47	2.02	49	-	-19	2	-20	19	90	0.0015
4	HHCOF	0.69	2.09	C ₄ F ₇ ClO	0.49	2.10	32	-	24	2	-20	16	50	0.002
5 ^d	HHCOF	7.09	2.13	C ₄ F ₇ ClO	0.49	2.12	47	-	0	1	-20	16	84	0.0015
6	HHCOF	0.38	1.14	C ₄ F ₇ BrO	0.32	1.14	13	-	24	1	-20	16	52	0.0015
									0	2				
									-20	1				

e) All the telomerizations were conducted in a 25 ml evacuated round bottomed flask; into Cs-tg first A was condensed then B.

b) H corresponds to hexafluoropropene oxide molarity. c) Conditions (I) apply to Cs-tg plus A; conditions (II) apply after B was introduced.

d) Stirring was very ineffective in this test.

TABLE 2

Product Distribution in Telomerization Reactions

Run No.	Products					
	R		RX		RXX	
	weight ^b %	recovery ^c %	weight ^b %	yield ^c %	weight ^b %	yield ^c %
1 ^d	20	29	54	53	17	13
2 ^d	23	34	42	41	21	16
3 ^d	33	47	40	39	14	10
4 ^e	19	32	56	55	8	5
5 ^e	29	47	18	17	16	11
6 ^{e,f}	7	13	61	60	19	13

a) R pertains to the acid fluoride employed; X denotes 4-chloroheptafluoro-1,2-epoxybutane segment in Runs 1-5 and 4-bromoheptafluoro-1,2-epoxybutane segment in Run No. 6.

b) This is the weight percent of a given product in the reaction mixture as determined from gas chromatography assuming each constituent to give the same response.

c) Based on the acid fluoride employed.

d) In this test $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$ was employed.

e) In this test $C_3F_7OCF(CF_3)COF$ was employed.

f) In this test 3% yield of RXX was obtained.

(compare tests No. 4 and 5). The yield of the mono-adduct (see Table 2) obtained utilizing the bromo-epoxide was higher than that observed under parallel conditions with the chloro-analogue; also the relative quantities of the di- and tri-adducts were increased. The major portion of the mono-adduct was collected in the condensable volatiles of which it constituted 84%.

The transformation of the $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_2CF_2Cl)COF$ telomer to the hydrogen terminated product, $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_2CF_2Cl)H$, using the ethylene glycol-sodium hydroxide process [7] was accomplished quantitatively. Unfortunately, the telomer mixture of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)COF$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CF_2OCF(CF_2CF_2Br)COF$

under these conditions afforded mainly products wherein both the carbonyl and the bromine entities were substituted by hydrogen.

In view of the failure to prepare the hydrogen-terminated, bromine-containing materials another terminal group had to be considered. As discussed previously methyl ester and carboxyl terminal groups cannot be utilized in processes employing ultraviolet irradiation. Nitriles are relatively readily prepared from acid fluorides; thus a nitrile termination could be considered. No literature data could be found regarding the behavior of perfluorinated nitriles under ultraviolet radiation in the presence of mercury. Apparently, nitriles are unaffected by ultraviolet radiation since the perfluoroalkylether nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, was recovered quantitatively after such a treatment in this laboratory. The nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$, was thus synthesized and subjected to ultraviolet radiation in the presence of mercury. The coupled product, $C_3F_7OCF(CF_3)CF_2OCF(CN)(CF_2)_4CF(CN)OCF_2CF(CF_3)OC_3F_7$, was obtained in a quantitative yield thereby establishing the feasibility of this overall process.

EXPERIMENTAL

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo.

Infrared spectra were recorded using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21, depending on the physical state of sample, e.g. as gas or neat liquid. Thermal analyses were conducted using a DuPont 951/990 Thermal Analyzer system. The mass spectral analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 204, equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system.

The volatile products were separated using high vacuum fractionation techniques. Their purity was determined by gas chromatography and the materials were characterized by vapor density molecular weights (when applicable) and mass spectral fragmentation patterns.

Preparation of 4-Bromoheptafluorobutene-1

The sodium salt, $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CO}_2\text{Na}$ (12.23 g, 35.25 mmol), was heated under vacuum at $268\text{--}300^\circ\text{C}$ for 4.0 hr. The reaction was carried out in a 100 ml round bottom flask attached to a vacuum system via three liquid nitrogen cooled traps. The product, which collected mainly in the first liquid nitrogen cooled trap, was purified by vacuum fractionation from a warming trap through -63 , -78 , -96 into -196°C cooled traps. Fractions -63 (5.79 g) and -78°C (2.45 g) were composed of 98% ($\text{VP}_{0^\circ\text{C}} = 88$ mm; MW, 258; Calcd. for $\text{C}_4\text{F}_7\text{Br}$, 260.9) and 95% pure $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2$, respectively, the other components being $\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$, $\text{CF}_2=\text{CFCF}=\text{CF}_2$, $\text{CF}_2\text{HCF}_2\text{CF}=\text{CF}_2$, $\text{ClCF}_2\text{CF}=\text{CF}_2$, $\text{BrCF}_2\text{CF}=\text{CFCF}_3$ and $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{CF}_3$. Based on fractions -63 and -78°C the yield of the olefin, $\text{BrCF}_2\text{CF}_2\text{CF}=\text{CF}_2$, was 87%. The presence in the mass spectrum of the parent ions, m/e 260, 262 (11.8, 11.6%), in conjunction with infrared spectral data were in agreement with the structural assignment.

