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Abstract

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REARRANGEMENT OF α,α-DIFLUOROALKYL AZIDES

The well-known rearrangement of acid azides (Curtius rearrangement), leading to the formation of isocyanates, according to current concepts, may be regarded as a process of α-elimination from the nitrogen atom with formation of nitrogen analogues of carbenes, which may be called "azacarbenes."

$$CF_3CFH{-}C(=O){-}N_3 \xrightarrow{-N_2} CF_3{-}CFH{-}C(=O){-}\ddot{N}$$

Azacarbenes are stabilized in the form of isocyanates through migration to the electrophilic nitrogen atom of the radical together with an electron pair

$$CF_3CFH{-}C(=O){-}\ddot{N} \longrightarrow CF_3CFH{-}N{=}C{=}O$$

β-Monohydroperfluoroalkyl azides, obtained by addition of hydrazoic acid to φ-olefins (see (1)), contain in the α-position to the azido group 2 fluorine atoms and are peculiar electronic analogues of acid azides

$$R{-}CO{-}N_3, \quad R{-}CF_2{-}N_3.$$

Therefore one could expect that upon heating they would undergo a rearrangement analogous to the Curtius rearrangement

$$CF_3CFHCF_2N_3 \xrightarrow{-N_2} (CF_3CFH){-}CF_2{-}\ddot{N} \longrightarrow CF_3CFH{-}N{=}CF_2$$

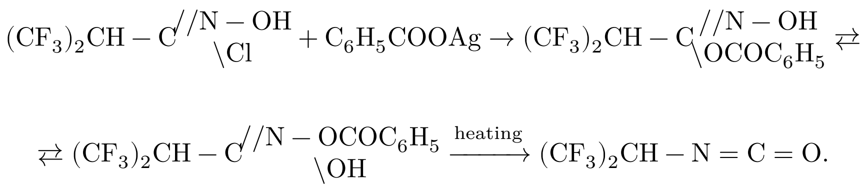
Indeed, on heating to 200° the corresponding carbimide fluorides were obtained from β-monohydroperfluoropropyl and β-monohydroperfluoroisobutyl azides. The structure of the carbimide fluorides obtained in the thermal rearrangement of α,α-difluoroalkyl azides required proof.

In the reaction of α-monohydroperfluoroisopropylcarbimide fluoride with aniline, a urea was obtained, identical with the urea obtained from α-monohydroperfluoroisopropyl isocyanate and aniline

$$(CF_3)_2CH{-}N{=}CF_2 \xrightarrow[H_2O]{C_6H_5NH_2} (CF_3)_2CH{-}NH{-}CO{-}NHC_6H_5 \xleftarrow{C_6H_5NH_2} (CF_3)_2CH{-}N{=}C{=}O.$$

To obtain this isocyanate, the reaction of φ-isobutylene with hydroxylamine was used (2). The fluoroanhydride of α-monohydroperfluoroisobutyrohydroxamic acid formed in this process, on interaction with liquid hydrogen chloride, was converted into the chloroanhydride of the same acid; on treatment of the latter with silver benzoate, the benzoyl derivative of α-monohydroperfluoroisobutyrohydroxamic acid was obtained, which

upon heating rearranged according to Lossen, giving α-monohydroperfluoroisopropyl isocyanate:



$$(CF_3)_2CH - C\begin{matrix}/\!/N - OH \\ \backslash Cl\end{matrix} + C_6H_5COOAg \rightarrow (CF_3)_2CH - C\begin{matrix}/\!/N - OH \\ \backslash OCOC_6H_5\end{matrix} \rightleftarrows$$

$$\rightleftarrows (CF_3)_2CH - C\begin{matrix}/\!/N - OCOC_6H_5 \\ \backslash OH\end{matrix} \xrightarrow{\text{heating}} (CF_3)_2CH - N = C = O.$$

The rearrangement of perfluoroalkenyl azides through the corresponding "perfluoroalkenylazacarbenes" might have been expected to lead to a compound with a three-membered nitrogen-containing ring:

$$CF_3 - \dot{C}F = CF - N_3 \longrightarrow CF_3C\dot{F} = CF \longrightarrow CF_3 - CF - CF$$

However, in reality, as reported earlier (^{2}), such "azacarbenes" rearrange by transfer to nitrogen of the fluorine atom from the γ-position. Probably this rearrangement, owing to conjugation of the bonds in

$$F_3C - CF = CF - \ddot{N}$$

takes place much more readily than "unpairing" of the electrons of the π bond, the electron density of which is depleted.

