CONVERSIONS OF α,α-DIFLUOROCARBONYL COMPOUNDS

VI. PHENYLHYDRAZONES OF FLUORINE-CONTAINING α-DIKETONES

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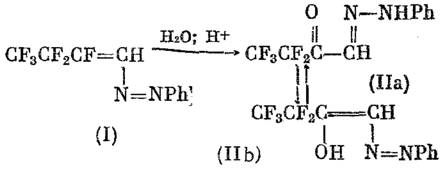
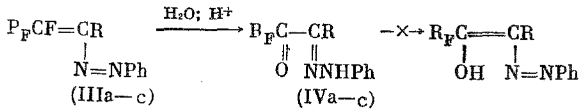
Earlier we reported [1] that 1-phenylazo-2,3,3,4,4,4-hexafluoro-1-butene (I) was easily hydrolyzed in acid solution to the phenylhydrazone of pentafluoroethylglyoxal (IIa) mixed with its tautomer (IIb).



$$\underset{\text{(I)}}{CF_3CF_2CF{=}CH{-}N{=}NPh} \xrightarrow{H_2O;\ H^+} \underset{\text{(IIa)}}{CF_3CF_2C(=O){-}CH{=}N{-}NHPh} \rightleftarrows \underset{\text{(IIb)}}{CF_3CF_2C(OH){=}CH{-}N{=}NPh}$$

In the present paper we investigate the hydrolysis of phenylazofluoroolefins which contain electron-donating and electron-accepting groups at the double bond and study some properties of the hydrolysis products: phenylhydrazones of fluorine-containing α-diketones.

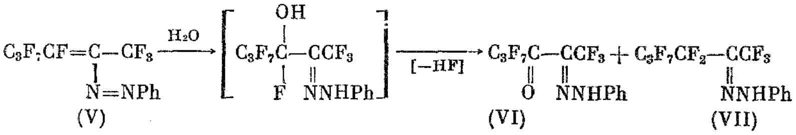
It was found that the azoolefins (IIIa-c)* hydrolyzed in acid medium to the phenylhydrazones of phenylpentafluoroethylglyoxal (IVa), methylpentafluoroethylglyoxal (IVb), and phenyldifluoromethylglyoxal (IVc), respectively.



$$\underset{\text{(IIIa—c)}}{P_FCF{=}CR(N{=}NPh)} \xrightarrow{H_2O;\ H^+} \underset{\text{(IVa—c)}}{B_FC(=O){-}CR(=NNHPh)} \xrightarrow{\times} R_FC(OH){=}CR(N{=}NPh)$$

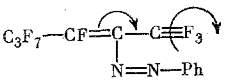
$R_F = C_2F_5$; $R = Ph$ (a); $R_F = C_2F_5$; $R = Me$ (b); $R_F = CF_2H$; $R = Ph$ (c).

The hydrolysis products were all exclusively in ketonic forms, in contrast to (IIa), and would not enolize even in the presence of triethylamine. Phenylazoperfluorohexene (V) in aqueous acetone at ~20°C yielded a mixture of the phenylhydrazones of trifluoromethylheptafluoropropylglyoxal (VI) and perfluoro-2-hexanone (VII).



$$\underset{\text{(V)}}{C_3F_7CF{=}C(N{=}NPh){-}CF_3} \xrightarrow{H_2O} \left[C_3F_7CF(OH){-}C(=NNHPh)CF_3\right] \xrightarrow[{[-HF]}]{} \underset{\text{(VI)}}{C_3F_7C(=O){-}C(=NNHPh)CF_3} + \underset{\text{(VII)}}{C_3F_7CF_2{-}C(=NNHPh)CF_3}$$

HF was eliminated during the formation of (VI) and added to the starting azoolefin (V) to produce (VII). This addition reaction did not occur with (IIIa-c) but was realized with (V) because of the hyperconjugation of the double bond with the trifluoromethyl group, resulting in the increase of electrophilicity of the olefin.



$$C_3F_7{-}CF{=}C(N{=}N{-}Ph){-}CF_3$$

Hydrolysis of azoolefin (V) in aqueous acetone in the presence of $NaHCO_3$ resulted in a quantitative yield of phenylhydrazone (VI), which existed as a tautomeric mixture of the ketonic (VIa) and enolic (VIb) forms in a ratio of 30:70.

