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Abstract

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NITROSOCHLORINATION OF OLEFINS AND THEIR DERIVATIVES BY AN IONIC MECHANISM

ANOMALOUS ADDITION TO CHLOROETHYLENES

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Nitrosation as substitution is realized for very active forms of unsaturated compounds, for example for enolate ions, similar to ArO^-:

$$RCH{=}CR{-}O^-$$

We also observed rapid nitrosation of mercury derivatives

$$RCH{=}CH{-}HgX,$$

similar to the reactions of Ar−HgX. However, for olefins themselves, under the action of nitrosating agents NOX, the formation of addition products

$$O{=}N{-}CR_2{-}CR_2{-}X$$

is characteristic.

According to the theory developed in 1941-1945 ([1–3]), the most active nitrosating agent is the nitrosyl cation

$$O{=}N^+,$$

owing to its maximal electrophilicity and coordination unsaturation and, consequently, its ability to form transition complexes through interaction with mobile and spatially accessible *p*- or π-electrons, for example, respectively, of amines R_2NH and olefins

$$R_2C{=}CR_2.$$

In particular, the preparation of nitrates

$$ON{-}CR_2{-}CR_2{-}ONO_2$$

by the action of a solution of N_2O_4 in conc. HNO_3 was considered as conjugate addition of ON^+ and NO_3^- to the π-bond of olefins ([2,3]).

The formation of nitrosochlorides

$$ON{-}CR_2{-}CR_2{-}Cl$$

with the less active

$$O{=}N^+ {-}Cl$$

proceeds readily only with reactive olefins. Nitrosochlorination of ethylene and, as a rule, of haloethylenes was not successful ([4–6]). For example, after prolonged standing (3-15 days at 20°) of mixtures of NOCl with chloro- and fluoroethylenes in sealed tubes, nitrochlorides ([4,5])

$$O_2N{-}CR_2{-}CR_2{-}Cl$$

were obtained along with other products; the authors believe these arose as a result of oxidation of nitrosochlorides by NOCl, and only in the case of 1,2-fluorochloroethylene was CHFCl–CCl=NOH isolated. In our opinion, the reaction is complicated by the equilibrium ([7])

$$2NOCl \rightleftarrows Cl_2 + 2NO \quad (0.5\%),$$

and, consequently, by chlorination of haloolefins and interaction of NO with nitroso compounds ([8]), which should lead to initiation of radical reactions $NO_2\cdot$, $NO_3\cdot$, and Cl·.

In accordance with the general theory of nitration–nitrosation, for the smooth and rapid preparation of nitrosochlorides of haloethylenes we successfully applied the action of solutions of halides of the type $AlCl_3$ in excess nitrosyl chloride at low temperatures. As has been known since 1938-1948 ([7]), these aprotic acids form with NOCl complexes of the type

$$[AlCl_4]^- NO^+,$$

which strongly dissociate into the ions

$$O{=}N^+$$

and

$$AlCl_4^-,$$

where the latter, or more probably the solvate

$$AlCl_4^- \rightarrow NO{-}Cl,$$

serves as a donor of chloride ions. The conjugate addition of NO^+ and Cl^- may be represented by the scheme in which the arc denotes the π-bond and the dotted lines the distribution of π-electron density in transition complex I:

$$O{=}N^+ + \begin{pmatrix} CR_2 \\ CR_2 \end{pmatrix} \rightarrow O{=}N^+ \begin{matrix} CR_2 \\ \vdots \\ CR_2 \end{matrix} \xrightarrow[-\,NO^+\cdot AlCl_4^-]{Cl^- \quad NO\cdot AlCl_4^-} O{=}N{-}CR_2{-}R_2C{-}Cl \quad (1)$$

(I)

Similarly, we succeeded in carrying out the addition of $SOCl^+$, SO_2Cl^+, PCl_2^+ and Cl^- to olefins and vinyl chloride by means of solutions of $AlCl_3$ in $SOCl_2$, SO_2Cl_2, PCl_3, which serves as additional confirmation of the ionic mechanism of our method of nitrosochlorination.

In contrast to related reactions, in particular nitrofluorination ([9]), in the nitrosochlorination of chloroethylenes an anomalous orientation of NO^+ and Cl^- was observed. Thus, in the reaction with vinylidene chloride $CH_2 = CCl_2$, 1,1,2-trichloro-1-nitrosoethane, $ON{-}CCl_2{-}CH_2{-}Cl$, was obtained. We believe that the cause of this deviation from Markovnikov' s rule is the conjugation effect of the halide and the nitroso group according to the scheme

$$Cl{-}CR_2{-}N{=}O.$$

This effect, according to our observations, is strongly manifested in the high mobility of chlorine in *gem*-chloronitroso compounds, for example in the reaction with Ag^+, in the ease of their conversion with OH^- into $R_2C{=}NOOH$ and Cl^-, with N_2H_4 into $R_2C{=}NOH$ (see below), and in similar transformations, as well as in the comparative difficulty of their oxidation and isomerization into the oxime form. According to this hypothesis, the mechanism of anomalous nitrosochlorination, for example of 1-chloroethene, should be expressed as follows:

$$O{=}N^+ + \begin{pmatrix} CH_2 \\ CHCl \end{pmatrix} \rightarrow ON{-}\begin{matrix} CH_2^{+\delta} \\ | \\ CH{-}Cl \end{matrix} \xrightarrow[-\,NO^+\cdot AlCl_4^-]{Cl{-}NO\cdot AlCl_4^-} ON{-}CH(Cl){-}CH_2Cl \quad (2)$$

