known mixtures of (I) and (V) and the second product had a spectrum identical to that of
the known (IVb), obtained according to [4].

**Interaction of (I) with Zinc and Hydrochloric Acid.** To the mixture of 12.5 ml (0.1
mole) of (I), 6.7 g of zinc, and 20 ml of abs. benzene were added, with stirring at ~20°C,
8 ml (0.1 mole) of concentrated HCl in the course of 20 min. The temperature was thereby
raised to the boiling point. The reaction mixture was stirred for 1 h and was left at ~20°C
for 2 days. To the mixture were added 30 ml of 10% HCl in portions. The solution obtained
was extracted with ether (3 × 50 ml) and the ether extracts were washed with water until a
neutral pH was obtained. The extracts were dried with MgSO₄ and the solvent was evaporated
in vacuo prior to distillation. The yield of 6.85 g of the product was obtained; it had the
bp 75-73°C (10 mm) and the np₂⁰ 1.4358. According to the PMR data, the ratio of (I) : (V)
is 23:4.

**LITERATURE CITED**

2549 (1988).
2. N. S. Vul'fson and L. Kh. Vinograd, Reactions and Methods of the Investigation of Or-

**NITRATION OF FLUOROETHYLENES BY NITRATING MIXTURE (HNO₃ + H₂SO₄ + SO₃)**

I. V. Martynov, V. I. Uvarov, V. K. Bre'l',
V. I. Anufriev, and A. V. Yarkov

UDC 542.958.1:547.413.1

The nitration of fluoroethylenes with sulfuric-nitric mixtures and added sulf-
uric anhydride was studied. It was shown that acid fluorides of halogenonitro-
acetic acids are formed in the nitration of fluoroethylenes containing the fluoro-
chloromethylene fragment, whereas nitroethylfluorosulfates are the main reaction
product in the nitration of ethylenes having the difluoromethylene grouping. The
structure of the compounds obtained was shown by the data of ¹⁹F and ¹H NMR and
IR spectroscopy.

The nitration of fluorinated ethylenes has been studied in detail. Two most practica-
ble methods of nitration are known: the radical nitration with oxides of nitrogen [1] and
the ionic nitration with nitrating mixture [2]. The ionic nitration is the most convenient
for the synthesis of halogenonitrocarbonyl compounds. The mechanism of the nitration of
halogenoethylenes, assuming the formation of acid fluorides of halogenonitrocarboxylic acids
as the intermediate compounds, was proposed; however they could not be isolated or detected
[3].

With the object of widening the synthetic possibilities of ionic nitration, as well as
specifying the mechanism of the reaction, we developed a method for the nitration of fluoro-
olefins using the mixture of HNO₃, H₂SO₄, and SO₃. The addition of SO₃ to the nitrating
mixture leads to the binding of water and prevents the hydrolysis of the resulting acid

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Fluoride. It is also known that SO₃ promotes the formation of the nitronium cation [4]. We showed that the nitration of fluoroethylenes of the general formula CRX=CFCI by the nitrat- ing mixture consisting of HNO₃ (99%), H₂SO₄ (100%), and oleum (60%) at 5-15°C leads to the formation of halogenonitroacetyl fluorides (I)-(III) [5].

\[
\text{CRX=CFCI + HNO₃ + H₂SO₄ + SO₃} \rightarrow \text{O₃NCRXC(O)F \quad (I)-(III)}
\]

When the nitration was carried out under analogous conditions, but without the added oleum, the corresponding halogenonitroacetic acids (VIII) and (IX) were obtained. The acid fluorides (I)-(III) are readily volatile liquids, fuming in air. The reaction with alcohols results in the formation of the corresponding esters. The structure of (I)-(III) was esta- blished using spectral data (Table I). The intense absorption bands of the carbonyl group (1600-1560 cm⁻¹) and the nitro group (1835-1880 cm⁻¹) are present in the IR spectrum. The shift of the absorption band of the \(\equiv\text{C=O} \) group to the high-frequency region is associated with the influence of the electron-acceptor substituents and is in agreement with the data for trifluoroacetyl fluoride [6]. The PMR spectra of (I) and (II) contain the doublet signal with \(\delta 6.0-6.5 \text{ ppm (J}_\text{H-F} = 1-3 \text{ Hz)} \). The \(^{19}\text{F} \) NMR spectra in the region of 95-110 ppm have the characteristic signals of acid fluorides [7] and (III) has the additional signal of

