NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.
TRANSLATION

DERIVATIVES OF PERFLUODICARBONIC ACIDS

By

I. L. Knunyants and M. P. Krasnaya

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

WRIGHT-PATTERSON AIR FORCE BASE
OHIO
UNEDITED ROUGH DRAFT TRANSLATION

DERIVATIVES OF PERFLUOROCARBONIC ACIDS

BY: I. L. Knunyants and M. P. Krasuska

English Pages: 6

SOURCE: Russian Periodical, Izvestiya AN SSSR, Oth, Nr. 1, 1963, pp 190-192

8/62-63-0-1

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-afb, OHIO.

Date 26 May 1963
DERIVATIVES OF PERFLUODICARBONIC ACIDS

by

I. L. Knunyants and M. P. Krasuskaia

In a report published previously there is a description of obtaining higher perfluodicarboxylic acids by the oxidation of \(\text{CF}_2\) \text{CF} \((\text{CF}_2)\_n \text{CF} = \text{CF} \text{NaO} \) \(\text{HOOC} \) \((\text{CF}_2)\_n \text{COOH}\) (1)

\[
\begin{align*}
\text{CF}_2 &= \text{CF} - (\text{CF}_2)\_n \text{CF} = \text{CF} \text{NaO} \\
\text{HOOC} &= (\text{CF}_2)\_n \text{COOH}
\end{align*}
\]

In continuing the work in the synthesis and use of perfluodicarboxylic acids we prepared some bifunctional derivatives of perfluorodicarboxylic, perfluorobisacetic, and perfluododeca-methylene-dicarbonic acids obtained by oxidation of perfluorodecadiene, perfluorododecadiene, and perfluorohexadecadiene, respectively. There were prepared chloranhydrides, esters, amides, nitriles, and amidines of the acids indicated by the following procedure:

\[
\begin{align*}
\text{HOOC} - (\text{CF}_2)\_n \text{COOH} + \text{H}_2\text{COO} & \xrightarrow{\text{NaOH}} \text{C}_2\text{H}_4\text{OOC} - (\text{CF}_2)\_n \text{COOC}_2\text{H}_4\text{NH}_2 \xrightarrow{\text{H}_2\text{NCO} (\text{CF}_2)\_n \text{CONH}_2} \\
\end{align*}
\]

(2)

From the same perfluodicarboxylic acids—perfluorodicarboxylic, perfluorobisacetic, and perfluododeca-methylene-dicarbonic—through the reduction of their ethyl esters by sodium borohydride in diglyme in the presence of anhydrous ammonium chloride there were synthesized the respective \(\sigma, \omega\)-tetrahydro-perfluorododecadiene and \(\sigma, \omega\)-tetrahydro-perfluorohexadecadiene:

\[
\begin{align*}
\text{C}_2\text{H}_4\text{OC}O - (\text{CF}_2)\_n \text{COOC}_2\text{H}_4 \xrightarrow{\text{NaBH}_4, \text{AnhCl}} \text{CH}_4\text{OCH}_2 - (\text{CF}_2)\_n \text{CH}_2\text{OH}
\end{align*}
\]

(3)

The method of reduction of the sodium borohydride was taken by us for the first time for the reduction of esters of perfluodicarboxylic acids, and it showed a number of advantages over reduction by lithium-aluminum-hydride in ether solutions.

Some bifunctional derivatives of perfluodicarboxylic acids; for example, amidines and \(\sigma, \omega\)-tetrahydro-perfluorododecadiene, were used for obtaining polymer compounds.

PMD-74-545/1 + 2
Experimental Part

Obtaining derivatives of perfluoricarbonic acids Esters. 0.05 of a mole of perfluoricarbonic acid are dissolved in 30 to 50 ml of abs. ethanol, there is added 1.5 ml of fluosulfonic acid, and the whole is heated in a boiling-water bath for 1.5 hours. The solution is poured into cold water, and the flaked oil is taken into ether, washed with a solution of NaHCO₃ and water, dried and distilled. One gets diethyl esters of perfluoradipic acid, b. p. 96—97°/7 mm, nD²⁰ 1.3541, d₂⁰ 1.426, yield 90%; perfluorobasic acid, b. p. 118—120°/5 mm, nD²⁰ 1.3424, d₂⁰ 1.578, yield 95%; perfluododeca-methylene-dicarbonic acid, b. p. 142—143°/5 mm, nD²⁰ 1.3408, d₂⁰ 1.606, yield 70%. There were found %: C 28.22; H 1.14; F 61.63; C₁₈H₁₀O₄F₂₄. Computed %: C 28.95; H 1.34; F 61.12.

