N-HALOGENO-N-NITROAMINES

1. SYNTHESIS AND PROPERTIES OF N-CHLORO-N-NITROAMINES

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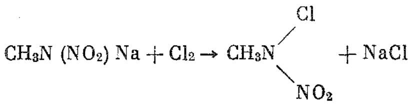
Unlike the aryl-N-chloro-N-nitroamines described in the last century [1], their aliphatic analogs are little-known compounds. In [2, 3] it was shown that N-chloro-N-nitroamines are formed during nitration of N,N'-dichloroamines, but isolation of the nitration products involves considerable difficulties. The only product which could be isolated (with a yield of 5%) was N,N'-dichloro-N,N'-dinitroethylenediamine.

We have found that the action of chlorine on aqueous solutions of the salts of primary nitroamines leads to the formation of N-chloro-N-nitroamines with high yield:



$$CH_3N(NO_2)Na + Cl_2 \rightarrow CH_3N\begin{matrix}\diagup Cl\\ \diagdown NO_2\end{matrix} + NaCl$$

The reaction was used to obtain N-chloro derivatives of alkylnitroamines, dinitroamines, polynitroamines, and polynitroalkylnitroamines. While studying the stability of the various N-chloro-N-nitroamines on storage, we found that the stability of the respective N-chloro derivatives decreased with increase in the acidity. The previously described N-chloronitrourethane [4] and the N-chlorosulfamide (VI) which we obtained were found to have low stability, while the chloronitroamine (VII) did not change after storage for several years. In the chlorination of primary nitroamines without previously converting them into salts the ease of the reaction is affected by the homogeneity of the medium and by the temperature. The reaction is accelerated by increase in temperature. Since increase in temperature causes an increase in the degree of dissociation of the primary nitroamines in water [5], the dissociated form of the nitroamine is evidently subject to chlorination.

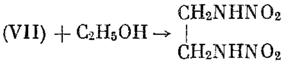
In the IR spectra of N-chloro-N-nitroamines (Fig. 1) absorption bands belonging to the $N-NO_2$ grouping were found in the 1250 and 1600 cm^{-1} regions. Introduction of chlorine into the primary nitroamine molecule leads to the disappearance of absorption bands belonging to the NH group in the 3200 cm^{-1} region. Absorption bands corresponding to the $-CH_2-$ group, which are masked in the primary nitroamines by the strong band of the NH group vibrations, are clearly seen in the 2900-2300 cm^{-1} region.

N-Chloro-N-nitroamines readily oxidize potassium iodide in aqueous solution:

$$CH_3N(NO_2)Cl + 2KI \rightarrow CH_3N(NO_2)K + I_2 + H_2O$$

The reaction was used for iodometric determination of the "active" chlorine in the molecule. Further investigation of the chemical properties in N-chloro-N-nitroamines revealed strongly electrophilic character in the chlorine atom in these compounds.

Reaction with potassium cyanide, sodium azide, and sodium nitrite leads to the formation of nitroamine salts. On heating ethanol reduces N-chloro-N-nitroamine quantitatively to the primary nitroamine:



$$(VII) + C_2H_5OH \rightarrow \begin{matrix}CH_2NHNO_2\\ |\\ CH_2NHNO_2\end{matrix}$$

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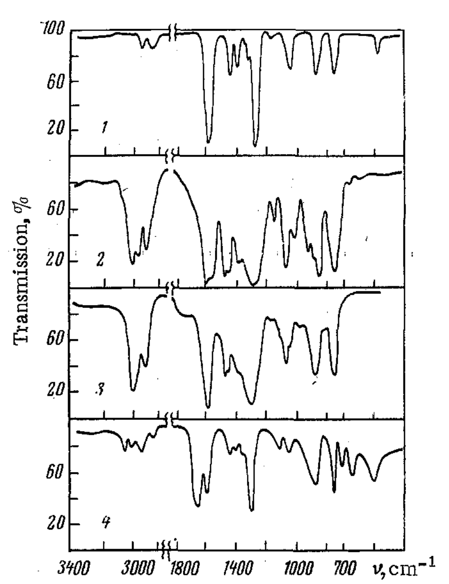
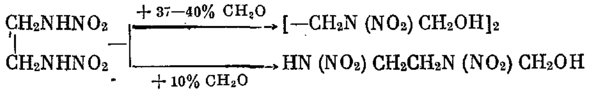


Fig. 1. Infrared spectra: 1) N-chloro-N-nitromethylamine; 2) N-chloro-N-nitropropylamine; 3) N-chloro-N-nitrobutylamine; 4) N-chloro-N-nitroaminoethanol nitrate.