This ratio was independent of the polarity of the solvent and remained the same in the presence of the base (pyridine), indicating that the chelating structure of the enolic form was favorably stabilized. The proton chemical shift of the OH group in (VIb) was 13 ppm, in contrast to that in the enol (IIb), which was 7 ppm and in which the ratio was strongly dependent on the polarity of the solvent [1].

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*Described in [2, 3].

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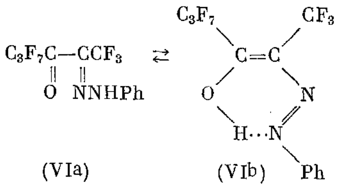
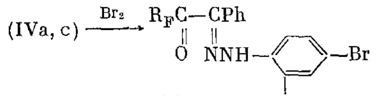


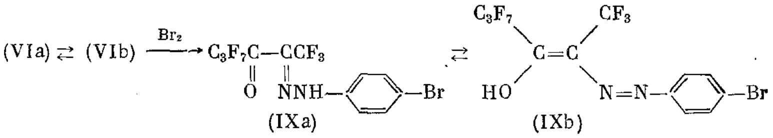
It is supposed that the formation of the tautomeric mixture of α-ketohydrazones (IVa-c) and (VI) depended on the electronic character of the substituent groups adjacent to the phenylhydrazone group. In the case of methyl and phenyl, these substituents increased the basicity of the NH group, so that enolization could not occur. On the other hand, the electron-accepting group CF_3 increased the acidity of the NH group, thus facilitating the formation of enolic form.

At a higher temperature phenylhydrazones (IVa,c) were brominated in the ortho and para positions of the N-phenyl ring.

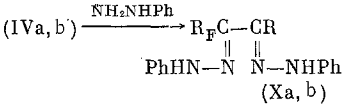


$R_F = C_2F_5$ (a); CF_2H (c).

The products (VIIIa,c) existed only in the ketonic forms. By bromination of the tautomeric mixture of (VIa,b) at 20°C, a mixture of tautomeric ketonic (IXa) and enolic (IXb) forms of p-bromophenylhydrazones with the same tautomeric ratio as the starting material was obtained.

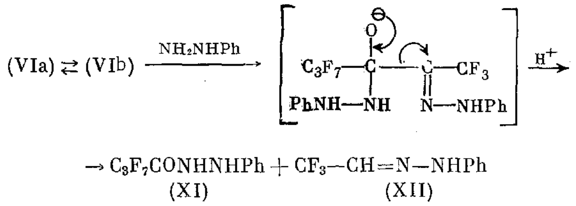


Phenylhydrazones (IVa,b) reacted with phenylhydrazine, yielding bisphenylhydrazones (Xa,b).

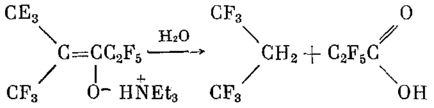


$R_F = C_2F_5$; $R = Ph$ (a); $R_F = C_2F_5$; $R = Me$ (b).

Reaction of phenylhydrazine with the tautomeric mixture of (VIa) and (VIb) produced compounds resulting from haloform cleavage: phenylhydrazide perfluorobutyric acid (XI) and phenylhydrazone trifluoroacetaldehyde (XII).



Haloform cleavage of the enolic form was made easier in the presence of amines as evidenced in the example of hexafluoroisopropyl pentafluoroethyl ketone and its enolic form [4].



EXPERIMENTAL

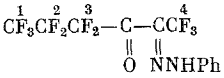
The PMR and ^{19}F NMR spectra were recorded on an R-32 spectrometer with TMS and CF_3COOH as external standards. The mass spectra were recorded on a Varian MAT apparatus, and IR spectra on a UR-10 spectrometer.

Phenylhydrazone of Phenylpentafluoroethylglyoxal (IVa). A mixture of 3.4 g of 1-phenyl-1-phenylazo-hexafluoro-1-butene (IIIa) (10 mmole), 2 ml of conc. HCl, and 30 ml of C_2H_5OH was boiled for 15 min, diluted with H_2O, and extracted with ether. The ether layer was washed with H_2O and dried with $MgSO_4$. After evaporation of the ether, the residue was distilled under vacuum at 179-180°C (2 mm Hg). The yield was 2.7 g (78%) of a viscous orange oil. IR spectrum, cm^{-1}: 1560 (s, C=N), 1685 (s, C=O), 3310 (s, NH). Found, %: C 55.81; H 3.44; F 28.13; N 8.02. $C_{16}H_{11}F_5N_2O$. Calculated, %: C 56.14; H 3.22; F 27.78; N 8.19. Mass spectrum: 342 (M^+), 322 (M^+ – HF). ^{19}F NMR spectrum (δ, ppm, CCl_4): 2.2 (s, CF_3), 36.0 (s, CF_2). PMR spectrum (δ, ppm, CCl_4): 6.7-6.9 (m, Ph), 9.4 (bs, NH) with integral intensity 10:1.

