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SYNTHESIS AND PROPERTIES OF SYMM-TRIAZINES.

3*. REACTIONS OF 2-ALKYL-4,6-BISTRICHLOROMETHYL-symm-TRIAZINES

CONTAINING HIGHER ALKYL GROUPS WITH AMMONIA AND ALIPHATIC AMINES

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The reaction of 2-alkyl-4,6-bistrichloromethyl-symm-triazines containing higher alkyl groups with ammonia or aliphatic amines results, depending on the reaction conditions, in the replacement of one or both trichloromethyl groups. On heating these symm-triazines with aqueous ammonia or dimethylamine, 2-oxo-4-amino-6-alkyl-1(3)H-symm-triazines are obtained.

Continuing the synthesis of symm-triazines containing higher alkyl groups, we have prepared some 2-amino-4-alkyl-6-trichloromethyl-symm-triazines, which are of interest as additives for polymers, oils, and fuels.

The starting materials for the preparation of these symm-triazines were the 2-alkyl-4,6bistrichloromethyl-symm-triazines (Ia, b). It is known [3, 4] that trichloromethyl groups attached to the symm-triazine ring react with nucleophiles, being cleaved as the anion, which then adds a proton to give chloroform. For this reason, trichloromethyl-symm-triazines are convenient starting materials for the preparation of symm-triazines containing a variety of functional groups (HO, RO, NH₂, COOR, CN, etc.).

There have been few reports of similar reactions of 2-alkyl-4,6-bis(trichloromethyl)symm-triazines containing longer alkyl radicals [5, 6]. These reports described the reactions of 2-nonyl- and 2-heptadecyl-4,6-bis(trichloromethyl)-symm-triazines with ethylamine, but the reaction methods and conditions received only a superficial description.

With a view to extending studies in this area, we have examined the reaction of 2-dodecyl- (Ia) and 2-heptadecyl-4,6-bis(trichloromethyl)-symm-triazine (Ib) with ammonia and some simple aromatic amines. It was found that replacement of the trichloromethyl groups in these compounds takes place stepwise, and depending on the reaction conditions either one or both of the Cl₃C groups are replaced cleanly.

*For communication 2, see [1].

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II, III a,c,e $R = C_{12}H_{25}$; b,d,f $R = C_{17}H_{35}$; a,b $R^1 = R^2 = H$; c,d $R^1 = R^2 = CH_3$; e.f $R^1 = H$, $R^2 = C_3H_7$

Treatment of triazines (Ia) and (Ib) with aqueous ammonia or dimethylamine at 30-35°C results in the replacement of only one of the Cl₃C groups, to give high yields of the 2amino- (IIa, b) or 2-dimethylamino-4-alkyl-6-trichloromethyl-symm-triazines (IIc, d). The replacement of one of the trichloromethyl groups in (Ia) and (Ib) by the n-propylamine residue takes place under similar conditions in inert solvents (benzene or dioxane).

When triazines (Ia, b) are reacted with aqueous ammonia at higher temperatures (90-100°C), instead of the expected 2,4-diamino-6-alkyl-symm-triazines (IIIa, b), the 2-hydroxy-4-amino-6-alkyl-symm-triazines (IVa, b) were isolated from the reaction mixture. These compounds were assigned to oxo-tautomeric structure, with the hydrogen attached to the ring nitrogen, i.e., 2-oxo-4-amino-6-alkyl-1(3)H-symm-triazines (Va, b) on the basis of spectral data.



The formation of compounds (Va, b) may be rationalized by assuming that the intermediate triazines (IIa, b) which appear in the reaction mixture following replacement of the first trichloromethyl group, undergo hydrolysis much more rapidly than ammonolysis under these conditions. The same oxo-derivatives (Va, b) are formed on heating the pure compounds (Ia, b) with aqueous ammonia at 100°C.

The replacement of both trichloromethyl groups in (Ia, b) by amino or dimethylamino could only be effected by carrying out the reaction under more severe conditions in nonaqueous media. 2,4-Diamino- (IIIa, b) and 2,4-bisdimethylamino-6-alkyl-symm-triazines (IIIc, d) were obtained by passing gaseous ammonia into solutions of (Ia) or (Ib) in DMF at 150-155°C, and 2,4-bis(propylamino)-6-alkyl-symm-triazines (IIIe, f) by heating (Ia, b) with an excess of propylamine in dioxane under pressure at 120-130°C. Similar conditions may be used to obtain mixed N-substituted 2,4-diamino-6-alkyl-symm-triazines. For example, on passing ammonia into a solution of triazine (IIc) or (IIe) in DMF at 150-155°C, or dimethylamine into a solution of (IIa) or (IIb), good yields of the 2-amino-4-dimethylamino-6-alkyl-symm-triazines (IIIg, h) are obtained.