Reaction of compound (VIII) (Table 1) with aldehydes also leads to the formation of a primary nitroamine, but (as shown before [6]) reaction with diluted formalin gives the monomethylol derivatives of ethylene dinitroamine (EDNA). While investigating the reaction of compound (VII) with 37-40% formalin, we were able to isolate the previously undescribed 2,5-dinitro-2,5-hexane-1,6-diol:

$$\text{(VII)} + CH_2O + H_2O \rightarrow HOCH_2N(NO_2)CH_2CH_2N(NO_2)CH_2OH$$

The question arose as to what part the chlorine played in the formation of dinitroaminomethylol, since the monomethylol derivative of this compound is formed during condensation of EDNA with formalin [7, 8]. For this purpose we investigated the condensation of EDNA with formalin and found that both the mono- and dimethylol derivatives of EDNA can be formed, depending on the concentration of formalin:



$$\begin{matrix} CH_2NHNO_2 \\ | \\ CH_2NHNO_2 \end{matrix} \begin{cases} \xrightarrow{+\,37-40\%\ CH_2O} [-CH_2N(NO_2)CH_2OH]_2 \\ \xrightarrow[+\,10\%\ CH_2O]{} HN(NO_2)CH_2CH_2N(NO_2)CH_2OH \end{cases}$$

It can be supposed that N-chloro-N-nitroamines are reduced by formalin to primary nitroamines, and the latter are converted into nitroaminomethylols. The formation of the various condensation products from EDNA is consistent with the following scheme [9]:

$$RN(NO_2)CH_2OH \rightleftharpoons RNHNO_2 + CH_2O$$

In dilute aqueous solutions the equilibrium is almost completely shifted to the right. Reaction with a concentrated solution of formalin leads to displacement of the equilibrium to the left owing to separation of the reaction product from the solution.

EXPERIMENTAL

The initial primary nitroamines were obtained by the methods described in [2, 3, 8, 10-15].

3,3-Dinitrobutylnitroamine. This was obtained by nitration of N-3,3-dinitrobutylmethyl carbamate [16] by the usual procedure [8] followed by hydrolysis of the nitrocarbamate with aqueous ammonia. The yield was 74%, and the product melted at 38°C (from chloroform). Found, %: C 23.42, H 3.95, N 26.33. $C_4H_8N_4O_6$. Calculated, %: C 23.07, H 3.83, N 26.92.

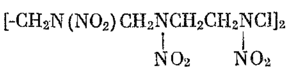
2,2-Dinitroaminodiethyl Ether. This was obtained in a similar manner from 2,2-diaminodiethyl ether [17]. The yield was 85%, and the melting point 65-66°C (from chloroform). Found, %: C 24.66, H 4.92, N 28.59. $C_4H_{10}N_4O_5$. Calculated, %: C 24.79, H 5.15, N 28.86.

Typical Method for Chlorination of Nitroamines for the Example of EDNA. A moderate stream of chlorine was passed through 30 ml aqueous solution containing 1.6 g sodium hydroxide and 3.0 g EDNA at 0-5°C, and a flocculent white precipitate was formed. As the compound accumulated the reaction mixture was filtered, and the mother liquor was made alkaline and again treated with chlorine. The product was washed with iced water, dried in air, and dissolved in 25 ml ether. The ethereal solution was filtered and partly evaporated. As the solvent was removed the product crystallized as fine needles. The yield was 4.3 g (94%) and the melting point 44°C. According to date from [2] the melting point is 41-41.6°C. The product was identified by a mixed melting test.

A moderate stream of chlorine was passed through a solution of 3.0 g EDNA in 100 ml water at 60°C, and a heavy light-yellow oil was formed. When the reaction mixture no longer increased in weight the oil was separated in a separating funnel and washed with iced water, and the whole mass solidified. The yield was 4.2 g (92%), and the melting point after purification as described above was 44°C.

