4-Hydroxy-4-phenylethynyl-2,2,6,6-tetramethylpiperidine (IV). A mixture of 155 g of (I) in 150 ml of EtOH, 250 ml of 20% ethanolic KOH solution, 102 g of phenylacetylene, and 300 ml of liquid NH₃ was kept in an autoclave for 8 h at ~20 °C. After the same workup as in the synthesis of (III), we obtained 146 g (56.8%) of (IV) as a white crystalline powder with mp 108 °C (hexane). Found: C 79.35; H 8.87; N 5.31%; mol. wt. 257 (mass spectrometry). C₁₇H₂₃NO. Calculated: C 79.38; H 8.95; N 5.45%.

CONCLUSIONS

A convenient method was proposed for the preparation of acetylenic carbinols of the 2,2,6,6-tetramethyl-piperidine series by the ethynylation of 2,2,6,6-tetramethyl-4-oxopiperidine in liquid ammonia in the presence of alcoholic alkali.

LITERATURE CITED


REDUCTION OF PERFLUOROCARBOXYLIC ACID ANHYDRIDES TO 1,1-DIHYDROPERFLUORO ALCOHOLS

G. D. Kolomnikova, M. I. Kalinkin, Z. Ts. Tskhurbaeva, Z. N. Parnes, and D. N. Kursanov

1,1-Dihydroperfluoroalcohols are usually obtained by the reduction of perfluorocarboxylic acids or their derivatives with aluminum lithium hydride [1]. Methods for the catalytic hydrogenation of perfluorocarboxylic acid derivatives have received little study. Trifluoroacetic anhydride [2] and trifluoroacetamide [3] are hydrogenated to trifluoroethanol on Adams catalyst. Copper chromite catalyzes the hydrogenation of perfluorocarboxylic esters to the corresponding alcohols at 210 °C and a pressure of 250 atm [4].

Recently it was proposed [5] to use trimethylsilane for the reduction of perfluoro acid fluorides in the presence of Pt/C, ZnCl₂, and KF. The reaction is run in an autoclave at 160–210 °C, and the yield of the formed esters or lactones in the case of dibasic acids is 10–30%. The drastic conditions of the last reaction can be explained by the absence of a sufficiently strong electrophilic agent in the reaction sphere, which activates the carbonyl group for reaction with the silane.

We found that perfluorocarboxylic anhydrides are easily reduced by organohydroxilanes in the presence of the corresponding acids (Table 1). The reaction proceeds under mild conditions, is preparatively simple, and leads to a mixture of the alcohol and its ester with the starting acid. The triethyl- and diphenylsilanes give comparable results in the reduction of the perfluoro anhydrides.

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TABLE 1. Reduction of Perfluoro Anhydrides with Triethylsilane Et₃SiH: \( \text{RFCO}_2\text{O}:\text{RFCOOH} = 2.2:1.5 \) (moles), 50 °, 3 h

<table>
<thead>
<tr>
<th>Anhydride</th>
<th>Reaction products</th>
<th>( \delta_{\text{CH}} ) ppm</th>
<th>( J_{\text{HF}} ) Hz</th>
<th>Total yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (\text{CF}_2\text{CO})_2\text{O} )</td>
<td>( \text{CF}_3\text{CH}_2\text{OH} ) [\text{CF}_3\text{CH}_2\text{OCOCF}_3 ]</td>
<td>3.8</td>
<td>8</td>
<td>60</td>
</tr>
<tr>
<td>( (\text{CF}_3\text{CO})_2\text{O} )</td>
<td>( \text{CF}_3\text{CH}_2\text{OH} ) [\text{CF}_3\text{CH}_2\text{OCOCF}_7 ]</td>
<td>3.8</td>
<td>13</td>
<td>60</td>
</tr>
<tr>
<td>( (\text{C}_3\text{F}_6\text{CO})_2\text{O} )</td>
<td>( \text{HOOC}\left(\text{CF}_2\right)_3\text{CH}_2\text{OH} ) *</td>
<td>3.9</td>
<td>11</td>
<td>80</td>
</tr>
</tbody>
</table>

*It was not ascertained whether the product is formed as the hydroxy acid or as the lactone.

