HERBICIDAL HYDROXYLAMINE DERIVATIVES

X. Reactions of Chloro-sym-triazines with Hydroxylamine and its N-Substituted Derivatives*

I. A. Mel'nikova and Yu. A. Baskakov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 4, No. 4, pp. 751–755, 1968

UDC 547.873: 542.952.6: 630.57

The synthesis of 2-alkyl(dialkyl)amino-4-chloro-sym-triazine derivatives of hydroxylamine, N-methylhydroxylamine, and N-phenylhydroxylamine has been effected and their properties have been studied. The thermal and catalytic polycondensation of the 2-alkyl(dialkyl)amino-4-chloro-6-N-phenyl(methyl)hydroxyamino-sym-triazines accompanied by the liberation of hydrogen chloride and the formation of linear polycondensates with 3-4 members has been observed.

In preceding investigations [1,2] we have studied the reaction of 2-alkyl(dialkyl)amino-4,6-dichloro-sym-triazines with alkoxy amines and have shown that in such reactions feebly basic alkoxy amines replace chlorine with the ease which is generally characteristic only of strongly basic aliphatic amines [3] and form with high yields completely stable 2-alkoxyamino-4-alkyl(dialkyl)amino-6-chloro-sym-triazines. A similar type of anomaly for other cases has been explained by the capacity of compounds containing a mobile hydrogen atom for forming with the molecule of a triazine derivative, associates with structures of the hydrogen bond or of the "triazinium" ion types [4–7].

In contrast to the O-alkylhydroxylamines [8], the reaction of cyanuric chloride with equimolecular amounts of hydroxylamine or N-methyl- and N-phenylhydroxylamines does not stop at the stage of the replacement of one chlorine atom even when the reaction is carried out under the mildest possible conditions: at −15 to −5° C in a current of nitrogen and in the presence of an excess of sodium hydrogen carbonate or sodium acetate. Under these conditions a complex mixture is obtained of polysubstitution products, of products of the hydrolysis of the hydroxylamine derivatives formed, and of products of other side reactions with a total chlorine content in the mixture of 8–19%, as compared with the theoretical 29–36% corresponding to the 2,4-dichloro hydroxylamine derivatives. An attempt to separate the mixture of products obtained was unsuccessful.

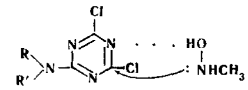
The reaction of N-phenylhydroxylamine with 2-dialkylamino-4,6-dichloro-sym-triazines, in which the chlorine is deactivated by the presence of an amino group, takes place at 40°–45° C with the replacement of only one chlorine atom to form 2-chloro-4-dialkylamino-6-N-phenylhydroxyamino-sym-triazines.

Performing the reaction in an atmosphere of an inert gas (argon, nitrogen) prevents the oxidation of the N-phenylhydroxylamine and the reaction products by atmospheric oxygen and considerably (by about 20%) raises the yield of the normal reaction products.

The reaction of the more reactive unsubstituted hydroxylamine and N-methylhydroxylamine with 2-alkylamino-4,6-dichloro-sym-triazines, unlike that with phenylhydroxylamine, takes place at an anomalously low temperature of about 0° C and is complete in 1 hr. As in the case of N-phenylhydroxylamine, it is important to keep the mixture neutral or faintly acid (pH ~8) for the whole time of the reaction.

The increased reactivity of the hydroxylamines in reactions with substituted sym-triazines can be explained, in our opinion, by the formation of hydrogen bonds, with the participation of the hydroxy group which are stronger than in the case of the O-alkylhydroxylamines. The reaction of 2-alkyl(dialkyl)amino-4,6-dichloro-sym-triazines with hydroxylamine can be represented as a simultaneous attack of the hydrazine molecule at two centers.

In the first place, this is a nucleophilic attack of the nitrogen atom in the amine and in the second place it is the reaction of a free hydroxyl with a heterocyclic nitrogen atom with the formation of an intramolecular hydrogen bond:



These two factors facilitate the splitting out of the first chlorine atom and increase the mobility of the second.

The 2-alkylamino-4-chloro-6-N-methylhydroxyamino-sym-triazines and 2-chloro-4-isopropylamino-6-hydroxyamino-sym-trazines are solid crystalline substances extremely unstable to heat and having no definite melting points. In view of this, their purification is possible only by reprecipitation from benzene solution with n-pentane and petroleum ether in the cold or by washing out the impurities with a suitable solvent.