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>PMR spectrum (δ, ppm)</th>
<th>(^{19}\text{F} ) NMR spectrum (δ, ppm; J, Hz)</th>
<th>IR spectrum (ν, cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>O₃NCHClC(O)F</td>
<td>6.58 d (1H, CHCl)</td>
<td>106.17 d (1F, COF, (\text{J}_{\text{F-H}} = 0.9))</td>
<td>2980 1860 1598</td>
</tr>
<tr>
<td>(II)</td>
<td>O₃NCHBrC(O)F</td>
<td>6.08 d (1H, CHBr)</td>
<td>99.08 d (1F, COF, (\text{J}_{\text{F-H}} = 3.1))</td>
<td>3010 1875 1600</td>
</tr>
<tr>
<td>(III)</td>
<td>O₃CF₂C(O)F²</td>
<td>-</td>
<td>(\delta_1 = 11.93 \text{ d, t} ) (\text{J}<em>{\text{F-N}} = 10.8); (\delta_2 = 93.9) d (1F, COF, (\text{J}</em>{\text{F-F}} = 10.8))</td>
<td>- 1835 1558</td>
</tr>
<tr>
<td>(IV)</td>
<td>O₃CF₂C₂O₂SO₂F³</td>
<td>-</td>
<td>(\delta_1 = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 10.5); (\delta_2 = -6.58 \text{ t, d (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_3 = 128.7 \text{ t (1F, SO}<em>2\text{F)} (\text{J}</em>{\text{F-F}} = 141.0); (\delta_4 = 82.38 \text{ d, t (1F, CHF)} (\text{J}<em>{\text{F-F}} = 3.65 \text{ m}); (\delta_5 = 126.8 \text{ t (1F, SO}<em>2\text{F)} (\text{J}</em>{\text{F-F}} = 8.4); (\delta_6 = 3.75 \text{ m (1F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_7 = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_8 = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_9 = 3.75 \text{ m (1F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta</em>{10} = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4);</td>
<td>- 1485 (as) 1560 (s)</td>
</tr>
<tr>
<td>(V)</td>
<td>O₃NCHF₂C(OSO₂F)²</td>
<td>6.2 d, t (1H, CHF)</td>
<td>(\delta_{11} = 46.5) (\text{J}<em>{\text{H-F}} = 141.0); (\delta</em>{12} = 8.4) (\text{J}<em>{\text{H-F}} = 8.4); (\delta</em>{13} = 3.65 \text{ m (1F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{14} = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{15} = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4);</td>
<td>- 1485 (as) 1560 (s)</td>
</tr>
<tr>
<td>(VI)</td>
<td>O₃NCFC(O)H</td>
<td>9.17 t (1H, COH)</td>
<td>(\delta_{16} = 2.7) (\text{J}<em>{\text{H-F}} = 2.7); (\delta</em>{17} = 5.95 \text{ t, d (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.0); (\delta_{18} = 127.53 \text{ t (1F, SO}<em>2\text{F)} (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{19} = 3.75 \text{ m (1F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{20} = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{21} = 3.75 \text{ m (1F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{22} = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4);</td>
<td>2850 1740 1600</td>
</tr>
<tr>
<td>(VII)</td>
<td>O₃NCH₂CF₂OSO₂F³</td>
<td>5.93 t (2H, CH₃)</td>
<td>(\delta_{23} = 9.0) (\text{J}<em>{\text{H-F}} = 2.7); (\delta</em>{24} = 5.95 \text{ t, d (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.0);</td>
<td>2995 1480 (as) 1595</td>
</tr>
<tr>
<td>(VIII)</td>
<td>O₃NCFCICOOH</td>
<td>11.80 s (1H, OH)</td>
<td>(\delta_{25} = 3.50 \text{ s (1F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{26} = 3.75 \text{ m (1F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{27} = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{28} = 3.75 \text{ m (1F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4); (\delta_{29} = 25.3 \text{ t (2F, CF}<em>2) (\text{J}</em>{\text{F-F}} = 8.4);</td>
<td>3550 3550</td>
</tr>
<tr>
<td>(IX)</td>
<td>O₃NCHClCOOH</td>
<td>11.08 s (1H, CHCl)</td>
<td>-</td>
<td>3500 3150 1750 1558</td>
</tr>
</tbody>
</table>