SYNTHESIS AND THERMAL DECOMPOSITION OF HALOALKOXY-sym-TRIAZINES

5.* THERMAL DECOMPOSITION OF 2-METHOXY(METHYLTHIO)-4-[1,3-DICHLOROPROPOXY(3-CHLORO-1-PROPOXY)]-6-DIMETHYLAMINO-sym-TRIAZINES

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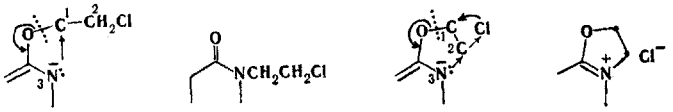
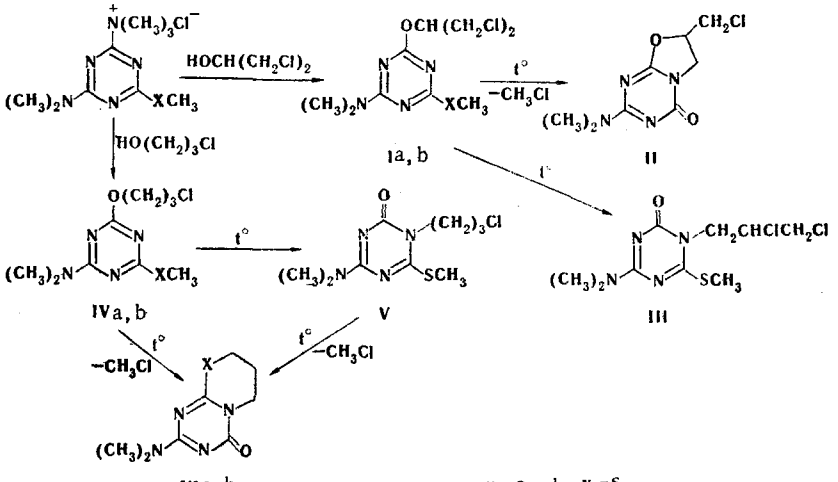
2-Methoxy(methylthio)-4-(1,3-dichloropropoxy)- and 2-methoxy(methylthio)-4-(3-chloro-1-propoxy)-6-dimethylamino-sym-triazines were synthesized and subjected to thermolysis, as a result of which chloromethyltetrahydrooxazolo-, N-2,3-dichloropropyl-sym-triazines and tetrahydrooxazino- and tetrahydrothiazino-sym-triazines, respectively, were obtained. The thermolysis of haloalkoxy-sym-triazines proceeds via a concerted mechanism.

The rearrangement of 2-methylthio(ethoxy, propoxy)-4-(2-chloroethoxy)-6-dialkylamino-sym-triazines to N-2-chloroethyl derivatives [1, 2] could have taken place either with the formation of a bond between the N_3 atom and the C_1 atom of the 2-chloroethoxy group, i.e., without the participation of the chlorine atom in the transition state, or with the formation of a bond between the nitrogen atom and the C_2 atom and migration of the chlorine atom to the C_1 atom:



A

The formation of [2-dialkylamino-4-alkoxy(methylthio)-6,7-dihydrooxazolo[3,2-a]-sym-triazinium] chlorides (structure A) when 2-chloroethoxy derivatives are heated in water still does not make it possible to make a choice, since the indicated salts could be formed after the formation of the N-2-chloroethyl derivatives, which are known [1] to undergo conversion to triazinium salts (A) when they are heated in water.



I, IV, VI a X=O; b X=S

*See [4] for communication 4.

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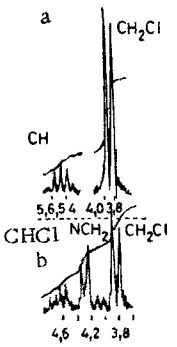
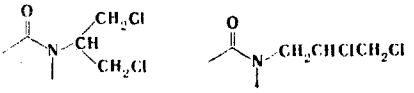


Fig. 1. PMR spectra:
a) Ib; b) III.

In order to shed some light on this problem we synthesized Ib, in the thermolysis of which both the N-1,3-dichloro-2-propyl and N-2,3-dichloropropyl derivatives could have formed, depending on the transition state:



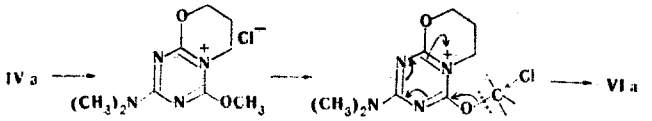
Compound III was obtained by thermolysis of Ib. The PMR spectrum of Ib (Fig. 1a) contains two signals characteristic for an AB_4 system for the 1,3-dichloropropyl group. A spectrum with the same character, also should have been expected for III in the case of retention of the 1,3-dichloropropyl grouping. However, three signals at 4.27 (d, 2H, NCH_2), 3.82 (d, 2H, CH_2Cl), and 4.67 ppm (m, 1H, CHCl) with a ratio of the integral intensities (2:1:2), that is characteristic for an A_2BC_2 system of the protons of the $CH_2CHClCH_2Cl$ group, are observed in the PMR spectrum of III. Thus, III is the N-2,3-dichloropropyl derivative. This means that the rearrangement of the 2-chloroethoxy derivative to the N-2-chloroethyl derivative in the case of 2-methylthio(ethoxy, propoxy)-sym-triazines proceeds with the formation of a bond between the N_3 atom and the C_2 atom and migration of the chlorine atom to the C_1 atom.

