recrystallized from ethanol (220 ml for 1 g product) to yield 3 g (15%) yellow crystals mp 235-236°C. Proton NMR spectrum (ppm): 1.33 (t, CH_3); 4.34 (q, CH_2); 11.40 (s, NH); centers of aromatic proton multiplets at 7.25 and 7.85 ppm (peri). UV spectrum in methanol, λ_{max}, nm (log ε): 252 (4.51); 371 (4.16); 392 (4.28), 418 (4.13). Found, %: C 52.4, H 4.5, N 7.8, S 8.8; M 364. $C_{16}H_{16}N_2O_6S$. Calculated, %: C 52.8, H 4.4, N 7.7, S 8.8.

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SYNTHESIS AND PROPERTIES OF DERIVATIVES OF sym-TRIAZINE.

5.* SYNTHESIS AND MASS SPECTROMETRIC STUDY OF CARBAMIDE DERIVATIVES OF sym-TRIAZINE

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The reaction of 2-amino- and 2,4-diamino-sym-triazines with nitrourea and phenyl isocyanate was studied; it gives N-mono- and N,N'-disubstituted ureas that contain sym-triazine segments. General features were established for the decomposition of carbamide derivatives of sym-triazine under electron impact.

Among the carbamide derivatives of sym-triazine are substances having bactericidal and antitumor properties, fungicides, and prospective herbicides [2-4]. But until now such sym-triazine derivatives have been difficult to obtain in spite of a number of partial or multistep methods of synthesis [5-8].

The present work is a study of the reaction of a number of 2-amino-4,6-disubstituted sym-triazines (I-VII) and 2,4-diamino-6-alkyl(aryl)-sym-triazines (VIII-XIII) with nitrourea and phenyl isocyanate.

*For Communication 4, see [1].

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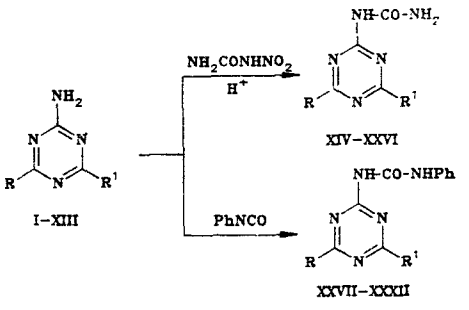
TABLE 1. Properties of Synthesized Compounds[a]