IIIg $R = C_{12}H_{25}$; h $R = C_{17}H_{35}$

The structures of the amino- (IIa-e) and diamino-symm-triazines (IIIa-h) are in good agreement with their elemental analyses, IR and PMR spectra. In addition, the structures of some of the compounds were confirmed by direct synthesis. For example, triazines (IIa) and (IIb) were obtained in high yield on prolonged boiling (18-24 h) of the appropriate N-acylguanidines (VIa, b) in an excess of trichloroacetonitrile.

 $\frac{R-CO-NH}{VI}C \bigvee_{NH_{2}}^{NH} + CI_{3}C-CN \qquad H_{2}O \qquad H_{3}A, b$ VI.a, b VI.a R=C₁₂H₂₅; b R=C₁₇H₃₅

Compounds (IIIa, b) were synthesized by a literature method [7], by cyclocondensation of the appropriate alkyl nitriles with dicyandiamide. Triazines (IIIg, h) were prepared by cyclocondensation of methyl tridecanoate or methyl stearate with NN-dimethylbiguanide. All the compounds obtained by direct synthesis were fully identical with the compounds obtained by the nucleophilic replacement of the trichloromethyl groups in (Ia, b).

The IR spectra of all the amino-symm-triazines (IIa-f) and diamino-symm-triazines (IIIa-h) showed absorption of varying intensity at 1570-1560, 1412-1405, 1115-1100, 1010-990

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TABLE 1. Properties of (IIa-f), (IIIa-h), and (Va, b)

	mo •c=	_{R₄} b	Found, %				Empirical	Calc., %				Yield,	
Comp			с	н	Cl	N	formula	с	н	CI	N	8	
IIa IIb IIc IIf IIIa IIIb IIIb IIIb IIIb IIIb IIIb	$\begin{array}{c} 140-141,5\\ 162-163\\ 61-62\\ 80-81,5\\ 0i1d\\ 108-109\\ 116-117.5^{e}\\ 0i1d\\ 54-55d\\ 37-38d\\ 0i1d\\ 172-173\\ 167-168\\ 225-226\\ 216-217,5 \end{array}$	0,50 (A) 0,48 (A) 0,62 (A) 0,52 (A) 0,72 (B) 0,28 (B) 0,28 (B) 0,20 (B) 0,28 (A) 0,50 (B) 0,50 (B) 0,50 (B) 0,52 (B) 0,34 (B) 0,34 (B) 0,0 0,0	50,2 55,7 52,6 57,4 53,7 58,4 64,6 68,7 68,0 71,0 69,3 72,1 66,5 70,1 64,4 68,5	7,1 8,2 7,6 8,6 7,7 10,4 11,2 11,1 11,5 11,4 11,8 10,8 11,3 10,0 10,8	27,7 23,8 25,8 22,5 25,0 19,3 	14,9 12,3 13,8 11,5 13,4 11,2 24,9 20,1 20,7 17,5 19,4 16,1 22,6 18,6 19,9 16,2	$\begin{array}{c} C_{16}H_{27}Cl_3N_4\\ C_{21}H_{37}Cl_3N_4\\ C_{12}H_{31}Cl_3N_4\\ C_{22}H_{41}Cl_3N_4\\ C_{19}H_{33}Cl_3N_4\\ C_{19}H_{33}Cl_3N_4\\ C_{16}H_{29}N_5\\ C_{20}H_{39}N_5\\ C_{20}H_{39}N_5\\ C_{24}H_{47}N_5\\ C_{24}H_{47}N_5\\ C_{24}H_{47}N_5\\ C_{26}H_{51}N_5\\ C_{17}H_{33}N_5\\ C_{17}H_{33}N_5\\ C_{22}H_{48}N_4O\\ C_{20}H_{38}N_4O \end{array}$	50,4 55,8 52,7 57,6 53,8 64,5 68,8 68,1 71,1 69,4 72,0 66,4 70,4 64,3 68,6	7,1 8,2 7,6 8,5 7,8 8,7 10,5 11,2 11,0 11,6 11,3 11,8 10,7 11,4 10,0 9	27,9 23,6 26,0 22,2 25,1 19,1 — — — — — — — — — — — —	$\begin{array}{c} 14,7\\12,4\\13,7\\11,7\\13,2\\11,3\\25,1\\20,0\\20,9\\17,3\\16,2\\22,8\\18,6\\20,0\\16,0\\\end{array}$	86 (92) 82 (90) 85 80,5 78 82 65 (73) 72 (70) 74 70 74 87 87 84 83 (84) 84 88	

