

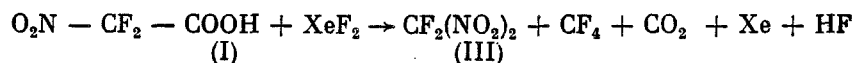
REACTION OF FLUOROCHLORONITROACETIC AND DIFLUORONITROACETIC ACIDS  
WITH XENON DIFLUORIDE

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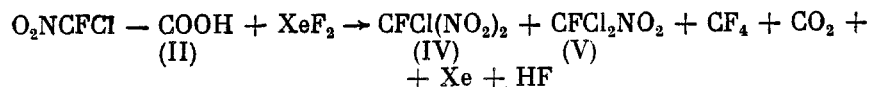
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The use of xenon difluoride in preparative organic chemistry has recently been expanded [1]. Thus, carboxylic acids react with  $\text{XeF}_2$  to undergo decarboxylation with subsequent fluorination [2, 3].  $\text{XeF}_2$  has been used by Shachelford [4] and Shaw [5] as a convenient fluorinating reagent. The reaction of  $\text{XeF}_2$  with nitro compounds has virtually not been studied [6].

We studied the reaction of  $\text{XeF}_2$  with difluoronitroacetic (I) and fluorochloronitroacetic acids (II) in a study of the reactivity of halonitrocarboxylic acids [7]. In contrast to unsubstituted carboxylic acids [2, 3], (I) and (II) react with  $\text{XeF}_2$  for dihalodinitromethanes (III) and (IV) and a series of side products.



$\text{XeF}_2$  reacts with (I) in  $\text{CH}_2\text{Cl}_2$  with cooling to give difluorodinitromethane (III) identical to the compound described by Eremenko [8].  $\text{CF}_4$ ,  $\text{Xe}$ , and  $\text{CO}_2$  were detected by mass spectrometry in the gaseous products. The formation of  $\text{CF}_4$  was also indicated by  $^{19}\text{F}$  NMR spectroscopy ( $\delta$  13.8 ppm) [9].



Under analogous conditions,  $\text{XeF}_2$  reacts with (II) to give fluorochlorodinitromethane (IV),  $\text{CF}_4$ ,  $\text{CO}_2$ ,  $\text{Xe}$ ,  $\text{HF}$ , and fluorodichloronitromethane (V). These reactions probably proceed through the formation of dihalonitromethyl radicals [6], which may react with the initial (I) and (II), or, upon decomposition, may serve as sources of  $\text{NO}_2$  and  $\text{Cl}$  radicals. Recombination with these radicals leads to nitromethanes (III)-(V).

EXPERIMENTAL

The  $^{19}\text{F}$  NMR spectra were obtained on a Bruker CXP-200 spectrometer at 188 MHz relative to  $\text{CF}_3\text{CO}_2\text{H}$ . The IR spectra were taken on a Specord IR-75 spectrometer for  $\text{CCl}_4$  solutions. The mass spectra were taken on a Finnigan mass spectrometer at 70 eV. The temperature of the ionization chamber was 120°C.