The tendency toward strengthening of the conjugation shown in the complex with NO^+ leads to addition of the chloride ion to carbon 2. In a similar way one may represent the slow nitrosochlorination of $O{=}N^+{-}Cl$, as a donor of NO^+ and Cl^-, all the more so since its ability to form complexes through interaction with π-electrons is known ([3]).

Nitrosochlorination was most vigorously activated by $AlCl_3$; $FeCl_3$, $SbCl_5$, and $SnCl_4$ were also used successfully. Additions of $ZnCl_2$ acted considerably more weakly owing to the smaller polarization of NOCl in the adduct

$$O{=}N{-}Cl \longrightarrow ZnCl_2.$$

Activation by $AlCl_3$ and $FeCl_3$ had, to one degree or another, a catalytic character owing to dissociation of their complexes with nitroso chlorides. Under the action of $NO^+BF_4^-$ on $CH_2{=}CCl_2$ and of NO^+ on C_2F_4 in HF ([9]), nitrofluorination of haloethylenes was observed.

By our method of nitrosochlorination, vinylidene chloride gave 1,1,2-trichloro-1-nitrosoethane $CH_2Cl{-}CCl_2{-}NO$; trichloroethylene gave 1,1,2,2-tetrachloro-1-nitrosoethane $CHCl_2{-}CCl_2{-}NO$; 1,2-dichloroethylene gave the acid chloride of dichloroacetohydroxamic acid $CHCl_2{-}CCl{=}NOH$ (the oxime form of nitroso chloride); vinyl chloride gave $CH_2Cl{-}CCl{=}NOH$. Nitrosochlorination of ethylene initially gave 1,2-nitrosochloroethane $CH_2Cl{-}CH_2{-}NO$, which, through chlorination of its oxime form, was converted into $CH_2Cl{-}CCl_2{-}NO$; the same compound is formed on chlorination of $CH_2Cl{-}CCl{=}NOH$. Thus, $CH_2Cl{-}CCl_2{-}NO$ can be obtained both directly from $CH_2{=}CCl_2$ and from $CH_2{=}CHCl$ or $CH_2{=}CH_2$. Photochemical nitrosochlorination of vinylidene chloride with NOCl in a stream of NO, initiated by $Cl\cdot$ through photolysis of $O{=}N{-}Cl$, also gave $CH_2Cl{-}CCl_2{-}NO$,

$$CH_2{=}CCl_2 + Cl\cdot \rightarrow CH_2Cl{-}\dot{C}Cl_2 \xrightarrow{NO} CH_2Cl{-}CCl_2{-}NO, \qquad (3)$$

but in this case it was the product of normal addition by a radical mechanism.

Tetrachloroethylene did not undergo nitrosochlorination by the ionic mechanism owing to its increased electrophilicity and steric hindrance, but photochemical nitrosochlorination of C_2Cl_4 according to an equation of type 3 proceeded rapidly on irradiation with a mercury lamp. In the seeming contra-

In this connection, tetrafluoroethylene, despite its gaseous state, reacted with $NO^+AlCl_4^-$ and gave a good yield of $Cl{—}CF_2{—}CF_2{—}NO$. The activity of C_2F_4 is due to the greater conjugation effect in the group $F{—}C{=}C$, of the type $\overset{\downarrow}{F}{—}C{=}C$, than in its chlorine analogue $Cl{—}C{=}C$, owing to the closeness of the sizes of the orbitals of C and F.

The conjugation of halides according to the scheme $X{—}C{=}C$ may be called a vicinal effect, while that considered in equation 2 may be

called a geminal effect. From what has been said above it follows that in F atoms, in ionic nitrosochlorination, the vicinal effect predominates, whereas in Cl atoms the geminal effect does. In accordance with this conclusion, $CF_2 = CH_2$, in contrast to $CCl_2 = CH_2$, gave in this reaction $CF_2Cl—CH = NOH$, $CHF = CHCl—CHFCl—CCl = NOH$, $CF_2 = CFCl—CF_2Cl—CFCl—NO$. The formation of $Cl—HCCl—CCl_2—NO_2$ from $CHCl = CCl_2$, $Cl—CHF—CCl_2—NO_2$ from $CHF = CCl_2$, and $Cl—CF_2—CFCl—NO_2$ from $CF_2 = CFCl$ in slow reactions with NOCl as such (see above), in the light of our data, can be rationally represented as occurring through oxidation of the corresponding nitrosochlorides. In prolonged nitrosochlorination of $CF_2 = CFCl$ by means of $NO^+AlCl_4^-$, we also detected the formation of the nitrochloride along with the nitrosochloride, the principal reaction product. In a recent work ([10]) on the nitrosochlorination of fluorochloroethylenes in the presence of $FeCl_3$ at 45° in a flow system, orientation in agreement with our hypothesis was also observed, although the authors themselves do not take into account the fundamental role of $FeCl_3$.