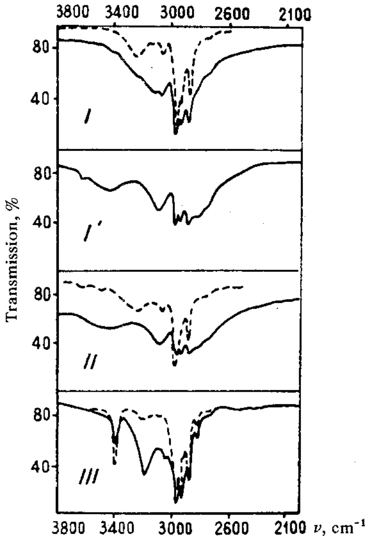
The IR spectra of the 2-dialkylamino-4-chloro-6-N-phenylhydroxyamino-sym-triazines are given in the figure, together with the spectrum of 2-chloro-4-di-n-propylamino-6-methoxyamino-sym-triazine, which has been described previously [9], for comparison.

A feature of the spectra of the 2-chloro-4-dialkylamino-6-N-phenylhydroxyamino-sym-triazines (I and II) given in the figure is the absence in clear form of bands corresponding to the stretching vibrations of the OH group. The spectra of I and II also lack the bands of the stretching vibration of an NH group, which are present in the 3380–3400 cm^{-1} region in the case of

---

*For part IX see [9].

the methoxyamino derivative III. Characteristic for 2-chloro-4-dialkylamino-6-N-phenylhydroxyamino-sym-triazines is an intense absorption band in the 3000–3500 cm^{-1} region.



IR spectra of 2-chloro-4-dialkylamino-6-N-phenylhydroxyamino-sym-triazines: I) 2-chloro-4-diethylamino-6-N-phenylhydroxyamino-sym-triazine, solution in CCl_4; I') the same, KBr tablet; II) 2-chloro-4-di-n-propylamino-6-N-phenylhydroxyamino-sym-triazine, KBr tablet; III) 2-chloro-4-di-n-propylamino-6-methoxyamino-sym-triazine, solution in CCl_4.

When a solution is diluted, one band remains in the spectrum with a frequency of 3250 cm^{-1} and the strong absorption in the region of the stretching vibrations of CH almost disappears. Thus, the band with a frequency of 3250 cm^{-1} for these compounds corresponds only to an intramolecular hydrogen bond with the participation of the OH group, and the absorption in the region of the stretching vibrations of the CH group takes place through the formation of a very strong intermolecular hydrogen bond of the hydroxy group.

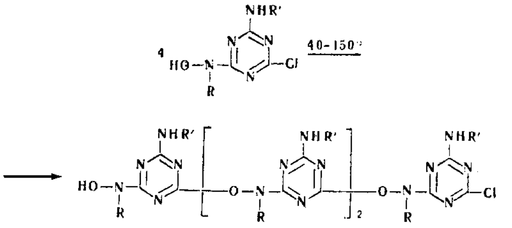
The 2-chloro-4-dialkylamino-6-N-phenylhydroxyamino-sym-triazines are soluble at room temperature in dilute solutions of caustic soda and of strong mineral acids and precipitate from the solutions only in the pH range from 5 to 7. However, they are so little dissociated that they can be extracted with chloroform even from a cooled aqueous caustic soda solution. With ferric chloride solution, the 2-chloro-4-alkyl(dialkyl)amino-sym-triazine derivatives of hydroxylamine, N-methylhydroxylamine, and N-phenylhydroxylamine give dark blue-red colorations.

The mobility of the chlorine atom of the hydroxylamine derivatives of sym-triazine is confirmed by their hydrolysis under the action of 2 N caustic soda solution, which takes place to the extent of 75% in half an hour at 35°–40° C, and also by the thermal instability of the substances.

The thermal lability of the hydroxylamine derivatives is shown in an attempt to recrystallize the 2-chloro-4-dialkylamino-6-N-phenylhydroxyamino-sym-triazines from boiling benzene or chloroform.

In a more detailed study of the stability to heating of the 2-alkylamino-4-chloro-6-N-methylhydroxyamino-sym-triazines with the isopropylamino derivative as an example, it was found that the compounds decompose at 40–70° C with the liberation of hydrogen chloride, which becomes more intense on careful slow heating at 120°–150° C (the slightest overheating leads to resinification) and is accompanied by foaming.

The analytical determination of the chlorine content in the product of the thermal decomposition of 2-chloro-4-isopropylamino-6-N-methylhydroxyamino-sym-triazine gave a value 3–4 times less than in the initial substance. A determination of the molecular weight of the product by the isothermal boiling method [10] also gave an approximately four-fold value. The coloration with ferric chloride was less intense. All this permits the deduction that in this case linear thermal polycondensation takes place with the splitting out of hydrogen chloride as the result of an intermolecular reaction of the chlorine atom with the hydroxyl of the amino group in the following way:



Under the reaction conditions that we studied, the polycondenstation reaction leads to the formation of a mixture of tri- and tetramers. It was impossible to carry out dimerization. The polycondensation process easily proceeds further. The liberated hydrogen chloride catalyzes this process. In the presence of small amounts of phosphoric acid, intermolecular condensation takes place even at room temperature, but more feebly than on heating.

