ARYLAZOPOLYFLUOROALKENES FROM TERMINAL PERFLUOROOLEFINS

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The reactions of perfluoro-1-hexene and perfluoro-1-butene with phenylhydrazine gives phenylhydrazones of acid fluoride derivatives of the corresponding polyfluorocarboxylic acids. The dehydrofluorination of these products using triethylamine gives conjugated arylazopolyfluoroalkenes. The dehydrofluorination of the phenylhydrazone of α-hydroperfluorocaproyl fluoride by the action of phenylhydrazine leads to the phenylhydrazone of perfluoro-2-pentenoyl fluoride (IV).

The growing interest in arylhydrazones is attributed to the possibility of their use as reagents for constructing heterocyclic systems such as pyrazoles and pyrimidines. These compounds have a broad range of biological activity [1].

Special interest is found in arylazofluoroolefins. The first such compounds were synthesized in our laboratory using the reaction of polyfluoroaldehydes [1] and polyfluoroketones [3, 4] with phenylhydrazine.

$$R_f-CF_2-\underset{\underset{O}{\|}}{C}-R \xrightarrow{1)\ H_2NNHPh\ \ 2)\ KOH} R_f-CF=CR-N=N-Ph$$

R = H, alkyl, aryl, or fluoroalkyl.

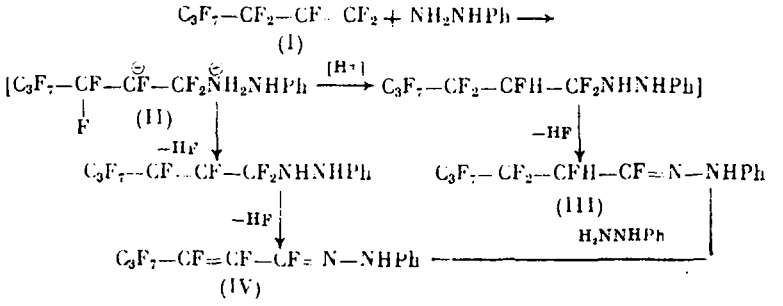
In the present work, we report a new approach to the synthesis of various arylazofluoroolefins based on the reaction of readily available terminal fluoroolefins with phenylhydrazine and subsequent treatment of the phenylhydrazones formed with triethylamine.

$$R_f-CF=CF_2 \xrightarrow{1)\ H_2NNHPh,\ 2)\ NEt_3} R_f-CH=CF-N=N-Ph$$

$R = CF_3, C_2F_5, C_3F_7$.

The reaction of terminal fluoroolefins with phenylhydrazine has been described only in the case of perfluoropropylene [5].

The reaction of perfluoro-1-hexene (I) with phenylhydrazine at about 20°C gives the trans isomer of phenylhydrazone of perfluoro-2-pentenoyl fluoride (IV) in about 10% yield in addition to the expected phenylhydrazone of α-hydroperfluorocaproyl fluoride (III) (as in the work of Carboni and Lindsey [5]).



The intermediate formation of carbanion (II) is proposed. The stabilization of (II) leads to (III) by the addition of a proton or to phenylhydrazone (IV) due to loss of a

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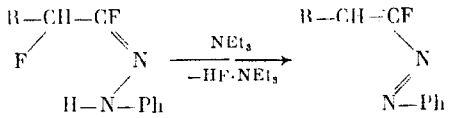
fluoride anion. The dehydrofluorination of phenylhydrazone (III) in the presence of phenylhydrazine, which also leads to (IV), is not excluded. Indeed, phenylhydrazone (IV) was separated quantitatively upon the action of excess phenylhydrazine on (III) or perfluoro-1-hexene.

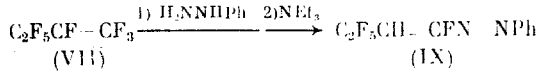
The dehydrofluorination of phenylhydrazone (III) in the presence of triethylamine unexpectedly led to 1-phenylazo-2-hydroperfluoro-1-hexene (V)* in quantitative yield.



R = C_4F_9 (III); CF_3 (VI); C_4F_9 (V), CF_3 (VII).