Compound	mp, °C[b]	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
III	85—86,5	73,2	11,8	15,0	$C_{23}H_{44}N_4$	73,4	11,7	14,9	45
IV	97—98	77,8	12,6	10,1	$C_{37}H_{72}N_4$	77,6	12,6	9,8	42
V	140—141,5	50,2	7,1	14,9	$C_{16}H_{27}Cl_3N_4$	50,3	7,1	14,7	94
VI	118—119	74,5	9,5	15,6	$C_{22}H_{34}N_4$	74,6	9,6	15,8	89
VII	124—125	76,2	10,2	13,5	$C_{26}H_{42}N_4$	76,1	10,2	13,7	82
IX	170—172	65,4	10,7	24,1	$C_{16}H_{31}N_5$	65,5	10,6	23,9	84
X	167—168	70,2	11,5	18,3	$C_{22}H_{43}N_5$	70,0	11,4	18,6	81
XI	304—305	58,2	9,5	26,0	$C_{13}H_{25}N_5O$	58,4	9,4	26,2	82
XIV	188,5—190	19,4	1,0	18,5	$C_6H_3Cl_6N_5O$	19,2	0,8	18,7	91
XV	152—154	65,9	4,4	23,8	$C_{16}H_{13}N_5O$	66,0	4,5	24,0	75
XVI	295—297	68,5	10,6	16,9	$C_{24}H_{45}N_5O$	68,7	10,7	16,7	76
XVII	268—269	74,3	12,0	11,3	$C_{38}H_{73}N_5O$	74,1	11,9	11,4	77
XVIII	30—31[c]	48,0	6,5	16,7	$C_{17}H_{23}Cl_3N_5O$	48,1	6,6	16,5	82
XIX	103—104	69,3	8,9	17,8	$C_{23}H_{35}N_5O$	69,5	8,8	17,6	85
XX	78—80	71,6	9,4	15,7	$C_{27}H_{43}N_5O$	71,5	9,5	15,4	88
XXI	205—206	42,8	6,0	43,1	$C_7H_{12}N_6O$	42,9	6,1	42,9	80
XXII	248—250	60,8	9,5	24,7	$C_{17}H_{32}N_6O$	60,7	9,5	25,0	77
XXIII	136—138	65,6	10,4	20,2	$C_{23}H_{44}N_6O$	65,7	10,5	20,0	78
XXIV	327—328	54,3	8,3	26,9	$C_{14}H_{26}N_6O_2$	54,2	8,4	27,1	90
XXV	240—242	48,3	3,9	36,1	$C_{11}H_{11}N_7O_2$	48,4	4,0	35,9	92
XXVI	227—228	47,4	4,4	32,5	$C_{12}H_{13}N_7O_3$	47,5	4,3	32,3	91
XXVII	124—125	55,2	6,4	19,8	$C_{23}H_{32}Cl_3N_5O$	55,1	6,4	20,0	86
XXVIII	228—230	74,9	8,8	13,3	$C_{33}H_{47}N_5O$	74,8	8,9	13,2	94
XXIX	255—257,5	57,4	5,8	40,1	$C_{13}H_{16}N_6O$	57,3	5,9	30,9	85
XXX	54—56	62,4	7,7	21,5	$C_{20}H_{30}N_6O_2$	62,3	7,8	21,8	95
XXXI	324—326	65,0	4,5	23,1	$C_{23}H_{19}N_7O_2$	64,9	4,5	23,0	91
XXXII	277—278	63,4	4,7	21,3	$C_{24}H_{21}N_7O_3$	63,3	4,6	21,5	89

[a]Compounds I [19], II [20], VIII [21], XII and XIII [22] were synthesized by known procedures.
[b]Compounds were recrystallized: III, VI, XIV, XV, XXV, and XXVII from 1:1 alcohol:water; IV, V, VII, X, XI, and XXI from n-butyl alcohol; IX from 2.5:1 hexane:alcohol; XVI from ethylene glycol; XVII and XXX from alcohol; XIX, XXIV, XXVI, XXVIII and XXXI from 1:1 acetone:water; XX and XXII from 2:1 alcohol:water; XXIII and XXIX from 5:1 alcohol:water; XXXII from aqueous DMFA.
[c]Compound SVIII was purified by column chromatography on Al_2O_3, eluent 15:1 benzene:methanol.

The initial 2-amino-4,6-dialkyl-sym-triazines (III, IV) were synthesized by cyclocondensation of the respective alkyl nitriles with guanidine (molar ratio 2:1) in the presence of sodium ethylate. The 2-amino-4-alkyl-6-substituted sym-triazines (V-VII) were synthesized by the reaction of N-acylguanidines with trichloroacetonitrile or benzonitrile. The 2-amino-4-dimethylamino-6-alkyl-sym-triazines (VIII-X) were synthesized by cyclocondensation of N,N-dimethylbiguanide with esters of the respective acids, while XI was synthesized by cyclocondensation of N-(β-hydroxy-ethyl)biguanide with ethyl pelargonate.



