REACTION OF TETRAFLUOROHYDRAZINE WITH OXIMES

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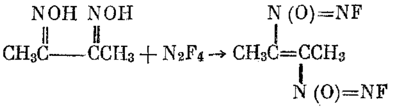
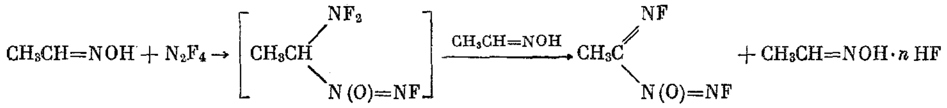
It was reported earlier that the reaction of tetrafluorohydrazine with p-quinone dioxime leads to p-bis-(N-fluoroazoxy)benzene [1]. In an analogous reaction with some aliphatic oximes gem-difluoroamino-N-fluoroazoxyalkanes were obtained [2].

In the present work it has been shown that the reaction of tetrafluorohydrazine with dimethylglyoxime in tetrahydrofuran in a glass reaction vessel proceeds on heating to 60-65°C for 4-5 h. After removal of the solvent the residue represented a yellowish liquid, which quickly became darker on storage and vigorously decomposed on slight heating to give nitrous oxide.* According to elemental analysis and its determined molecular weight this compound corresponds to 2,3-bis(N-fluoroazoxy)-2-butene (I), and it can then be supposed that the reaction is similar to the reaction with p-phenone dioxime [1], which also has two conjugated oxime groups, and proceeds by the following scheme:



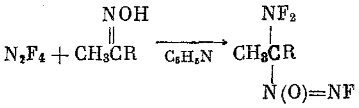
$$CH_3\overset{\overset{NOH}{\|}}{C}-\overset{\overset{NOH}{\|}}{C}CH_3 + N_2F_4 \rightarrow CH_3\overset{\overset{N(O)=NF}{|}}{\underset{\underset{N(O)=NF}{|}}{C}}=CCH_3 \qquad (1)$$

The reaction of tetrafluorohydrazine with acetaldoxime in a glass reaction vessel occurs at 70-75°C. From the reaction products the poorly stable N-fluoroimido-N-fluoroazoxyethane (II) was obtained in small yield together with acetaldoxime hydrofluoride, which makes it possible to suggest the following reaction scheme:



$$CH_3CH=NOH + N_2F_4 \rightarrow \left[CH_3CH\begin{matrix}NF_2\\N(O)=NF\end{matrix}\right] \xrightarrow{CH_3CH=NOH} CH_3C\begin{matrix}{=}NF\\N(O)=NF\end{matrix} + CH_3CH=NOH\cdot nHF$$

It should be noted that in our earlier attempts to carry out the reaction of the oximes by passing tetrafluorohydrazine through a solution of the oxime in an inert solvent in a bubbling column at 75-80°C it was not possible to isolate reaction products which were fluorinated at the nitrogen atom, although strong absorption of tetrafluorohydrazine was observed under these conditions. However, by addition of 0.7-0.8 mole pyridine per mole original oxime to the reaction mixture it was possible to obtain the respective difluoroamino-N-fluoroazoxyalkanes with satisfactory yield from acetoxime and methyl ethyl ketoxime:



$$N_2F_4 + CH_3\overset{\overset{NOH}{\|}}{C}R \xrightarrow[C_5H_5N]{} CH_3\overset{\overset{NF_2}{|}}{\underset{\underset{N(O)=NF}{|}}{C}}R$$

(III) $R=CH_3$; (IV) $R=C_2H_5$

Thus, unlike the reactions with the true C-nitroso compounds (which as a rule take place spontaneously [3-8]), the reaction of tetrafluorohydrazine with isonitroso compounds requires moderate heating of the

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*The formation of nitrous oxide has been observed earlier in the decomposition of 2-chloro-2-N-fluoroazoxypropane [3] and also in our experiments when 2-difluoroamino-2-N-fluoroazoxypropane was heated to 100-120°C.

