## THE PREPARATION OF 1-HYDROPERFLUOROHEXYNE, OCTYNE AND DECYNE

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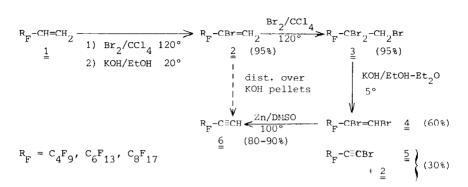
### SUMMARY

1-hydroperfluoroalkynes ( $R_F^{C\equiv CH}$ ,  $R_F^{}=C_4^{F_9}$ ,  $C_6^{F_{13}}$ ,  $C_8^{F_{17}}$ ) were prepared from the corresponding alkenes by a multistep process involving bromination, dehydrobromination and debromination reactions. The influence of the perfluorinated chain's length on chemical reactivity is illustrated by the important changes in experimental procedure, with respect to the lower terms, needed for the bromination and debromination steps. Physical data are reported for compounds  $R_F^{CBr}_{2}CH_{2}Br$ ,  $R_F^{CBr=CHBr}$  and  $R_F^{C=CH}$ .

# INTRODUCTION

The lower 1-hydroperfluoroalkynes  $R_F^{-C \equiv CH}$  ( $R_F^{-} = CF_3^{-}$ ,  $C_2F_5^{-}$  and  $iC_3F_7^{-}$ ) have been reported by Cullen et al. [1], but their chemistry has received little attention [1,2]. The development of long-chain homologues which are potential intermediates for the introduction of longer perfluoroalkyl chains has become desirable because of the unique properties these chains confer on the compounds which contain them. One of these properties is their capacity to dissolve large quantities of gases and thus to serve as oxygen carriers for biological uses. These uses require that pure, univocally defined materials be made available, which goal may be attained more effectively by chemical than by electrochemical methods [3,4]. For this purpose we recently prepared highly fluorinated dienes from 1-hydroperfluoroalkynes as starting materials [4]. We now wish to report the preparation of the latter. Meanwhile, another preparation of one of them,  $C_8F_{17}^{-C \equiv CH}$ , has been reported [5].

The preparative approach we used [6] for the synthesis of 1-hydroperfluoroalkynes is derived from the general scheme developed by Henne and Nager [7] and Haszeldine and Leedham [8] for the lower terms:



However, the procedures described were found to be ineffective for the longer terms in the bromination and debromination steps. Indeed, we found that bromination requires thermal (120°) or photochemical activation to be achieved in quantitative yields. In the same way, the debromination of  $\frac{4}{2}$  by zinc dust in EtOH could not be used for the higher terms. Instead, by using dimethylsulfoxide as the solvent,  $\frac{6}{2}$  was obtained in 80-85% yields. The preparation of the vinylic bromides  $\frac{2}{2}$  has been reported previously [9].

Direct preparation of the alkyne  $\underline{6}$  by dehydrobromination of  $\underline{2}$  was attempted, but the low yields (<u>ca</u>.20%) obtained made us prefer the bromination ( $\underline{2} \rightarrow \underline{3}$ ) - dehydrobromination ( $\underline{3} \rightarrow \underline{4}$ ) - debromination ( $\underline{4} \rightarrow \underline{6}$ ) sequence, whose overall yields are better (45-50%). Thermal or photochemical bromination of  $\underline{2}$  could be achieved in high yields, but dehydrobromination of  $\underline{3}$ giving  $\underline{4}$  was accompanied by debromination leading back to  $\underline{2}$  and by double dehydrobromination giving the bromoalkyne  $\underline{5}$ . The amount of these two side products could not be reduced to less than <u>ca</u>. 30%.  $\underline{5}$  was isolated by independent synthesis [10].

These results again stress the important effects of the chain length on the reactivity of the double bond. Its inertness is further increased by the presence of an additional perfluorinated chain, as was previously observed [9] in compounds of the type  $R_pCH=CHR_p$ , where thermal (24h at 200°) or photochemical bromination was unsuccessful. Likewise, the double bond was only partially hydrogenated over Raney nickel or oxidised by alkaline potassium permanganate, in spite of drastic conditions.

The new compounds were identified by  ${}^{19}$ F and  ${}^{1}$ H NMR (Table I). The  ${}^{19}$ F NMR results are thought to be useful, since there is a lack of data on such perfluoroalkyl derivatives; moreover, because the R<sub>F</sub> chains are long, the relative shifts observed for the CF<sub>2</sub>  $\alpha$  and  $\beta$  to the function

TABLE I

<sup>19</sup> F and <sup>1</sup> H NMR data for  $CF_2 CF_2 CF_2 CF_2 CF_2 CF_2 CF_3$  in compounds  $\frac{3}{2}$ ,  $\frac{4}{2}$  and  $\frac{6}{2}$ 

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Compound	όFα <sup>a</sup>	δFβ	δFγ	δFδ	δFε	ôf c	δFη	δCF <sub>3</sub>	q <sup>H§</sup>	J(H-Fα) <sup>C</sup>
$c_{AF_{Q}CBr_{2}CH_{2}Br^{d}}$	102.5	115.4	126.2					81.6	4.25	0
C <sub>E13</sub> CBr <sub>3</sub> CH <sub>3</sub> Br	102.5	114.5	122.0	122.0	126.4			81.6	4.23	0
$c_{BF_17}^{CBF_2CH_2BF}$	102.5	114.1	121.6	121.6	121.6	121.6	125.8	81.2	4.25	0
$c_{4^{\mathbf{F}}9}^{\mathbf{CBr}=\mathbf{CHBr}}$	106.1	121.4	126.2					81.6	7.70	0
c <sub>6</sub> F <sub>13</sub> CBr=CHBr	105.9	120.1	122.2	122.2	126.4			81.6	7.80	ں ح
c <sub>8</sub> F <sub>17</sub> cbr=chbr	105.9	120.4	122.0	122.0	122.0	122.0	126.6	81.2	(7.45) <sup>e</sup> 7.76	Q Z
с₄ғ <sub>9</sub> с≡сн	99.6	124.0	126.2					81.6	(7.41) <sup>~</sup> 2.96	5.5
c <sub>6</sub> F <sub>13</sub> -c≞ch	6.66	121.6	122.9	122.9	126.6			81.6	2.90	ы
c <sub>8</sub> F <sub>17</sub> −c≘cн	100.3	118.3	118.3	118.3	118.3	118.3	126.6	82.0	2.90	ហ