I, XIV R=R¹=CCl_3; II, XV R=R¹=Ph; III, XVI R=R¹=$C_{10}H_{21}$; IV, XVII R=R¹=$C_{17}H_{35}$; V, XVIII R=CCl_3, R¹=$C_{12}H_{25}$; VI, XIX R=Ph, R¹=$C_{13}H_{27}$; VII, XX R=Ph, R¹=$C_{17}H_{35}$; VIII, XXI R=Me, R¹=Me_2N; IX, XXII R=$C_{11}H_{23}$, R¹=Me_2N; X, XXIII R=$C_{17}H_{35}$, R¹=Me_2N; XI, XXIV R=C_8H_{17}, R¹=$NHCH_2CH_2OH$; XII R=Ph, R¹=NH_2; XIII R=2-$MeOC_6H_4$, R¹=NH_2; XXV R=Ph, R¹=$NHCONH_2$; XXVI R=2-$MeOC_6H_4$, R¹=$NHCONH_2$; XXVII R=CCl_3, R¹=$C_{12}H_{25}$; XXVIII R=Ph, R¹=$C_{17}H_{35}$; XXIX R=Me, R¹=Me_2N; XXX R=C_8H_{17}, R¹=$NHCH_2CH_2OH$; XXXI R=Ph, R¹=NHCONHPh; XXXII R=2-$MeOC_6H_4$, R¹=NHCONHPh

TABLE 2. Mass Spectra of sym-Triazinylureas

Compound	m/z (relative peak intensity, %)[a]	W_M, %
XIV	371[b] (M^+, 8,5), 355[b] (12), 354[b] (20), 336[b] (17), 328[b] (35), 301[b] (100), 266[b] (23), 117[b] (52), 108[b] (25)	2,6
XV	291 (M^+, 31), 275 (8), 274 (14), 248 (27), 247 (5), 144 (100), 117 (8), 104 (11), 103 (52), 44 (24)	10,2
XVI	419 (M^+, 23,5), 403 (21), 376 (15), 306 (24), 293 (100), 277 (10), 250 (18), 180 (82), 167 (18), 44 (15)	6,7
XVII	615 (M^+, 26), 599 (15), 598 (6), 582 (44), 391 (100), 371 (28), 358 (11), 304 (20), 180 (64), 167 (13)	7,6
XVIII	423[b] (M^+, 4), 407[b] (25), 388[b] (35), 380[b] (12), 353[b] (100), 282[b] (20), 269[b] (57), 198 (11), 117[b] (37), 108[b] (13)	1,1
XIX	397 (M^+, 14), 381 (24), 380 (18), 354 (20), 242 (27), 229 (100), 186 (54), 145 (14), 139 (35), 103 (18)	4,3
XX	453 (M^+, 18,5), 437 (20), 436 (14), 420 (15), 242 (33), 229 (100), 196 (9), 126 (12), 103 (83), 93 (14)	6,6
XXI	196 (M^+, 15), 181 (32), 180 (6), 179 (12), 163 (55), 162 (9), 148 (18), 135 (100), 126 (10), 93 (13)	4,7
XXII	336 (M^+, 5), 320 (22), 319 (13), 293 (24), 209 (8), 196 (100), 153 (56), 112 (80), 83 (10), 44 (55)	1,2
XXIII	420 (M^+, 7), 404 (27), 403 (17), 387 (71), 286 (9), 209 (13), 196 (100), 168 (8), 163 (14), 126 (7)	2,4
XXIV	310 (M^+, 2,5), 294 (12), 293 (5), 279 (100), 267 (17), 266 (42), 236 (7), 225 (12), 212 (8), 44 (76)	0,8
XXV	273 (M^+, 28), 257 (10), 256 (5), 230 (100), 214 (62), 213 (11), 187 (32), 104 (55), 103 (16), 44 (24)	7,7
XXVI	303 (M^+, 32), 287 (12), 286 (9), 274 (14), 273 (52), 270 (100), 254 (10), 253 (7), 170 (38), 103 (27)	10,3
XXVII	499[b] (M^+, 35), 464[b] (37), 429[b] (100), 407[b] (11), 394 (15), 358[b] (18), 345[b] (57), 310 (14), 117[b] (15), 108[b] (5)	11,0
XXVIII	529 (M^+, 48), 437 (15), 436 (22), 420 (12), 318 (27), 317 (10), 305 (100), 202 (9), 196 (13), 103 (24)	15,8
XXIX	272 (M^+, 43), 257 (10), 202 (9), 187 (24), 180 (12), 179 (8), 163 (40), 148 (22), 135 (100), 93 (12)	14,4
XXX	386 (M^+, 36), 355 (100), 342 (16), 294 (10), 293 (8), 288 (25), 267 (64), 262 (32), 236 (18), 223 (12)	10,3
XXXI	411 (M^+, 35), 319 (16), 318 (12), 302 (52), 210 (11), 209 (8), 199 (100), 193 (30), 192 (10), 90 (23)	10,5
XXXII	361 (M^+, 39), 332 (9), 331 (28), 269 (14), 268 (10), 252 (72), 222 (100), 160 (18), 143 (22), 119 (34)	9,8