Chloranhydrides. 0.02 of a mole of perfluoricarbonic acid was mixed with 0.08 to 0.1 of a mole of SOCl₂, there is added 0.01 of a mole of KOH and 2 to 3 drops of pyridine, and the whole is heated in a boiling-water bath for several hours (until complete solution of the acid). The excess of SOCl₂ is evaporated out and the product of the reaction is distilled. One gets chloranhydrides: of perfluoradipic acid, b. p. 130—132°, nD²⁰ 1.3484, yield 78%, perfluorobasic acid, b. p. 115—117°/40 mm, m. p. 29—30°, yield 78%; perfluododeca-methylene-dicarbonic acid, b. p. 161°/50 mm, m. p. 92—95°, yield 74%. There were found %: C 23.37; F 61.84; Cl₂₁O₉F₂₄. Computed %: C 23.10, F 62.72.

Amides. 0.05 of a mole of ethyl esters of perfluoricarbonic acid are dissolved in 50 to 60 ml of abs. ester, and a current of dry NH₃ is passed through until saturation. One gets amides of perfluoricarbonic acids with a yield of 95—98%; amide of perfluoradipic acid, m. p. 235 to 238°, amide of perfluorobasic acid, m. p. 233—239°, amide of perfluododeca-methylene-
dichrbonic acid, m. p. 242—244°. There were found %: C 24.01; H 0.72; F 66.41; N 3.48; C14H02F22N2. Computed %: C 24.41; H 0.59; F 66.28.

**Nitriles.** 0.02—0.05 of a mole of amide of perfluodicarbonic acid is mixed with 0.1—of a mole of P2O5 and heated in Wood's bath at 100—300° with simultaneous evaporation of nitrile being formed. In obtaining the nitrile of perfluododeca-methylene-dicarbonic acid the evaporation is done in a vacuum. The nitriles obtained are distilled once more: nitrile of perfluoradipic acid, b. p. 63°, yield 77%; nitril of fluosebacid acid, b. p. 147—148°, nD 1.3039, d = 1.673, yield 80%. There were found %: C 26.10; F 67.63; H 6.70; C10F16N2. Computed %: C 26.54; F 67.25; H 6.19; nitril of perfluododeca-methylene-dicarbonic acid, b. p. 115—120°/10 mm, m. p. 78 (from acetone). There were found %: C 26.08; F 69.25 H 4.34; C14F24N2.

**Amidines.** 0.02—0.05 of a mole of perfluodicarbonic acid are placed in a two-necked retort with a reverse cooler for dry ice (CO2); one adds from a dropping funnel in 2—3 operation 30—40 ml of liquid ammonium, maintains at room temperature for 2 hours, and then leaves for evaporation of the ammonium. In the deposit one gets amidines of perfluodicarbonic acids with a yield of 96—99% in the form of white or yellowish powders. On crystallizes from acetone; one obtains: amide of perfluoradipic acid, m. p. 154° (literature data 147—125°). There were found %: C 25.39; H 2.02; F 52.67; N 19.80; C6H02F24N4. Computed %: C 25.10; H 2.0; F 53.15; N 19.58; amidine of perfluosebacid acid, m. p. 173—175° (with Diff.). There were found %: C 24.40; H 1.40; F 62.12; N 11.02; C10H6F16N4. Computed %: C 24.69; H 1.23; F 62.55; N 11.52. For obtaining amine of perfluododeca-methylene-dicarboxylic acid a mixture of nitrile and liquid ammonia is kept at room temperature for 10 to 12 hours in a closed steel test tube. After removing the ammonia the amine dodecamethylene-dicarbonate is washed with acetone.
and ether, m. p. 187—190° (with Diff.) There were found %: C 24.20; 
H 0.94; F 66.60; N 7.96; C_{14}H_{6}F_{24}N_{21}. Computed %: C 24.48; H 0.87; 
F 66.47; N 8.16.