In their physical properties, the polycondensation products are sharply distinguished from the initial compounds. The mixture of tri- and tetramers obtained is stable up to ~250° C and melts at about 300° C with marked browning. It is sparingly soluble in organic solvents.

EXPERIMENTAL

2-Chloro-4-diethylamino-6-N-phenylhydroxyamino-sym-triazine. In a current of nitrogen at 35° C, 11.5 g (0.05 mole) of 2,4-dichloro-6-diethylamino-sym-triazine in 30 ml of dioxane was added over 20–30 min to a mixture of 0.82 g (0.075 mole) of phenylhydroxylamine in 50 ml of dioxane and 27.2 g (0.02 mole) of $CH_3COONa \cdot 3H_2O$ in 50 ml of water. The reaction mixture was heated at 40°–45° C for 2 hr 30 min to 3 hr, cooled, and poured into a double volume of water. The aqueous dioxane layer was decanted off and the oily residue was treated with ice water; the water was decanted off and then the product was treated with the minimum amount (~10 ml) of cold benzene. The addition of pentane (~30 ml) to the benzene solution precipitated the 2-chloro-4-diethylamino-6-N-phenylhydroxyamino-sym-triazine, which was filtered off and dried to give 6.8 g (46%) of practically pure product, mp 96°–98° C. After two reprecipitations from chloroform with n-pentane, mp 98°–99° C (decomp.). Found, %: C 53.14, 53.30; H 5.36, 5.74; Cl 12.35, 12.45; N 24.08, 24.12. Calculated for $C_{13}H_{16}ClN_5O$, %: C 53.15; H 5.49; Cl 12.07; N 23.84.

2-Chloro-4-di-n-propylamino-6-N-phenylhydroxyamino-sym-triazine. In a current of nitrogen at room temperature, 13.6 g (0.1 mole) of $CH_3COONa \cdot 3H_2O$ in 35 ml of water was added to a solution of 6.25 g (0.025 mole) of 2,4-dichloro-6-di-n-propylamino-sym-triazine in 20 ml of dioxane, the pH of the medium being ~7. At 35° C, 4.05 g (0.037 mole) of phenylhydroxylamine in 30 ml of dioxane was added dropwise over 30 min. The reaction mixture was stirred at 40°–45° C for 2 hr 30 min to 3 hr and was then cooled and poured into a double volume of water. A greenish oil precipitated which crystallized on strong cooling (acetone + dry ice). The dirty green crystals were filtered off and washed on the filter with cold pentane (~15 ml). After drying in air, 4.35 g (54%) of 2-chloro-4-di-n-propylamino-6-N-phenylhydroxyamino-sym-triazine was obtained with mp 99°–100° C (decomp.). After two recrystallizations from petroleum ether, mp 103°–103.5° C. Found, %: C 56.55, 56.67; H 6.40, 6.44, Cl 11.02, 10.67; N 21.66, 21.60. Calculated for $C_{15}H_{20}ClN_5O$, %: C 55.96; H 6.93; Cl 11.02. N 21.76.

After 3 to 4 recrystallizations, the substance became slightly yellow and its chlorine content fell to 9.23–9.28%.

2-Chloro-4-alkylamino-6-N-methylhydroxyamino-sym-triazines. In a current of nitrogen, a solution of 2.1 g (0.025 mole) of N-methylhydroxylamine hydrochloride in 5 ml of water at a temperature of −10 to −5° C was neutralized with 2.5 g (0.027 mole) of $NaHCO_3$ in 10 ml of water, the pH of the medium being ~6–7. At 0° C, 4.2 g (0.05 mole) of $NaHCO_3$ in 20 ml of water and 5.2 g (0.025 mole) of 2,4-dichloro-6-isopropylamino-sym-triazine in 35 ml of dioxane were added simultaneously at such a rate that the pH of the medium was about 7. Time of addition was about 10 min. The reaction mixture was stirred at −2° to +4° C for 1 hr and the slightly grayish precipitate that had deposited was filtered off and washed with distilled water until it was free from chloride ion (test with $AgNO_3$). The crystals were pressed out on the filter, dried in the air, and washed with cold (10° C) petroleum ether to eliminate the initial 2,4-dichloro-6-isopropylamino-sym-triazine. This gave 3.7 g (70%) of 2-chloro-4-isopropylamino-6-N-methylhydroxyamino-sym-triazine. Found, %: C 38.29, 38.40; H 5.21, 5.38; Cl 16.34, 16.46. Calculated for $C_7H_{12}ClN_5O$, %: C 38.62; H 5.50; Cl 16.29. On melting with an open thermometer (Terent'ev apparatus), the substance lost hydrogen chloride (litmus) at 40°–60° C and this process was particularly vigorous at 120°–150° C; at 220°–230° C, a vitreous substance was formed which melted with decomposition at 265°–275° C.

