

3 - H Y D R O P E R F L U O R O - 2 - B U T A N O N E

A N D I T S R E A C T I O N S

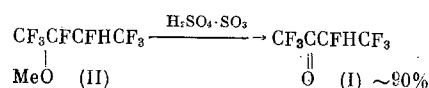
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It is known that the strong electron-acceptor effect of polyfluoroalkyl substituents, found α to the carbonyl group, facilitates nucleophilic attack on the ketone and hinders considerably the reaction with electrophiles [1]. Thus, perfluoroketones form stable adducts with NH_3 , H_2O , and alcohols, are reduced by complex metal hydrides [1], undergo haloform decomposition under the influence of aqueous alkali [2], but react with difficulty with PCl_5 [3].

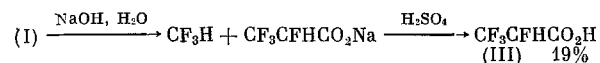
The behavior of hydrogen when α to the carbonyl group of a perfluoroketone lowers the electrophilicity of the latter and opens up the possibility of realizing reactions that involve the α -hydrogen atom. However, the reactivity of such ketones was studied only for pentafluoroacetone (PFA) [4].

The purpose of the present paper was to study the reactivity of a higher PFA homolog - specifically, 3-hydroperfluoro-2-butanone (I). We synthesized (I) by the hydrolysis of 2-methoxy-3-hydroperfluorobutane (II), which was obtained as described in [5]:



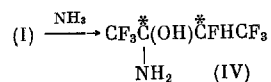
In contrast to PFA, it proved that ketone (I) does not undergo autocondensation in the presence of bases [4], apparently due to the steric hindrance created by replacing the α -F atom in PFA by the CF_3 group.

Ketone (I) reacts with aqueous NaOH solution only when refluxed vigorously, and here it undergoes hydrolysis to give trifluoromethane and the Na salt of 2,3,3,3-tetrafluoropropionic acid:

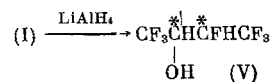


It is obvious that the difficult decomposition of (I) is explained by the possibility of a competing process, namely the deprotonation of (I) and the formation of the mesomeric carbanion.

When (I) is reacted with NH_3 , it exhibits the properties of a perfluoroketone and forms a stable adduct, which represents a 1:1 mixture of diastereomers (^{19}F NMR):

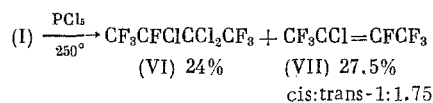


The reduction of (I) with LiAlH_4 in ether gave a mixture of the diastereomers of alcohol (V) in a 2.6:1 ratio (GLC, ^{19}F NMR), which confirms the scheme proposed in [6] for the reduction of trans-perfluoro-2-butene oxide:



When (I) is reacted with PCl_5 , the carbonyl oxygen and the α -H atom are replaced by chlorine to give (VI) and (VII):

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E X P E R I M E N T A L

The ^1H and ^{19}F NMR spectra were taken on a Perkin-Elmer R-32 spectrometer at 90 MHz using TMS (^1H) as the external standard and at 84.6 MHz and using CF_3COOH (^{19}F) as the external standard, and also on a Tesla BS-497 spectrometer at 100 MHz using TMS (^1H) as the internal standard and at 94 MHz using C_6F_6 (^{19}F) as the internal standard. The IR spectra were obtained on a UR-20 spectrometer. The purity of the products was established by GLC on an LKM-72 chromatograph, which was equipped with a katharometer as the detector, a 6 m \times 4 mm steel column packed with 5% SKTFT-100 deposited on Chromosorb G, and helium was used as the carrier gas.

3-Hydroperfluoro-2-butanone (I). With stirring, to 80 g of 60% oleum was added 40 g (0.17 mole) of (II), the mixture was refluxed for 0.5 h, and then the (I) was distilled. Distillation over conc. H_2SO_4 gave 31 g (91%)

of (I), bp 34-35°. $\text{CF}_3\text{COC}^2\text{FHC}^3\text{F}_3$. ^{19}F NMR spectrum (δ , ppm): -0.3 m (3F, CF_3), 135.3 d. sept (1F, CF^2), 1.2 d (3F, CF_3), $J_{1-2} = J_{2-3} = 11.3$, $J_{2-\text{H}} = 45.3$ Hz.

PMR spectrum (external standard TMS, δ , ppm): 4.81 d. qu. Infrared spectrum (ν , cm^{-1}): 1790 (C = O). Found: C 24.01; F 67.25%. $\text{C}_4\text{HF}_7\text{O}$. Calculated: C 24.24; F 67.17%.

Reaction of (I) with NaOH. To 10.5 g (0.053 mole) of (I) was added dropwise a solution of 2.2 g (0.055 mole) of NaOH in 3.2 ml of H_2O and the stirred mixture was refluxed for 3.5 h. The gas was collected, and the residue was distilled twice over conc. H_2SO_4 to give 320 ml (0.0143 mole) (27%) of CF_3H (identified by GLC using a standard) and 1.5 g of (III) (19%), bp 140-142°C [7]. ^{19}F NMR spectrum (C_6F_6 , δ , ppm): -40.82 d. qu (1F, CF), 87.6 d. d (3F, CF_3), $J_{\text{CF}_3-\text{CF}} = 11.6$, $J_{\text{CF}_3-\text{H}} = 6.6$, $J_{\text{H}-\text{F}} = 45.6$ Hz. PMR spectrum (δ , ppm, internal standard

TMS): 5.3 d. qu. (1H, CH), 8.8c (1H, COOH). Infrared spectrum (ν , cm^{-1}): 1770 (C = O), 3610 (OH).

