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# TRANSFORMATIONS OF $\alpha$ , $\alpha$ -DIFLUOROCARBONYL COMPOUNDS V. REACTION OF PERFLUORO-2-HEXANONE WITH PHENYLHYDRAZINE

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It has already been shown that ketones containing  $\alpha$ -difluoromethylene groups form with excess of phenylhydrazine base or phenylhydrazine acetate, at an elevated temperature, bisphenylhydrazones of  $\alpha$ -dicarbonyl compounds, or products of their dehydrofluorination, the corresponding pyrazoles. The  $\alpha$ -difluoromethylene group of the ketones transforms into the phenylhydrazone group as the result of the initial reaction with the C=O group; in the monohydrazone formed, the F atoms of the neighboring CF<sub>2</sub> group become mobile due to the electron-donor phenylhydrazone grouping. Incompletely fluorinated ketones, such as penta-fluoroacetone, methyl heptafluoropropyl ketone, phenyl heptafluoropropyl ketone, can also participate in this reaction [1].

It was interesting to clarify whether this reaction can be extended to perfluoro ketones, i.e., whether the electron-donor ability of the phenylhydrazone group is sufficient to activate the  $\alpha$ -difluoromethylene group in the perfluoro compounds, where this electron-donor ability should be distributed between two neighboring strongly electrophilic groupings. The present work describes the study of the reaction of perfluoro-2-hexanone with phenylhydrazine.

It was found that perfluoro-2-hexanone does not react with phenylhydrazine under the conditions previously used by us (in the presence of acetic or sulfuric acid, at 100°C). But when AcOH or  $H_2SO_4$  are replaced by CF<sub>3</sub>COOH, 1-phenyl-3-trifluoromethyl-4-phenylazo-5-pentafluoroethylpyrazole (I) is readily formed



Pyrazole (I) is formed as the result of successive transformations of perfluoro-2-hexanone into monohydrazone (II), azoolefin (III), and bisphenylhydrazone (IV), which is dehydrofluorinated to (I). To confirm the formation mechanism of pyrazole (I), we attempted to synthesize the above intermediate products.

The azoolefin (III) cannot be obtained under mild conditions described previously in [1]. Compound (III) is formed in good yield when product (II) is decomposed by solid KOH

$$(II) \xrightarrow{\text{KOH}} \begin{bmatrix} CF_3 - (CF_2)_2 - CF \swarrow_{||}^C - CF_3 \\ F & N \\ K & NPh \end{bmatrix} \xrightarrow{-[KF]} (III)$$

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1092–1095, May, 1981. Original article submitted July 15, 1980. The azoolefin (III) is considerably more stable than the azoolefins previously obtained by dehydrofluorination of monohydrazones of partially fluorinated ketones or aldehydes. Thus, (III) is stable under normal conditions for several months, while azoolefins of the type  $R_{F}$ - CF=C(Z)N=NPh, where Z = Me, H, Ph, for example, when Z = H, are stable for a few hours only. With respect to stability, the azoolefins obtained can be arranged in the following series:  $Z = CF_3 > Ph > Me > H$ . The azoolefin (III) readily reacts with phenylhydrazine, forming bisphenylhydrazone (IV) in a yield of ~100%.

It has already been shown that bisphenylhydrazones of  $\alpha$ -dicarbonyl compounds with a  $\alpha$ -difluoromethylene group are dehydrofluorinated at elevated temperature in the presence of the BF<sub>3</sub> · NR<sub>3</sub> complex with the formation of pyrazoles [1]. The dehydrofluorination of bisphenylhydrazone (IV) occurs at ~ 20°C, and, in the presence of Et<sub>3</sub>N, pyrazole (I) is formed in a yield of ~ 100%.

It is known that in the presence of an excess of phenylhydrazine, at elevated temperature, bisphenylhydrazones of perfluoro- $\alpha$ -ketoaldehydes form trisphenylhydrazones of the corresponding tricarbonyl compounds [2]. We found that even at ~20°C, bisphenylhydrazone (IV) reacts with excess of phenylhydrazine to form tetrakisphenylhydrazone of 1,1,1,6,6,6-hexafluorohexanetetraone (V) in a quantitative yield.



On boiling with methanol in the presence of catalytic amounts of an acid, compound (V) transforms in a  $\sim 100\%$  yield into the phenylhydrazone of trifluoromethyl 1-phenyl-4-phenylazo-5-trifluoromethylpyrazolyl ketone (VI)



A similar transformation of polyphenylhydrazones of polycarbonyl compounds into pyrazoles with the elimination of a phenylhydrazine molecule is known. Thus, when boiled in methanol, the trisphenylhydrazone of mesoxalic aldehyde transforms into 1-phenyl-4-phenylazopyrazole (VII) with the elimination of phenylhydra-zine [3]



### EXPERIMENTAL

PMR spectra were recorded on the Perkin–Elmer R-12 spectrometer (external standard TMS); <sup>19</sup>F NMR spectra, on the Hitachi H-6013 spectrometer (56.456 MHz) and R-32 with  $CF_3COOH$  as external standard; and mass spectra, on the Varian Mat CH-8 apparatus at the energy of the ionizing electrons of 70 eV and temperature of the ionic source of 40, 50, and 55°C.