Under similar conditions, 2.1 g (0.025 mole) of N-methylhydroxylamine hydrochloride, 4.8 g (0.05 mole) of $(NH_4)_2CO_3$, and 4.85 g (0.025 mole) of 2,4-dichloro-6-ethylamino-sym-triazine yielded 2 g (40%) of 2-chloro-4-ethylamino-6-N-methylhydroxyamino-sym-triazine. Purification: at 15° C, 1 g of the crystals was treated with 3 ml of benzene. The insoluble residue was filtered off and it was repeatedly washed free from traces of the initial compound with cold benzene (3 ml), giving 0.5 g of 2-chloro-4-ethylamino-6-N-methylhydroxylamino-sym-triazine. Found, %: Cl 17.69, 17.83. Calculated for $C_6H_{10}ClN_5O$, %: Cl 17.41. On melting with an open thermometer (Terent'ev apparatus), at ~70° C the substance lost hydrogen chloride (litmus) and this process took place particularly vigorously at 140°–170° C. At 295°–300° C the decomposition products resinified completely.

2-Chloro-4-isopropylamino-6-hydroxyamino-sym-triazine. Under similar conditions, 5.2 g (0.025 mole) of 2,4-dichloro-6-isopropylamino-sym-triazine, 1.75 g (0.025 mole) of hydroxylamine hydrochloride, and 6.4 g (0.075 mole) of $NaHCO_3$ yielded 1.9 g (40%) of 2-chloro-4-isopropylamino-6-hydroxyamino-sym-triazine. After the end of the reaction, the mixture was extracted with benzene at room temperature (3 × 15 ml); a small amount of white precipitate at the boundary of the two phases was filtered off. The product was precipitated with petroleum ether (2 volumes). For analysis, this reprecipitation in the cold (5° C) was repeated 3-5 times. On melting with an open thermometer (Terent'ev apparatus), the 2-chloro-4-isopropylamino-6-hydroxyamino-sym-triazine foamed without melting at 115°–120° C and evolved hydrogen chloride vigorously at 120°–140° C. Found, %: Cl 17.05, 16.96. Calculated for $C_6H_{10}ClN_5O$, %: Cl 17.41.

Thermal polycondensation of 2-chloro-4-isopropylamino-6-N-methylhydroxyamino-sym-triazine. 2-Chloro-4-isopropylamino-6-N-methylhydroxyamino-sym-triazine (0.62 g) was heated for ~2 hr in a thermostat at 50° C, then for 3–4 hr in a silicone bath at 110°–115° C, and then for about 4 hr at 135°–140° C until the evolution of hydrogen chloride ceased (test with litmus). This gave 0.54 g of faintly yellowish crystals which vitrified at 220°–230° C and melted with pronounced browning at 265°–275° C. Found, %: Cl 5.48, 5.35; mol. wt. 564 ± ± 30. Calculated, %: Cl 6.12; mol. wt. 579.5 (for the trim $C_{21}H_{34}ClN_{15}O_3$); Cl 4.67%; mol. wt. 760.5 (for the tetramer $C_{28}H_{45}ClN_{20}O_4$).

REFERENCES

1. Yu. A. Baskakov and I. A. Mel'nikova, KhGS, collection 1, p. 430, 1967.
2. I. A. Mel'nikova, I. S. Beskina, and Yu. A. Baskakov, KhGS, collection 1, p. 440, 1967.
3. J. T. Thurston, J. R. Dudley, D. W. Kaiser, J. Hechenbleikner, F. C. Schaefer, and D. Holm-Hansen, J. Am. Chem. Soc., 73, 2981, 1951.
4. M. Goi, Yuki Gosei Kagaku Kyokaishi, 18, 337, 1960; C. A., 54, 19702, 1960.
5. C. K. Banks, J. Am. Chem. Soc., 66, 112, 1944.
6. H. Zollinger, Angew. Che., 73, 125, 1961.
7. C. K. Banks, O. M. Gruhzit, E. W. Tilliston, and J. Controulis, J. Am. Chem. Soc., 66, 1771, 1944.
8. J. T. Shaw, E. R. Nicottra, and R. K. Madison, J. Org. Chem., 27, 4054, 1962.
9. P. V. Tibanov, A. F. Vasil'ev, and Yu. A. Baskakov, KhGS [Chemistry of Heterocyclic Compounds], 4, 746, 1968.
10. L. M. Shuter and B. Yu. Gordinskii, ZhAKh, 13, 150, 1958.

9 July 1966

All-Union Scientific-Research
Institute for Chemical Plant
Protection Agents, Moscow