Epoxidation Reactions

The procedures employed for the synthesis of 4-chloro- and 4-bromoheptafluoro-1,2-epoxybutanes were essentially identical; consequently only the preparation of the latter is given in detail. To 4-bromoheptafluorobutene-1, 2.87 g (which was condensed into the reaction flask at -196°C in vacuo, warmed to -20°C , and brought to atmospheric pressure with nitrogen), was added at -20°C 60% hydrogen peroxide (2.5 ml) followed by methanol (2.2 ml). Subsequently to the stirred mixture was introduced over a period of 45 min a methanolic potassium hydroxide solution (2.22 g in 5.4 ml of methanol). The reaction mixture was then stirred at -21 to -19°C for 6 hr; this was followed by vacuum distillation at -23°C into traps kept at -196°C via a column packed with calcium chloride and Drierite. The product thus obtained was fractionated repeatedly from a warming trap through traps held at -47 , -63 , -78 into a -196°C trap to remove the methanol which was largely retained in the -47°C trap. Finally the material collected in the -63 and -78°C traps was distilled onto freshly dried calcium chloride and was further purified by passing through an Ascarite-packed column. In the case of 4-chloroheptafluoro-1,2-epoxybutane in the fractionation process an additional trap held at -112°C was employed; the product was retained in the -78 and -112°C traps.

TABLE 3

Epoxide Preparations

Epoxide	Yield %	VP _{0°C} mm	MW		M.S.
			Found	Calcd	
C ₄ F ₇ ClO	35	199	233	232.48	Table 4
C ₄ F ₇ BrO	36	99	273	276.90	Table 5

The materials were free from olefin as determined by infrared spectral analysis; no separation of the epoxide and olefin was possible by gas chromatography using even a Porapak Q column. The mass spectral patterns given in Tables 4 and 5 confirmed the structural arrangements.

Telomerization Reactions of Acid Fluoride and Halo-epoxide

The telomerization reactions are summarized in Tables 1 and 2. In a typical procedure to prepare the cesium fluoride complex, onto the denoted quantity of cesium fluoride and tetraglyme was condensed the perfluoroalkyl-ether acid fluoride; this was then followed by stirring at the specified temperature for specified periods of time. Subsequently the epoxide was condensed (at -196°C) onto the cesium complex-tetraglyme solution and the telomerization reaction was carried out at -20°C for a given period of time. At the conclusion of the reaction the unreacted reagents and the volatile products were removed in vacuo, originally at -20°C , then at 0°C , and finally at room temperature. The volatiles were fractionated using high vacuum line techniques and the individual fractions were analyzed as the methyl esters by GC-MS using $\sim 10' \times 1/8''$ 4% OV-101 on Chromosorb-G column. The room temperature involatile residues were analyzed in an analogous fashion. The materials were unequivocally identified by their mass spectral breakdown patterns; the most characteristics peaks are given in Table 6.

TABLE 4

Ion Fragments and Intensities Relative to Base Peak of
4-Chloroheptafluoro-1,2-Epoxybutane^a

m/e		m/e		m/e		m/e	
31	71.8	69	91.0	97	29.2	131	57.1
35	8.9	70	6.3	100	33.4	132	5.9
47	38.2	74	6.8	109	6.6	135	28.1
49	4.3	78	8.5	112	11.0	137	15.8
50	39.0	81	21.8	116	<u>100.</u>	147	16.2
62	11.1	85	94.9	117	9.6	149	8.2
66	17.7	87	50.0	118	52.1	166	4.6
68	8.1	93	17.5	119	23.5	169	19.3
				128	4.8	185	4.9

a) Peaks having intensities less than 3% of the base peak are not reported.

TABLE 5

Ion Fragments and Intensities Relative to Base Peak of
4-Bromoheptafluoro-1,2-Epoxybutane^a

m/e		m/e		m/e		m/e	
31	47.3	79	9.0	119	29.2	162	59.4
47	29.6	81	35.0	129	57.3	169	35.9
50	39.7	91	4.0	131	<u>100.</u>	179	20.7
62	9.6	93	30.5	132	10.7	181	19.9
66	3.4	97	33.2	141	3.8	191	9.1
69	61.4	100	42.4	143	3.6	193	9.6
70	3.7	110	15.4	147	4.0	210	16.5
74	6.8	112	22.2	160	62.2	212	14.2

a) Peaks having intensities less than 3% of the base peak are not reported.

