REACTION OF TETRAFLUOROHYDRAZINE
WITH 1,1',2,3,4,4'-HEXAFLUOROBUTADIENE
AND HEXAFLUOROCYCLOBUTENE

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The ability of conjugated polyenes of variable structure to become fully saturated with difluoroamino groups employing tetrafluorohydrazine was described recently in a number of patents [1-4]. It was also found [5] that butadiene when reacted with tetrafluorohydrazine forms two isomers of the 1:1 adduct, with a predominance of 1,4-bis-(difluoroamino)-2-butene

\[ CH_2=CH-H=CH_2 + N_2F_4 \rightarrow CH_2=CH-N=CF_2 \]

whereas 1,1,2-trifluorobutadiene gives only 1,4-bis-(difluoroamino)-1,1',2-trifluoro-2-butene. It proved [6] that 2-chloro-1,3-butadiene also adds tetrafluorohydrazine only in the 1 and 4 positions of the diene, forming 1,4-bis-(difluoroamino)-2-chloro-2-butene. It was found [7] that 1,1',4,4'-tetrafluorobutadiene reacts with tetrafluorohydrazine to give a mixture composed of 61% of 1,4-bis-(difluoroamino)-1,1',4,4'-tetrafluoro-2-butene and 35% of 1,2-bis-(difluoroamino)-1,1',4,4'-tetrafluoro-3-butene:

\[ F_2C=CH-CF_2 + N_2F_4 \rightarrow F_2C=CH-N=CF_2 + F_2C=CH-CH=CF_2 \]

The given examples of the reaction of tetrafluorohydrazine with butadienes, and also its ability to add to haloethylenes [5, 7-11] under the conditions of the radical process, are responsible for the interest in the attempt to add tetrafluorohydrazine to perfluorobutadiene and its cyclic isomer, namely perfluorocyclobutene, all the more so since statements exist [5] that the reactivity of olefins toward tetrafluorohydrazine decreases in measure with depletion of the \( \pi \)-bond, caused by the effect of substituents. Experiment disclosed that perfluorobutadiene reacts with tetrafluorohydrazine, both at room temperature and a pressure of approximately 1.5 atm, and in an autoclave under autodeveloping pressure. The product of this reaction is the 1:1 adduct, the \( F_19 \) NMR spectrum of which is characterized by three signals, with chemical shifts of 412.5, 537.5, and 583.8 ppm. The presence of only one signal (412.5 ppm), characteristic for the difluoroamino group (the other two signals respectively belong to the CF2 and CF = CF groups), indicates that the adduct has a symmetrical structure, which is assured only if the adduct has the structure of 1,4-bis-(difluoroamino)-1,1',2,3,4,4'-hexafluoro-2-butene:

\[ CF_2=CF-CF_2 + N_2F_4 \rightarrow F_2N-CF_2-CF = CF-CF_2-NF_2 \]

Under the same conditions, 1,1',4,4'-tetrafluorobutadiene reacts somewhat more vigorously with tetrafluorohydrazine, forming a mixture that is composed of 1,4-bis-(difluoroamino)tetrafluoro-2-butene and a much smaller amount of 1,2-bis(difluoroamino)tetrafluoro-3-butene (up to 6%) than was described in [7].

The experiments with perfluorocyclobutene proved to be especially interesting. The addition of tetrafluorohydrazine to this olefin could be accomplished by heating the reaction mixture in an autoclave for 10 h at 110°C. The physicochemical constants of the product of this reaction, and also the \( F_19 \) NMR spectrum, composed of signals with chemical shifts of 413, 537, and 582.8 ppm, proved to be practically identical with...
the constants and spectrum of the 1,4-bis-(difluoroamino)perfluoro-2-butene obtained by the reaction of
tetrafluorohydrazine with perfluorobutadiene. From these results it follows that the reaction of tetrafluoro-
hydrazine with perfluorocyclobutene is not a simple reaction of addition to the double bond of the olefin
and is complicated by processes that lead to an opening of the ring:

\[
\begin{align*}
\text{CF}_3\text{--CF} & \quad \xrightarrow{\text{F}_2\text{NCF}_3\text{--CF}\xrightarrow{\text{CF}3\text{NF}_2}\text{NO}_3}\to \text{O}_2\text{NCF}_3\text{CF}3\text{NO}_3, \\
\text{CF}_3\text{--CF} & \quad \xrightarrow{\text{N}_2\text{O}_4\text{140}^\circ}\to \text{CF}_3\text{--CF}\xrightarrow{\text{CF}3\text{--NO}_3,}\text{CF}_3\text{--CF}.
\end{align*}
\]