Experimental Part

1. α-Monohydroperfluoroisopropylcarbylamine fluoride. Through a glass tube placed in a tubular electric furnace, at 205–210° there was passed 4.7 g of 2-monohydroperfluoroisobutyl azide. The pyrolysis product was collected in a trap cooled with solid carbon dioxide. Distillation gave 2-monohydroperfluoroisopropylcarbylamine fluoride—a colorless liquid with the odor of phosgene, b.p. 36°, $d_4^0 1.5350$; $n_D < 1.3$. Mol. wt.: found 221, calculated for C_4HF_8N 215. Found F 70.50%; calculated F 70.70%.

A sample of the carbylamine fluoride obtained was dissolved in aniline water, heated for 5 min, and the fluorine was titrated. Found 17.85% F; theoretically, two fluorine atoms correspond to 17.70%.

2. α-Monohydroperfluoroethylcarbylamine fluoride. Pyrolysis of 2-monohydroperfluoropropyl azide was carried out in the same way as in experiment 3. 2-Monohydroperfluoroethylcarbylamine fluoride–a colorless liquid with b.p. 24°, $d_4^0 1.5000$. Mol. wt.: found 167, calculated for C_3F_6HN 165. Found F 68.74%; calculated F 69.09%. A sample of the carbylamine fluoride obtained was dissolved in aniline water, heated for 5 min, and the fluorine was titrated. Found 11.30% F; theoretically, two fluorine atoms correspond to 11.51%.

3. Phenylhexafluoroisopropylurea. 0.5 g of α-monohydroperfluoroisopropylcarbylamine fluoride was dissolved in ether, and an ethereal solution of aniline was added. Evolution of heat was observed. The ether was distilled off, and the remaining sticky crystalline mass was recrystallized from aqueous alcohol. M.p. 210° (after two recrystallizations). Determination of the melting point of a mixed sample with an authentic sample of $(CF_3)_2CHNHCONHC_6H_5$ gives no depression.

Found, %: C 42.08; H 2.70; N 9.68

$C_{10}H_8F_6N_2O$. Calculated, %: C 41.96; H 2.80; N 9.89

4. **Acid chloride of α-monohydroperfluoroisobutyrohydroxamic acid.** Into a steel tube, with cooling, were introduced 22.5 g of the ether complex of the acid fluoride of α-monohydroperfluoroisobutyrohydroxamic acid and 25 ml of liquid hydrogen chloride. The contents of the tube were stirred at room temperature for 3 h on a shaker, after which the tube was cooled, opened, and slowly brought to room temperature. The contents of the tube were transferred to a separatory funnel containing ether and washed several times with small portions of water until the aqueous layer became clear. The ether layer was separated, dried over calcium chloride, and distilled. The acid chloride of α-monohydroperfluoroisobutyrohydroxamic acid is a colorless liquid with a sharp odor. B.p. (after the second distillation) 58° at 38 mm, $d_4^{20} 1.4780$; $n_D^{20} 1.3570$.

$$[(CF_3)_2CHC(Cl) = NOH]_4 (C_2H_5)_2O.$$

Found, %: C 24.88; H 1.83; N 5.67; F 45.70; Cl 14.15
Calculated, %: C 24.15; H 1.82; N 5.77; F 45.97; Cl 14.32

5. **Benzoyl derivative of α-monohydroperfluoroisobutyrohydroxamic acid.** 10 g of the acid chloride of α-monohydroperfluoroisobutyrohydroxamic

acid was added to a suspension of 27.6 g of silver benzoate in 50 ml of dry ether. The reaction mixture was stirred for 2 days at room temperature. The precipitate was then filtered off, and the filtrate was distilled. After removal of the ether, crystals remained in the residue, m.p. (aqueous alcohol) 175°.

$$C_{11}H_7O_3F_6N.$$

Found, %: F 34.92; N 4.56
Calculated, %: F 36.18; N 4.44

6. **Phenylhexafluoroisopropylurea.** In a round-bottom flask equipped with a reflux condenser were placed 3 g of the benzoyl derivative of α-monohydroperfluoroisobutyrohydroxamic acid and 10 ml of nitrobenzene. The end of the condenser was connected to an ampoule immersed in a Dewar vessel with a cooling mixture. The flask was heated at the boiling temperature of nitrobenzene. A liquid collected in the ampoule; upon addition of aniline to it, white crystals precipitated, m.p. after recrystallization from aqueous alcohol 211°.

$$C_{10}H_8OF_6N_2$$

Found, %: C 42.08; H 2.89; F 39.50; N 9.54
Calculated, %: C 44.96; H 2.80; F 39.86; N 9.89

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Note: Figure translations are in progress. See original paper for figures.