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Abstract

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ON NEW INTERESTING CASES OF THE FORMATION OF NITROSO COMPOUNDS

In 1956–1957 the results of investigations on the nitration of perfluoroolefins with nitrogen dioxide were published (^{1}), and a new extensive class of organofluorine compounds was found: α-nitroperfluorocarboxylic acids and their numerous derivatives: complex esters, chloro-, bromo-, and fluoroanhydrides, amides, nitriles, etc. The study of the chemical properties of α-nitroperfluorocarboxylic acids and their derivatives, in particular derivatives of nitrodifluoroacetic acid, unexpectedly led to the discovery of a new and interesting reaction proceeding with the formation of difluorochloronitrosomethane.

This reaction was first observed upon heating the ethyl ester of nitrodifluoroacetic acid with hydrochloric acid, when a blue gas with b.p. -36° was formed. The boiling point, quantitative analysis, molecular weight, etc., made it possible to identify this gas as difluorochloronitrosomethane.

$$\mathrm{O_2N-CF_2-COOR+HCl\longrightarrow CF_2ClNO+CO_2+ROH}$$

The mechanism of this reaction is very interesting and has features in common with the conversion of nitroparaffins into carboxylic acids and hydroxylamine, which occurs under the action of concentrated acids. Upon heating difluoronitroacetic acid with concentrated hydrochloric acid, decarboxylation occurs with the formation of the aci-form of difluoronitromethane:

$$\mathrm{F_2CNO_2-COOH\longrightarrow F_2C=N(O)OH+CO_2}$$

The formation of aci-forms of nitroparaffins during decarboxylation of nitrocarboxylic acids is well proved by the example of the decarboxylation of nitroacetic acid in the presence of bromine, leading to the formation of bromonitromethane. The latter could have formed from the aci-form, since it is well known that nitroparaffins are brominated only in the form of aci-forms.

$$CH_2NO_2 - COOH \xrightarrow[-CO_2]{} H_2C = N(O)OH \xrightarrow{Br_2} CH_2Br - NO_2 + HBr$$

The acid difluoronitromethane formed during the decarboxylation of difluoronitroacetic acid is an incomparably weaker acid than hydrochloric acid and, with respect to the latter, plays the role of a base.

$$F_2C = N(O)OH + H^+ \longrightarrow [CF_2 = N = O]^+ + H_2O$$

Next, the cation thus formed is attacked by the chloride anion and is converted into a chloronitroso compound.

$$\begin{bmatrix} CF_2 \\ N \\ O \end{bmatrix}^+ + Cl^- \longrightarrow CF_2Cl - N = O$$

As is evident from the scheme given below, this reaction is analogous to the above-mentioned decomposition of nitroparaffins. In the case of acid difluoronitromethane, the absence of a hydrogen atom at the carbon atom bonded to nitrogen leads to arrest of the reaction at the stage of formation of the nitroso compound. Analogously, it has been shown that the introduction of the sodium salts of 2-nitropropane and nitrocyclohexane into an ethereal solution of hydrogen chloride leads to

$$R - CH_2 - NO_2 \rightarrow R - CH = N(= O)OH \xrightarrow{H^+} [R - CH = N = O]^+ + H_2O$$

$$[R - CH = N = O]^+ \rightarrow R - \overset{+}{C}H - \overset{:}{N} = O \xrightarrow{Cl^-} R - CH(Cl) - NO \rightarrow R - C(Cl) = NOH \xrightarrow{H_2O} R - COOH + NH$$

$$O_2N - CF_2 - COOH \xrightarrow{-CO_2} F_2C = N(= O)OH \xrightarrow{H^+} [F_2C = N = O]^+ + H_2O$$

$$[F_2C = N = O]^+ \rightarrow F_2\overset{+}{C} - \overset{:}{N} = O \xrightarrow{Cl^-} F_2C(Cl) - NO$$

to the formation of stable chloronitroso compounds:

$$(CH_3)_2CH - NO_2 \xrightarrow{RONa} (CH_3)_2C = N(O)ONa \xrightarrow{HCl} (CH_3)_2C(Cl)NO$$

$$\text{Nitrocyclohexane} \xrightarrow{R'ONa} \text{sodium salt of aci-nitrocyclohexane} \xrightarrow{HCl} 1,1\text{-chloronitrosocyclohexane}$$

By this method it proved possible to obtain 2,2-chloronitrosopropane and 1,1-chloronitrosocyclohexane in high yield.

