Bis[4-phenyl-5-(p-tolyl)-1,2,4-triazol-3-yl] Disulfide (XII). A solution of 1.3 g (5 mmole) of iodine in 50 ml of ethanol was added dropwise with thorough stirring and ice cooling in the course of 30 min to a solution of 2.89 g (10 mmole) of VII in 25 ml of ethanol. After all of the iodine had been added, the reaction mixture was stirred at room temperature for another 30 min. The resulting precipitate was separated by filtration.

Similar iodination of VIII gave bis[4-phenyl-5-(p-nitrophenyl)-1,2,4-triazol-3-yl] disulfide (XIII).

4-Iodomethyl-4,5-dihydro-6-(p-tolyl)thiazolo[2,3-c]-1,2,4-triazole Hydriodide (XIV). A solution of 2.54 g (10 mmole) of iodine in 100 ml of ethanol was added dropwise with thorough stirring and ice cooling to a solution of 2.31 g (10 mmole) of III in 15 ml of ethanol. After all of the iodine solution had been added, the reaction mixture was stirred for another 30 min at room temperature. The precipitate was removed by filtration and washed with ether.

Thiazolo[2,3-c]triazoles XV-XVII were similarly obtained by iodination of IV-VI.

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SYNTHESIS OF 2-(4'-METHYL-1',3'-IMIDAZOLIDON-1'-YL)-sym-TRIAZINES

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N-Cyano-N-allylamino-sym-triazines, which were synthesized by the reaction of allyl bromide and the potassium salts of cyanoamino-sym-triazines, were converted to 2-(4'-methyl-1',3'-imidazolidon-1'-yl)-sym-triazines by the action of hydrogen peroxide in an alkaline medium. A similar transformation occurred in hydrochloric acid or under the influence of hydrogen chloride in alcohol. The structures of the products were confirmed by IR and mass-spectral data and alternative synthesis.

sym-Triazine derivatives have great practical value as chemical agents for the protection of plants. Epoxypropylamino-sym-triazines could be of definite interest as herbicides if one takes into account their structural similarity to the preparation "metoprotrin" [2-methylmercapto-4-isopropylamino-6-(3-methoxypropylamino)-sym-triazine], which displays pronounced selectivity with respect to grain crops [1].

In order to study the possibility of obtaining epoxypropylamino derivatives of sym-triazines we synthesized N-cyano-N-allylamino-sym-triazines and studied their behavior under epoxidation conditions. The synthesis of N-cyano-N-allylamino-sym-triazines I-IX (see Table 1) was accomplished by the reaction of the potassium salts of cyanoamino-sym-triazines with allyl bromide.

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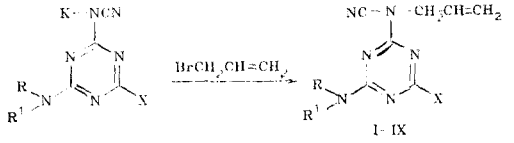
TABLE 1. N-Cyano-N-allylamino-sym-triazines

Compound	R	R'	X	mp, °C	R_f	Empirical formula	N, % found	N, % calc.	Yield, %
I	CH_3	CH_3	$N(CH_3)_2$	87—89	0,54	$C_{11}H_{17}N_7$*	39,35	39,65	90
II	i-C_3H_7	H	NHC_3H_7-i	110—112	0,65	$C_{13}H_{21}N_7$	35,35	35,63	89
III	C_2H_5	H	NHC_2H_5	66—68	0,69	$C_{11}H_{17}N_7$	39,60	39,68	90
IV	CH_3	CH_3	OCH_3	88—90	0,51	$C_{10}N_{14}N_6O$	36,11	35,89	85
V	i-C_3H_7	H	OCH_3	78—80	0,49	$C_{11}H_{16}N_6O$	33,49	33,87	76
VI	CH_3	CH_3	SCH_3	89—90	0,63	$C_{10}H_{14}N_6S$	34,01	33,60	90
VII	i-C_3H_7	H	SCH_3	—†	0,69	$C_{11}H_{16}N_6S$	32,11	31,80	70
VIII	CH_3	CH_3	Cl	84—85	0,35	$C_9H_{11}N_6Cl$	35,61	35,22	83
IX	s-C_4H_9	H	Cl	—†	0,41	$C_{11}H_{15}N_6Cl$	31,16	31,51	78

*Mass spectrum, m/z (%): 247 (100), 246 (46), 232 (58), 218 (12), 207 (54), 163 (50), 96 (86), 71 (70), 69 (54), 44 (78), 43 (55), and 41 (80).

†A viscous undistillable liquid.