<u>1-Phenyl-3-trifluoromethyl-4-phenylazo-5-pentafluoroethylpyrazole (I)</u>. a) A mixture of 2.6 g (24 mmoles) of phenylhydrazine, 2.8 g (24 mmoles) of CF<sub>3</sub>COOH, 5 ml of absolute ethanol, and 1.9 g (6 mmoles) of perfluoro-2-hexanone was heated for 5 h at 100°C. After cooling, the reaction mixture was diluted with water, the precipitate separated, and washed 4 times with boiling water. By recrystallization of the air-dried product (from alcohol, then from benzene), 0.9 g (34%) of (I), mp 179-181°C, was obtained. IR spectrum ( $\nu$ , cm<sup>-1</sup>):

1550 s (C= N). <sup>19</sup>F NMR spectrum (δ, ppm, benzene): -17 s (CF<sub>3</sub>), 5 t (CF<sub>3</sub>), 29 m (CF<sub>2</sub>). Mass spectrum (m/z): M<sup>+</sup> 434, (M<sup>+</sup>- F) 415, (M<sup>+</sup>- Ph) 357. Found: C 49.98; H 3.53; N 13.04%. C<sub>18</sub>H<sub>10</sub>F<sub>8</sub>N<sub>4</sub>. Calculated: C 49.89; H 2.33; N 12.90%.

b) A 0.1 g (10 mmoles) portion of triethylamine in 3 ml of ether was added to 0.2 g (4 mmoles) of the bisphenylhydrazone of perfluoromethylpropylglyoxal (IV) in 3 ml of absolute ether. The ether was then evaporated off, and the solid residue recrystallized from hexane. Yield, 0.15 g (82%) of (I), mp 180–181°C, which was identical with an authentic sample according to IR and <sup>19</sup>F NMR spectra.

<u>2-Phenylazoperfluoro-2-hexene (III).</u> To 2.7 g (7 mmoles) of the phenylhydrazone of perfluoro-2-hexanone in 20 ml of absolute ether, 2 g (35 mmoles) of KOH powder was added in portions. The mixture was stirred for 10 min, and then the solution separated from the precipitate, ether removed in vacuo, and the solid residue pyrolyzed by heating over a flame of a burner. The liquid was distilled, and by fractional distillation 1.7 g (66%) of (III), bp 78-79°C (3 mm), was obtained. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1670 (C=C). Found: C 36.89; H 1.16; F 53.21%. C<sub>12</sub>H<sub>5</sub>F<sub>11</sub>N<sub>2</sub>. Calculated: C 37.31; H 1.30; F 54.15%. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): -16.9 d (CF<sub>3</sub><sup>1</sup>), 3.8 m (CF<sub>3</sub><sup>2</sup>), 35.4 q.m (CF <sup>3</sup>), 35.6 m (CF<sub>2</sub><sup>5</sup>), 49.2 m (CF<sub>2</sub><sup>4</sup>), J<sub>CF<sub>3</sub>-CF = 34 Hz. C<sup>2</sup>F<sub>3</sub>C<sup>3</sup>F<sub>2</sub>.</sub>

C<sup>1</sup>F<sub>2</sub>

Mass spectrum:  $M^+ 386$ ,  $(M^+ - F) 367$ ,  $(M^+ - Ph) 309$ .

Bisphenylhydrazone of Perfluoromethylpropylglyoxal (IV). A 1.9 g (17 mmoles) portion of phenylhydrazine was added dropwise to 3.0 g (8 mmoles) of 2-phenylazoperfluoro-2-hexene (III) in 15 ml of ether. The mixture was held for 1 h at ~20°C, and then the solution was separated from the precipitate, washed with 10% HCl, water, dried over MgSO<sub>4</sub>, ether distilled off, and the residue distilled in vacuo. Yield, 3.1 g (84%) of (IV), bp 131-132°C ( $6 \cdot 10^{-3}$  mm) as orange glassy mass. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1560 s and 1570 s (C= N), 3310 and 3325 m (NH). Found: C 45.53; H 2.56; N 12.60; F 40.80%. C<sub>18</sub>H<sub>12</sub>F<sub>10</sub>N<sub>4</sub>. Calculated: C 45.57; H 2.53; N 11.81; F 40.08%. Mass spectrum: M<sup>+</sup>474, (M<sup>+</sup>- HF) 454, (M<sup>+</sup>- 2HF) 434. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm, CCl<sub>4</sub>): -15.0 t (CF<sub>3</sub>), 1.78 t (CF<sub>3</sub>), 28.7 m (CF<sub>2</sub>), J<sub>CF<sub>3</sub>-CF<sub>2</sub> = 5.6; J<sub>CF<sub>3</sub>-CF<sub>2</sub> = 10.3 Hz. PMR spectrum ( $\delta$ , ppm, CCl<sub>4</sub>): 8.0 s (NH), 7.7 s (NH), 7.0 s (Ph), integral intensity 1:1:10.</sub></sub>

