REARRANGEMENTS IN THE HALOALKOXY(MERCAPTO, AMINO)-sym-TRIAZINE SERIES.

4.* REARRANGEMENT OF 2-CHLOROETHOXY-sym-TRIAZINES

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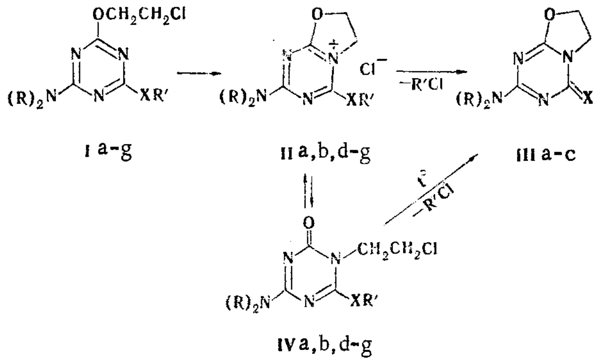
UDC 547.873'787.3

It is shown by means of an O^{18} label that the thermolysis of 2-methoxy-4-(2-chloroethoxy)-6-dialkylamino-sym-triazines to give oxazolo-sym-triazines in an inert medium proceeds without the formation of intermediate N-2-chloroethyl derivatives. In contrast to this, the thermolysis of 2-ethoxy(propoxy)-4-(2-chloroethoxy) derivatives gives N-2-chloroethyl derivatives, which upon prolonged heating are converted to oxazolo-sym-triazines. Triazinium salts are formed when both 2-chloroethoxy and N-2-chloroethyl derivatives are heated in water. The triazinium salts undergo rearrangement to N-2-chloroethyl derivatives when the water is removed. On the basis of the data obtained it is assumed that the thermolysis of 2-chloroethoxy-sym-triazines in an inert medium proceeds via a concerted mechanism, whereas thermolysis proceeds via an ionic mechanism in water. Data from the UV, IR, and PMR spectra are presented.

The rearrangement of 2-methoxy-4-(2-chloroethoxy)-6-dialkylamino-sym-triazines (Ia,b) to oxazolo-sym-triazines (IIIa,b) [2] may proceed via one of the schemes indicated below:



I—IV a $R=CH_3$, $R'=CH_3$, $X=O$; b $R=C_2H_5$, $R'=CH_3$, $X=O$; c $R=CH_3$, $R'=CH_3$, $X=O^{18}$; d $R=CH_3$, $R'=CH_3$, $X=S$; e $R=C_2H_5$, $R'=CH_3$, $X=S$; f $R=CH_3$, $R'=C_2H_5$; $X=O$; g $R=CH_3$, $R'=C_3H_7$, $X=O$

Attempts to isolate N-2-chloroethyl derivatives (IVa,b) in the course of the reaction or to detect traces of them during prolonged standing of Ia,b at room temperature did not give positive results. Oxazolo-sym-triazine IIIc obtained by thermolysis of Ic with an O^{18}-labeled methoxy group contains an oxygen label in the carbonyl group, as indicated by the appearance in the IR spectrum of the only new, as compared with the absorption of the unlabeled oxazolo-sym-triazine IIIa, absorption in the region characteristic for its C=O vibrations, the mass effect of which is 10 cm^{-1}. The rearrangement of Ia,b to IIIa,b consequently proceeds without the formation of IVa,b intermediates, for otherwise the oxygen label would have been observed in the oxazolidine ring.

On the other hand, as we have previously shown, Id,e form IVd,e [1]. Compounds If,g behave similarly. When they are heated briefly in toluene, they are converted to IVf,g, which form oxazolotriazines IIIa with the elimination of RCl when they are heated for a long time.

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*See [1] for communication 3.

Armenian Agricultural Institute, Yerevan 375009. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 124-127, January, 1979. Original article submitted December 7, 1977; revision submitted April 24, 1978.

