### REACTION OF DIFLUORO- AND FLUOROCHLORONITROACETIC

# ACIDS WITH MERCURIC OXIDE

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The mercuric salts of haloacetic acids are known to be reactive compounds. The most well-studied of these compounds are the salts of perhalo acids [1, 2]. The reactions of the mercury salts of halonitrocarboxylic acids have not been studied. In a continuation of a study on halonitrocarboxylic acids, we investigated the reaction of difluoro- and fluorochloronitroacetic acids with mercuric oxide:

$$NO_{2}CF_{2}COOH + HgO \longrightarrow \begin{pmatrix} Et_{2}O \\ WO_{2}CF_{2}COO\right)_{2}Hg + H_{2}O \\ \downarrow RPh \qquad (I) \\ RPh \\ NO_{2}CF_{2}COOHgC_{6}H_{4}R \\ (II) - (IV) \end{pmatrix}$$

Fokin et al. [3] have shown that difluoronitroacetic acid reacts with HgO in ether to form mercury salt (I) [3]. We have found that upon carrying out this reaction in aromatic solvents, mercuration of the aromatic ring occurs with formation of arylmercury salts of difluoronitroacetic acid (II)-(IV). These compounds were also obtained by heating salts (I) in aromatic solvents at 70-90°C, which is in accord with the results of the analogous reaction for trichloro- and trifluoroacetic acids [4, 5]. Salts (II)-(IV) are crystalline compounds with low solubility in acetone, ether, and benzene. Their structure was proven using IR, <sup>19</sup>F NMR, and mass spectroscopy (Table 1). Thus, the mass spectrum of (I) has strong signals corresponding to the molecular ion M<sup>+</sup> 419 and fragment ions. The fragmentation proceeds initially with the loss of a CO<sub>2</sub> molecule ([M - CO<sub>2</sub>]<sup>+</sup> 375) and subsequent loss of the NO<sub>2</sub> group ([M - CO<sub>2</sub> - NO<sub>2</sub>]<sup>+</sup> 329).

In contrast to difluoronitroacetic acid, fluorochloroacetic acid reacts with yellow HgO in absolute ether to form previously unreported di(fluorochloronitromethyl)mercury [6]:

$$NO_{2}CFCICOOH + HgO - \overbrace{(V)}^{Et_{2}O} (NO_{2}CFCl)_{2}Hg + CO_{2} + H_{2}O \xrightarrow{(V)} (V)$$

$$R = H (VI), Me (VII), F (VIII).$$

The reaction proceeds in this case as for trichloroacetic acid through the formation of mercury fluorochloronitroacetate and subsequent spontaneous decarboxylation [7]. Salt (V) is a white crystalline compound which is stable in organic solvents but decomposes upon prolonged standing as a result of intramolecular nucleophilic attack of the chlorine atom with the formation of mercuric chloride. The structure of (V) was established by spectral methods (see Table 1).

Carrying out the reaction in aromatic solvents leads to the formation of aryl derivatives of mercuric chloride. The reaction likely proceeds as in the case of difluoronitroacetic acid but, as a consequence of their low stability, arylmercury salts of fluorochloronitroacetic acid decarboxylate to form (VI)-(VIII). The physicochemical indices of arylmercuric chlorides (V)-(VIII) are in full accord with literature values [8]. The spectral indices are given in Table 1.