TABLE 6

Characteristic Mass Spectral Peaks of
 $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_2CF_2X)CO_2Me$ Compounds

	m/e	m/e	m/e
X = Cl n = 1	59, CO_2Me (100%) ²	541, M-Cl (13.0%)	391, 393, M-185 (11.0%) (3.7%)
X = Br n = 1	81, C_3F_5 (100%) ³	541, M-Br (37.5%)	435, 437, M-185 (18.7%) (20.1%)
X = Cl n = 2	59, CO_2Me (100%) ²	707, M-Cl (9.2%)	557, 559, M-185 (4.8%) (1.7%)

Preparation of $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_2CF_2Cl)H$

The volatile condensibles from the telomerization experiments No. 1 and 2 (see Table 2) which consisted of a 1:1 mixture of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)COF$ and $C_3F_7O[CF(CF_3)CF_2O]_2CF(CF_2CF_2Cl)COF$ were washed with water followed by addition of 2.5 ml of 0.92 N sodium hydroxide. Water was then removed at $\sim 60^\circ C$ using a stream of nitrogen. After addition of ethylene glycol (1.13 g) the resulting mixture was heated at $175-190^\circ C$ for 3 hr under nitrogen by-pass with the outlet leading to a liquid nitrogen cooled trap. Following cooling to room temperature the condensible volatiles were collected in vacuo in a trap cooled to $-196^\circ C$. This condensate consisted of two layers, the bottom layer (350 mg, 60% yield) was found by GC-MS to be composed of $C_3F_7[OCF(CF_3)CF_2]_2OCF(CF_2CF_2Cl)H$ (characteristic MS peaks: m/e 665, 667 (29.9, 10.9%), M-F; m/e 649 (12.3%), M-Cl; m/e 167, 169 (96.3, 100%), $CF(CF_2CF_2Cl)H$) and $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$ (characteristic MS peaks: m/e 433 (6.8%), M-F; m/e 101 (100%), $CF(CF_3)H$) in a 1:3 ratio. The relative loss of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)H$ is attributed to its higher volatility and therefore greater rate of evaporation during the final separation of the two phases, which was conducted under atmospheric conditions.

Attempted Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)H$

The procedure adopted was that described for the chloro-analogue. The material used (348 mg) was the involatile fraction of Test No. 6 (Table 1) which consisted of equal portions of telomers, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)COF$ and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CF_2OCF(CF_2CF_2Br)COF$. The volatiles collected in the liquid nitrogen cooled traps during the heating period and the subsequent evacuation as determined by GC-MS contained as major products $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2H)H$ (characteristic MS peaks: m/e 465 (10.8%), M-F; m/e 69 (100%), no m/e 79, Br) and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2H)CF_2OCF(CF_2CF_2H)H$. The above two compounds were admixed with smaller quantities of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)H$ (characteristic MS peaks: m/e 483 (15.7%), M-Br; m/e 211, 213 (66.4, 60.4%), $CF(CF_2CF_2Br)H$; m/e 69 (100%), CF_3) and $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2H)CF_2OCF(CF_2CF_2Br)H$.

Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$

To the acid fluoride, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)COF$ (137.7 mg, 0.226 mmol; Test No. 6, Table 1, condensible volatiles), was added in vacuo methanol (1.344 mmol). After 1 hr (at room temperature) the excess of methanol was removed; the amount consumed was 0.281 mmol. Subsequently, onto the methyl ester ammonia was condensed and the pressure drop occurring on warming was monitored. This was repeated 4 times until no further pressure drop was observed. At this stage the amide formation was assumed to be completed. The amide was then heated with P_2O_5 (200 mg) under 450 mm of nitrogen (in a closed system) at 180–190°C for 2.5 hr. After cooling to room temperature the product was distilled in vacuo and purified by vacuum fractionation from a warming trap through traps held at 0, -23, -47, and -196°C. The material present in the -23 and -47°C cooled traps (55 mg) was found by GC-MS to consist of 95% pure nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$, $VP_{23.5^\circ C} = 1.8$ mm. Its mass spectrum was consistent with the assigned structure based on m/e 508 (46.5%) M-Br, and m/e 179, 181 (36.1, 31.0%), CF_2CF_2Br ; m/e 69 (100%).

Preparation of $C_3F_7OCF(CF_3)CF_2OCF(CN)(CF_2)_4CF(CN)OCF_2CF(CF_3)OC_3F_7$

The nitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_2CF_2Br)CN$ (45 mg), was sealed in vacuo with mercury (2.37 g) in a 20 ml Vycor tube. The resulting mixture was shaken horizontally and irradiated with a 450 watt Hanovia lamp over a period of 14 hr; only a trace (~2 mg) of condensable volatiles were collected. The room temperature involatile residue was taken up in Freon-113 and subjected to GC-MS analysis. Based on this analysis the main component (90%) dissolved in the Freon-113 was the desired coupled product. Although no parent peak m/e 1016 was recorded, the M-F peak m/e 997, was present in high abundance (23.3%), as well as other peaks such as m/e 990 (33.1%), M-CN; m/e 831 (9.2%), M- OC_3F_7 ; m/e 665 (43%), M- $OCF_2CF(CF_3)OC_3F_7$; m/e 167 (100%), C_3F_7 .

ACKNOWLEDGEMENTS

This investigation was supported by U. S. Air Force Materials Laboratory, under Contract F33615-76-C-5054. The authors are indebted to Drs. R. C. Evers and W. H. Gumprecht for helpful discussions and suggestions.

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