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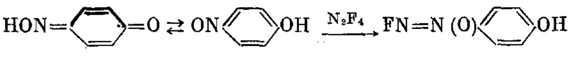
TABLE 1

Compound No.	Bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found, %		Molecular formula	Calculated, %	
				F	N		F	N
I	—	—	1,42	20,52	29,33	$C_4H_6F_2N_4O_2$	21,11	31,11
II	68—69(152)	1,3968	1,318	29,16	33,67	$C_2H_3F_2N_3O$	30,89	34,15
V	83—84 *	—	—	11,83	17,61	$C_6H_5FN_2O_2$	12,18	17,95
VI	101 (1)	—	—	9,10	14,33	$C_8H_{17}FN_2O_3$	9,58	14,15

* Melting point.

† Mp 35-60°C.

reaction mixture. An exception is the reaction of tetrafluorohydrazine with p-quinone dioxime, which proceeds at room temperature [1]. In this connection it is interesting to note that when tetrafluorohydrazine is passed through a solution of p-nitrosophenol in chloroform, where the isonitroso form of nitrosophenol predominates [9], a vigorous reaction accompanied by appreciable resin formation takes place even at ~0°C. p-N-Fluoroazoxyphenol (V) is isolated in small yield from the reaction products:



(V)

This result evidently also shows that tetrafluorohydrazine has greater affinity towards the nitroso and not the isonitroso group.

Compound (V) is a slightly yellowish crystalline powder, which dissolves comparatively well in most organic solvents. In the impure form it decomposes vigorously in isolated cases even on heating to 80-90°C. It is more stable in the recrystallized form but is almost completely converted into resinous substances after storage for 1-2 months at room temperature. p-N-Fluoroazoxyphenyl acetate (VI) was obtained by acylation of Compound (V) with acetyl chloride:

$$p\text{-}HOC_6H_4N(O){=}NF + CH_3C(O)Cl \rightarrow p\text{-}CH_3C(O)OC_6H_4N(O){=}NF \quad (VI)$$

Unlike Compound (V), Compound (VI) does not change even after storage for a year. The properties of the newly prepared compounds are given in Table 1.

EXPERIMENTAL

2-Difluoroamino-2-N-fluoroazoxypropane (III). Into a glass bubbling column 350 mm long and 16 mm in diameter, provided with a jacket for heating, were placed 10.6 g acetoxime, 8.6 g pyridine, and 15 ml Freon-112. Nitrogen was blown through the apparatus, and tetrafluorohydrazine was then passed for 7-8 h at 79-80°C at a rate of 0.4-0.5 liter/h. Nitrogen was then passed again, and the reaction mixture was rinsed twice with 50-ml portions of 5% hydrochloric acid and dried over magnesium sulfate. The solvent was removed under vacuum. Fractional distillation gave 8.2 g (35%) colorless liquid boiling at 54°C (30 mm); n_D^{20} 1.3950; d_4^{20} 1.325. Published data [2] gives: bp 54°C (30 mm); n_D^{20} 1.3952; d_4^{20} 1.324.

p-N-Fluoroazoxyphenol (V). Into a 200-ml glass reaction vessel, provided with a bubbler, was placed 5 g p-nitrosophenol in 150 ml chloroform. Nitrogen was blown through the reactor, and tetrafluorohydrazine was then passed until it ceased to be absorbed. Nitrogen was again passed, the solvent was removed under vacuum, and the residue was recrystallized from hexane. A 1.9-g (30%) yield of light-brown crystalline compound, melting at 83-84°C, was obtained.

p-N-Fluoroazoxyphenyl Acetate (VI). A 3-g sample of p-N-fluoroazoxyphenol and 15 ml acetyl chloride were boiled under a reflux condenser for 16 h. Fractional distillation gave 1.7 g (45%) colorless compound, boiling at 101°C (1 mm) and melting at 55-56°C.

CONCLUSIONS

Reaction of tetrafluorohydrazine with dimethylglyoxime, acetaldoxime, and p-nitrosophenol gave the corresponding N-fluoroazoxy derivatives. Some special features of the process were investigated.

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