 $^{\rm a}$  in ppm from CCl $_3{\rm F}$  as internal reference, CCl $_4$  solution  $^{\rm b}$  in ppm from TMS as internal reference, CCl $_4$  solution

c<sub>in Hz</sub>

dccl<sub>3</sub>F solution emajor isomer:Z (minor isomer:E)

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TABLE II

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Compound	Yield	B.p./mmHg	M.p.	υ	ч Н	ſIJ	Br	υ	Н	Бц	Br
C ,F ,CBr ,CH , Br	80%	74°/12		14.85	0.41	35.26	49.48	14.81	0.39	35.34	49.14
4 y 2 2 C <sub>6</sub> F <sub>13</sub> CBr <sub>2</sub> CH <sub>2</sub> Br	94%		28,5°	16.41	0.34	42.22	41.02		0.35	42.25	40.76
C <sub>RF17</sub> CBr <sub>2</sub> CH <sub>2</sub> Br	95%		62°	17.51	0.30	47.15	35.03	17.31	0.26	46.76	34.90
c4FqcBr=CHBr	58%	55°/20		17.82	0.25	42.33	39.60	17.79		42.26	39.42
C <sub>F13</sub> CBr=CHBr	62%	72°/12		19.04	0.20	49.00	31.75	19.24	0.23	49.24	31.69
c <sub>g</sub> F <sub>1,7</sub> CBr=CHBr	60%	56°/0.5		19.87	0.17	53.47	26.49	20.34	0.23	53.95	25.30
c _ F _ C≡CH	60%	41°/760		29.51	0.41	70.08		29.56		69.40	
ς F <sub>13</sub> c≅ch	°06	95°/760		27.90	0.29	71.80		27.66	0.19	72.05	
c t cgF <sub>1</sub> γc≘cH	80%	40°/15		27.02	0.23	72.75		27.12	0.24	72.80	

can be taken as characteristic of the net effect of these functions on the chemical shift. The infrared, on the other hand, provides a convenient means of identification for the 1-bromo and 1-hydroperfluoroalkynes  $(v(C=C) = 2230 \text{ and } 2150 \text{ cm}^{-1} \text{ respectively})$ . The mass spectra exhibit the expected fragmentation of the perfluoroalkyl chains, with allylic or propargylic splitting when double or triple bonds are present [11].

The NMR spectra of  $\frac{4}{2}$  shows the presence of two isomers, as expected from the dehydrobromination reaction, in <u>ca</u>. 80/20 ratio. This is also found by VPC. However, the assignment of the NMR signals is not straightforward: the magnitude of the <sup>5</sup>J(H-F) coupling cannot be used reliably, since there seem to be no data available yet on such compounds, and those available for related compounds cannot be rationalized in a simple way [12,13]. Only a tentative assignment to the Z isomer of the most downfield signals, which correspond to the major compounds, was made, on the basis that chemical shifts generally appear to be greater when the hydrogen and the perfluoroalkyl chains are *cis* [9,12,13].

#### EXPERIMENTAL

The <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a JEOL C-60 HL spectrometer, the IR spectra on a Perkin-Elmer model 577 and the mass spectra on a CEC 21-130 spectrometer. Analytical and preparative VPC were performed on a Carlo Erba Fractovap 2400 chromatograph. Analyses were carried out on a 2 mm x 2 m column packed with 10% QF1 on Chromosorb W 80-100 mesh. Preparative columns (10 mm x 2 m) were packed with 25% QF1 on Chromosorb W 40-60 mesh. The yields, physical constants and analyses of compounds  $\underline{3}$ ,  $\underline{4}$  and  $\underline{6}$  are summarized in Table II.

# 1,1-dihydro 1,2,2-tribromoalkanes 3

These compounds were obtained from  $\frac{2}{2}$  by a method previously described for the bromination of  $\frac{1}{2}$  [9].

## 1-hydro 1,2-dibromoperfluoroalkenes 4

One equivalent of a <u>ca</u>. 2M ethanolic solution of potassium hydroxide was added dropwise to a stirred ethereal solution of  $\underline{3}$ , below 5°. After 2 h at room temperature the KBr precipitate was filtered off. The filtrate was washed with 10% HCl, then twice with water, and dried over MgSO<sub>A</sub>. After solvent evaporation, the distillation afforded two fractions. The more volatile fraction (about 30% in weight) was a mixture of  $\underline{2}$  and  $\underline{5}$ . The second one (60%) contained pure  $\underline{4}$ . The residue was unreacted  $\underline{3}$ .

#### 1-hydroperfluoroalkynes 6

 $\frac{4}{2}$  (0.1 mole) was added dropwise to a stirred suspension of 15 g of Zn dust and 0.5 g of ZnCl<sub>2</sub> in 300 ml of DMSO heated at 80°. The temperature rose gradually to 95-100° during the addition, and was then maintained at this level for 4 h. The crude  $\frac{6}{2}$  was separated from the mixture by distillation under reduced pressure, then washed twice with water, dried and redistilled.

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530