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TABLE 1. IR, <sup>19</sup>F NMR, and Mass Spectral Data for Compounds Synthesized (I)-(VIII)

| Compound | <sup>19</sup> F NMR<br>spectra, δF,<br>ppm | IR spectra,<br>v, cm <sup>-1</sup>                                             | Mass spectra                                                                                                                                                                                                                                                                                    |
|----------|--------------------------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| (I)      | 14,61                                      | 1718 (C=O)<br>1585 (NO <sub>2</sub> )                                          | 436[M-NO <sub>2</sub> ] <sup>+</sup> , 346[(M-2NO <sub>2</sub> -CO <sub>2</sub> )] <sup>+</sup> ,<br>202[Hg] <sup>+</sup>                                                                                                                                                                       |
| (11)     | 14,00                                      | 1702 (C=O)<br>1597 (NO <sub>2</sub> )<br>1648 (C <sub>6</sub> H <sub>5</sub> ) | 419M <sup>+</sup> , 375 [M–CO <sub>2</sub> ] <sup>+</sup> , 356[M–CO <sub>2</sub> –F] <sup>+</sup> ,<br>329[M–CO <sub>2</sub> –NO <sub>2</sub> ] <sup>+</sup> , 279[C <sub>6</sub> H <sub>5</sub> –Hg] <sup>+</sup> ,<br>202[Hg] <sup>+</sup> , 77[C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup> |
| (III)    | 14,50                                      | 1700 (C=O)<br>1597 (NO <sub>2</sub> )<br>1644 (C <sub>6</sub> H <sub>4</sub> ) | 433M+, 389[M–CO <sub>2</sub> ]+, 343[M–CO <sub>2</sub> –<br>NO <sub>2</sub> ]+, 293 [CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Hg]+, 91[CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ]+                                                                                                    |
| (IV)     | 13,90                                      | 1702 (C=O)<br>1587 (NO <sub>2</sub> )<br>1646 (C <sub>6</sub> H <sub>4</sub> ) | $437M+$ , $393[M-CO_2]+$ , $347[M-CO_2-NO_2]+$ , $202[Hg]+$ , $95[C_6H_4F]+$                                                                                                                                                                                                                    |
| (V)      | 2.75<br>$J_{F-C-Hg} = 817.4 Hz$            | 1560 (NO <sub>2</sub> )                                                        | 426M+, 380[M–NO <sub>2</sub> ]+, 334 [M–2NO <sub>2</sub> ]+,<br>299[M–2NO <sub>2</sub> –Cl]+                                                                                                                                                                                                    |
| (VI)     | -                                          | 1644 (C <sub>6</sub> H <sub>5</sub> )                                          | 314M+, 279[M–Cl]+, 77[M–Hg–Cl]+                                                                                                                                                                                                                                                                 |
| (VII)    |                                            | 1645 (C <sub>6</sub> H <sub>4</sub> )                                          | 328M+, 293[M-Cl]+, 91[M-Hg-Cl]+                                                                                                                                                                                                                                                                 |
| (VIII)   | _                                          | 1646 (C <sub>6</sub> H <sub>4</sub> )                                          | 332M+, 297[M-Cl]+, 95[M-Hg-Cl]+                                                                                                                                                                                                                                                                 |

#### EXPERIMENTAL

The <sup>19</sup>F NMR spectra were taken on a Bruker CXP-200 spectrometer at 188 MHz with  $CF_3CO_2H$  as the external standard. The IR spectra were taken on a Specord IR-75 spectrometer, while the mass spectra were taken on a Finnigan mass spectrometer with a direct inlet system. The ionization chamber temperature was 150°C, and the ionizing voltage was 70 and 18 eV.

A sample of mercuric difluoronitroacetate (I) was obtained according to Fokin et al. [3].

<u>Phenylmercury Salt of Difluoroacetic Acid (II)</u>. A sample of 80 ml benzene was added to 4.81 g (0.01 mole) (I) and heated at 70-100°C until (I) was completely dissolved. The reaction mixture was evaporated, and the isolated precipitate was dried in vacuum to yield 3.14 g (75%) (II), mp 85°C (dec.). Found: F 9.00; N 2.98%. Calculated for  $C_8H_5F_2$ HgNO<sub>4</sub>: F 9.03; N 3.24%.

