ALIPHATIC FLUORO NITRO COMPOUNDS

COMMUNICATION 1. CONJUGATED NITROFLUORINATION OF OLEFINS

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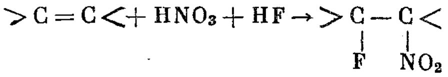
Aliphatic fluoro nitro compounds have not received adequate study, largely because of the absence of convenient methods of preparation [1-3]. Recently, Titov and co-workers have shown that trichloroethylene, vinylidene chloride, and vinyl chloride react with a mixture of nitric acid and hydrogen fluoride with formation of the corresponding β-fluoro nitro compounds [4].

We have found that the reaction of olefins with nitric acid in anhydrous hydrogen fluoride is a general method for the preparation of β-fluoro nitro compounds. This method consists in the simultaneous addition of a nitro group and a fluorine atom to an olefin molecule, the result of the reaction of conjugated nitrofluorination:



$$>C=C< + HNO_3 + HF \rightarrow >\underset{F}{C}-\underset{NO_2}{C}<$$

We studied the conjugated nitrofluorination of vinyl chloride, allyl chloride, methyl acrylate, vinylidene fluoride, trifluoroethylene, tetrafluoroethylene, perfluoropropene, and 1,1,1,4,4,4-hexafluoro-2-butene.

It was found that the conjugated nitrofluorination of olefins goes readily without pressure at low temperatures. The rate of nitrofluorination does not depend greatly on the excess of hydrogen fluoride and is determined by the character of the double bond of the olefin. For example, vinyl chloride reacts with nitric acid and hydrogen fluoride even at −60°, but if the electron density of the double bond of the olefin is reduced as a result of the presence of a powerful electronegative substituent, the reaction rate falls sharply. This indicates the electrophilic character of the nitrofluorination reaction. Thus, at −60°, the rate of reaction of trifluoroethylene is only one-sixth of that of vinyl chloride, and chlorotrifluoroethylene and tetrafluoroethylene do not react at all with nitric acid and hydrogen fluoride. Only at 10-20° does the slow nitrofluorination of chlorotrifluoroethylene and tetrafluoroethylene occur. Further reduction in the electron density of the double bond of the olefin leads to a still greater reduction in reaction rate. Thus,

Reaction of Olefins with Nitric Acid in Anhydrous Hydrogen Fluoride

Olefin	Fluoro nitro compound	Reaction temp.°C	Yield, %
$CHCl=CH_2$	$CHFCl-CH_2NO_2$	−60	58,7
$CH_2Cl-CH=CH_2$	$CH_2Cl-CHF-CH_2NO_2$ $CH_2Cl-CH(NO_2)-CH_2F$	−10	18,8
$CH_2=CH-COOCH_3$	$CH_2X-CH(NO_2)COOCH_3$*	0	~10
$CF_2=CH_2$	$CF_3-CH_2NO_2$	−60	57,6
$CF_2=CFH$	$CF_3-CFHNO_2$	−60	85,8
$CF_2=CFCl$	$CF_3-CFClNO_2$, $CF_2Cl-CF_2NO_2$	10	88,1
$CF_2=CF_2$	$CF_3-CF_2NO_2$	20	93,1
$CF_3-CF=CF_2$	—	20	Does not react
$CF_3-CH=CH-CF_3$	—	150	The same

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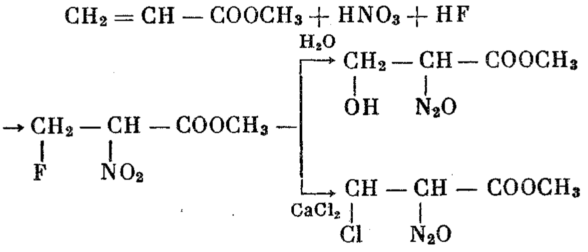
*X = Cl or OH.

perfluoropropene does not react at 20°, and 1,1,1,4,4,4-hexafluoro-2-butene does not react with nitric acid in anhydrous hydrogen fluoride even when the mixture is heated in an autoclave to 150°.

As will be seen from the table, the conjugated nitrofluorination of olefins usually leads to the formation of one reaction product in high yield. However, when the polarization of the double bond of the olefin is not marked, two isomeric products may be formed. Thus, in the reaction of allyl chloride with HNO_3 and HF, we obtained 1-chloro-2-fluoro-3-nitropropane and 1-chloro-3-fluoro-2-nitropropane in relative amounts of 1 : 2, as was shown by the NMR spectrum of F^{19} in the mixture obtained:

$$CH_2Cl-CH=CH_2+HNO_3+HF$$
$$\to CH_2Cl-CHF-CH_2NO_2+CH_2Cl-CH(NO_2)-CH_2F$$

The reaction of methyl acrylate with nitric acid and hydrogen fluoride went in accordance with the usual reaction scheme for conjugated nitrofluorination. When hydrogen fluoride was removed from the reaction mixture after the reaction by washing with water, the replacement of fluoro by hydroxyl occurred, and instead of the expected methyl 3-fluoro-2-nitropropionate we obtained methyl 3-hydroxy-2-nitropropionate. If, however, hydrogen fluoride was removed by treatment with calcium chloride, fluorine was replaced by chlorine with formation of methyl 3-chloro-2-nitropropionate:



$$CH_2=CH-COOCH_3+HNO_3+HF$$
$$\to \underset{F}{CH_2}-\underset{NO_2}{CH}-COOCH_3 \xrightarrow{H_2O} \underset{OH}{CH_2}-\underset{N_2O}{CH}-COOCH_3$$
$$\to \underset{F}{CH_2}-\underset{NO_2}{CH}-COOCH_3 \xrightarrow{CaCl_2} \underset{Cl}{CH}-\underset{N_2O}{CH}-COOCH_3$$

In all the other cases, when the reaction mixture was treated with water or calcium chloride the replacement of the fluorine atom did not occur.

EXPERIMENTAL

Vinyl chloride, HF, and HNO_3. A mixture of 130 ml of anhydrous HNO_3 and 300 ml of HF was prepared in a steel reactor, and in the course of 90 min at −60°, 2.8 moles of vinyl chloride was passed in. The mixture was stirred further for 1 h and then poured onto ice and extracted ten times with ether. The ethereal solution was washed with water, dried with calcium chloride, and distilled. We obtained 208.6 g (58.7%) of 1-chloro-1-fluoro-2-nitroethane; b.p. 64-67° (30 mm); $n^{20}D$ 1.4279, d^{20}_4 1.4740; symmetric and antisymmetric valence vibrations of the NO_2 group at 1380 and 1575 cm^{-1}. NMR spectrum of F^{19}: one peak with a chemical shift corresponding to the CHFCl group. Found: C 18.81, 18.60; H 2.30, 2.12; F 14.85, 15.15%. MR 21.74; mol. wt. 126. $C_2H_3FClO_2N$. Calculated: C 18.83; H 2.37; F 14.90%; MR 21.82; mol. wt. 127.5.

Allyl chloride, HF, and HNO_3. Seventy-six g of allyl chloride was added over a period of 2 h at −10° to a mixture of 86 ml of HNO_3 and 300 ml of HF. The mixture was stirred further for 1 h and then poured onto ice and extraced five times with ether. The combined ethereal solutions were washed with saturated aqueous urea solution and with water, dried with calcium chloride, and distilled. The distillate, which boiled over a wide range, was fractionated through a column, and we obtained 26.7 g (18.8%) of a mixture of 1-chloro-2-fluoro-3-nitropropane and 1-chloro-3-fluoro-2-nitropropane; b.p. 64-69° (3 mm); $n^{20}D$ 1.4487; d^{20}_4 1.4156. The symmetric valence vibration of the NO_2 group gave a broad absorption band at 1365-1380 cm^{-1}; the antisymmetric vibration of the NO_2 group was at 1565 cm^{-1}. NMR spectrum of F^{19}: two peaks of relative areas 2 : 1. The larger peak had a chemical shift characteristic for the CH_2F group, and the smaller peak, for the CHF group.

Found: C 25.20, 25.16; H 3.49, 3.33; F 14.01, 14.15%; MR 26.79; mol. wt. 141. $C_3H_5FClO_2N$. Calculated: C 25.47; H 3.56; F 13.43; MR 26.44; mol. wt. 141.5.

Methyl acrylate, HF, and HNO_3. Eighty-six g of methyl acrylate was added over a period of 2 h at 0° to a mixture of 100 ml of HF and 47 ml of HNO_3. The mixture was stirred further for 2 h and then either (1) anhydrous calcium chloride was sprinkled in, or (2) the mixture was diluted with water; it was then extracted with ether. We obtained: 1) methyl 3-chloro-2-nitropropionate; b.p. 60-62° (1.5 mm); $n^{20}D$ 1.4620; d^{20}_4 1.3941; symmetric and antisymmetric valence vibrations of the NO_2 group 1370 and 1560 cm^{-1}, valence vibrations of the $C=O$ group 1730 cm^{-1}. Found: C 28.75, 28.93; H 3.39, 3.45; Cl 20.69, 20.83; N 8.59, 8.44%; MR 33.04; mol. wt. 169. $C_4H_6ClO_4N$. Calculated: C 28.66; H 3.60; Cl 21.15; N 8.36%; MR 32.81; mol. wt. 167. 2) Methyl 3-hydroxy-2-nitropropionate, m.p. 46-47° (hexane-chloroform). Symmetric and antisymmetric valence vibrations of the NO_2 group 1378 and 1560 cm^{-1}, valence vibrations of the $C=O$ group 1730 cm^{-1}. Found: C 32.17, 31.97; H 4.69, 4.68; N 9.35, 9.26%; mol. wt. 149. $C_4H_7O_5N$. Calculated: C 32.22; H 4.73; N 9.39%; mol. wt. 149.