It was also possible to show that introducing the salt of acinitrocyclohexane into a 50–40% solution of anhydrous hydrogen fluoride in ether is accompanied by the ether solution turning an intense blue color. Evaporation, even in vacuo, of the ethereal solution washed free of excess hydrogen fluoride and dried leads to disappearance of the blue color and the appearance of colorless crystals with m.p. 65–68°.

Dissolving the colorless compound thus obtained in benzene is accompanied by an intense blue coloration. In the melt the substance likewise becomes blue. The substance obtained contains no fluorine; its behavior is entirely similar to that of crystalline dimers of nitroso compounds. It may be assumed that in the molecule of the initially formed 1,1-fluoronitrosocyclohexane the carbon–fluorine bond is considerably weakened by the presence of the electron-donor nitroso group, and this compound spontaneously splits off a molecule of hydrogen fluoride, forming nitrosocyclohexene:

$$\text{Nitrocyclohexane} \xrightarrow{\text{RONa}} \text{sodium salt of aci-nitrocyclohexane} \xrightarrow{\text{HF}} \text{aci-nitrocyclohexane} \rightarrow$$

$$\rightarrow [\text{cyclohexylidene-N} = \text{O}]^{+} \xrightarrow{-\text{F}^{-}} \text{1-fluoro-1-nitrosocyclohexane} \xrightarrow{-\text{HF}} [\text{nitrosocyclohexene}]_2$$

blue in solution

colorless, m.p. 65–68°,
blue in solution and in the melt

In dilute solutions nitrosocyclohexene exists in monomeric form, and therefore its solutions are colored; in crystalline form it is a colorless dimer. Nitrosocyclohexene is a rare example of a nitroso compound containing a nitroso group attached to a carbon atom with a multiple bond.

Dimerization of aliphatic nitroso compounds is evidently connected with the coordinative unsaturation of the nitrogen atom and, in its character, resembles salt formation:

$$2\,R-N=O \;\longrightarrow\; R-N^{+}(O^{-})-N(=O)-R$$

The more electronegative the character of the radical, the lower the tendency of the nitroso compound toward dimerization. It is precisely this circumstance that explains the fact that difluorochloronitrosomethane, like trifluoronitrosomethane, is monomeric also in the liquid state (b.p. −36°). An attempt to extend the method for forming chloronitroso compounds to examples of other nitroso compounds encountered unexpected limitations. In the case of salts of nitromalonic ester and nitroform, chloronitroso compounds cannot be obtained.

Experimental Part

I. Difluorochloronitrosomethane

From ethyl nitrodifluoroacetate. Into a flask fitted with a reflux condenser and an outlet to a gasometer were introduced 4.4 g of ethyl nitrodifluoroacetate and 5 ml of 21% hydrochloric acid. The flask was heated on a boiling water bath until the ether layer disappeared. The blue gas formed in this process was collected in the gasometer and fractionated. B.p. of the substance: $-35, -36°$.

CF_2ClNO.	Found %:	F 34.2; Cl 30.5
	Calculated %:	F 32.9; Cl 30.8

From tetrafluoroethylene and nitrogen oxides. a) Preparation of an aqueous solution of nitrodifluoroacetic acid. Into a hermetically closing steel reactor of 70 ml capacity, cooled with liquid oxygen, air, or nitrogen, were introduced successively: nitrogen dioxide (10 g), dry carbon tetrachloride (20 ml), and tetrafluoroethylene (15 g). After sealing, the reactor was placed in a steel block chamber and kept there at room temperature for not less than 5 days. After the reactor had been opened and the temperature of its contents brought to 0°, the reaction mass was poured into a three-necked flask cooled with an ice-salt mixture and equipped with a reflux condenser, a dropping funnel, and a vigorously operating stirrer. To the reaction mass was added 20 ml of water at such a rate that the temperature of the contents of the flask did not rise above 0°. After all the water had been added, the mixture was vigorously stirred for another 15 min, after which the aqueous layer was separated, and the organic layer was washed once more with 10 ml of water, which was combined with the first portion. The freshly obtained aqueous solution of nitrodifluoroacetic acid, after alkalimetric determination of its content in the solution, was used to obtain difluorochloronitrosomethane.

b) Into a three-necked flask of 1.5 l capacity, fitted with a reflux condenser, a dropping funnel, and a thermometer, were introduced 400 ml of concentrated hydrochloric acid. After heating in a water bath to boiling, addition was begun of a solution of 48 g of nitrodifluoroacetic acid in 200 cm^3 of water. The blue-colored gas formed was collected over a saturated aqueous solution of sodium chloride. A total of 26.3 g of substance was collected, which after fractionation had b.p. $-35, -36°$.