2-Dimethylamino-4-oxo-7-chloromethyl-4,5,6,7-tetrahydrooxazolo[3,2-a]-sym-triazine (II) is formed in the thermolysis of Ia.

The thermolysis of I proceeds more rapidly than the thermolysis of the corresponding 2-chloroethoxy derivatives* (see the experimental section), which is explained by the smaller degree of orderliness in the transition state (two chloromethyl groups of I and one in the 2-chloroethoxy derivatives).

In a previous communication, we presented evidence in favor of a concerted mechanism for the rearrangement of haloalkoxy-sym-triazines. From this point of view the thermolysis of IV is of interest. 2-Dimethylamino-4-oxo-4,5,6,7-tetrahydrooxazine[3,2-a]-sym-triazine (VIa) is formed in the thermolysis of IVa. Under the same conditions (120°C for 6.5 h) IVb does not undergo any changes. The latter undergoes rearrangement under more severe conditions (in n-octane for 20 h) to give V.

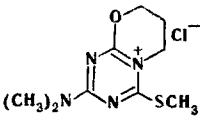
If the formation of VIa is regarded as a series of two isolated acts that include the



initial formation of a triazinium salt without participation of the 2-OCH_3 group of the sym-triazine ring (an ionic mechanism), the corresponding salt or the product of rearrangement of this salt should have been formed in the case of thermolysis of IVb under the same conditions. However, as indicated above, this does not occur. A variant involving

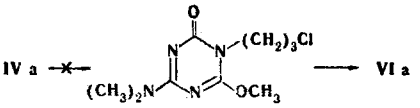
*According to refined data, 2.5 and 3.5 h, respectively, are required for complete thermolysis of 2-methoxy- and 2-methylthio-4-(2-chloroethoxy)-6-dimethylamino-sym-triazines at 120°C.

conversion of IVb to the salt by heating and rearrangement to the starting compound upon cooling is also excluded, since salts of this sort, like oxazolo-sym-triazinium salts, can

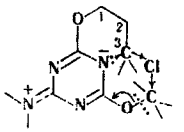


be cleaved only at the O—C_6 bond and cannot be cleaved at the 6 position of the condensed ring [1].

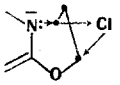
In addition, as in the case of 2-methoxy-4-(2-chloroethoxy)-6-dialkylamino-sym-triazines [1], an intermediate N-3-chloropropyl derivative that subsequently eliminates CH_3Cl cannot be formed in the thermolysis of IVa since, as we established in the thermolysis of IVb,



this sort of rearrangement requires more severe conditions. It remains to assume that in the case of thermolysis of IVc in an inert medium the substituent in the 2 position of the sym-triazine ring participates in the transition state i.e., the formation and cleavage



of the N—C_3 and C_3—Cl bonds proceed in a concerted fashion with the elimination of CH_3Cl and cleavage of the O—CH_3* bond. The transition state of the thermolysis of IVa has a lower energy barrier than the transition state without participation of the substituent in the 2 position of the sym-triazine ring, which leads to the formation of an N-3-chloropropyl derivative (V):



Thus, an increase of one CH_2 group as compared with the 2-chloroethoxy derivatives does not change the scheme of the thermolysis, which in the case of IV proceeds under more severe conditions (a greater degree of orderliness in the transition state). The thermolysis of 2-alkoxy(methylthio)-4-(2-chloroethoxy)- and 2-methoxy(methylthio)-4-(3-chloropropoxy)-6-dialkylamino-sym-triazines in a neutral medium proceeds via a concerted mechanism. Six electrons participate in the transition state, and the terminal fractions of the orbitals coincide with respect to phase — according to the theory of the boundary orbitals of concerted reactions, the reaction is permitted [4].

The difference in the course of the thermolysis on passing from the 2-methoxy-substituted compound to the 2-ethoxy(propoxy)-substituted compound, which consists in the direct elimination of CH_3Cl with the formation of N-2-chloroethyl-sym-triazines [1] can be explained by steric hindrance during attack by the chlorine atom of the alkoxy group (a bulky alkyl group in place of a hydrogen atom), whereas in the case of the thermolysis of 2-methylthio-sym-triazinesit can be explained by the lower polarity of the C—S bond as compared with the C—O bond.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of the compounds were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. The UV spectra were recorded with a Specord spectrophotometer. The purity of the compounds was monitored by thin-layer chromatography (TLC) on Silufol plates.