[a]The ten most intense peaks of the mass spectrum are shown.
[b]Ions containing the ^{35}Cl isotope.

It was established that the condensation of 2-amino-sym-triazines I-XI with nitrourea should be carried out by boiling equimolar amounts of the reagents (for 2,4-diamino-sym-triazines XII and XIII, at a molar ratio of 1:2) in alcohol in the presence of concentrated H_2SO_4 catalyst. Heating of the reaction mixture was continued until evolution of nitrogen oxides ceased (8-10 h). Under these conditions the yields of 2-carbamido-4,6-disubstituted (XIV-XXIV) and 2,4-dicarbamido-6-substituted sym-triazines (XXV, XXVI) were 75-92% (Table 1).

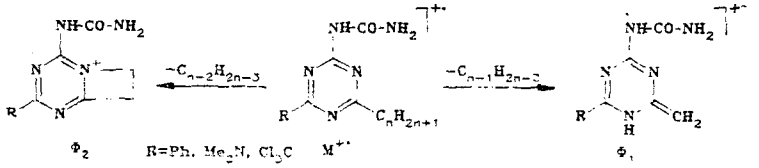
The reaction of 2-amino (V, VI, VIII, XI) and 2,4-diamino-sym-triazines (XII, XIII) with phenyl isocyanate was carried out by heating equimolar amounts of the reagents for several hours in an inert solvent (dioxane, diglyme, DMFA). 2-(N-Phenylcarbamido)- (XXVII-XXX) and 2,4-bis(N-phenylcarbamido)-sym-triazines (XXXI, XXXII) form in 85-95% yield.

The structures of compounds XIV-XXXII were confirmed by IR, PMR, and mass spectral data. The IR spectra show intense absorption maxima in the 1570-1560, 1415-1400, 1110-1090, 1010-995, 820-805, and 715-700 cm^{-1} regions that are typical of the valence and deformational vibrations of the triazine ring [9-11]. The carbonyl valence vibrations appear as intense absorption bands in the 1685-1648 cm^{-1} region; according to the data of [8] these correspond to the carbonyl vibrations of the carbamide segment in sym-triazines. When compared with the IR spectra of the initial amino-sym-triazines I-XIII, in which the NH deformational vibrations appear in the 1670-1655 cm^{-1} region, the spectra of XIV-XXVI show a significant shift of this band to a lower frequency. In the IR spectra of N-monosubstituted ureas XIV-XXVI an intense maximum at 1635-1625 cm^{-1} corresponds to the deformational vibrations of the primary amine NH group. Such a band assignment in the 1700-1600 cm^{-1} region is made by analogy with the corresponding vibrations (of the amide-I and amide-II band) in the spectra of amides and urea [12]. A number of bands of various intensities in the 1565-1545 and around 1250 cm^{-1} correspond to imine NH deformation vibrations and to

C–N bond valence vibrations, respectively [13]. In the low frequency of the spectrum the NH, amino, and imino valence vibrations overlap one another, and appear as a broad multiplet band in the 3320-3075 cm^{-1} region with a very weakly delineated separation of maxima. The location and shape of this band are evidence that the amino group takes part in intermolecular association.