The obtaining of α, α, γ, ω-tetrahydro-perfluodiol In a three-necked retort with a stirrer, reverse cooler, and a dropping funnel one dissolves 0.04 of a mole of NaBE in 25—30 of dry diglyme (dimethyl ether of dimethylene glycol); from the dropping funnel one adds a solution of 0.015 moles of freshly sublimated AlCl₃ in 25—30 ml of diglyme and afterwards a solution of 0.02 moles of ethyl ether of perfluoricarbonic acid in diglyme at such a rate that the reaction takes place with moderate cooling. After finishing the addition of the ether one stirs for about 1 hour at room temperature, then while heating in a water bath at 50—60° during the course of 30 to 40 min. After cooling the reaction mixture is gradually transferred to 100 to 200 ml of ice water, made acid by 10 to 15 ml of concentrated hydrochloric acid. The solution obtained goes two or three times through ether extraction. The extract is washed several times with water, dried, and distilled. After evaporation of the ether and a small quantity of diglyme one get crystalline or oil-like residue, which begins to crystallize with the addition of a small amount of chloroform. For final purification of the diols obtained they are distilled in a vacuum or crystallized from CHCl₃ or CCl₄. One gets α, α, γ, ω-tetrahydrohexandiol HOCH₂{(CF₂)₄CH₂OH, b. p. 118—120°/11 mm, m. p. 67—68°, yield 80%; phenylurethane, b. p. 140° (from CCl₄). There were found %: C 48.37; H 3.29; F 31.04; C_{20}H_{16}F_{10}O₂. Computed %: C 48.00; H 3.60; F 30.40; α, α, γ, ω-tetrahydroperfluoredecandiol HOCH₂{(CF₂)₆CH₂OH, b. p. 135—136°, yield 90%. There were found %: C 25.85; H 1.18; F 68.18; C_{10}H₆F₁₆O₂. Computed %: C 25.96; H 1.29; F 67.96, phenylrethane, b. p. 140—141° (from CCl₄). There were found %: C 41.44; H 2.44; F 43.35; N 3.98; C_{26}H_{16}F₁₆O₄.
Computed \%: C 41.14; H 2.25; O 43.42. *or, a, a,*, -tetrahydroperfluorotetradecandiol HOCH$_2$(CF$_2$)$_{12}$CH$_2$OH, b. p. 163—184$^\circ$, yield 67\%. There were found \%:

C 25.27; H 0.93; F 69.68. \( \text{C}_{14}\text{H}_2\text{O}_2\text{F}_{24} \). Computed \%: C 25.37; H 0.90; F 69.88.

Phenylurethane, b. p. 153—154$^\circ$. There were found \%: C 37.6\%; H 1.61;

F 50.01; C$_{20}$H$_{16}$O$_4$F$_{24}$H$_2$. Computed \%: C 37.33; H 1.77; F 50.66.

**Conclusions**

1. From the above perfluoricarbonic acids of the general formula HOOC — (CF$_2$)$_n$COOH, where \( n = 4, 8, 12 \) obtained from products of telomerisation of tetrafluorethyene by trifluodichloro-iodethane there were synthesised bi-functional derivatives—chloranhydrides, esters, amides, nitriles and amidines.

2. By reduction of esters of perfluoradipic, perfluosebacic, and perfluodecimethylene-dicarbonic acids using sodium borhydride in the presence of anhydrous ammonium chloride, there were obtained the corresponding \( \alpha, \omega, \omega, \omega - \text{tetrahydroperfluorodiols of the general formula HOCH}_2 — (\text{CF}_2)_n\text{CH}_2\text{OH}, where } n = 4, 8, 12. $$

**Literature Cited**


# DISTRIBUTION LIST

## DEPARTMENT OF DEFENSE

<table>
<thead>
<tr>
<th>Agency</th>
<th>Nr. Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFSC</td>
<td>1</td>
</tr>
<tr>
<td>SCFDD</td>
<td>1</td>
</tr>
<tr>
<td>DDC</td>
<td>25</td>
</tr>
<tr>
<td>TDEBL</td>
<td>5</td>
</tr>
<tr>
<td>TDEDP</td>
<td>2</td>
</tr>
<tr>
<td>TDRX (Honaker)</td>
<td>1</td>
</tr>
<tr>
<td>ASD (ASYIM)</td>
<td>2</td>
</tr>
<tr>
<td>ESD (ESY)</td>
<td>1</td>
</tr>
<tr>
<td>SSD (SSF)</td>
<td>2</td>
</tr>
</tbody>
</table>

## HEADQUARTERS USAF

<table>
<thead>
<tr>
<th>Agency</th>
<th>Nr. Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFCIN-3D2</td>
<td>1</td>
</tr>
<tr>
<td>ARL (ARB)</td>
<td>1</td>
</tr>
</tbody>
</table>

## OTHER AGENCIES

<table>
<thead>
<tr>
<th>Agency</th>
<th>Nr. Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIA</td>
<td>1</td>
</tr>
<tr>
<td>NSA</td>
<td>6</td>
</tr>
<tr>
<td>DIA</td>
<td>9</td>
</tr>
<tr>
<td>AID</td>
<td>2</td>
</tr>
<tr>
<td>OTS</td>
<td>2</td>
</tr>
<tr>
<td>AEC</td>
<td>2</td>
</tr>
<tr>
<td>PWS</td>
<td>1</td>
</tr>
<tr>
<td>NASA</td>
<td>1</td>
</tr>
<tr>
<td>ARMY (FSTC)</td>
<td>3</td>
</tr>
<tr>
<td>NAVY</td>
<td>3</td>
</tr>
<tr>
<td>NAFEC</td>
<td>1</td>
</tr>
<tr>
<td>RAND</td>
<td>1</td>
</tr>
<tr>
<td>AFCRL (CRXLR)</td>
<td>1</td>
</tr>
</tbody>
</table>