An analogous product, 1-phenylazo-2-hydrotetrafluoro-1-propene (VII), was obtained by the dehydrofluorination of the phenylhydrazone of 2,3,3,3-tetrafluoropropionyl fluoride (VI) previously obtained by Carboni and Lindsey [5].

The reaction of perfluoro-1-butene (VII) with phenylhydrazine and subsequent treatment of the reaction mixture by triethylamine gave 1-phenylazo-2-hydroperfluoro-1-butene (IX)† in about 40% yield.



The dehydrofluorination of (III) using triethylamine is stereoselective, while the dehydrofluorination of (VI) is stereospecific (azoolefin (VII) is formed as a 5:1 mixture of the cis and trans isomers).

The difference in the pathways for the dehydrofluorination of phenylhydrazone (III) is probably related to the difference in the basicity of the bases used. Thus, a "soft" CH proton is abstracted in the case of phenylhydrazine (pK_b 8.8) [7], while a "hard" NH proton is abstracted in the case of triethylamine (pK_b 3.3) [7].

The structures of all these compounds were supported by IR, PMR, and ^{19}F NMR spectroscopy and mass spectrometry.

EXPERIMENTAL

The PMR and ^{19}F NMR spectra were taken on an R-32 spectrometer with TMS and CF_3CO_2H as the internal standards. The mass spectra were taken on a Varian MAT mass spectrometer. The IR spectra were taken on a UR-10 spectrometer.

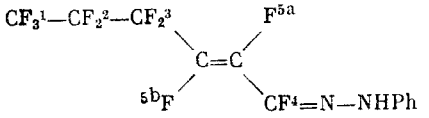
Phenylhydrazone of 2-Hydroperfluorocaproyl Fluoride (III). A mixture of 20 g (0.067 mole) perfluoro-1-hexene (I) and 15 g (0.14 mole) phenylhydrazine in 100 ml diethyl ether was maintained for 12 h at 25°C. The solution was separated from the precipitate, washed with 5% hydrochloric acid, and then water until the washings were neutral. The solution was dried over $MgSO_4$. Ether was removed on a rotary evaporator and the residue was distilled in vacuum to give 3 g of a fraction with bp 70-124°C (8 mm), containing 80% phenylhydrazone (IV) as indicated by PMR spectroscopy, and 18.5 g (72%) phenylhydrazone (III), bp 125-127°C (8 mm). Found: C, 37.55; H, 1.80; F, 53.87; N, 7.20%. Calculated for $C_{12}H_7F_{11}N_2$: C, 37.11; H, 1.63; F, 53.86; N, 7.21%. IR spectrum (ν, cm^{-1}): 1520 s (C=N), 3360 s (NH). Mass spectrum: 388 (M^+), 368 (M^+ - HF). PMR spectrum in CCl_4 (δ, ppm): 5.2 d.d.t (CH), 6.7-7.4 m (NH, C_6H_5) with 1:6 integral intensity, J_{HF-gem} 42.2 Hz, J_{HF-vic} 5.7 Hz, J_{H-CF_2} 14.1 Hz. ^{19}F NMR spectrum in CCl_4 (δ, ppm): 3.3 m (CF_3), 7.8 m (CF), 40.0 m (CF_2), 46.0 (CF_2), 48.7 m (CF_2), 121.5 (CFH) with 3:1:2:2:2:1 integral intensity.

Phenylhydrazone of Perfluoro-2-pentenoyl Fluoride (IV). A. A mixture 6.0 g (0.02 mole) perfluoro-1-hexene and 7.0 g (0.065 mole) phenylhydrazine in 50 ml diethyl ether was maintained for 72 h at 25°C. The solution was separated from the precipitate, washed with 5% hydrochloric acid, washed with water, and dried over $MgSO_4$. Ether was evaporated and

*This reaction was first reported in [6].

