THE PREPARATION OF 1-HYDROPERFLUOROHEXYNE, OCTYNE AND DECYNE

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SUMMARY

1-hydroperfluoroalkynes (R_F C^{$= C_4F_9$, C_6F_{13} , C_8F_{17}) were prepa-} red 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 $R_{\rm F}$ CBr₂CH₂Br, $R_{\rm F}$ CBr=CHBr and $R_{\rm F}$ CECH.

INTRODUCTION

The lower 1-hydroperfluoroalkynes $R_p-C\equiv CH$ ($R_p = CF_3$, C_2F_5 and IC_3F_7) have been reported by Cullen et al. $\begin{bmatrix} 1 \end{bmatrix}$, but their chemistry has received little attention $\lceil 1,2 \rceil$. 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. Theseuses 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 l-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} -CECH, has been reported [5].

The preparative approach we used $[6]$ for the synthesis of 1-hydroper-Eluoroalkynes is derived from the general scheme developed by Henne and Nager [7] and Haszeldine and Leedham [S] 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, 6 was obtained in 80-85% yields. The preparation of the vinylic bromides 2 has been reported previously $[9]$.

Direct preparation of the alkyne 6 by dehydrobromination of 2 was attempted, but the low yields $(ca.20%)$ 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 (45-508). Thermal or photochemical bromination of 2 could be achieved in high yields, but dehydrobromination of 3 giving $\frac{4}{5}$ was accompanied by debromination leading back to $\frac{2}{5}$ and by double dehydrobromination giving the bromoalkyne 5 . The amount of these two side products could not be reduced to less than ca. 30% . $\frac{5}{2}$ was isolated by preparative VPC and identified by comparison with a sample prepared by independent synthesis [IO] .

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_FCH=CHR_F, 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 $R_{\rm p}$ chains are long, the relative shifts observed for the CF₂ α and β to the function

TABLE I

¹⁹ and ¹H NMR data for CF₂CF₂CF₂CF₂CF₂CF₂CF₂ in compounds $\frac{3}{2}$, $\frac{4}{4}$ and $\frac{6}{4}$

	đ	$B \quad Y \quad S \quad S \quad T$								
Compound	$\delta_{\rm F\alpha}$ a	$6F\beta$	δ F γ	5F5	$5F\epsilon$	555	6Fn	6CF ₃	$\sigma_{\rm H3}^{\rm H9}$	J (H-F α) $^{\rm C}$
$\mathbf{C_4}\mathbf{F_9}\mathbf{C}\mathbf{Br_2}\mathbf{CH_2}\mathbf{Br}^{\mathbf{d}}$	102.5	115.4	126.2					81.6	4.25	0
$\mathbf{C_6F_1}_3\mathbf{CBr_2CH_2Br}$	102.5	114.5	122.0	122.0	126.4			81.6	4.23	0
$\mathrm{C_{gF_{17}CBr_{2}CH_{2}Br}}$	102.5	114.1	121.6	121.6	121.6	121.6	125.8	81.2	4.25	O
c_4^{F} c $\rm{Br=CHBr}$	106.1	121.4	126.2					81.6	7.70	
$c_{6}r_{13}c_{\rm Br}$ -char	105.9	120.1	122.2	122.2	126.4			81.6		o S
$\mathrm{C_{g}F_{17}CBr=CHBr}$	105.9	120.4	122.0	122.0	122.0	122.0	126.6	81.2	(7.30) (7.45) e (7.45) e (7.41) e	О S
$c_4r_9c=\text{CH}$	99.6	124.0	126.2					81.6	2.96	5.5
$\mathrm{C_{6}F_{13}-C\Xi CH}$	99.9	121.6	122.9	122.9	126.6			81.6	2.90	LΩ
$\mathsf{C}_{\mathsf{B}}\mathsf{F}_{17}$ –с=сн	100.3	118.3	118.3	118.3	118.3	118.3	126.6	82.0	2.90	ь٥

 a_{1n} ppm from CCl₃F as internal reference, CCl₄ solution
b_{in} ppm from TMS as internal reference, CCl₄ solution