TABLE 2. Catalytic Reduction of Perfluoro Acid Anhydrides (catalyst 0.02 g, anhydride 1-1.5 g, acid 1-1.5 g)

<table>
<thead>
<tr>
<th>Anhydride</th>
<th>Yield of [\text{Et}_3\text{SiCHO}_2\text{COOR} : \text{Et}_3\text{SiCH}_2\text{OH} ], %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (\text{CF}_3\text{CO})_2\text{O} )</td>
<td>55</td>
</tr>
<tr>
<td>( (\text{CF}_3\text{CO})_2\text{O} )</td>
<td>60</td>
</tr>
<tr>
<td>( (\text{CF}_3\text{CO})_2\text{O} )</td>
<td>80</td>
</tr>
</tbody>
</table>

It may be assumed that the reaction begins with the hydrosilylation of the carbonyl group of the anhydride to give product A, which is converted by the acid to compound B, the reaction of which with the acid and silane leads to the ester:

\[
\begin{align*}
\text{(R}_{2}\text{CO})_2\text{O} + \text{Et}_3\text{SiH} & \rightarrow \text{R}_{2}\text{CH(OEt}_3\text{)}\text{OCOR} \text{B} \\
\text{R}_{2}\text{CH(OEt}_3\text{)}\text{OCOR} + \text{Et}_3\text{SiH} & \rightarrow \text{R}_{2}\text{CH(OEt}_3\text{)}\text{OCOR} + \text{Et}_3\text{SiOCOR} \\
\end{align*}
\]

The intermediate compounds A and B were recorded via the PMR spectrum of the mixture (quadruplets at 5.7 and 7.3 ppm, \( J_{\text{HF}} = 3 \) Hz) when the reaction was run with a catalytic amount of \( \text{CF}_3\text{CO}_2\text{H} \). In the comparable \( \text{R-CH(OOCF}_3\text{)}_2 \) compounds the chemical shift of the methine protons is 6 ppm [6].

In the reduction of carbonyl compounds the system silane-\( \text{CF}_3\text{COOH} \) resembles certain hydrogenating systems of composition: \( \text{H}_2 - \text{catalyst-}\text{CF}_3\text{COOH} \) [7]. We found that when perfluoro acid anhydrides are reduced in the corresponding acids as the medium, in the presence of homogeneous [\( (\text{Ph}_3\text{P})_2\text{PtCl}_2 \) and \( \text{Ru(OOCF}_3\text{)}_3 \)] and heterogeneous (Pto₂) catalysts, the same products are formed as when they are reduced with silanes.

The catalytic hydrogenation proceeds by the following overall equation:

\[
\begin{align*}
\text{catalyst} & \rightarrow \text{R}_{2}\text{CH}_2\text{OCOR} + \text{H}(\text{H}_2) \\
\text{R}_{2}\text{CH}_2\text{OCOR} & \rightarrow \text{R}_{2}\text{CH}_2\text{OCOOR} + \text{H}2 \\
2\text{R}_{2}\text{CH}_2\text{OCOR} & \rightarrow \text{R}_{2}\text{CH}_2\text{OCOR} + \text{H}2 \\
\end{align*}
\]

The yields of the reduction products, calculated using this equation, are given in Table 2.

A comparison of the data given in Tables 1 and 2 reveals that all of the studied hydrogenation systems give close results in the reduction of perfluorocarboxylic acid anhydrides.

**EXPERIMENTAL**

The compounds \( (\text{CF}_3\text{CO})_2\text{O} \) and \( (\text{C}_3\text{F}_7\text{CO})_2\text{O} \) were obtained by distilling the corresponding acids over \( \text{P}_2\text{O}_5 \), bp 39.5-40.5 and 106-106.5°, respectively (cf. [8, 9]). The compound \( (\text{C}_3\text{F}_6\text{CO})_2\text{O} \) was obtained as described in