REACTION OF SECONDARY AMINES WITH
HEXAFLUOROPROPYLENE DIMERS

V. F. Snegirev, E. V. Zakharova,
K. N. Makarov, and I. L. Knunyants

The reaction of hexafluoropropylene dimers (perfluoro-4-methyl-2-pentene (I) and perfluoro-2-methyl-2-pentene (II)) with secondary amines has already been studied. The reaction of (I) with diethylamine leads exclusively to enamine (IV) [1], and the reaction of (II) with piperidine to a mixture of enamines (IV) and (V) [2]. The formation of isomeric enamines (IV) and (V) is explained by the isomerization of (I) into (II), and of (II) into (III) under the reaction conditions

\[
\begin{align*}
(CF_3)_2CFCF=CFCF_3 & \rightleftharpoons (CF_3)_2C=CFCF_3 \\
(CF_3)_2C=CFCF_3 & \rightarrow (CF_3)_2C=CCF_3 \\
(X) & \rightarrow (IV), (V)
\end{align*}
\]

In the present work, we studied the reactions of olefins (I) and (II) with different secondary amines, such as dimethylamine, diethylamine, piperidine, pyrrolidine, and hexamethyleneimine. It was found that on transition from (I) to (II), the relative amount of enamine (IV) increases. A similar increase is observed with increase in the steric hindrances in the attack by the secondary amine (Table 1). It is clear that here the steric factor is the main one, and predetermines the ratio of the enamines of different structures. A similar conclusion is also obtained in the study of reactions of secondary amines with perfluoro-2-pentene [3].

A more detailed investigation of the reaction of (II) with secondary amines showed that the addition of a half-equimolar amount of the amine leads to a complete disappearance of the olefin (II), but there was no separation of crystals of the secondary amine hydrofluoride. It was found that the HF evolved in this reaction binds with olefin (II) with the formation of 2-hydroperfluoro-2-methylpentane (VI)

\[
2 (II) + HNR_2 \rightarrow (IV)/(V) + (CF_3)_2CHCF_2CF_2CF_3
\]

Thus, the reaction proceeds further only via the dehydrofluorination of alkane (VI) and subsequent reaction of the olefin formed with the amine. As known [4], the dehydrofluorination of (VI) by the NEt_3-BF_3 complex leads to a mixture of olefins (II) and (III), with (II) predominating. However, in the reaction of (VI) with secondary amines, the terminal olefin (III) is apparently preferentially formed. In fact, the (IV):(V) ratio increases when alkane (VI) is used as the starting material (see Table 1). In the reaction of (II) with the addition of the secondary amine this ratio gradually increases.

It is known that perfluoro-2-methyl-2-butene reacts with secondary amines without isomerization [5]. It is possible that the replacement of the trifluoromethyl group by the more bulky perfluoroethyl group adjacent to the reaction center of the olefin molecule was also the reason for the appreciable difference in the reactions of these homologs.

We also showed that secondary amines of a different structure readily and unequivocally react with the cyclic analog of olefin (II), perfluoro-1-methylcyclopentene (VII). The only product in this reaction, enamine (VIII), is formed by substitution of the "vinyl" fluorine atom. It is interesting to note that, as shown by special experiments, this reaction proceeded without the formation of the corresponding monohydroperfluorocycloalkane. Enamine (VIII) readily hydrolyzes into enamine (IX), with two fluorine atoms present in the allyl position to the double bond being saponified, as is characteristic of cyclic enamines [6, 7].

TABLE I. Reaction of Perfluoro-4-methyl-2-pentene (I), Perfluoro-2-methyl-2-pentene (II) and 2-Hydroperfluoro-2-methylpentane (VI) with Secondary Amines

<table>
<thead>
<tr>
<th>Secondary amine</th>
<th>Initial compound</th>
<th>Ratio between products, %</th>
<th>Overall yield, %</th>
<th>Secondary amine</th>
<th>Initial compound</th>
<th>Ratio between products, %</th>
<th>Overall yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(V)</td>
<td>(IV)</td>
<td>(V)</td>
<td>(IV)</td>
<td>(V)</td>
<td>(IV)</td>
<td>(V)</td>
</tr>
<tr>
<td>HN=C=O</td>
<td>(I) *</td>
<td>14</td>
<td>0</td>
<td>HN=C=O</td>
<td>(I)</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>(II)</td>
<td>55</td>
<td>45</td>
<td>(II)</td>
<td>(I)</td>
<td>12</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>(VI)</td>
<td>43</td>
<td>57</td>
<td>(VI)</td>
<td>(I)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>HN=C=O</td>
<td>(I)</td>
<td>39</td>
<td>61</td>
<td>HNEt2</td>
<td>(I)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>(II)</td>
<td>13</td>
<td>87</td>
<td></td>
<td>(II)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>(VI)</td>
<td>11</td>
<td>89</td>
<td></td>
<td>(VI)</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

* The main product is allylamine (X).

The result of the reaction of olefin (I) with pyrrolidine, a relatively nonbulky and strongly basic amine, was unexpected. It was found that it readily reacts directly (i.e., without isomerization) with (I) to form allylamine (X), while no enamine (IV) was detected, and only 14% of (V) was formed. Hence, in the case of the reaction with pyrrolidine, the isomerization of (I) into (II) is inappreciable, and further transformation into (III) does not generally occur.

The structure of aminoolefin (X), which is relatively stable in an ether solution, was unequivocally confirmed by spectral methods, but attempts to isolate it in a pure state were unsuccessful. On storage, allylamine (X) gradually converts into a nitrogen-containing bicyclic olefin (XI).

It is clear that the mobile F₂ atom splits in the form of an anion, while the cationoid particle (A) formed is stabilized by elimination of a proton from the α-carbon atom of the pyrrolidine ring. The intramolecular cyclization of the zwitterion (B) leads to the formation of compound (XI).* Besides (XI) compound (XII) was isolated, which clearly was obtained as the result of a nucleophilic substitution of the vinyl F atom in the molecule of (XI) by the action of excess of pyrrolidine. The structure of compounds (XI) and (XII) was confirmed by spectral methods.

Aminoolefin (X)† is readily hydrolyzed in a weakly acid medium and converts into vinyl ketone hydrate (XIII). Vinyl ketone (XIV) was isolated by distillation from H₂SO₄

* Similar intramolecular reactions are described in [8].
† A solution of aminoolefin (X) in ether was used, which was obtained immediately after olefin (I) and pyrrolidine were mixed.