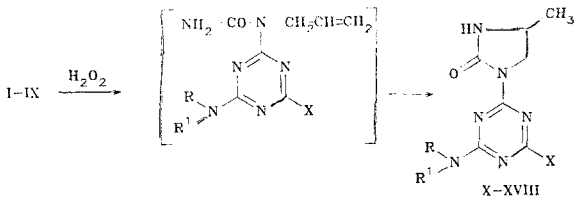


I–IX

Absorption bands at 2240 (νC≡N), 3090 and 3030 (νC—H), 1640 (νC=C), and 990, 950, and 920 cm^{-1} (δCH_2=CH) are present in the IR spectra of all of the compounds obtained.

In addition to the maximum peak of a molecular ion (M^+) with mass number 247, peaks of ions at 218* ($[M - NCH_3]^+$) and at 207 and 163, which are formed as a result of the successive elimination of allyl and dimethylamino groups by M^+, are present in the mass spectrum of I (Table 1). These mass-spectrometric data confirm the structure of I.

We have established that the corresponding epoxy compounds are not formed in the action of hydrogen peroxide on I-IX in the presence of potassium carbonate and that substituted triazinylurea derivatives, which subsequently undergo cyclization to give 2-(4'-methyl-1',3'-imidazolidon-1'-yl)-sym-triazine derivatives, are formed, evidently as a result of initial hydrolysis of the cyano group.



X–XVIII

This intramolecular heterocyclization reaction proceeds in the same way as the formation of 3-aryl-4-methylene-5-alkyl(5,5-dialkyl)oxazolidin-2-ones from alkynyl esters of arylcarbamic acids [2] or the synthesis of 5-methyl-3,3-diphenylpyrrolidin-2-one from 2,2-diphenylpenten-4-oic acid nitrile [3].

The IR spectra of X-XVIII contain absorption bands at 1690 cm^{-1} that are due to an amide C=O group, but absorption bands of C≡N, CH_2—CH=CH_2, and CH_2—CH—CH_2 groups are absent.

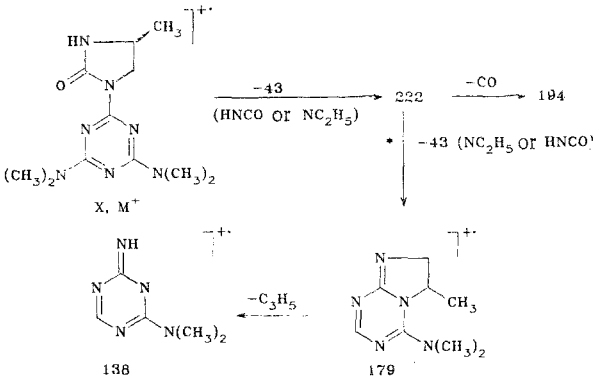
The formation of an imidazolidone ring is confirmed by data from the mass spectrum of X, in which, first, the $[M - C_3H_4]^+$ ion peak that is characteristic for allylarylamines (see the ion at 207 in the spectrum of I) is absent, and, second, ion peaks at 222, 194, 179, and 138 (see Table 2), which are formed in different stages of the dissociative ionization, are observed:

*Here and subsequently, the numbers that characterize the ions are the m/z values.

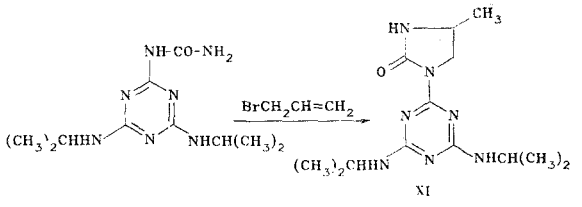
TABLE 2. 2-(4'-Methyl-1',3'-imidazolidon-1'-yl)-4,6-Substituted sym-Triazines

Compound	R	R'	X	mp, °C	R_f	Empirical formula	N, % found	N, % calc.	Yield, %
X	CH_3	CH_3	$N(CH_3)_2$	169—170	0,30	$C_{11}H_{19}N_7O$*	37,00	36,97	78
XI	i-C_3H_7	H	NHC_3H_7-i	146—147	0,40	$C_{13}H_{23}N_7O$	33,6	33,44	76
XII	C_2H_5	H	NHC_2H_5	138—140	0,42	$C_{11}H_{19}N_7O$	36,8	36,98	85
XIII	CH_3	CH_3	OCH_3	118—120	0,55	$C_{10}H_{16}N_6O_2$	33,5	33,2	75
XIV	i-C_3H_7	H	OH	318—320	0,47	$C_{10}H_{16}N_6O_2$	33,1	33,3	66
XV	CH_3	CH_3	SCH_3	140—141	0,50	$C_{10}H_{16}N_6SO$	31,4	31,3	83
XVI	i-C_3H_7	H	SCH_3	142—143	0,55	$C_{11}H_{18}N_6SO$	29,9	29,7	85
XVII	CH_3	CH_3	Cl	141—142	0,60	$C_9H_{13}N_6ClO$	32,5	32,7	70
XVIII	s-C_4H_9	H	OH	120—122	0,52	$C_{11}H_{18}N_6O_2$	31,7	31,5	64