Yield based on nitrodifluoroacetic acid: 67%.

CF_2ClNO.	Found %:	F 32.0; Cl 31.0
	Calculated %:	F 32.9; Cl 30.8

Molecular weight found: 116.5; calculated: 115.5.

II. 1,1-Chloronitrosocyclohexane

To 8 g (0.052 mole) of nitrocyclohexane, cooled with an ice-salt mixture, with continuous stirring, was added an alcoholic solution of sodium ethylate prepared from 1.2 g of sodium and 15 ml of absolute ethyl—

ethyl alcohol. To the reaction mixture, 20 ml of dry sulfuric ether was added and the mixture was thoroughly stirred. The precipitated salt of aci-nitrocyclohexane was filtered off and washed twice on the filter with dry ether. The salt, ground to a powder, was added in small portions with stirring to ether saturated with hydrogen chloride and cooled with an ice-salt mixture. The volume of ether was 100 ml.

Addition of the salt was accompanied by the appearance of a persistent blue color. After the entire amount of salt had been added, the ethereal solution of 1,1-chloronitrosocyclohexane was washed with cold water, twice with a saturated sodium bicarbonate solution, again with water, and dried with ignited magnesium sulfate. After removal of the ether, the product was distilled in vacuo. There was collected 7.2 g of a dark-violet liquid with b.p. 49–50°/11 mm. From the residue in the flask, 1.2 g of nitrocyclohexane returned from the reaction was isolated.

The yield of 1,1-chloronitrosocyclohexane, based on the nitrocyclohexane that entered into the reaction, was 93%; d_4^{20} 1.0552; molecular weight found 144.5, calculated 147.6.

$C_6H_{10}ONCl$.	Found, %:	N 9.32;	Cl 23.85
	Calculated, %:	N 9.48;	Cl 24.02

III. 2,2-Chloronitrosopropane

By the procedure described for 1,1-chloronitrosocyclohexane, the interaction was carried out between the salt of aci-nitropropane, obtained from 2 g of 2-nitropropane and a solution of 0.43 g of metallic sodium in 10 ml of absolute ethyl alcohol, and hydrogen chloride dissolved in 45 ml of absolute ether. Introduction of the salt into the ethereal solution of hydrogen chloride was accompanied by the appearance of a persistent blue color. After the entire amount of salt had been added, the ethereal solution of 2,2-chloronitrosopropane was washed with cold water, twice with a saturated aqueous solution of sodium bicarbonate, again with water, and then dried with magnesium sulfate. After removal of the ether, the residue was distilled in vacuo. There was collected 2.2 g of an intensely violet liquid with b.p. 33–34°/108 mm. The yield of 2,2-chloronitrosopropane was about 90%; d_4^{20} 1.001; molecular weight found 110.10, calculated 107.54.

IV. Nitrosocyclohexene

To 50 ml of sulfuric ether, cooled with an ice-salt mixture, 20 ml (1 mole) of liquid hydrogen fluoride was added in small portions with constant stirring. To the resulting solution, also with vigorous stirring, 15.2 g (0.1 mole) of dry, thoroughly pulverized sodium salt of aci-nitrocyclohexane was added. Introduction of the salt was accompanied by the solution becoming intensely blue.

After the entire amount of salt had been added, the solution was carefully poured into 200 ml of ice water. The ether layer was separated, washed three times with water, and dried with ignited magnesium sulfate. Removal of the ether in vacuo was accompanied by decoloration of the solution and precipitation of white crystals. The crystals were filtered off from the remaining nitrocyclohexane and washed with a small amount of ether. There was collected 2.5 g of crystals. From the reaction, 4.5 g of nitrocyclohexane was recovered. The yield of crystalline dimer, based on the nitrocyclohexane that entered into the reaction, was about 25%. In benzene the colorless crystals dissolve with the formation of an intense blue color. After recrystallization from benzene, the substance melts at 65-68° and contains no fluorine.

C_6H_9ON.	Found, %:	N 13.1
	Calculated, %:	N 12.62

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CITED LITERATURE

1. I. L. Knunyants, A. V. Fokin, *DAN*, **111**, No. 5, 1035 (1956); **112**, No. 1, 67 (1957); *Izv. AN SSSR, OKhN*, 1957, No. 12, 1440.

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