Chemistry

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Abstract

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ON THE REACTION OF SIMPLE VINYL ETHERS WITH NITROSYL CHLORIDE

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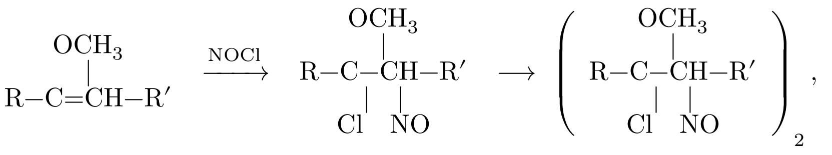
Upon consideration of the extensive literature material it becomes obvious that the addition of nitrosyl chloride to olefins proceeds the more readily, the greater the density of the π-electron cloud of the multiple bond. Therefore NOCl adds more readily to di- and trisubstituted olefins ($^{1-4}$) than to monosubstituted ethylene hydrocarbons (^{5}). Electron-accepting nonhydrocarbon substituents at the double bond strongly inhibit the reaction (^{6,7}), whereas electron-donating substituents, for example CH_3O—in ortho- and para-methoxystyrenes (^{7}), facilitate the addition reaction of nitrosyl chloride.

In this connection it could be assumed that simple methylvinyl ethers would react vigorously with nitrosyl chloride, owing to the strong effect of the CH_3O-group, which increases the electron density of the double bond.

We have investigated the reaction of nitrosyl chloride with three simple vinyl ethers: methylisopropenyl (I), methylpropenyl (II), and methyl-α-phenylvinyl (III). The reaction with all three ethers proceeds very rapidly already at -60° in dilute solutions of diethyl ether. The reaction conditions and the structure of the reaction products speak in favor of an ionic mechanism of addition.

At first the ethereal solution becomes blue owing to the formation of a monomeric chloronitroso compound, after which colorless crystals of dimeric nitroso chlorides begin to precipitate from the solution: 2-chloro-1-nitroso-2-methoxypropane (IV), 1-chloro-2-nitroso-1-methoxypropane (V), and α-chloro-β-nitroso-α-methoxyethylbenzene (VI), with yields of 98, 95, and 65%, respectively.



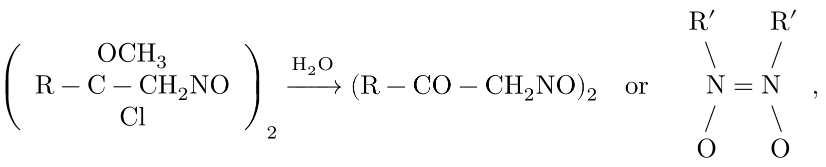
$$\underset{\text{(I) – (III)}}{\mathrm{R{-}\overset{\overset{\displaystyle OCH_3}{|}}{C}{=}CH{-}R'}} \xrightarrow{\mathrm{NOCl}} \mathrm{R{-}\overset{\overset{\displaystyle OCH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}{-}\underset{\underset{\displaystyle NO}{|}}{CH}{-}R'} \longrightarrow \underset{\text{(IV) – (VI)}}{\left(\mathrm{R{-}\overset{\overset{\displaystyle OCH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}{-}\underset{\underset{\displaystyle NO}{|}}{CH}{-}R'}\right)_2},$$

(I) – (III) (IV) – (VI)

where for I and IV: $R = CH_3,\ R' = H$; for II and V: $R = H,\ R' = CH_3$; for III and VI: $R = C_6H_5,\ R' = H$.

All the dimeric nitroso chlorides obtained at −60° are extremely unstable; they decompose rapidly and violently in air, even below 0°, and are somewhat more stable in solutions in benzene and CCl_4, which are blue in color.

The structure of dimers IV and VI was proved by hydrolysis of them, under cooling, into dimeric α-nitroso ketones (yield 60-65%). α-Nitroso ketones and their dimers with the nitroso group at the primary carbon atom had not been known until now. IR spectra indicate the cis form of the obtained dimers of nitrosoacetone (absorption at 1350 and 1315 cm^{-1}; according to (^{8}), for cis-$(RNO)_2$ a doublet at 1323-1344, 1330-1420 cm^{-1}) and of ω-nitrosoacetophenone (absorption at 1345 and 1310 cm^{-1}). It follows from this that the dimeric nitroso chlorides IV and VI are likewise in the labile cis form.



$$\left(\begin{array}{c} OCH_3 \\ R-C-CH_2NO \\ Cl \end{array}\right)_2 \xrightarrow{H_2O} (R-CO-CH_2NO)_2 \quad \text{or} \quad \begin{array}{ccc} R' & & R' \\ \backslash & & / \\ N & = & N \\ / & & \backslash \\ O & & O \end{array},$$

cis.
cis-

where $R = CH_3,\ C_6H_5;\ R' = RCOCH_2$.

According to the data of Gowenlock (^{9}) and Smith (^{10}), true dimeric C-nitroso compounds at low temperatures are likewise obtained in the cis form, and only on heating or in nonpolar solvents do they pass into the more stable trans form.