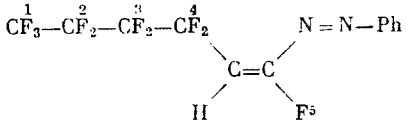
†This experiment was carried out with the participation of A. M. Belostotskii.

the solid residue was recrystallized thrice from hexane to give 5.3 g (73%) (IV), mp 83–84°C (trans isomer). Found: C, 39.21; H, 1.57; N, 7.89%. Calculated for $C_{11}H_7F_{10}N_2$: C, 39.13; H, 1.63; N, 7.61%. IR spectrum (ν, cm^{-1}): 1535 s (C=N), 1630 s (C=C), 3350 s (NH). Mass spectrum: 368 (M^+), 349 (M^+ - F), 243 (M^+ - C_2F_5). ^{19}F NMR spectrum in CCl_4 (δ, ppm, J, Hz): 2.4 t (CF_3^1), 11.8 d.d (CF^4), 40.0 d.d.q (CF_2^3), 50.6 m (CF_2^2), 80.0 d.d.t.t (CF^{5a}), 80.5 d.d.m (CF^{5b}) with 3:1:2:2:1:1 integral intensity, J_{1-3} 9.5, J_{2-5a} 7.5, J_{3-5a} 28.2, J_{4-5t} 35.2, J_{a-b} 132.0.



B. A mixture of 0.5 g (1.35 mmoles) phenylhydrazone (III) and 0.2 g (1.85 mmoles) phenylhydrazine in 3 ml CCl_4 was maintained for 72 h at 25°C. The solution was separated from the precipitate and washed with 5% hydrochloric acid and water. The solvent was evaporated and the solid residue was recrystallized from hexane to give 0.3 g (65%) (IV), mp 83–84°C, which was identical in its melting point and ^{19}F NMR spectrum to an authentic sample.

1-Phenylazo-2-hydroperfluoro-1-hexene (V). A mixture of 13.0 g (0.033 mole) phenylhydrazone (III), 3.6 g (0.035 mole) triethylamine, and 15 ml pentane was maintained for 48 h at 25°C. The solution was separated from the crystalline precipitate, washed with water, and dried over $MgSO_4$. The solvent was distilled off and the residue was distilled in vacuum to give 11.2 g (91%) (V) as a bright red liquid, bp 79–80°C (10 mm). Found: C, 39.12; H, 1.71; N, 7.85%. Calculated for $C_{12}H_6F_{10}N_2$: C, 39.13; H, 1.63; N, 7.61%. IR spectrum (ν, cm^{-1}): 1680 s (C=C). Mass spectrum: 368 (M^+), 349 (M^+ - F).



PMR spectrum of the cis isomer (δ, ppm): 5.5 d.t (CH), 6.5–7.3 m (C_6H_5) with 1:5 integral intensity, J_{H-F} 33.8 Hz, J_{H-CF_2} 18.8 Hz. ^{19}F NMR spectrum (δ, ppm, J, Hz): 4.1 t.t (CF_3^1), 22.2 d.t.t (CF^5), 31.8 d.d.t (CF_2^4), 44.7 m (CF_2^3), 48.9 d.t.q (CF_2^2) with integral intensity 3:1:2:2, J_{1-2} 9.4, J_{1-3} 2.8, J_{3-4} 11.3, J_{3-5} 7.5, J_{4-5} 33.8.

1-Phenylazo-2-hydrotetrafluoro-1-propene (VII). By analogy to the previous procedure, 4.5 g (0.019 mole) phenylhydrazone (VI), whose synthesis was described by Carboni and Lindsey [5], and 2.0 g (0.02 mole) triethylamine in 15 ml pentane gave 3.9 g (95%) (VII) as a bright red liquid, bp 64–65°C (20 mm) (5:1 mixture of cis and trans isomers). Found: C, 49.31; H, 2.75; N, 12.12%. Calculated for $C_9H_6F_4N_2$: C, 49.54; H, 2.75; N, 12.84%. IR spectrum (ν, cm^{-1}): 1685 s (C=C). Mass spectrum: 218 (M^+), 199 (M^+ - F). PMR spectrum of the cis isomer (δ, ppm): 5.3 d.q (CH), 6.7–7.1 m (C_6H_5), J_{H-F} 23.0 Hz, J_{H-CF_3} 7.5 Hz. ^{19}F NMR spectrum of the cis isomer (δ, ppm): -18.9 d.d (CF_3), 23.4 d.q (CF) with 3:1 integral intensity, J_{F-CF_3} 16.0 Hz. PMR spectrum of the trans isomer (δ, ppm): 5.3 d.q (CH), 6.7–7.1 m (C_6H_5), J_{H-F} 6.1 Hz, J_{H-CF_3} 7.5 Hz. ^{19}F NMR spectrum of the trans isomer (δ, ppm): -23.4 d.d (CF_3), 26.0 d.q (CF), J_{F-CF_3} 12.2 Hz.