2-Hydroxy-2-amino-3-hydroperfluorobutane (IV). Into a solution of 6 g (0.034 mole) of (I) in 50 ml of ether at 0° was passed 0.5 g of dry NH_3 , and then the ether was evaporated. We obtained 4.5 g (69%) of (IV), mp 65-67° (CHCl_3). ^{19}F NMR spectrum (δ , ppm): -5.1 m (6F, 2 CF_3); -0.7 m (3F, CF_3); 0.9 m (3F, CF_3); 130.9 m (2F, 2CFH). PMR spectrum (internal standard TMS, δ , ppm): 5.3 d. qu (1H, CFH); $J_{\text{H}-\text{F}} = 46.0$; $J_{\text{H}-\text{CF}_3} = 6.7$ Hz; 2.8 br. s (1H, OH); 6.2 br. s (2H, NH_2). Infrared spectrum (ν , cm^{-1}): 1610, 3320, 3400 (N-H); 3200 (OH). Found: C 22.05; H 1.94; F 61.52; N 6.81%. $\text{C}_4\text{H}_4\text{F}_7\text{NO}$. Calculated: C 22.32; H 1.86; F 61.86; N 6.51%.

2,3-Dihydroperfluoro-2-butanol (V). To a stirred suspension of 4.2 g of LiAlH_4 in 100 ml of ether was added dropwise 41 g (0.21 mole) of ketone (I) and the stirring was continued for another hour, after which 10% HCl solution was added, the ether layer was separated, and the aqueous layer was extracted with ether. The combined extract was dried over MgSO_4 , the ether was distilled off, and the residue was distilled over conc. H_2SO_4 to give 31 g (75%) of (V), bp 80.5-82.5°. The IR, PMR, and ^{19}F NMR spectra coincide with those given in [6].

Reaction of (I) with PCl_5 . A mixture of 40 g (0.202 mole) of (I) and 45 g (0.215 mole) of PCl_5 was shaken in a 200-ml steel autoclave for 6 h at 250°. The reaction mass was poured into ice water, and the lower layer was separated, dried over MgSO_4 , and distilled to give 12 g (27.5%) of (VII), bp 32° [8, 9]. cis:trans = 1:1.75

(^{19}F NMR), and 14 g (24%) of (VI), bp 96° [8, 9]. $\text{CF}_3\text{CCl}_2\text{CFCIC}^3\text{F}_3$. ^{19}F NMR spectrum (δ , ppm): -5.5 d. qu (3F, CF_3); -3.9 d. qu (3F, CF_3); 42.7 qu. qu (F, CF); $J_{1-2} = 11.3$; $J_{1-3} = 7.6$; $J_{2-3} = 5.3$ Hz.

C O N C L U S I O N S

1. 3-Hydroperfluoro-2-butanone was synthesized in ~90% yield by the hydrolysis of 2-methoxy-3-hydroperfluorobutane with 60% oleum.

2. The haloform splitting of 3-hydroperfluoro-2-butanone is hindered when compared with perfluoroketones.

3. The action of NH_3 , LiAlH_4 , and PCl_5 respectively gave 2-hydroxy-2-amino-3-hydroperfluorobutane, 2,3-dihydroperfluoro-2-butanol, and a mixture of 2,2,3-trichloroheptafluorobutane and 2-chloroheptafluoro-2-butene.

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R E A C T I O N S O F A R O M A T I C A C E T Y L E N I C E T H E R S W I T H T R I E T H Y L G E R M A N E

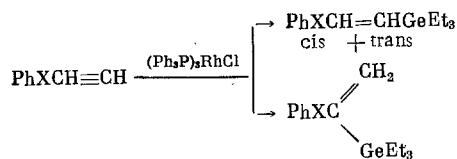
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The hydrogermylation of aromatic acetylenic ethers was studied for the example of compounds of type $\text{ArXC} \equiv \text{CH}$, $\text{ArXCH}_2\text{C} \equiv \text{CH}$, $\text{ArXC} \equiv \text{CCH}_3$, and $\text{ArXCH} = \text{C} = \text{CH}_2$ ($\text{X} = \text{O}, \text{S}$) in the presence of Speier catalyst [1-3].

As an expansion of these studies it seemed of interest to study the stereochemical direction of the hydrogermylation of heteroatomic acetylenic compounds using triphenylphosphinerhodium chloride as another catalyst. According to [4], the latter is active in the hydrosilylation of olefins. In the present paper we used the terminal acetylenes $\text{ArXC} \equiv \text{CH}$ and $\text{ArXCH}_2\text{C} \equiv \text{CH}$ ($\text{X} = \text{O}, \text{S}$) as the starting compounds.

The acetylenic ether and sulfide $\text{PhXC} \equiv \text{CH}$ add Et_3GeH in the presence of the rhodium catalyst by the following scheme:



Consequently, the hydrogermylation of these compounds is both nonstereo- and nonregiospecific. In contrast to them, the propargyl ethers of phenol and of the o-bromo- and p-chloro-2,5-dimethylphenols react with hydrogermane to give the gem and trans isomers with a substantial predominance of the latter.

When compared with 3-phenoxy-1-propyne, phenyl propargyl sulfide forms the same isomers, but in reverse ratio (Table 1). For the example of these compounds it was found that replacing the Speier catalyst by $(\text{Ph}_3\text{P})_3\text{RhCl}$ has no effect on the ratio of the isomers and the direction of the given reaction.

The structure of the obtained compounds was confirmed by elemental analysis and the PMR spectra (see

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