<u>p-Tolylmercury Salt of Difluoronitroacetic Acid (III).</u> This salt was obtained by analogy with (II) from (I) and toluene in 68% yield, mp 140°C (dec.). Found: F 9.41: N 3.15% Calculated for  $C_9H_7F_2HgNO_4$ : F 9.03; N 3.24%.

<u>p-Fluorophenylmercury Salt of Difluoronitroacetic Acid (IV)</u>. This salt was obtained by analogy with salt (II) from (I) and fluorobenzene in 73.1% yield, mp 125°C (dec.). Found: 13.28; N 3.82%. Calculated for  $C_8H_4F_3NO_4$ : F 13.07; N 3.21%.

<u>Di(fluorochloronitromethyl)mercury (V).</u> A sample of 4.1 g (19 mmoles) yellow HgO was added with stirring to a solution of 6 g (38 mmoles) fluorochloronitroacetic acid in 20 ml abs ether at 20°C. The reaction mixture was stirred for 5 h and left overnight. The solution was filtered, and the filtrate was evaporated to give 9.4 g (58%) (V), mp 107°C (dec.). Found: F 9.11; N 6.61%. Calculated for  $C_2F_2Cl_2HgN_2O_4$ : F 8.92; N 6.80%.

Phenylmercuric Chloride (VI). A sample of 13.08 g (0.06 mole) yellow HgO was added in small portions with rapid stirring to a solution of 9.45 g (0.06 mole) fluorochloronitroacetic acid in 40 ml of benzene. Unreacted HgO was removed after 3 h, and the residue was evaporated. The isolated salt was dried in vacuum to yield 4.04 g (70% relative to reacted HgO) (VI), mp 250°C [8].

p-Tolylmercuric chloride (VII) was obtained by analogy with (VI) from toluene in 65% yield, mp 230°C [8].

p-Fluorophenylmercuric chloride (VIII) was obtained by analogy with (VI) from fluorobenzene in 75% yield, mp 280°C [8].

#### CONCLUSIONS

The reaction of difluoronitroacetic acid with mercuric oxide in aromatic hydrocarbons proceeds by mercuration of the aromatic ring and formation of arylmercury salts of difluoronitroacetic acid. Aryl derivatives of mercuric chloride are obtained in the case of fluorochloronitroacetic acid.

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# CHLORINATION OF 3,6-DI-TERT-BUTYL-0-BENZOQUINONE BY SULFURYL CHLORIDE

| v. | Α. | Garnov, V. I. | Nevodchikov, G. A. Abakumov,     | UDC 542.944:547.567:546. |
|----|----|---------------|----------------------------------|--------------------------|
| v. | ĸ. | Cherkasov, L. | G. Abakumova, and Yu. A. Kurskii | 226'131-31               |

In order to expand the range of sterically hindered o-benzoquinones, we studied the chlorination of 3,6-di-tert-butyl-o-benzoquinone (I) by  $SO_2Cl_2$ . Ershov et al. have shown that the reactions of HCl with (I) [1] or of  $Cl_2$  and 3,6-di-tert-butylpyrocatechol (II) [2] cannot introduce two chlorine atoms. However, Peratoner [3] established that the reaction of two equivalents of  $SO_2Cl_2$  with pyrocatechol in absolute ether in the cold leads to the formation of 4,5-dichloropyrocatechol. In the present work, we have shown that under analogous conditions, (II) gives 5,6-dichloro-3,6-di-tert-butyl-3-cyclohexene-1,2-dione (III):



Here and subsequently, X = t-Bu.

The action of diethylamine on (III) in pentane gives 4-chloro-3,6-di-tert-butyl-obenzoquinone (IV) [1], which reacts with one equivalent of  $SO_2Cl_2$  in the presence of HCl to give 4,5,6-trichloro-3,6-di-tert-butyl-3-cyclohexene-1,2-dione (V). Upon treatment with amine, dione (V) is converted to 4,5-dichloro-3,6-di-tert-butyl-o-benzoquinone (VI):

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