Reaction of Compound (VII) with Sodium Azide. To a solution of 2.58 g compound (VII) in 30 ml acetone was added dropwise a solution of 2.23 g sodium azide in 30 ml water; the mixture was left for 20 min after evolution of gas had ceased. It was diluted with water and acidified with hydrochloric acid, and the

TABLE 1. N-Chloro-N-nitroamines

Compound No.	Compound	Yield, %	Mp, °C	Bp, °C (p, mm)	d_4^{20}	n_D^{20}	*MR* found	*MR* calculated	Found, % N	Found, % Cl	Molecular formula	Calculated, % N	Calculated, % Cl
I	$CH_3N(NO_2)Cl$	90,5	—	33 (25)	1,4033	1,4603	21,35	21,89	25,07	32,29	$CH_3N_2O_2Cl$	25,45	32,51
II	$O_2NOCH_2CH_2N(NO_2)Cl$	91	—24	—	1,5011	1,4872	34,07	33,17	22,34	30,18	$C_2H_4N_3O_5Cl$	22,63	29,91
III	$n\text{-}C_3H_7N(NO_2)Cl$	90	—	68 (33)	1,2253	1,4551	30,59	30,26	20,31	25,65	$C_3H_7N_2O_2Cl$	20,22	25,61
IV	$n\text{-}C_4H_9N(NO_2)Cl$	48	—	69 (25)	1,1732	1,4541	35,05	34,88	18,58	23,30	$C_4H_9N_2O_2Cl$	18,42	23,27
V	$CH_3C(NO_2)_2CH_2CH_2N(NO_2)Cl$	78	57	—	—	—	—	—	23,20	14,72	$C_4H_7N_4O_6Cl$	23,14	14,66
VI	$CH_3C_6H_4SO_2N(NO_2)Cl$	60	44—45	—	—	—	—	—	10,59	14,20	$C_7H_7N_2O_4SCl$	11,22	14,16
VII	$[-CH_2N(NO_2)Cl]_2$ *	93	43	—	—	—	—	—	—	—	—	—	—
VIII	$O[CH_2CH_2N(NO_2)Cl]_2$	89	7—8	—	1,4902	1,5091	—	—	24,32	27,02	$C_4H_8N_4O_9Cl_2$	24,61	26,98
IX	$C(NO_2)_2[CH_2CH_2N(NO_2)Cl]_2$	87	50	—	—	—	—	—	24,02	20,22	$C_5H_8N_6O_8Cl_2$	23,93	20,22
X	$Cl[N(NO_2)CH_2CH_2]_3N(NO_2)Cl$ *	95	121—122	—	—	—	—	—	28,11	17,66	$C_6H_{12}N_8O_8Cl_2$	28,43	17,92
XI	 $[\text{-}CH_2N(NO_2)CH_2\underset{NO_2}{\underset{\mid}{N}}CH_2CH_2\underset{NO_2}{\underset{\mid}{N}}Cl]_2$	94	119	—	—	—	—	—	31,13	12,82	$C_8H_{16}N_{12}O_{12}Cl_2$	31,02	13,02

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* Compounds (VI) and (X) have been described before [2, 3], but Compound (X) was not isolated in pure form.

precipitate was filtered off. The yield of EDNA was 0.93 g (35%), and the melting point was 176°C. The product was identified by a mixed melting test with a known sample.

Reaction of Compound (VII) with Ethanol. To 15 ml ethanol was added 2.2 g compound (VII) and the mixture was heated to boiling. After removal of the solvent 1.5 g (100%) EDNA remained; the melting point was 176°C. Without heating the reaction takes 1.5-2 h.

2,5-Dinitro-2,5-diazahexane-1,6-diol. An 11 g sample of compound (VII) was dissolved in 10 ml 36% formalin at 60-70°C and kept at this temperature for 5 min. The syrup which formed crystallized after standing for 2 days. The yield was 10.1 g (96%), and the melting point was 82-84°C. Found, %: C 23.15, H 4.87, N 26.74. $C_4H_{10}N_4O_6$. Calculated, %: C 22.85, H 4.76, N 26.66.

The structure of the compound was confirmed by conversion to 2,5-dinitro-2,5-diazahexane-1,6-diol acetate, which has been described before [18]. On boiling with CH_3COCl in $(CH_2Cl)_2$ the diol gave a product melting at 83°C. No melting point depression was obtained with a known sample [18].

CONCLUSIONS

1. A convenient method has been developed for preparation of aliphatic N-chloro-N-nitroamines.

2. The chemical stability of the N-chloro-N-nitroamine decreases with increased acidity in the original primary nitroamine.

3. 2,5-Dinitro-2,5-diazahexane-1,6-diol was obtained for the first time.

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