Subsequently, in special experiments a similar phenomenon, but not expressed as quantitatively,
could be observed when a mixture of perfluorocyclobutene and nitrogen tetraoxide was heated in an auto-
clave. The F\text{13} NMR spectrum of the nitration products obtained in this case indicated that they consist
of a mixture of 1,2-dinitroperfluorocyclobutane (~80%) and 1,4-dinitroperfluoro-2-butene, which is smoothly
obtained by the nitration of perfluorobutadiene [12]:

\[
\text{CF}_3\text{--CF} \quad \xrightarrow{\text{O}_2\text{NCF}_3\text{CF}3\text{NO}_3}\to \text{CF}_3\text{--CF} \xrightarrow{\text{CF}3\text{--NO}_3,}\text{CF}_3\text{--CF}.
\]

As a result, it can apparently be assumed that the opening of the perfluorocyclobutene ring when the
olefin is heated in the presence of particles having a radical nature bears a quite general character.

A similar phenomenon was encountered in [13], where the formation of 1,2,3,4-tetrahydroperfluoro-
butane was observed when a mixture of perfluorocyclobutene and hydrogen iodide was heated for a long
time:

\[
\text{CF}_3\text{--CF} \quad \xrightarrow{\text{HI} \text{275--900}^\circ}\to \text{CF}_3\text{--CF} \xrightarrow{\text{HCF}_3\text{--CF}3\text{H}H}.
\]

However, coping with the fact of the reversible thermal perfluorobutadiene - perfluorocyclobutene
interconversion, which takes place at temperatures of 500° and higher:

\[
\text{CF}_3\text{--CF} \quad \xrightarrow{\text{HI} \text{275}^\circ}\to \text{CF}_3\text{--CF} \xrightarrow{\text{CF}3\text{--CF}3\text{H}H}.
\]

the formation of tetrahydroperfluorobutene was explained in [13] by the reaction of HI with perfluorobuta-
diene, and not with perfluorocyclobutene. For further discussion it is important to mention that the reaction
of perfluorocyclobutene with HI has as it were a temperature threshold; at 210° and a contact time of
65 h the reaction does not go, but at 275° and a contact time of 24 h the yield of tetrahydroperfluorobutene
is 90%. The obtained results give reason to believe that the opening of the perfluorocyclobutene ring by
tetrafluorohydrazine (110°), nitrogen tetraoxide (140°), and apparently by HI [13] (275°), is not associated
with an obligatory prior isomerization of perfluorocyclobutene to perfluorobutadiene, which is observed
only at temperatures of 500° and higher [13].

The thermal perfluorocyclobutene - perfluorobutadiene equilibrium, bearing a general character, is
caused by the thermodynamic properties of the cyclic biradical, which has unpaired electrons on adjacent
carbon atoms and is found in resonance with two saturated states:

\[
\begin{align*}
\text{CF}_3\text{--CF} & \quad \xrightarrow{\text{CF}3\text{--CF}3\text{H}H} \\
\text{CF}_3\text{--CF} & \quad \xrightarrow{\text{CF}3\text{--CF}3\text{H}H} \\
\text{CF}_3\text{--CF} & \quad \xrightarrow{\text{CF}3\text{--CF}3\text{H}H}.
\end{align*}
\]

The temperature "threshold" of this isomerization (which, as is emphasized in [13], is not associated
with migration of the halogen) practically coincides with the temperature interval (400° and higher) for
opening the \(\pi\)-bond of tetrafluoroethylene with the formation of perfluorocyclobutane [14, 15]:

\[
\text{CF}_3\text{--CF} \quad \text{CF}_3\text{--CF} \quad \text{CF}_3\text{--CF} \quad \text{CF}_3\text{--CF}.
\]