SYNTHESIS AND THERMAL DECOMPOSITION OF HALOALKOXY-sym-TRIAZINES.

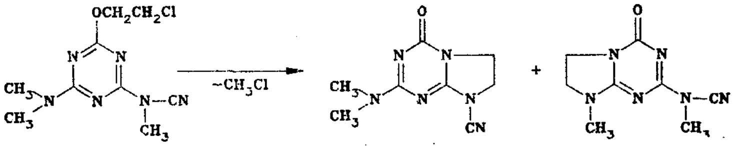
11.* SYNTHESIS AND THERMOLYSIS OF 2-(2-CHLOROETHOXY)-4-N-METHYL-N-METHOXYAMINO-6-DIMETHYLAMINO-sym-TRIAZINE

V. V. Dovlatyan, V. A. Pivazyan, K. A. Éliazyan,
and R. G. Mirzoyan

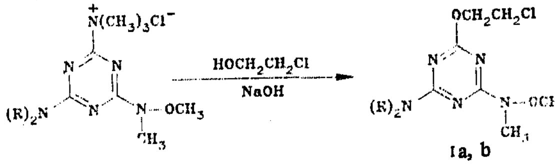
UDC 547.491'781.3.07:541.11

2-(2-Chloroethoxy)-4-N-methyl-N-methoxyamino-6-dialkylamino-sym-triazines were synthesized. In the case of the dimethylamino derivative it was established that thermolysis gives a mixture of oxooxazolo- and oxoimidazo-sym-triazines, the structures of which were proved by data from the IR, PMR, and mass spectra. A probable scheme for the rearrangement—cyclization reaction is proposed.

The thermolysis of 2-(2-chloroethoxy)-4-N-methyl-N-cyanoamino-6-dialkylamino-sym-triazines is accompanied by the elimination of methyl chloride; a methyl radical is eliminated from both the dimethylamino and methylcyanoamino groups, and this leads to the formation of a mixture of two imidazo-sym-triazines [1].



In the present paper we present the results of a study of the specificity of a similar reaction in the case of 2-(2-chloroethoxy)-4-N-methyl-N-methoxyamino-6-dialkylamino-sym-triazines Ia, b, which were obtained from (4-N-methyl-N-methoxyamino-6-dialkylamino-sym-triazin-2-yl) trimethylammonium chlorides and ethylene chlorohydrin in the presence of alkali at low temperatures [2].



Ia, b

Ia R=CH_3; b R=C_2H_5

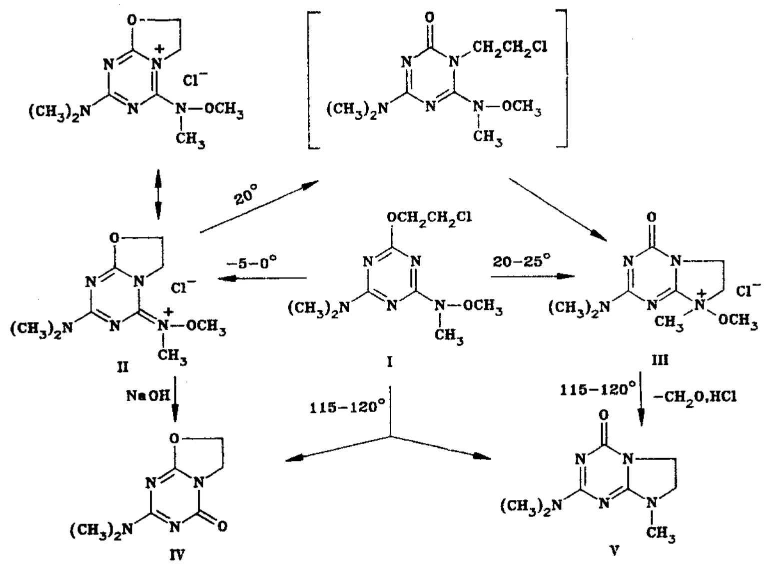
The indicated chlorides undergo thermolysis when they are heated briefly at 115-120°C. We found that a mixture of two substances, viz., 2-dimethylamino-4-oxo-4,5,6,7-tetrahydro-oxazolo[3,2-a]- (IV) and 2-dimethylamino-4-oxo-8-methyl-6,7-dihydroimidazo[1,2-a]-sym-triazine (V), respectively, is formed by alkaline treatment of the products of thermolysis of triazine Ia. A detailed study of this transformation provided a basis for proposing a scheme that includes the following consecutive reactions:

---

*See [5] for communication 10.

Armenian Agricultural Institute, Yerevan 375009. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1125-1128, August, 1985. Original article submitted April 17, 1984; revision submitted November 20, 1984.