 $c_{\rm in~Hz}$

 α CCl₃F solution

major isomer:Z (minor isomer:E)

TABLE II

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 ($V(C=CC)$ = 2230 and 2150 cm⁻¹ 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 4 shows the presence of two isomers, as expected from the dehydrobromination reaction, in ca. 80/20 ratio. This is also found by VPC. However, the assignment of the NMR signals is not straiqhtforward: the magnitude of the 5 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 $\left[12,13\right]$. 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 ¹H and ¹⁹F 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% QFl on Chromosorb W 80-100 mesh. Preparative columns (10 mm x 2 m) were packed with 25% QFl on Chromosorb W 40-60 mesh. The yields, physical constants and analyses of compounds 2, 4 and 6 are summarized in Table II.

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

These compounds were obtained from 2 by a method previously described for the bromination of $1 \nvert 9$.

1-hydro 1,2-dibromoperfluoroalkenes 4

One equivalent of a ca. 2M ethanolic solution of potassium hydroxide was added dropwise to a stirred ethereal solution of 3 , below 5° . After 2 h at room temperature the KRr precipitate was filtered off. The filtrate was washed with 10% HCl, then twice with water, and dried over MgSO₄. After solvent evaporation, the distillation afforded two fractions. The more volatile fraction (about 30% in weight) was a mixture of 2 and 5 . The second one (60%) contained pure $\frac{4}{5}$. The residue was unreacted $\frac{3}{5}$.

1-hydroperfluoroalkynes 5

1 (0.1 mole) was added dropwise to a stirred suspension of 15 g of Zn dust and 0.5 g of ZnCl₂ in 300 ml of DMSO heated at 80 $^{\circ}$. The temperature rose gradually to 95-100' during the addition, and was then maintained at this level for 4 h. The crude 6 was separated from the mixture by distillation under reduced pressure, then washed twice with water, dried and redistilled.

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REFERENCES

1 a) M.I. Bruce and W.R. Cullen, Fluorine Chem. Rev. 4 (1969) and references therein; b) W.R. Cullen and M.C. Waldman, Can. J.Chem. 47 (1969) 3093 a) W.R. Cullen and M.C. Waldman, J. Fluorine Chem. 1 (1971) 41 _ b) J.H. Atherton and R. Fields, J. Chem. Soc.(C) (1968) 1507 c) F.G.A. Stone, J. Chem. Soc. (A) (1968) 1765 d) D.F. Howarth and R.G. Sherwood, Can. J. Chem. 51 (1973) 1655 Symposium on Inert Organic Liquids for Biological Oxygen Transport, Fed. Proc. 29 (1970) 1695-1820; J.G. Riess, Ann. Anesth. Fr., in press F. Jeanneaux, G. Santini, M. Le Blanc, A. Cambon and J.G. Riess, Tetrahedron, 30 (1974) 4197. 5 R.J. De Pasquale, C.D. Padgett and R.W. Rosser, J.Org.Chem.40 (1975)811 G. Santini, Thesis, Nice, Januarv 1973 7 A.L. Henne and M. Nager, J. Amer. Chem. Soc. 73 (1951) 1042 8 R.N. Haszeldine and K. Leedhan, J. Chem. Soc. (1952) 3483 9 G. Santini, M. Le Blanc and J.G. Riess, Tetrahedron 29 (1973) 2411 10 M. Le Blanc, G. Santini and J.G. Riess, in preparation 11 J.L. Cotter, Org. Mass Spect. 5 (1971) 851 12 R.N. Haszeldine, D.W. Keen and A.E. Tipping, J.Chem.Soc.(C)(1970) 414 13 W.R. Cullen and M.C. Waldman, Can. J. Chem. 47 (1969) 3093. -

530