1-Phenylazo-2-hydroperfluoro-1-butene (IX). A mixture of 8.5 g (0.055 mole) perfluoro-1-butene (VIII), 9.6 g (0.088 mole) phenylhydrazine, and 100 ml diethyl ether was maintained for 48 h at 20°C and then treated with an equal volume of 5% hydrochloric acid. The mixture was washed with water until neutral and dried over $MgSO_4$. Ether was removed on a rotary evaporator and a solution of 6.0 g $BF_3 \cdot NEt_3$ in 50 ml abs. monoglyme was added to the residue. The solution was heated at reflux for 1.5 h. A sample of 80 ml hexane and 100 ml water were added to the cooled solution. The organic layer was washed with water, dried over $MgSO_4$, evaporated on a rotary evaporator at ~20°C, and distilled in vacuum to give 4.5 g (38%) (IX), bp 78–79°C (5 mm) as a red liquid (7:2 mixture of cis and trans isomers). Found: C, 45.00; H, 2.3%. Calculated for $C_{10}H_6F_6N_2$: C, 44.8; H, 2.2%. Mass spectrum (m/z): 268 (M^+). ^{19}F NMR spectrum (δ, ppm): 8.4, 8.7 m (CF_3), 21.0 (CF), 29.6, 35.1 m (CF_2). PMR spectrum in $CDCl_3$ (δ, ppm): 5.2 m (CH), 6.0–7.2 m (C_6H_5).

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REACTION OF O-TRIPHENYLPHOSPHIMINOFORMYLISOBUTYROHYDROXIMOYL CHLORIDE WITH HEXAFLUOROACETONE

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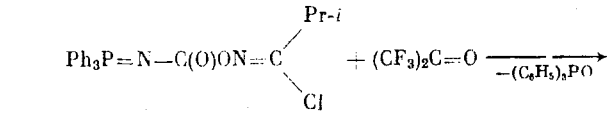
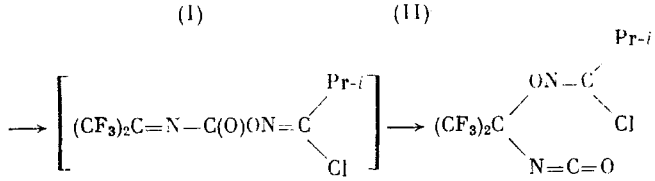
O-Triphenylphosphiminoformylisobutyrohydroximoyl chloride reacts with hexafluoroacetone to give the product of a sigmatropic rearrangement, namely, α-(O-isopropylchloroformimino)hexafluoroisopropyl isocyanate.

Phosphazo compounds react with perfluoroketones to form the corresponding N-substituted imine derivatives, including N-carbalkoxy derivatives [1]. Thus, we might have expected that treatment of O-triphenylphosphiminoformylisobutyrohydroximoyl chloride (I) with hexafluoroacetone (HFA) (II) would give the corresponding HFA imine (III). However, isocyanate (IV) was the only fluorine-containing product. The formation of (IV) is apparently related to the 1,3-sigmatropic rearrangement of (III) due to the presence of the electron-withdrawing oxime group at the carbonyl carbon atom. The nucleophilic properties of this oxime group are the driving force for this isomerization.



(I) (II)



(III) (IV)

The structure of (IV), which was synthesized in our previous work by a different method [2], was supported by IR and NMR spectroscopy and some chemical transformations. Thus, (IV) reacts exothermally with diphenylphosphonous acid and 3,4-dichloroaniline to give the corresponding phosphine oxide (V) and urea (VI).

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