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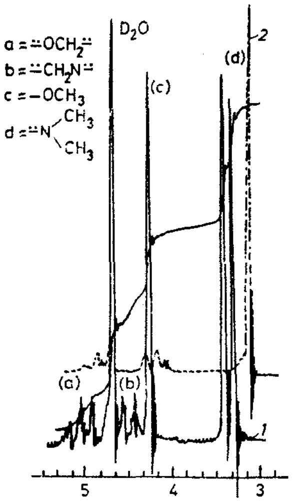
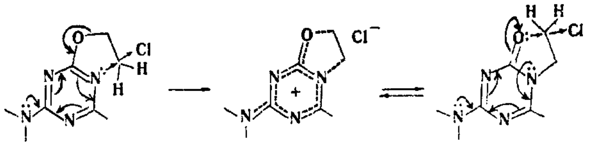


Fig. 1. PMR spectra: 1) IIa; 2) IIIa.

One might have expected that during the thermolysis of I in water salts II, the formation of which has been assumed, would be stabilized as a result of solvation and could not be detected. In fact, I, which are only slightly soluble in water, dissolve to give salts II upon brief heating. The appreciable shift of the methylene and dimethylamino protons in the PMR spectrum of IIa (Fig. 1) to the weak-field side as compared with the spectrum of IIIa [0.25, 0.24, and 0.21 ppm, respectively, for NCH_2, $N(CH_3)_2$, and OCH_2] is due to distribution of the positive charge over the entire cation.

Salts II are readily formed by heating IV in water. The identical character of the PMR spectra of salts II obtained from both I and IV constitutes evidence that the rearrangement of I in water and in an inert medium proceeds exclusively in the 5 position; the shift of the electrons involves the dialkylamino group (rotation about the exocyclic C–N bond is inhibited, Fig. 1) and is directed toward the 5-N atom in the case of I and toward the oxygen atom of the carbonyl group in the case of IV.



Salts II are stable only in aqueous solutions. When aqueous solutions of salts II are evaporated at room temperature, the salts undergo rearrangement to IV. The formation of N-2-chloroethyl derivatives when water is removed from salts IIa,b indicates that salts IIa,b are not formed as intermediates in the thermolysis of Ia,b in an inert medium, since if they were formed, their subsequent stabilization should have led to the formation of N-2-chloroethyl derivatives, and this does not actually occur. Although the thermolysis of Ia,b and Id-g in an inert medium proceeds via different schemes, there is no basis whatsoever to assume that it also proceeds via a different mechanism. It may therefore be assumed that the thermolysis of 2-chloroethoxy-sym-triazines in an inert medium proceeds without the formation of intermediate II, i.e., via a concerted mechanism, whereas it proceeds via an ionic mechanism in water; the change in the mechanism does not involve the reaction center, which is the 5-N atom in both variants.

EXPERIMENTAL

The UV spectra of ethanol (I and VI) and water (II) solutions of the compounds were recorded with a Specord spectrophotometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of solutions of the compounds in 10% D_2O (II) and CCl_4 (I and IV) were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard. The individuality of the compounds was determined by thin-layer chromatography (TLC) on Silufol UV-254 plates in an acetone–hexane system (1:2).

Compounds If,g were obtained by a method similar to that described in [2] through the intermediate formation of [2-ethoxy(propoxy)-6-dimethylamino-sym-triazin-4-yl]trimethylam-

TABLE 1. 2-Alkoxy-4-(2-chloroethoxy)-6-dimethylamino-sym-triazines (If,g) and 2-Alkoxy-(2-chloroethyl)-4-oxo-6-dialkylamino-3,4-dihydro-sym-triazines (IVa,b,f,g)[a]

Compound	mp, °C	Found, %		Empirical formula	Calc., %		R_f	PMR spectrum, δ, ppm		IR spectrum, ν, cm⁻¹		UV spectrum, λ_{max}, nm (log ε)	Yield,[c] %
		Cl	N		Cl	N		XCH_2[b]	CH_2Cl	C=O	C=N		
If	44—46	14,2	23,0	$C_9H_{15}ClN_4O_2$	14,4	22,7	0,76	4,45	3,69	—	1591 1538	229 (4,49)	94
Ig	34—35	13,3	21,6	$C_{10}H_{15}ClN_4O_2$	13,6	21,5	0,64	4,47	3,70	—	1590 1535	228 (4,20)	89
IVa	102—103	15,0	24,4	$C_8H_{13}ClN_4O_2$	15,3	24,1	0,19	4,08	3,63	1704	1620 1565 1555 1500	235 (4,12)	57
IVb	63—65	13,4	21,8	$C_{10}H_{17}ClN_4O_2$	13,6	21,5	0,36	4,09	3,63	1705	1622 1557 1550 1505	238 (4,21)	43
IVf	98—99	14,2	22,9	$C_9H_{15}ClN_4O_2$	14,4	22,7	0,19	4,08	3,66	1692	1615 1572 1555 1505	236 (4,37)	92
IVg	99—100	13,4	22,6	$C_{10}H_{17}ClN_4O_2$	13,6	21,5	0,20	4,09	3,67	1700	1620 1572 1560 1505	237 (4,37)	90