It should be noted that the nature of the ring substituents in sym-triazines XIV-XXXII has a strong effect on the location of only two spectral bands: the carbonyl valence vibrations and the imino NH deformational vibrations. For example, when the ring contains the electronegative Cl_3C group, the IR spectra show a significant shift of both bands toward lower frequency.

Mass spectral study of the synthesized urea derivatives also confirms the proposed structure. By means of mass spectrometry the molecular weights of XIV-XXXII were determined; they agreed with the calculated values. Furthermore the nature of the subsequent fragmentations, confirmed by metastable transitions, agrees with the proposed structures. The mass spectra of all the syn-triazinylureas XIV-XXXII (see Table 2) contain molecular ion peaks, M^+, the stability of which depends on the tendency of the substituents to undergo fragmentation under electron impact. The least stable (W_M = 0.8-1.2) are M^+ of derivatives XVIII, XXII, and XXIV, while the most stable (W_M = 9.8-15.8) are M^+ of the N,N'-disubstituted ureas XXVII-XXXII. Formation of $[M - H]^+$ ions is not typical of these compounds; the intensities of these ions do not exceed 1% of the maximum.



The primary M^+ decomposition processes of sym-triazines XIV-XXXII proceed along several competing directions. The principal M^+ decomposition of compounds containing long alkyl radicals (XVI-XX, XXII, XXIII, XXVII, and XXVIII) involves β-cleavage of the alkyl C–C bond and elimination of a $C_{n-1}H_{2n-2}$ alkene by a MacLafferty rearrangement. Here the fragment Φ_1 ions form; their peak intensity is maximal in the mass spectra of this type of compound (except for XVIII and XXVII).

To a lesser extent the mass spectra of these compounds show the elimination of a $C_{n-2}H_{2n-3}$ alkyl radical to give Φ_2 ions, the peak intensity of which is 20-27% of maximal. For the dialkyl-sym-triazines XVI and XVII further decomposition of Φ_1 ions involves the easy detachment of a $C_{n-2}H_{2n-3}$ radical because of the second alkyl radical. The peaks of the corresponding $[M - C_{n-1}H_{2n-2}]^+$ and $[M - C_{n-2}H_{2n-3}]^+$ ions (Φ_3 ion, m/z 180) are 64-82% of maximal (see Table 2). The ejection from ion Φ_1 of the second alkene molecule $C_{n-1}H_{2n-2}$ (ion Φ_4, m/z 167) is more difficult. The mass spectra of sym-triazines containing long alkyl radicals also show low-intensity peaks that correspond to the ejection of C_mH_{2m+1} radicals (m = 1, ..., n – 3).

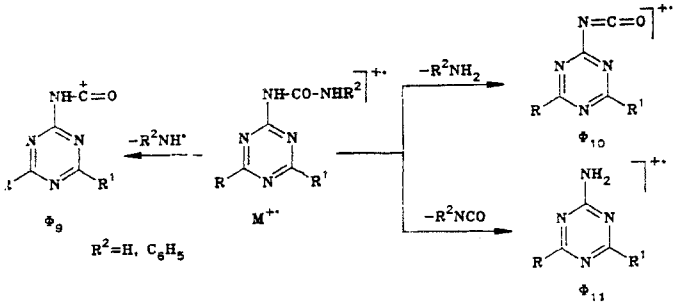
The mass spectra of XIX, XX, and XXVIII show significant peaks of $[M - C_{n-1}H_{2n-2}]^+$ and $[M - NCC_6H_5]^+$ ion Φ_5, due to the ejection of a benzonitrile molecule from ion Φ_1. Such a process is typical of aryl-substituted sym-triazine derivatives [14]. It should be noted that similar processes involving scission of the triazine ring and the formation of the intense Φ_6 fragment ions $[M - C_{n-1}H_{2n-2}]^+$ and $[M - NCNMe_2]^+$ also appear in the mass spectra of the sym-triazinylureas XXII and XXIII.