^a Compounds recrystallized as follows: (IIa, b, d) from ethanol-water (1:2); (IIc) from acetone-water, 1:1; (IIIa, b) from propan-2-ol; (IIId) from absolute ethanol-hexane, 1:5; (IIIg) from absolute ethanol-hexane, 1:2.5; (IIIh) from butan-1-ol; and (Va, b) from DMF. ^b Solvent system given in brackets. ^c Yields of compounds obtained by direct synthesis given in brackets. ^d Compounds purified on alumina columns; np²⁰ (compound): 1.5239 (IIe); 1.5170 (IIf); 1.5209 (IIc); 1.5180 (IIIf). ^e According to [14], mp 115-118°C.

812-805, and 710-705 cm⁻¹, characteristic of the stretching and deformational vibrations of the triazine ring (Table 2) [8-10]. In the spectra of the symm-triazines containing only a single primary amino-group (IIa, b) and (IIIg, h), two broadened absorption bands are seen in the N-H stretching region. One of these is shifted towards longer wavelengths, occurring at 3180-3100 cm⁻¹ ($v_{\rm SN-H}$), and the other is of shorter wavelength, at 3455-3290 cm⁻¹ ($v_{\rm aSN-H}$). The position and shape of the N-H stretching doublet indicates that in the crystalline state stable hydrogen bonds are formed [8]. The absorption maxima of varying intensity at 1675-1655 cm⁻¹ are attributed to the planar deformational vibrations of the N-H bond in primary amino-groups, such as is typical of amino-symm-triazines [11]. It is noteworthy that the third substituent in the ring has a considerable influence on the positions of both the stretching and deformational N-H vibrations in the spectra of these compounds. For instance, in the IR spectra of (IIa, b), which contain the Cl₃C group which has a strong -I effect, these bands are shifted strongly towards the lower frequency region of the spectrum as compared with (IIIg, h), which contain the electron-donor dimethylamino-group.

In the IR spectra of the 2,4-diamino-6-alkyl-symm-triazines (IIIa, b), four absorption bands are seen in the high-frequency region; two of these are narrow and of high frequency (3472-3465 and 3420 cm⁻¹), and two broad and of lower frequency (3315 and 3155 cm⁻¹). This is evidence of the presence in the crystalline state of two types of hydrogen bond. By analogy with the vibrational spectra of melamine and ammeline (2-hydroxy-4,6-diamino-symm-triazines) [8, 11],the following assignments of these frequencies may be made. The two narrow, short-wavelength bands are probably due to antisymmetrical and symmetrical stretching vibrations of the N-H bonds in the amino-groups participating in weak hydrogen bonding, and the two longer-wavelength, broad bands to the analogous vibrations of the amino-groups which are strongly hydrogen-bonded.

Support for the view that in the crystalline state the symm-triazines (Va, b) exist as the oxo-tautomers is provided by the presence in the spectra of these compounds of strong absorption at 1680-1675 cm⁻¹, which is characteristic of the vibrations of carbonyl groups in oxoheterocycles [12]. Several absorption bands are seen in the N-H stretching region, namely, at 3425, 3378-3370, 3200-3195, 3075, and 2890 cm⁻¹. This gives grounds for assuming that these oxo-tautomers form strong intermolecular hydrogen bonds of the N-H.*.O=C type [12]. The last of these bands is apparently due to stretching vibrations of the ring NH group. This assignment of the absorption at 2980 cm⁻¹ was made by comparison with the IR spectrum of cyanuric acid [11], in which this absorption is highly characteristic. In the spectra of (Va, b), the planar ring stretching vibrations are somewhat shifted to higher frequencies,