On dissolving the cis dimer of ω-nitrosoacetophenone in dichloroethane and precipitating it with n-hexane, the trans dimer of ω-nitrosoacetophenone was obtained (in the IR spectra, very strong absorption at 1210 cm^{-1}, characteristic of trans dimers $(RNO)_2$ (^{8})).

The synthesized dimeric nitroso ketones isomerize on melting into the well-known isonitroso ketones.

$$(R-CO-CH_2NO)_2 \rightarrow R-CO-CH_2NO \rightarrow R-CO-CH=NOH,$$

where $R = CH_3$ and C_6H_5.

The structure of dimer V was proved by converting it into methylglyoxime (58%) by treating the reaction mixture with an aqueous solution of potash and hydroxylamine hydrochloride.

$$\text{(V)} \xrightarrow{H_2O} [CH_3CH(NO)CHO]_2 \xrightarrow{NH_2OH} CH_3C(=NOH)CH=NOH.$$

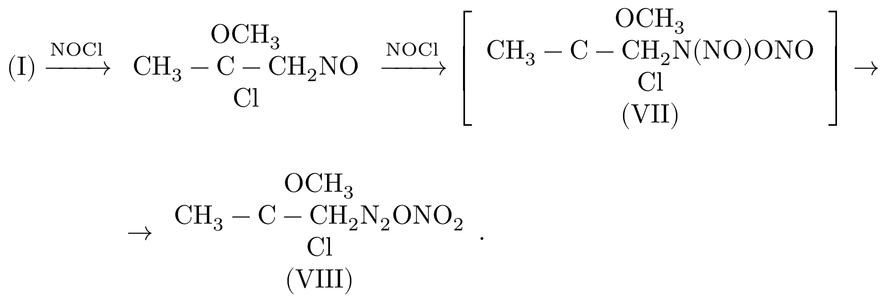
The dimer of 2-nitrosopropanal could not be isolated, since it rapidly turns into a colorless polymer.

Cis dimer V is extremely unstable in air and decomposes violently in vacuum already at –35°. If the reaction of ether II with NOCl is carried out at –5°, and dimer V is isolated after 2 hours, a relatively stable trans form is obtained (IR spectrum 1530 cm^{-1} (in CCl_4), 1205 cm^{-1}; according to (^{8}), 1539–1621 cm^{-1} ($N=O$ in the monomer), 1176–1290 cm^{-1} in trans dimers $(RNO)_2$).

Of greatest interest is the course of the reaction of nitrosyl chloride with ether I at 10–15° in diethyl ether. Under these conditions, the initially obtained blue solution gradually turns yellow, and a crystalline precipitate colored light brown separates from it (yield 30–40%). In all its properties and elemental composition the crystals correspond to 2-chloro-2-methoxypropyldiazonium nitrate (VIII). The insolubility of compound VIII in organic solvents (simple and complex ethers, hydrocarbons, halogen derivatives, ketones, etc.), except for alcohol and acetic acid, in which it slowly decomposes, also indicates such a structure*. In water compound VIII is instantly hydrolyzed and the solution contains the NO_3^- ion. On heating, the crystals decompose at 46–48° with evolution of one mole of nitrogen.

The exceptional sensitivity to the slightest traces of moisture made it impossible to obtain a distinct IR spectrum of compound VIII. Diazonium nitrate VIII is apparently the product of radical addition of NO to the monomeric chloronitroso compound. The resulting derivative of bisnitrosohydroxylamine VII then rearranges into diazonium nitrate VIII.

$$NOCl \rightleftarrows \dot{N}O + \cdot Cl$$



$$\text{(I)} \xrightarrow{NOCl} CH_3-\underset{Cl}{\overset{OCH_3}{C}}-CH_2NO \xrightarrow{NOCl} \left[\underset{\text{(VII)}}{CH_3-\underset{Cl}{\overset{OCH_3}{C}}-CH_2N(NO)ONO}\right] \to$$

$$\to \underset{\text{(VIII)}}{CH_3-\underset{Cl}{\overset{OCH_3}{C}}-CH_2N_2ONO_2}\ .$$

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* Or to the structure of 2-chloro-2-methoxypropyldiazonium nitrate.

Several dozen experiments were carried out to obtain diazonitrate VIII. The best conditions were: 0.8 g-mol of NOCl per 1 g-mol of ether I, 1 g of NOCl in 4-5 ml of diethyl ether, and a temperature of 10-15°. At a concentration of 1 g of NOCl in 10-20 ml of ether, dimer IV is formed in 20-30% yield, while upon dilution of 1 g of NOCl with 40-50 ml of diethyl ether no crystalline products are separated from the solution.