0009-3122/85/2108-0942$09.50



Intramolecular quaternization product II is formed when I is allowed to stand at −5°C to 0°C; II is then converted to triazinoimidazolinium chloride III, evidently through the N-2-chloroethyl derivative. Salt III is also obtained when I is allowed to stand at 20-25°C. Thus in the case of I we were able for the first time to isolate triazinooxazolinium (II) and triazinoimidazolinium (III) salts, the intermediate formation of which was previously proposed in a study of the thermolysis of various 2-chloroethoxy-sym-triazines [2]; however, because of their instability, they were obtained only in aqueous solutions [3].

Compounds IV and V, respectively, are formed in the alkaline treatment of II and thermolysis product III. Two peaks with mass numbers 182 and 195 are observed in the mass spectrum of the product of thermolysis of I in the high m/z region.

The peak with mass number 182 corresponds to the molecular mass of IV, and the character of its fragmentation coincides almost completely with the mechanism of the fragmentation of the previously investigated oxooxazolo-sym-triazine [3, 4], which we isolated in the alkaline treatment of II (Fig. 1c).

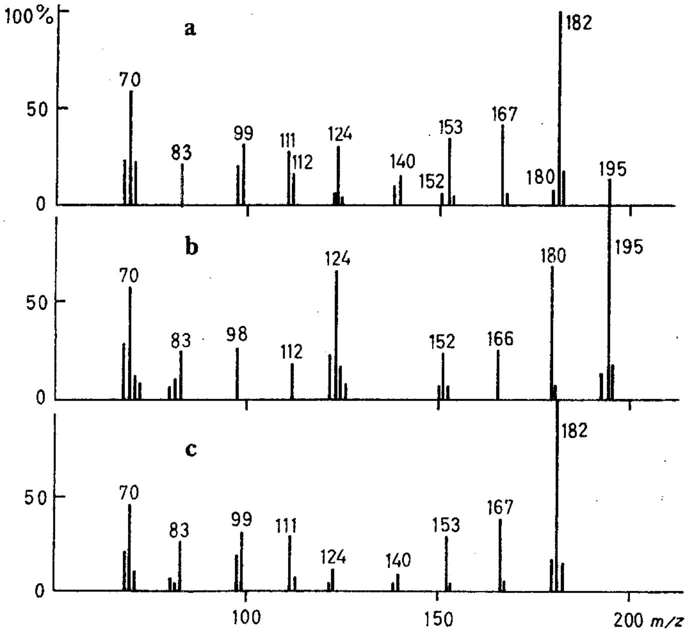


Fig. 1. Mass spectra: a) product of thermolysis of I; b) V; c) IV.

The peak with mass number 195 corresponds to the molecular mass of V; however, because of the low intensity of the peak of this ion, it is difficult to isolate the characteristic peaks of the fragment ions. Despite this, a comparison of mass spectra a, b, and c, where b is the mass spectrum of V, obtained by thermolysis of III and by thermolysis of 2-(2-chloroethoxy)-4,6-bis(dimethylamino)-sym-triazine [2], makes it possible to isolate the peaks of ions with m/z 180, 152, and 124, which are fragments of V.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions in deuteropyridine were obtained with a Varian T-60 spectrometer with tetramethylsilane (TMS) as the internal standard. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the samples into the ion source at an ionizing voltage of 30 eV. The individuality of the substances was verified by thin-layer chromatography (TLC) on Silufol UV-254 plates.

2-(2-Chloroethoxy)-4-N-methyl-N-methoxyamino-6-dialkyl-amino-sym-triazines Ia, b. These compounds were obtained by the method in [2]. Compound Ia, with mp 52-54°C, was obtained in 75% yield. Found: Cl 13.7; N 26.5%. $C_9H_{16}ClN_5O_2$. Calculated: Cl 13.6; N 26.8%. This product had R_f 0.57 [acetone—hexane (1:4)]. Compound Ib, with mp 40-42°C, was obtained in 79% yield. Found: Cl 12.5; N 24.4%. $C_{11}H_{20}ClN_5O_2$. Calculated: Cl 23.3; N 24.2%. R_f 0.44.

Thermolysis of Ia. A suspension of 1.3 g (5 mmole) of Ia in 5 ml of absolute toluene was heated at 115-120°C for 3 h, after which the toluene was decanted, and the residue was triturated with absolute ether. Filtration gave 1.1 g of a substance with mp 122-126°C (dec.). This product was treated with aqueous sodium hydroxide solution until a solution with pH 6-7 was obtained. This solution was evaporated at 20-25°C, and the mixture of IV and V was extracted with ethanol. Evaporation of the ethanol gave 0.6 g of a substance with mp 144-145°C. The mass spectrum of the thermolysis product is presented in Fig. 1a.