*On the basis of previous data [1] one can arrive at the same conclusion also for 2-methoxy-4-(2-chloroethoxy)-6-dialkylamino-sym-triazines.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp, °C	R_f[a]	Found, %					Empirical formula	Calc., %					Yield, %
			C	H	Cl	N	S		C	H	Cl	N	S	
Ia	106—107	0,52	38,2	4,8	25,4	19,6	—	$C_9H_{14}Cl_2N_4O_2$	38,4	5,0	25,3	19,9	—	96
Ib	107—108	0,70	36,2	4,5	24,1	18,7	10,9	$C_9H_{14}Cl_2N_4OS$	26,4	4,7	23,9	18,9	10,8	95
II	179—181	0,10	41.5	4,8	15,2	24,4	—	$C_8H_{11}ClN_4O_2$	41,6	4,8	15,4	24,3	—	97
III	111—113	0,20	36,5	4,9	24,9	19,1	11,0	$C_9H_{14}Cl_2N_4OS$	36,4	4,7	25,1	18,9	10,8	96
IVa	62—64	0,47	44,0	6,0	14,3	22,6	—	$C_9H_{15}ClN_4O_2$	43,8	6,1	14,4	22,7	—	90
IVb	63—65	0,75	41,0	5,6	13,7	21,0	12,4	$C_9H_{15}ClN_4OS$	41,1	5,7	13,5	21,3	12,2	85
V	149—151	0,50	43,3	5,8	13,4	21,2	12.2	$C_9H_{15}ClN_4OS$	43,1	5,7	13,5	21,3	12,2	94
VIa	169—172	0,14	48,7	6,3	—	28,8	—	$C_8H_{12}N_4O_2$	49,0	6,1	—	28,6	—	97
VIb	161—163	0,12	45,5	5,9	—	26,5	14,9	$C_8H_{12}N_4OS$	45,3	5,7	—	26,4	15,1	89

[a]In the case of elution with acetone—hexane (1:1) for II, V, and VIa; acetone—hexane (1:2) was used for the remaining compounds.

TABLE 2. Spectral Characteristics of the Synthesized Compounds

Compound	UV spectra,[a] λ_{max}, nm (log ε)	IR spectra, cm^{-1}		PMR spectra,[b] δ, ppm				
		ν_{CO}	ν triazine ring	CH	CH_2Cl	CH_2N	CH_2O	C-CH_2-C
Ib	234 (4,59)	—	1593, 1580, 1506	5,39	3,83	—	—	—
II	237 (4,56)	1712	1645, 1575, 1500	5,26	3,90	4,20	—	—
III	257 (4,59) 236 (4,47) 218 (4,38)	1681	1615—1585, 1556, 1545	4,67	3,82	4,27	—	—
IVa	227 (4,33)	—	1593, 1542	—	3,67	—	4,37	2,16
V	257 (4,30) 235 (4,44) 217 (4,50)	1685	1590, 1540	—	3,57	4,01	—	2,16
VIa	235 (4,54) 214 (4,57)	1700	1620—1595, 1570, 1515	—	—	3,91	4,47	2,22
VIb	267 (4,38) 236 (4,49) 217 (4,54)	1685	1585—1560	—	—	4,00	3,17 (CH_2S)	2,30

[a]The UV spectra of solutions of the compounds in C_2H_5OH were recorded. [b]The PMR spectra of Ib, III, and IVa were recorded from solutions in CCl_4; the remaining PMR spectra were obtained from solutions in $CDCl_3$.

Compounds I and IV were obtained by a previously described method with glycerol 1,3-dichlorohydrin and propylene chlorohydrin, respectively, in place of ethylene chlorohydrin. In the preparation of I the solutions, afterthe dropwise addition of NaOH solution, were allowed to stand for 30 min to 1 h (from 3 h to 3.5 h in the case of IV). Data on the synthesized compounds is presented in Tables 1 and 2.

2-Dimethylamino-4-oxo-7-chloromethyl-4,5,6,7-tetrahydrooxazolo[3,2-a]-sym-triazine (II). A suspension of 0.01 mole of Ia in 4 ml of toluene was heated at 120°C for 40 min, after which it was cooled, and ether was added to the precipitate. Compound II was removed by filtration.

2-Methylthio-3-(2,3-dichloropropyl)-4-oxo-6-dimethylamino-3,4-dihydro-sym-triazine (III). A suspension of 0.01 mole of Ib in 4 ml of toluene was heated at 120°C for 2 h, after which it was evaporated on a water bath. The residue was refluxed with petroleum ether and removed by filtration to give III.

2-Methylthio-3-(3-chloropropyl)-4-oxo-6-dimethylamino-3,4-dihydro-sym-triazine (V). A suspension of 0.01 mole of IVb in 4 ml of n-octane was refluxed for 20 h, after which it was cooled and dissolved in $CHCl_3$. The solution was evaporated, and the residue was triturated with petroleum ether and removed by filtration to give V.

2-Dimethylamino-4-oxo-4,5,6,7-tetrahydrooxazino[3,2-a]-sym-triazine (VIa). A suspension of 0.01 mole of IVa in 4 ml of toluene was heated at 120°C for 6.5 h, after which it was cooled and treated with ether. The precipitated VIa was removed by filtration.

2-Dimethylamino-4-oxo-4,5,6,7-tetrahydrothiazino[3,2-a]-sym-triazine (VIb). Compound V was heated at 180-185°C for 6.5 h, after which it was cooled. Compound VIb began to crystallize out when the product was triturated with toluene.

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