Reaction of Difluoronitroacetic Acid with  $\text{XeF}_2$ . A sample of 1.41 g (0.01 mole) (I) was dissolved in 5 ml  $\text{CH}_2\text{Cl}_2$ . A sample of 1.69 g (0.01 mole)  $\text{XeF}_2$  was added in portions with cooling to 5-10°C. The reaction mass turned dark red and gas evolution was noted. The gases were collected in two consecutive traps cooled to -70 and -196°C. At the end of the reaction, the residue was distilled to give 0.54 g (38%) (III), bp 36-38°C,  $n_D^{12}$  1.3462,  $d_4^{12}$  1.5697 [8]. Found, %: C 7.94; F 27.15; N 19.68.  $\text{CF}_2\text{N}_2\text{O}_4$ . Calculated, %: C 8.45; F 26.95; N 19.72.  $^{19}\text{F}$  NMR spectrum ( $\delta$ , ppm): -6.36 m ( $J_{\text{F-N}} = 11.5$  Hz). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1625 ( $\text{NO}_{2\text{AS}}$ ), 1305 ( $\text{NO}_{2\text{S}}$ ). Mass spectrum (m/z): 50 [ $\text{M} - \text{NO}_2$ ] $^+$ , 46 ( $\text{NO}_2$ ) $^+$ , 30 ( $\text{NO}$ ) $^+$ .  $\text{CF}_4$  was isolated from the gaseous products,  $^{19}\text{F}$  NMR spectrum ( $\delta$ , ppm): 13.8 s [9]. Mass spectrum (m/z): 69 [ $\text{M} - \text{F}$ ] $^+$ , 50 ( $\text{CF}_2$ ) $^+$ , 31 ( $\text{CF}$ ) $^+$  [10]. We also isolated  $\text{CO}_2$  (m/z 44) and xenon (m/z 129).

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**Reaction of Fluorochloronitroacetic Acid with XeF<sub>2</sub>.** The reaction was carried out by analogy to the above procedure to give (IV) in 28% yield, bp 86°C,  $n_D^{20}$  1.4093,  $d_4^{20}$  1.6198. Found, %: C 8.13; N 16.98. CFC1N<sub>2</sub>O<sub>4</sub>. Calculated, %: C 7.59; N 17.72. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 9.28 m ( $J_{F-N}$  = 11.5 Hz) [11]. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1615 (NO<sub>2as</sub>), 1326 (NO<sub>2s</sub>). Mass spectrum (m/z): 66.68 (CFC1)<sup>+</sup>, 46 (NO<sub>2</sub>)<sup>+</sup>, 30 (NO)<sup>+</sup>. The gaseous products CF<sub>4</sub>, CO<sub>2</sub>, and xenon were identified as in the preceding reaction. The <sup>19</sup>F NMR spectrum of (V) ( $\delta$ , ppm): 37.01 t ( $J_{F-N}$  = 11 Hz). Mass spectrum (m/z): 101 (CFC1<sub>2</sub>)<sup>+</sup>, 68 (CFC1)<sup>+</sup>, 46 (NO<sub>2</sub>)<sup>+</sup>, 31 (CF)<sup>+</sup>, and 30 (NO)<sup>+</sup>. IR spectrum ( $\nu$ , cm<sup>-1</sup>, gas phase): 1625 (NO<sub>2as</sub>), 1325 (NO<sub>2s</sub>) [12].

#### CONCLUSIONS

Dihalodinitromethanes are formed in the reaction of difluoronitroacetic and fluorochloronitroacetic acids with xenon difluoride.

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#### ENANTIOSELECTIVITY IN COPPER COMPLEXES OF $\alpha$ -AMINOALKYLPHOSPHONIC

#### ACIDS

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$\alpha$ -Aminoalkylphosphonic acids (APA) hold interest as phosphoric analogs of natural amino acids. Racemic APA have been studied in considerable detail [1, 2]. A series of APA and their derivatives have been obtained in optically active form [3, 4]. The absolute configuration has been established for some of these compounds [5, 6].

Enantioselective effects are very common in complexes of optically active amino acids [7]. We have shown such effects for labile mixed APA complexes by ligand-exchange chromatography [8]. In the present work, potentiometric titration was used to study enantioselectivity in labile copper complexes of racemic (R, S) and optically active (R)  $\alpha$ -aminobenzylphosphonic (H<sub>2</sub>L<sup>I</sup>) and  $\alpha$ -amino- $\alpha$ -methylbenzylphosphonic acids (H<sub>2</sub>L<sup>II</sup>). These systems were selected because enantioselective effects are clearly evident in the copper complexes of amino acids [7], while the methods for the synthesis and separation of the enantiomers of these APA are well known [4, 8]. The absolute configuration has not been established for (-)-H<sub>2</sub>L<sup>II</sup> (in 5 HCl) and has been arbitrarily taken as R.

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