The nature of the multiplet of the M^+ peaks in the mass spectra of carbamide derivatives containing trichloromethyl groups is evidence for the presence of six (compound XIV) or three (XVIII and XXVII) chlorine atoms in the molecule. Here the primary fragmentation of the molecular ions is due to successive elimination of three chlorines; the $[M - Cl_2]^+$ peaks have maximal intensity, while the $[M - Cl]^+$ peak intensities are 35-42% of the maximal. The mass spectra of these compounds also contain intense Cl_3C^+ and NCC^+Cl_2 peaks.

By nature of their dissociative ionization the sym-triazines containing β-hydroxyethyl segments (XXIV and XXX) differ sharply from the other test compounds. The β-hydroxyethyl groups tend to be cleaved easily, so that for M^+ of XXIV and XXX decompositions involving fragmentation of the alkyl radical are inhibited. In the spectra of these compounds the

maximal peaks correspond to $[M - CH_2OH]^+$ (ion Φ_7) due to "amine" decomposition [15]. The spectra of XXIV and XXX also show quite intense peaks of $[M - C_2H_4O]^+$ (ion Φ_8).

All the test sym-triazinylureas XIV-XXXII also show decompositions involving fragmentation of the carbamide group. These decompositions cause the peaks of three characteristic ions to appear: $[M - R^2NH]^+$ (ion Φ_9), $[M - R^2NH_2]^+$ (ion Φ_{10}), and $[M - R^2NCO]^+$ (ion Φ_{11}). This is in good agreement with the data on the behavior of N-substituted ureas under electron impact [16, 17].



Comparison of the mass spectra of the N-monosubstituted ureas XIV-XXVI and the N,N-disubstituted ureas XXVII-XXXII shows that with the latter class of compound, M^+ stability increases sharply and the intensity of its peak reaches 35-48% of maximal. Further fragmentation of Φ_{11} proceeds by the typical mechanism for amino-sym-triazines [18].

The mass spectra of the synthesized sym-triazinylureas XIV-XXXII are shown in Table 2.

EXPERIMENTAL

IR spectra were obtained with a UR-20 spectrophotometer in KBr tablets or in mineral oil. PMR spectra were recorded with a Tesla BS-487C spectrometer (80 MHz) in DMSO-D_6 or acetone-D_6 with HMDS as internal standard. Mass spectra were obtained with a LKB-2091 instrument using direct introduction of sample into the ion source (electron ionizing energy 70 eV, emission current 25 μA, ion source temperature 200°C), at 130-150° sample vaporization temperature. The course of the reaction and the purity of the compounds were monitored with TLC on Al_2O_3 of grade II activity in a solvent system of 10:1 benzene:methanol (a) or 20:1 benzene:methanol (b); development with iodine vapor.

2-Amino-4,6-didecyl-sym-triazine (III). To a solution of sodium ethylate prepared from 0.74 g (0.032 mole) of sodium in 40 ml of absolute ethanol was added 2.02 g (0.03 mole) of guanidine hydrochloride portionwise. The reaction mixture was boiled for 1 h and cooled to 0°, and the NaCl precipitate was filtered off. The filtrate was evaporated in vacuum. The residue was dissolved in 100 ml of n-butyl alcohol, 10.1 g (0.06 mole) of undecanoic nitrile was added, and the solution was boiled with stirring until ammonia evolution ceased and the original, nitrile had disappeared from the reaction mixture (20-23 h; monitored by TLC). The solvent was boiled off in vacuum, the residue was extracted with hot alcohol (4 × 20 ml), and the extract was evaporated to dryness to give triazine III. IR spectrum: 3385, 3180 (ν_{NH_2}), 2960, 2935, 2865 (ν_{C-H}), 1675 (δ_{NH_2}), 1560, 1415, 1110, 1000, 805, 710 cm^{-1} (sym-triazine ring). PMR spectrum (DMSO-D_6): 1.14 (6H, t, CH_3); 1.26-2.04 (32H, m, CH_2); 2.88 (4H, t, ring CH_2); 6.82-6.88 ppm (2H, br. s, NH_2).