Tetrakisphenylhydrazone of 1,1,1,6,6,6-Hexafluorohexanetetraone (V). A mixture of 1.5 g (3 mmoles) of the bisphenylhydrazone of perfluoromethylpropylglyoxal (IV), 2.0 g (13 mmoles) of phenylhydrazine, and 10 ml of diglyme was held for 3 days at ~20°C, and then the solution separated from the precipitate, diluted with 50 ml of 5% HCl, the precipitate separated, washed with hot water, dried in vacuo, and recrystallized from a hexanebenzene (1:1) mixture. Yield, 1.6 g (84%) of (V) yellow crystals, mp 189-190°C (dec.). PMR spectrum ( $\delta$ , ppm, ether): 6.5-7.0 m (Ph), 8.5 s (NH), 12.5 s (NH), integral intensity 20:2:2. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm, ether): -14.7 s (CF<sub>3</sub>). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1470, 1510, 1520, 1540, 1550, 1660 s (unsaturated bonds), 3040-3070 m (arom. CH), 3230 and 3320 br (NH). Found: C 59.62; H 4.10; N 17.88; F 18.19%. C<sub>30</sub>H<sub>24</sub>N<sub>8</sub>F<sub>6</sub>. Calculated: C 59.02; H 3.93; N 18.36; F 18.68%.

Phenylhydrazone of Trifluoromethyl 1-Phenyl-4-phenylazo-5-trifluoromethylpyrazolyl Ketone (VI). A 0.2 g portion of tetrakisphenylhydrazone (V) in 5 ml of methanol and 3 drops of HCl were boiled for 1 h, then the solution was diluted with water, the solid precipitate separated, washed with 5% HCl, water, dried in air, and recrystallized from ethanol (twice). Yield, 0.1 g (59%) of (VI), mp 81-82°C. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1555 s (C=N), 3310 and 3250 m (NH). Found: C 57.81; H 3.30; N 15.87%. C<sub>24</sub>H<sub>16</sub>F<sub>6</sub>N<sub>6</sub>. Calculated: C 57.37; H 3.19; N 16.73%. Mass spectrum: M<sup>+</sup> 502, (M<sup>+</sup>- PhNH) 410, (M<sup>+</sup>- PhN<sub>2</sub>) 397. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm, acetone): -23.1 s (CF<sub>3</sub>), -13.8 s (CF<sub>3</sub>). PMR spectrum ( $\delta$ , ppm, acetone): 6.7-7.6 (Ph), 9.6 s (NH), integral intenstity 15:1.

## CONCLUSIONS

1. Perfluoro-2-hexanone forms with excess of phenylhydrazine, at elevated temperature, in the presence of trifluoroacetic acid, 1-phenyl-3-trifluoromethyl-4-phenylazo-5-pentafluoroethylpyrazole.

2. It was shown for the first time that all the difluoromethylene groups of unbranched perfluoro ketones are transformed into the phenylhydrazone groups. In particular, tetrakisphenylhydrazone of 1,1,1,6,6,6-hexa-fluorohexanetetraone was obtained from perfluoro-2-hexanone.

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# REACTION OF PHOSPHOROUS ACID ESTERS WITH

#### $\alpha$ -FLUOROCARBONYL COMPOUNDS

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The reaction of trialkyl phosphites (TAP) with hexafluoroacetone (HFA) proceeds with the formation of tetrakistrifluoro-1,3,2-dioxaphospholanes [1], which at ~200°C decompose with the formation of the corresponding trialkyl phosphates and perfluorotetramethylethylene oxide [2]. In the reaction of ethyl ethylene phosphite with 1,1,1-trifluoroacetone (TFA) carried out under mild conditions, a bicyclic 1,4,2-dioxaphospholane is formed, which on heating readily isomerizes into 1,3,2-dioxaphospholane [3]. In the reactions of TAP with TFA, 1,4,2-dioxaphospholane, formed as an intermediate, isomerizes slowly at ~20°C into trialkoxy- $\alpha$ -trifluoromethyl- $\alpha$ -(1-methyl-2,2-difluoro)vinyloxyethylfluorophosphorane [4]; diethyltrimethylsilyl phosphate (DETMSP) forms with fluoro ketones the corresponding diethyl  $\alpha$ -trimethylsilyloxyphosphonates [5].

In a continuation of the study of the reactions of derivatives of P(III) with  $\alpha$ -fluorocarbonyl compounds, we studied the reaction of phosphorous acidesters with HFA and fluoral (FA). By <sup>31</sup>P NMR it was shown that in the reaction of triethyl phosphite with HFA at -100°C in an ether solution, 1,3,2-dioxaphospholane (X) is formed ( $\delta^{31}P + 55$  ppm, R = R' = Et, R" = CF<sub>3</sub>) according to the following scheme:



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