Aliphatic diazonitrates had not been known up to now. One possible route to the formation of aliphatic diazonitrates might be the Bamberger reaction ([11]), which proceeds well in the aromatic series. The negative results obtained quite recently in the reaction of nitric oxide with certain aliphatic nitroso compounds ([12]) led to the conclusion that the Bamberger reaction is impossible in the aliphatic series. Meanwhile, recently rather well-founded assumptions have been put forward concerning the formation of aliphatic diazonitrates as intermediates in reactions of nitric oxide with isobutylene ([13]), with dimeric nitrosocyclohexane ([14]), with various halogenated olefins ([15]), and in the reaction of the latter with nitrosyl chloride ([16]). In the reaction of nitric oxide with trifluoronitrosomethane, the formation of an unstable bisnitroso derivative of trifluoromethylhydroxylamine was proved by obtaining the stable salt of N-nitroso-N-trifluoromethylhydroxylamine ([17]). Similar bisnitroso derivatives had already been assumed by Bamberger ([18]), and subsequently also by other investigators ([12–14]), to be intermediates in the formation of diazonitrates.

Although in all the works cited the reaction of aliphatic nitroso compounds with nitric oxide apparently proceeded through the diazonitrate stage, in no case was it possible to isolate them.

Thus, 2-chloro-2-methoxypropyldiazonitrate (VIII) is the first representative of previously unknown aliphatic diazonitrates. With the other two vinyl ethers it was not possible to obtain analogous compounds. Some of the experiments with methylisopropenyl ether are described below.

Methylisopropenyl ether (I) was obtained by passing acetone dimethyl ketal (b.p. 77.8-78.5° at 760 mm, d_4^{20} 0.8500; n_D^{20} 1.3780) over magnesium pyrophosphate at 325-350° ([19]). B.p. 34.5° at 775 mm, d_4^{20} 0.7379, n_D^{20} 1.3881; according to ([20]), b.p. 33.5°, n_D^{20} 1.3827.

Reaction of methylisopropenyl ether (I) with nitrosyl chloride at −60°. To 13 g of I in 160 ml of diethyl ether at −60°, 9.7 g of nitrosyl chloride was introduced over 40 min. In the course of the reaction, colorless crystals of the dimer of 2-chloro-1-nitroso-2-methoxypropane (IV) precipitate from the blue solution. The crystals are filtered off in a stream of dry air at −20° to constant weight. Obtained: 19.8 g of IV, yield 98%. At ordinary temperature it decomposes vigorously in air. Solutions in benzene are colored blue.

cis-Dimer of nitrosoacetone. To 19.8 g of dimer IV, dried in vacuo at −20°, an excess of water is rapidly added; the crystals are quickly filtered off, washed with water, alcohol, and ether. Obtained: 6.54 g (65%) of cis-dimer of nitrosoacetone; a finely crystalline colorless substance, m.p. 81-83°, insoluble in the cold in ether, alcohol, water, acetic acid, hydrocarbons, and CCl_4.

Found, %: C 41.44; 41.51; H 5.97; 6.03; N 16.09; 15.73
$(C_3H_5NO_2)_2$. Calculated, %: C 41.38; H 5.79; N 16.09

In the IR spectra, absorption was noted at 1350 (s.) and 1315 cm^{-1} (medium). According to (^{8}), for cis-$(RNO)_2$ the doublet is 1323-1344, 1330-1420 cm^{-1}.

On heating 3.5 g of the dimer of nitrosoacetone in toluene to boiling, 3.3 g of colorless needles of isonitrosoacetone, m.p. 64.5° (from petroleum–

ethyl ether); a mixture with an authentic sample of isonitrosoacetone melts without depression, and the IR spectra are identical.

Reaction of methylisopropenyl ether (I) with nitrosyl chloride at 15°. To 14.7 g of I at +15° there was slowly added a solution of 11 g of nitrosyl chloride in 40 ml of diethyl ether. The initially blue solution soon turns yellow, and yellow flakes of 2-chloro-2-methoxypropyldiazonium nitrate (VIII) begin to precipitate from it. The reaction proceeds with considerable evolution of heat and requires intensive cooling. The precipitate VIII is filtered off in dry air, washed well with ether, and dried in vacuo to constant weight. The yellow crystals, weighing 3.3 g (30%), decompose instantly in the presence of moisture; they are insoluble in ether, hydrocarbons, and chlorides, and readily soluble in alcohol and acetic acid. In the hydrolysate of compound VIII the presence of the anion NO_3^- was demonstrated (blue coloration with a solution of diphenylamine in sulfuric acid, blue coloration on boiling with copper powder in the presence of ammonia, formation of a precipitate with nitron). The aqueous solution gives no reaction for the anion NO_2^- with Griess reagent.

Diazonium nitrate VIII can be purified by dissolution in cold absolute alcohol followed by precipitation with strongly cooled ether. Decomposition temperature 46-48°. Analysis is greatly hindered by the exceptional sensitivity to atmospheric moisture.

Found, %: Cl 18.09; 17.97; N 21.46; 21.52
$C_4H_8ClN_3O_4$. Calculated, %: Cl 17.95; N 21.27

On heating a weighed portion of the substance, 1 g-mol of nitrogen is evolved*.

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named after A. A. Zhdanov

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* In most experiments on thermal decomposition, less than one mole of nitrogen was evolved.

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

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