2-Amino-4,6-diheptadecyl-sym-triazine (IV) was obtained analogously from stearic nitrile. IR spectrum: 3420-3380, 3220 (ν_{NH_2}), 2965, 2960, 2872 (ν_{C-H}), 2965, 2960, 2872 (ν_{C-H}), 1670 (δ_{NH_2}), 1565, 1420, 1105, 995, 810, 705 cm^{-1} (sym-triazine ring).

2-Amino-4-trichloromethyl-6-dodecyl-sym-triazine (V). A mixture of 3.06 g (0.012 mole) of N-tridecanoylguanidine and 10.0 g (0.07 mole) of trichloroacetonitrile was boiled with stirring for 18-20 h until the initial N-acylguanidine had disappeared from the reaction mixture (monitored by TLC). The reaction mixture was evaporated to dryness in vacuum, and the residue was washed with ether to give triazine V. PMR spectrum (acetone-D_6): 1.16 (3H, t, CH_3); 1.28-1.90 (20H, m, CH_2); 2.82 (2H, t, ring CH_2); 6.74-6.80 ppm (2H, br. s, NH_2).

2-Amino-4-phenyl-6-tridecyl-sym-triazine (VI) was obtained analogously from N-tetradecanoylguanidine and benzonitrile after heating at 175-180° for 3 h. PMR spectrum (DMSO-D_6): 1.06 (3H, t, CH_3); 1.24-2.02 (22H, m, CH_2); 2.82 (2H, t, ring-CH_2); 6.74-6.82 (2H, br. s, NH_2); 6.92-7.46 ppm (5H, m, aromatic).

2-Amino-4-phenyl-6-heptadecyl-sym-triazine (VII) was obtained analogously from N-octadecanoylguanidine and benzonitrile (180°, 3 h). Mass spectrum, m/z (%): 410 (M^+, 8), 409 (3), 199 (21), 186 (100), 144 (10), 104 (45), 103 (24), 83 (11).

2-Amino-4-dimethylamino-6-undecyl-sym-triazine (IX). To a solution of sodium ethylate prepared from 1.4 g (0.061 mole) of sodium in 50 ml of absolute ethanol was added 9.93 g (0.06 mole) of dimethylbiguanide hydrochloride portionwise with stirring at 0-5°. The reaction mixture was stirred 30 min at 20°, and precipitated NaCl was filtered off and washed on the filter with 25 ml of cold alcohol. To the filtrate was added a solution of 12.8 g (0.06 mole) of methyl laurate in 20 ml of alcohol dropwise with stirring. Then the reaction mixture was boiled with stirring for 16-18 h until the methyl ester disappeared (monitored by TLC), and then evaporated to dryness at reduced pressure. The residue was washed several times with hot petroleum ether to give triazine IX. PMR spectrum (DMSO-D_6): 1.08 (3H, t, CH_3); 1.28-2.02 (18H, m, CH_2); 2.84 (2H, t, CH_2); 3.10 (6H, d, Me_2N, J = 5.5 Hz); 6.81-6.88 ppm (2H, br. s, NH_2).

2-Amino-4-dimethylamino-6-heptadecyl-sym-triazine (X) was obtained analogously from methyl stearate.

2-Amino-4-(β-hydroxyethyl)amino-6-octyl-sym-triazine (XI) was obtained analogously from N-(β-hydroxyethyl)biguanide hydrochloride and methyl pelargonate. PMR spectrum (DMSO-D_6): 1.14 (3H, t, CH_3); 1.38-1.86 (12H, m, CH_2); 2.88 (2H, t, ring-CH_2); 3.69-2.92 (4H, m, NH—CH_2CH_2—O); 4.64 (1H, s, OH); 5.74 (1H, s, NH); 6.94 ppm (2H, s, NH_2).