Phenylhydrazone of methylpentafluoroethylglyoxal (IVb) was obtained in the same way as (IVa) from 10 g of 2-phenylazo-3,4,4,5,5,5-hexafluoro-2-pentene (IIIb), 50 ml of conc. HCl, and 150 ml of C_2H_5OH. The yield was 9.1 g (91%) of the yellow crystals with mp 108-109°C (from hexane). IR spectrum, cm^{-1}: 1550 (s, C=N), 1675 (s, C=O), 3310 (s, NH). Found, %: C 46.99; H 3.13; N 9.78. $C_{11}H_9F_5N_2O$. Calculated, %: C 47.14; H 3.21; N 10.00. Mass spectrum: 280 (M^+), 261 (M^+ – F), 230 (M^+ – CF_2), 220 (M^+ – F – MeCN), 161 (M^+ – C_2F_5), 133 (M^+ – C_2F_5CO). PMR spectrum (δ, ppm, MeCN): 1.5 (s, Me), 7.0-7.3 (m, Ph), 9.0 (bs, NH) with integral intensity 3:5:1. ^{19}F NMR spectrum (δ, ppm, MeCN): 3.7 (s, CF_3), 36.3 (s, CF_2).

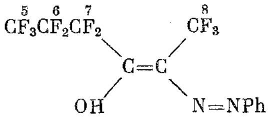
Phenylhydrazone of phenyldifluoromethylglyoxal (IVc) was obtained in the same way as (IVa) from 2 g of 1-phenylazo-1-phenyl-2,3,3-trifluoro-1-propene (IIIc), 3 ml of conc. HCl, and 20 ml of C_2H_5OH. The yield was 1.5 g (76%) of yellow crystals with mp 106-107°C (from hexane). IR spectrum, cm^{-1}: 1560 (s, C=N), 1680 (s, C=O), 3290 (s, NH). Found, %: C 66.27; H 4.52; F 13.89; N 10.14. $C_{15}H_{12}F_2N_2O$. Calculated, %: C 65.69; H 4.38; F 13.87; N 10.22. Mass spectrum: 274 (M^+), 254 (M^+ – HF). PMR spectrum (δ, ppm, acetone): 6.7 (t, CF_2H), 6.8-7.0 (m, Ph), 9.5 (bs, NH). J_{H-F} 53 Hz. ^{19}F NMR spectrum (δ, ppm, acetone): 49.0 (d, CF_2H).

Phenylhydrazone of Trifluoromethylheptafluoropropylglyoxal (VIa) and 2-Phenylazo-3-hydroxydecafluoro-2-hexene (VIb). a. A mixture of 3.5 g of 2-phenylazoperfluoro-2-hexene (V), 1 g of $NaHCO_3$, 5 ml of H_2O, and 30 ml of acetone was stirred for 1 h. It was then diluted with water and extracted with ether. The extract was washed with 5% HCl, water, and dried with $MgSO_4$. The solvent was evaporated and the residue distilled under vacuum at 105-112°C (2 mm Hg). The yield of orange liquid was 2.9 g (85%) of mixture of (VIa) and (VIb) with a ratio of 3:7. IR spectrum, cm^{-1}: 1525-1535 and 1560-1570 (s, C=N), 1640 (s, C=C), 1700 (s, C=O), 3375 (s, NH, OH). Found, %: C 37.76; H 1.61; F 48.60; N 7.49. $C_{12}H_6F_{10}N_2O$. Calculated, %: C 37.50; H 1.56; F 49.47; N 7.29. Mass spectrum: 384 (M^+), 365 (M^+ – F), 345 (M^+ – F – HF). PMR spectrum (δ, ppm): 6.2 (m, Ph), 8.7 (bs, NH), 13.1 (s, OH).