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a) The physicochemical and spectral data for IVd,e were presented in a previous communication. b) X = O for I, and X = N for IV. c) The yields are based on the converted Ia,b.

TABLE 2. [2-Dialkylamino-4-alkoxy(methylthio)-6,7-dihydrooxazolo[3,2-a]-sym-triazinium] Chlorides (II)

Compound II	Reflux time, min	Found, %	Empirical formula	Calc., %	PMR spectra, δ, ppm		UV spectrum, λ_{max} nm (log ε)	Yield,[a] %
		Cl^-		Cl^-	OCH_2	CH_2N		
a	2,5	15,0	$C_8H_{13}ClN_4O_2$	15,3	5,04	4,42	235 (4,46)	98
b	3,0	13,2	$C_{10}H_{17}ClN_4O_2$	13,6	5,06	4,42	238 (4,63)	97
c	2,5	14,1	$C_8H_{13}ClN_4OS$	14,3	5,07	4,45	240 (4,00)	99
d	3,5	12,8	$C_{10}H_{17}ClN_4OS$	13,0	5,05	4,43	243 (4,13)	98
e	2,5	14,0	$C_9H_{15}ClN_4O_2$	14,4	5,03	4,42	236 (4,41)	97
f	3,0	13,4	$C_{10}H_{17}ClN_4O_2$	13,6	5,02	4,41	237 (4,12)	98

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a) The yields were calculated from the percentage of Cl^- ions in solution.

monium chlorides in 93% yield in the case of the ethoxy derivative, with mp 110-111°C (dec.). Found: Cl 12.9; N 26.5%. $C_{10}H_{20}ClN_5O$. Calculated: Cl 13.2; N 26.7%.

The propoxy derivative, with mp 104-105°C (dec.) was obtained in 87% yield. Found: Cl 12.7; N 24.7%. $C_{11}H_{22}ClN_5O$. Calculated: Cl 12.9; N 24.8%.

Compounds Ic and IIIc were obtained by the method in [2] by means of $CH_3O^{18}H$. IR spectra: Ic 1066 cm⁻¹ (C-O^{18}-C); IIIc 1689 cm⁻¹ (C=O^{18}).

2-Alkoxy-3-(2-chloroethyl)-4-oxo-6-dialkylamino-3,4-dihydro-sym-triazines (IV, Table 1). A) Aqueous suspensions (10%) of Ia,b were heated with thorough stirring at 70°C for 1-1.5 h, after which the solutions were cooled and extracted with CCl_4. The aqueous solutions were evaporated at room temperature, and the residues were dried thoroughly in a desiccator over sulfuric acid. They were then treated with CCl_4 and filtered, and the filtrates were worked up to give IVa,b, which were recrystallized from hexane.

B) Suspensions of 30% solutions of If,g in toluene were heated at 125°C for 1 h, after which they were evaporated on a water bath, and the residues were recrystallized from petroleum ether.

2-Alkylamino-4-alkoxy(methyltrio)-6,7-dihydrooxazolo[3,2-a]-sym-triazinium Chlorides (II, Table 2). Aqueous suspensions (10%) of IV were refluxed at 120°C for 2-3 min, and the resulting solutions of II were cooled and analyzed. The purity of the solutions was monitored by means of the PMR spectra. Removal of the water gave the starting IV.

LITERATURE CITED

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2. V. V. Dovlatyan, K. A. Éliazyan, and A. V. Dovlatyan, Khim. Geterotsikl. Soedin., No. 7, 989 (1977).