N-Monosubstituted sym-triazinylureas (XIV-XXVI). A mixture of 0.01 mole of amino-sym-triazine I-XI, 1.4 g (0.01 mole) of nitrourea (in the case of XII and XIII, 0.02 mole of nitrourea) and several drops of concentrated H_2SO_4 in 50 ml of alcohol was boiled with stirring until evolution of nitrogen oxides ceased (8-10 h). The reaction mixture was cooled to 20° and poured into 200 ml of cold water. The precipitate was filtered off, washed on the filter with water, dried, and crystallized from an appropriate solvent.

N,N'-Disubstituted syn-triazinylureas (XXVII-XXXII). A mixture of 0.01 mole of amino-sym-triazine V, VI, VIII, or XI and 1.19 g (0.01 mole) of phenyl isocyanate (in the case of XII and XIII, 0.02 mole of phenyl isocyanate) was stirred at 80-90° in 50 ml of inert solvent (dioxane, diglyme, DMFA) for 10-12 h. The reaction mixture was cooled to 20° and poured into 200 ml of cold water. The precipitate was filtered off, washed on the filter with 20 ml of cold acetone, dried, and crystallized from an appropriate solvent.

Compounds XIV-XXXII have good solubility in alcohols, DMFA, DMSO, acetic acid, and hot aromatic solvents; they are insoluble in water, ether, acetone, heptane, and CCl_4.

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AROMATIC DERIVATIVES OF 1H-2,3-DIHYDROPYRAZOLO[4,5-b]-1,5-DIAZEPINE

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Aromatic derivatives of 1H-2,3-dihydropyrazole[4,5-b]-1,5-diazepine were obtained by the reaction of 1-phenyl-3-methyl-4,5-diaminopyrazole with chalcones and acetylarenes, catalyzed by acetic or sulfuric acid. The seven-membered ring in these compounds has a conformation of the boat type. The IR, UV, PMR, and mass spectra of the compounds are discussed.

It is known [1, 2] that the reaction of α,β-unsaturated ketones of the aromatic series (chalcones, their vinylogs) with 1,2-diamines under the conditions of base or acid catalysis leads to the formation of dihydrodiazepine systems. The aim of the present work was to study the reaction of aromatic ketones with 1-phenyl-3-methyl-4,5-diaminopyrazole (I), a convenient method for the synthesis of which was proposed in [3]. It was found that the initial components were recovered unchanged when alcohol solutions of the diamine (I) and chalcones, containing catalytic amounts of triethylamine, were boiled. Prolonged boiling (6-8 h) of the same compounds in pure triethylamine led to small yields (~20%) of compounds (II), but the process was accompanied by considerable resin formation. At the same time the reaction of the diamine (I) with chalcones took place smoothly when their methanol solutions were boiled for 1-3 h with catalytic amounts of acetic acid; 2,4-diaryl-6-methyl-8-phenyl-1H-2,3-dihydropyrazolo[4,5-b]-1,5-diazepines (IIa-c, e-m) were obtained (Table 1).

A second method for the synthesis of dihydrodiazepine derivatives is based on the reaction of 1,2-diamines with acetylarenes [4]. It was found that even the diamine (I) reacts with 4-R-acetophenones when their methanol solutions are boiled in the presence of catalytic amounts of concentrated sulfuric acid. The 2,4-diaryl-2,6-dimethyl-8-phenyl-1H-2,3-dihydropyrazolo[4,5-b]-1,5-diazepines (IIIa, b, d-g) were obtained (Table 1).

Compounds (II, III) were crystalline substances with colors ranging from light-yellow to orange-red. The fact that they belong to the dihydrodiazepines was confirmed by elemental analysis and spectral data. Thus, the electronic absorption spectra are typical of dihydro-

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