Vinylidene fluoride, HF, and HNO_3. A mixture of 600 ml of HF and 240 ml of HNO_3 was prepared in a steel reactor, and at −60° vinylidene fluoride was passed in at 150 liters/h. After 50 min the absorption of gas ceased (5.38 moles was absorbed), the mixture was poured onto 3 kg of ice, the lower layer was separated, and the upper layer was extracted three times with ether. The combined solutions were washed with water, dried with calcium chloride, and distilled through a fractionating column. We obtained 400 g (57.6%) of 1,1,1-trifluoro-2-nitroethane; b.p. 43° (106 mm); $n^{20}D$ 1.3300; $d^{20}{}_4$ 1.5122. Symmetric and antisymmetric valence vibrations of the NO_2 group 1365 and 1578 cm^{-1}. NMR spectrum of F^{19}: one peak with a chemical shift corresponding to the CF_3 group.

Found: C 18.85, 18.95; H 1.47, 1.38; F 44.58, 44.97%; MR 17.41; mol. wt. 130. $C_2H_2F_3O_2N$. Calculated: C 18.62; H 1.56; F 44.19%; MR 17.47; mol. wt. 129.

Trifluoroethylene, HF, and HNO_3. A mixture of 300 ml of HF and 95 ml of HNO_3 was prepared in a steel reactor, and at −60° trifluoroethylene was passed in at 15 liters/h. After 5.5 h the gas feed was stopped (2.0 moles was absorbed), the mixture was poured onto ice, the lower layer was separated, and the upper layer was extracted with ether. The combined solutions were washed with water, dried, and distilled through a fractionating column. We obtained 252.5 g (85.8%) of tetrafluoronitroethane; b.p. 56°; $n^{20}D$ 1.3019; $d^{20}{}_4$ 1.5552. Symmetric and antisymmetric valence vibrations of the NO_2 group 1352 and 1600 cm^{-1}. NMR spectrum of F^{19}: two peaks of relative areas 3 : 1. The larger peak had a chemical shift characteristic for the CF_3 group, and the smaller for the CHF group.

Found: C 16.40, 16.48; H 0.70, 0.67; F 51.69, 51.70%; MR 17.78; mol. wt. 146. $C_2HF_4O_2N$. Calculated: C 16.34; H 0.69; F 51.70%; MR 17.62; mol. wt. 147.

Chlorotrifluoroethylene, HF, and HNO_3. A mixture of 86 ml of HNO_3 and 200 ml of HF was prepared in a steel reactor, and at 10° chlorotrifluoroethylene was passed in. The gases leaving the reactor were washed with water and then passed through a column containing anhydrous calcium chloride and into a trap cooled to −20°. In the course of 7 h, 1.26 moles of gas was absorbed. The mixture was poured onto ice, and the lower layer was separated, washed with water, combined with the contents of the trap, dried, and distilled. We obtained 200 g of a mixture of 1-chlorotetrafluoro-1-nitroethane and 1-chlorotetrafluoro-2-nitroethane; b.p. 35-37°, $n^{20}D$ 1.3160; $d^{20}{}_4$ 1.5971. NMR spectrum of F^{19}: three signals with relative areas of 1 : 1 : 2.

Found: C 13.19, 13.02; F 41.21, 41.16%; MR 22.29; mol. wt. 179. $C_2H_4ClO_2N$. Calculated: C 13.23; F 41.87%; MR 22.48; mol. wt. 181.5.

Tetrafluoroethylene, HF, and HNO_3. A mixture of 300 ml of HF and 135 ml of HNO_3 was prepared in a steel reactor, and with stirring at 20° tetrafluoroethylene was passed for 7 h (64 liters at 750 mm and 20° was passed). The gases leaving the reactor were washed with water, passed through a column containing anhydrous calcium chloride, and condensed in a trap cooled to −100°. The condensate was fractionated through a low-temperature column. We obtained 46.6 liters of tetrafluoroethylene, 21.3 g of blue-colored pentafluoronitroethane, boiling from −4 to −2.4° and containing traces of pentafluoronitrosoethane, and 88 g of pentafluoronitroethane of b.p. from −2.4 to −2°. The total yield of pentafluoronitroethane was 93.1%. NMR spectrum of F^{19}: two peaks of relative areas 3 : 2. The larger peak had a chemical shift characteristic for the CF_3 group, and the smaller for the $C-CF_2-N$ grouping. Molecular weight: found 164.6, calculated from $C_2F_5O_2N$, 165. The literature [2] gives b.p. −1 to 0°.

SUMMARY

The conjugated nitrofluorination of olefins was studied. This reaction provides a convenient method for the synthesis of various β-fluoro nitro compounds.

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