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THE PREPARATION OF 1-HYDROPERFLUOROHEXYNE, OCTYNE AND DECYNE

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SUMMARY

1-hydroperfluoroalkynes ($R_F-C\equiv CH$, $R_F = C_4F_9, C_6F_{13}, C_8F_{17}$) 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 $R_F-C\equiv CH$.

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:

TABLE II

Yields, boiling or melting points and analyses of compounds 3, 4 and 6

Compound	Yield	B. p./mmHg	M. p.	A n a l y s e s							
				C	H	Required F	Br	C	H	Found F	Br
$C_4F_9CBr_2CH_2Br$	80%	74°/12		14.85	0.41	35.26	49.48	14.81	0.39	35.34	49.14
$C_6F_{13}CBr_2CH_2Br$	94%		28.5°	16.41	0.34	42.22	41.02	16.52	0.35	42.25	40.76
$C_8F_{17}CBr_2CH_2Br$	95%		62°	17.51	0.30	47.15	35.03	17.31	0.26	46.76	34.90
$C_4F_9CBr=CHBr$	58%	55°/20		17.82	0.25	42.33	39.60	17.79		42.26	39.42
$C_6F_{13}CBr=CHBr$	62%	72°/12		19.04	0.20	49.00	31.75	19.24	0.23	49.24	31.69
$C_8F_{17}CBr=CHBr$	60%	56°/0.5		19.87	0.17	53.47	26.49	20.34	0.23	53.95	25.30
$C_4F_9C\equiv CH$	60%	41°/760		29.51	0.41	70.08		29.56		69.40	
$C_6F_{13}C\equiv CH$	90%	95°/760		27.90	0.29	71.80		27.66	0.19	72.05	
$C_8F_{17}C\equiv CH$	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 ($\nu(\text{C}\equiv\text{C}) = 2230$ 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 straightforward: the magnitude of the $^5J(\text{H-F})$ 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 down-field 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 ^{19}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 3, 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 [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 KBr precipitate was filtered off. The filtrate was washed with 10% HCl, then twice with water, and dried over MgSO_4 . 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 4. The residue was unreacted 3.

1-hydroperfluoroalkynes 6

4 (0.1 mole) was added dropwise to a stirred suspension of 15 g of Zn dust and 0.5 g of $ZnCl_2$ 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 6 was separated from the mixture by distillation under reduced pressure, then washed twice with water, dried and redistilled.

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