The addition of NO^+ and X^- is accompanied by the formation of telomers $ON—(—CR_2—CR_2—)_n—X$, for example in the nitrosochlorination of $CF_2 = CFCl$ by means of $NO^+AlCl_4^-$, with molecular weight $\sim$ 500. To nitrosohalogenation we can apply a number of conclusions drawn in discussing nitrofluorination ([9]). It is possible that nitrosohalogenation and nitrofluorination of electrophilic unsaturated compounds of the type $X—C \equiv C—X$ or $(CF_3)_2C = CF_2$ will also proceed by a mechanism of nucleophilic addition, for example through the action of NOF and $C(NO_2)_4$ in the presence of $NR_4^+F^-$.

Judging from the chemical nature and electronic structure of the ring, cyclopropane compounds are also capable of adding NO^+ and Cl^- with formation of 1,3-nitrosochlorides ([2,3]).

We give a description of several nitrosochlorination experiments.

1. Into a reactor containing a solution of 2 g of $AlCl_3$ in 10 ml of NOCl at −20°, 25 g of $CH_2 = CCl_2$ was added dropwise with stirring over 30 min; then, after standing for 1-2 hr, the contents were poured onto ice, the nitrosochloride was separated off and dried with $CaCl_2$. After distillation in vacuum, about 30 g of dark-blue $CH_2Cl—CCl_2—NO$ was obtained, b.p. 36° at 40 mm; d_4^{20} 1.489; n_D^{20} 1.4660; molecular weight 159.

Found, %: N 8.7; Cl 65.8

It, as well as $CH_3—CCl_2—NO$, immediately reacts with $AgNO_3$ in alcohol. On prolonged standing of the product in HNO_3 of specific gravity 1.5, it is converted into $CH_2Cl—COOH$, identified in the form of the anilide, m.p. 133°.

2. Analogously, from 40 g of NOCl, 20 g of $AlCl_3$, and 40 g of $CHCl = CCl_2$, 23 g of tetrachloronitrosoethane was obtained, b.p. 56° at 40 mm.

Found, %: N 7.1; Cl 70.9

3. To a solution of 13.5 g of $AlCl_3$ in 40 g of NOCl at −30°, about 50 g of liquid vinyl chloride is added, and after 4-5 hr it is poured onto ice; the oil is quickly separated, dried with $MgSO_4$, and distilled in vacuum. More than 30 g of the acid chloride of chloroacetohydroxamic acid, $CH_2Cl—CCl=NOH$, is obtained, b.p. 78° at 10 mm.

Found, %: N 11.2; Cl 55.1

In a mixture with water, the product gave a reaction for Cl^- and hydroxamic acid; in HNO_3 it was rapidly converted into $CH_2Cl—COOH$, and upon chlorination in 5% HCl at 0°—into $CH_2Cl—CCl_2—NO$, described in experiment 1; it can be obtained in still better yield by chlorinating the mixture immediately after pouring it onto ice. Conversely, by adding $CH_2Cl—CCl_2—NO$ at 0° to an aqueous hydrazine solution, $CH_2Cl—CCl=NOH$ can be obtained in a yield > 80%; $CH_3—CCl_2—NO$ reacted analogously.

4. From 65 g of $NOCl$, 13.5 g of $AlCl_3$, and 60 g of 1,2-dichloroethylene under conditions similar to experiment 3, 31.2 g of $CHCl_2—CCl=NOH$ were obtained, with b.p. 86° at 15 mm; d_4^{20} 1.597; n_D^{20} 1.5187.

Found, %: N 8.8; Cl 65.2

In HNO_3 the product was converted into $CHCl_2—COOH$, identified as the anilide with m.p. 117°; upon chlorination, the resulting acid chloride of dichloroacetohydroxamic acid was converted into the tetrachloronitrosoethane of experiment 2.

5. Into a solution of 13.5 g of $AlCl_3$ in 40 g of $NOCl$, while cooling with solid CO_2 and vigorously stirring in a shaker for 6 h, a slow stream of ethylene was passed. After pouring onto ice, about 10 g of an oil with the properties of β-chloroacetaldoxime were obtained; 7 g of this, for identification, were converted by chlorination, as in experiment 3, into $CH_2Cl—CCl_2—NO$ in a yield of about 5 g.

6. Analogously, for 3 h, 6 l of C_2F_4 were passed through, and then the temperature was raised to +5°. After washing, drying, and cooling the exit gases at −50°, about 30 g of a blue liquid were obtained, from which $Cl—CF_2—CF_2—NO$, b.p. −5°, was isolated.

Found, %: F 44.5; Cl 21.6

The results of the iodometric determination of the ON group are close to theory.

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Note: Figure translations are in progress. See original paper for figures.