*Mass spectrum, m/z (%): 265 (58), 222 (42), 221 (27), 207 (50), 195 (25), 194 (16), 179 (25), 138 (25), 96 (100), 71 (75), and 44 (28).



The structure of 2-(4'-methyl-1',3'-imidazolidon-1'-yl)-4,6-bis(isopropylamino)-sym-triazine (XI) was confirmed by alternative synthesis by reaction of the corresponding triazinylurea [4] with allyl bromide.



We also carried out the acidic hydrolysis of I-IX with hydrochloric acid or in alcohol under the influence of hydrogen chloride. In an aqueous medium under conditions of peroxide-alkaline or acidic hydrolysis N-alkyl-N-cyanoamino-sym-triazines that contain a labile methoxy group or a labile chlorine atom in the 4 position and an amino hydrogen atom in the 6 position undergo hydrolysis to the corresponding hydroxy compounds (XIV, XVIII).

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer. The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionization energy of 50 eV. The individuality of the substances was monitored by thin-layer chromatography (TLC) on Silufol UV-254 with acetone—hexane (4:5) as the eluent and development with 2% $AgNO_3$ + 4% Bromphenol Blue + 4% citric acid.

2-N-Cyano-N-allylamino-sym-triazines (I-IX). A 1.4-g (0.011 mole) sample of allyl bromide was added to 0.01 mole of the potassium salt of the 2-cyanoamino-sym-triazine [obtained from 0.01 mole of the corresponding cyanoamino-sym-triazine [5, 6] and 0.7 g (0.011 mole) of ground potassium hydroxide in 15 ml of acetone], and the mixture was heated at 50-60°C for

3-4 h. The mixture was filtered, the acetone was removed from the filtrate, the residue was treated with water, and the aqueous mixture was filtered (Table 1). The products were recrystallized from octane. IR spectrum: 2240 (C≡N); 1540, 1600 (C=N); 3090, 3030, 1640, 940, 950, 920 cm^{-1} (CH=CH_2).

2-(4'-Methyl-1',3'-imidazolidon-1'-yl)-sym-triazines (X-XVIII). A) A 20-ml sample of a 4 N solution of K_2CO_3 was added with ice cooling to 0.01 mole of I-IX in 40 ml of methanol, after which 20 ml of 30% hydrogen peroxide was added dropwise, and the mixture was heated at 40-50°C for 6 h. The precipitate was removed by filtration to give X-XVIII (see Table 2).

B) An 8-ml sample of concentrated hydrochloric acid was added to 0.01 mole of I, II, or III, and the mixture was allowed to stand overnight. Water (10 or 15 ml) was added, and the mixture was neutralized with sodium carbonate. The resulting precipitate was removed by filtration and recrystallized from aqueous acetone (1:1). This method was used to obtain X-XII (Table 2). IR spectrum: 1690 (C=O); 3300 (NH); 1540, 1600 cm^{-1} (C=N).

2-(4'-Methyl-1',3'-imidazolidon-1'-yl)-sym-triazines (XIV-XVII). A 1.5-g sample of dry hydrogen chloride was passed through a solution of 0.01 mole of V-VIII in 15 ml of methanol, after which the mixture was allowed to stand overnight. Water (10 ml) was then added, and the mixture was neutralized with sodium carbonate. The precipitate was removed by filtration. This method was used to obtain XIV-XVII (Table 2).

2-(4'-Methyl-1',3'-imidazolidon-1'-yl)-4,6-bis(isopropylamino)-sym-triazine (XI). A mixture of 0.35 g (0.005 mole) of ground potassium hydroxide, 1.25 g (0.005 mole) of 2-carbamido-4,6-bis(isopropylamino)-sym-triazine, and 10 ml of acetone was stirred for 1 h, after which 0.7 g (0.005 mole) of allyl bromide was added, and the mixture was heated at 60-65°C for 8 h. The acetone was removed, and the residue was washed with water and removed by filtration to give 0.3 g (41%) of a product with mp 146-147°C; no melting-point depression was observed for a mixture of this product with XI obtained by method A.

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