$$\overset{1}{CF_3}\overset{2}{CF_2}\overset{3}{CF_2}-\underset{\underset{O}{\|}}{C}-\underset{\underset{NNHPh}{\|}}{C}\overset{4}{CF_3}$$

(VIa)

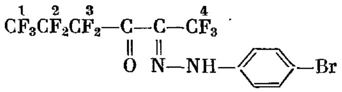


^{19}F NMR spectrum (δ, ppm): –17.9 (s, $\overset{4}{CF_3}$), –17.7 (tt, $\overset{8}{CF_3}$), 2.5 (t, $\overset{5}{CF_3}$), 2.7 (t, $\overset{1}{CF_3}$), 35.6 (q, $\overset{3}{CF_2}$), 39.0 (m, $\overset{7}{CF_2}$), 47.0 (s, $\overset{2}{CF_2}$), 47.2 (q, $\overset{6}{CF_2}$), J_{1-3} 10.4, J_{5-7} 9.4, J_{6-8} 4.7, J_{7-8} 17.9 Hz. b. A mixture of 3 g of compound (V), 1 ml of water, and 20 ml of acetone was kept at 20°C for 12 h. It was then diluted with 30 ml of ether, and washed with water. The ether layer was dried with $MgSO_4$ and distilled. The residue was kept in vacuum at 1 mm Hg for 3 h. The yield of orange-red oil was 2.7 g (90%). Based on ^{19}F NMR analysis it was a mixture of (VIa), (VIb), and the phenylhydrazone of perfluoro-2-hexanone (VII) in the ratio 1:2:1.

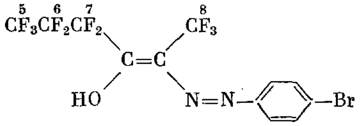
2,4-Dibromophenylhydrazone of Phenylpentafluoroethylglyoxal (VIIIa). A mixture of 1 g of (IVa), 1.6 g of bromine, 5 ml of ether, and 2 drops of water was heated in a sealed ampoule at 100°C for 30 min. It was then washed with water and dried with $MgSO_4$. The ether was then removed and a residue crystallized from C_2H_5OH. The yield of yellow crystals was 1.4 g (90%), mp 98-99°C. IR spectrum, cm^{-1}: 1560 (s, C=N), 1695 (s, C=O), 3295 (s, NH). Found, %: C 38.58; H 2.01; F 19.47; N 5.37. $C_{16}H_9Br_2F_5N_2O$. Calculated, %: C 38.40; H 1.80; F 19.00; N 5.60. Mass spectrum: 502–500–498 (M^+), 482–480–478 (M^+ – HF). PMR spectrum (δ, ppm, CCl_4): 7.4 (m, Ph), 9.1 (bs, NH) with integral intensity 3:1. ^{19}F NMR spectrum (δ, ppm, CCl_4): 2.4 (s, CF_3), 36.4 (s, CF_2).

2,4-Dibromophenylhydrazone of phenyldifluoromethylglyoxal (VIIIc) was obtained in the same way as (VIIIa) from 3 g of (IVc), 5 g of bromine, 20 ml ether, and 3 drops of water. The yield of yellow crystals was 3.4 g (92%) with mp 130-131°C (from hexane). IR spectrum, cm^{-1}: 1555 (s, C=N), 1690 (s, C=O), 3290 (s, NH). Found, %: C 42.26; H 2.36; N 6.48. $C_{15}H_{10}Br_2F_2N_2O$. Calculated, %: C 41.67; H 2.31; N 6.48. Mass spectrum: 434–432–430 (M^+), 414–412–410 (M^+ – HF). PMR spectrum (δ, ppm, acetone): 7.1 (t, CF_2H), 7.4 (m, Ph), 9.1 (bs, NH). J_{H-F} 31.6 Hz. ^{19}F NMR spectrum (δ, ppm, acetone): 4.8 (d, CF_2H).