Quaternary Triazinooxazolinium Salt II. A 2.6-g (10 mmole) sample of I was maintained at —5°C to 0°C for 3 months, after which the resulting precipitate was treated with ether, and the solid material was removed by suction filtration and stored in a desiccator over sulfuric acid to give 1.6 g (60%) of a product with mp 60-61°C and R_f 0.22 [acetone—hexane (1:4)]. PMR spectrum: 3.25 [6H, s, $N(CH_3)_2$], 3.5 (3H, s, $N—CH_3$), 4.05 (3H, s, $N—OCH_3$), and 5.07 ppm (4H, s, $CH_2—CH_2$). Found: Cl 14.1; N 26.4%. $C_9H_{16}ClN_5O_2$. Calculated Cl 13.6; N 26.8%. In contrast to triazine I, the indicated compound was quite soluble in water and contained ionic chlorine. A mixture of II and I melted at 36-37°C.

2-Dimethylamino-4-oxo-4,5,6,7-tetrahydrooxazolo[3,2-a]-symtriazine (IV). A 0.2-g (5 mmole) sample of NaOH was added to a solution of 1.3 g (5 mmole) of II in 2 ml of water, and the resulting solution was evaporated at 20-25°C. Compound IV was extracted with chloroform, and the chloroform extract was evaporated to give 0.7 g (77%) of a substance with mp 180-182°C and R_f 0.40. IR spectrum: 1690 (C=O); 1636, 1560, 1504 cm^{-1} (C=N). PMR spectrum: 3.11 [d, $(CH_3)_2$] and 4.41 ppm [m, $(CH_2)_2$]. Found: C 46.3; H 5.8; N 30.4%. $C_7H_{10}N_4O_2$. Calculated: C 46.2; H 5.5; N 30.8%. No melting-point depression was observed for a mixture of IV with the product of thermolysis of 2-methoxy-4-(2-chloroethoxy)-6-dimethylamino-sym-triazine [3].

Quaternary Triazinoimidazolinium Salt III. A 5.2-g (20 mmole) sample of I was allowed to stand at 20-25°C for 20-25 days, after which the precipitate was treated with ether, and III was removed by filtration and stored in a desiccator over sulfuric acid to give 1.8 g (35%) of a product with mp 118-120°C (dec.). PMR spectrum: 3.20 and 3.25 (3H each, s, $N—CH_3$), 3.6 (3H, s, $N—CH_3$), 3.95 (3H, s, OCH_3), and 4.85 ppm (4H, m, NCH_2CH_2N). Found: Cl 14.0; N 27.2%. $C_9H_{16}ClN_5O_2$. Calculated: Cl 13.6; N 26.8%.

2-Dimethylamino-4-oxo-8-methyl-6,7-dihydroimidazo[1,2-a]-sym-triazine (V). A 1.3-g (5 mmole) sample of III was heated in 3 ml of toluene at 115-120°C for 4 h until hydrogen chloride evolution was complete. Cooling of the toluene solution precipitated V, which was removed by filtration and washed with petroleum ether to give 0.75 g (77%) of a product with mp 168-170°C. IR spectrum: 1695 (C=O); 1620, 1570, 1515 cm^{-1} (C=N). PMR spectrum: 3.0 (3H, s, $N—CH_3$), 3.2 [6H, s, $N(CH_3)_2$], and 3.9 ppm (4H, m, $CH_2—CH_2$). Found: C 49.9; H 7.1; N 35.5%; M^+ 195. $C_8H_{13}N_5O$. Calculated: C 49.2; H 6.7; N 35.9%; M^+ 195. No melting-point depression was observed for a mixture of Vwith the product of thermolysis of 2-(2-chloroethoxy)-4,6-bis(dimethylamino)-sym-triazine [2].

LITERATURE CITED

1. V. V. Dovlatyan, V. A. Pivazyan, K. A. Éliazyan, and R. G. Mirzoyan, Khim. Geterotsikl. Soedin., No. 11, 1558 (1980).
2. V. V. Dovlatyan, K. A. Éliazyan, and L. G. Agadzhanyan, Khim. Geterotsikl. Soedin., No. 2, 262 (1977).
3. V. V. Dovlatyan, K. A. Éliazyan, and A. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 7, 989 (1977).
4. R. G. Mirzoyan, S. M. Saakyan, M. P. Demirchyan, P. B. Terent'ev, A. V. Dovlatyan, and V. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 1, 124 (1982).
5. V. V. Dovlatyan, N. Kh. Khachatryan, T. A. Gomktsyan, and S. M. Saakyan, Khim. Geterotsikl. Soedin., No. 12, 1689 (1981).