Bromination of Mixture (VIa)-(VIb). A mixture of 0.5 g (VIa) and (VIb) and 0.3 g of bromine in 5 ml pentane was kept at 20°C for 24 h. It was then succesively washed with solutions of $NaHCO_3$ and water, and dried with $MgSO_4$. The pentane was removed and a residue distilled in vacuum. The yield was 0.5 g (83%) of the mixture (IXa) and (IXb) with a ratio of 1:2 and with bp 145-152°C (4 mm Hg). IR spectrum, cm^{-1}: 1520-1540 and 1560-1580 (s, C=N), 1640 (s, C=C), 1715 (s, C=O), 3350-3370 (s, NH, OH). Found %: C 30.92; H 1.05; N 6.11. $C_{12}H_5BrF_{10}N_2O$. Calculated, %: C 31.10; H 1.08; N 6.05. Mass spectrum: 464-462 (M^+), 445-443 ($M^+ - F$). PMR spectrum (δ, ppm, CCl_4): 6.9-7.3 (m, Ph), 9.8 (bs, NH), 14.2 (s, OH).



(IXa)



(IXb)

^{19}F NMR spectrum (δ, ppm, CCl_4): −17.9 (s, $\overset{4}{CF_3}$), −17.7 (tt, $\overset{8}{CF_3}$), 2.5 (t, $\overset{5}{CF_3}$), 2.7 (t, $\overset{1}{CF_3}$), 35.6 (q, $\overset{3}{CF_2}$), 39.0 (m, $\overset{7}{CF_2}$), 47.0 (s, $\overset{2}{CF_2}$), 47.2 (q, $\overset{6}{CF_2}$), J_{1-3} 10.4, J_{5-7} 9.4, J_{6-8} 4.7, J_{7-8} 17.9 Hz.

Bisphenylhydrazone of Phenylpentafluoroethylglyoxal (Xa). A mixture of 1.7 g (IVa) and 2 g of phenylhydrazine in 10 ml of C_2H_5OH was boiled for 3 h. The mixture was then diluted with 30 ml of water. A precipitate formed, which was separated, washed with 5% HCl and then with water, and recrystallized from C_2H_5OH. The yield was 1.9 g (90%); mp 141-142°C. This agrees with the published data [2].

Bisphenylhydrazone of methylpentafluoroethylglyoxal (Xb) was obtained in the same way as (Xa) from 2.8 g of (IVb) and 1.5 g of phenylhydrazine in 15 ml of C_2H_5OH. The yield was 3 g (81%); mp 103-104°C. This agrees with the published data [2].

Interaction of Mixture of (VIa) and (VIb) with Phenylhydrazine. A 1.7-g portion of a mixture of (VIa) and (VIb) and 1 g of phenylhydrazine in 10 ml ether was kept at 20°C for 5 days. After the ether was removed, the residue was washed with 5% HCl, H_2O, and hexane. The yield was 1.2 g (85%) of compound (XII); mp 110-111°C (from hexane). IR spectrum, cm^{-1}: 1700 (s, C=O), 3260-3280 (s, NH). Found, %: C 39.43; H 2.13; N 9.32. $C_{10}H_7F_7N_2O$. Calculated, %: C 39.47; H 2.30; N 9.21. Mass spectrum: 304 (M^+). PMR spectrum (δ, ppm, acetone): 6.2-6.7 (m, Ph), 10.0 (bs, NH) with integral intensity 6:1. ^{19}F NMR spectrum (δ, ppm, acetone): 3.3 (t, CF_3), 43.0 (q, CF_2), 49.0 (s, CF_2), J_{F-F} 9.4 Hz. The hexane from washing and crystallization was evaporated to yield a residue, which was sublimed at 1 torr. The yield was 0.6 g (75%) of compound (XI); mp 71-72°C. IR spectrum, cm^{-1}: 1540 (m, C=N), 3330 (s, NH). Found, %: C 51.20; H 3.85; N 13.95. $C_8H_7F_3N_2$. Calculated, %: C 51.06; H 3.85; N 14.89. Mass spectrum: 188 (M^+). PMR spectrum (δ, ppm, ether): 6.5-7.0 (m, Ph, CH), 8.8 (bs, NH) with integral intensity 6:1. ^{19}F NMR spectrum (δ, ppm, ether): −12.4 (d, CF_3), J_{H-F} 4.7 Hz.

CONCLUSION

1. Phenylhydrazones of fluorine-containing α-diketones were produced by hydrolysis of phenylazofluoroolefins.

2. Reactions of phenylhydrazine with phenylhydrazones of α-diketones depend on the electronic character of the substituents adjacent to the phenylhydrazone group, resulting in bisphenylhydrazones of α-diketones or products of haloform cleavage from the starting compounds, namely phenylhydrazide derivatives of perfluorocarboxylic acids and the phenylhydrazone of perfluoroacetaldehyde.

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