. p			IR	spec							
unodu	ν _s . ν	δ _s N—H	ring vibrations ^a				other	PMR spectrum, ppm (δ scale)			
ပိ	N-H		ν	—Ъ	γ	β	vibrations				
IJa	3295, 3100	1655	1565 1405	1100 1005	800	710	1330, 1205 (vC-N), 772,	1,16 (3H, \pm , CH ₃); 1,28–1,90 (20H, m CH ₂); 2,82 (2H, \pm , CH ₂ -ring);			
IJc	-		1565 1412	1105 1002	805	710	1333, 1215 (vC-N), 775	1,15 (3H, t, CH ₃); 1,22–2,04 (20H, m, CH ₂); 2,86 (2H, t CH ₂ -ring); 1,22–2,04 (20H, t); 2,16 (2H, t); 2,16			
IĬè	3345	1525	1560 1405	1100 995	810	705	(C-CI) 1325, 1220 (vC-N), 780 (C-CI)	5,10 (07, d, N —CH ₃) 1,10 (3H,t, CH ₃); 1,20 (3H,t, CH₃ —CH ₂ CH ₂ NH); 1,26—2,10[22H, m, —(CH ₂) ₁₀ ; — CH ₂ —CH ₂ NH]; 2,88 (2H,t, CH ₂ -ring); 3,34 (2H, q, —CH ₂ NH); 5,557 (1H br			
IIIa	3472 3420 3315 3155	1675	1570 1410	1100 1005	805	710	1325, 1210 (vC—N)	NH) 1,16 (3H,t, CH ₃); 1,26–1,94 (20H, m, CH ₂); 2,90 (2H,t, CH ₂ -ring) ; 6,96–7,12 (4H, br. NH ₂)			
IIIf	3330	1515	1565 1406	1115 990	812	705	1325, 1220 (vC—N)	1,08 (3H, t, CH ₃); 1,18 [6H, t, CH ₃ —(CH ₂) ₂ NH]; 1,28—2,15 [34H, m —(CH ₂) ₁₅ —; 2CH ₂ —CH ₂ NH]; 2,90 (2H, t CH ₂ -ring) ; 3,30 (4H, 9 ,CH ₂ NH); 5,50—5,81 (2H, br,			
III B	3455 3180	1665	1570 1410	1115 1010	807	710	1380, 1240 1185, 1135 (vC—N)	(NH) 1,12 (3H, \pm , CH ₃); 1,30–1,96 (20H, m, CH ₂); 2,86 (2H \pm , CH ₂ ring); 3,08 (6H, d N–CH ₃); 6,80–6,91 (2H \pm , VH)			
Vр	3425 3375 3195 3077 2870	1655	1585 1445	1100 1005	810	705	1680 (C=O), 1325, 1225 (vC-N)	$ \begin{array}{c} (2100^{\circ}, 1012) \\ 1,16 & (3H, t, CH_3); \\ n, CH_2); \\ 2,84 & (2H, t, CH_2 \cdot ring); \\ 5,64-6,02 & (2H, br, NH_2); \\ 6,60 & (1H, br, NH ring) \end{array} $			

TABLE 2. Spectral Properties of the Compounds Prepared

 $\frac{a}{\gamma}$ denotes planar, and β extraplanar deformational vibrations of the ring. $\frac{b}{\gamma}$ "Breathing" vibrations of the ring.

being seen at 1585-1580 and 1450-1445 cm⁻¹, but the positions of the other bands remain almost unchanged.

In the PMR spectra of the compounds obtained, three groups of resonance signals, differing in intensity and chemical shifts, correspond to the protons of the alkyl groups. The methyl group signals comprise symmetrical triplets at 1.08-1.16 ppm. The complex multiplets in the range 1.26-2.16 ppm are assigned to the methylene chain protons, and the nonsymmetrical triplets shifted to lower field (3.06-3.18 ppm) to the CH₂ groups directly bonded to the triazine ring [5]. All the signals for the amino-group protons are seen as broadened singlets of the appropriate intensity. For the primary amines, these signals are seen at 6.78-7.32 ppm, and for the secondary amino-groups (in IIe, f and IIIe, f), at 5.50-6.40 ppm. In the spectra of the symm-triazines containing dimethylamino-groups (IIc, d and IIIc, d, g, h) the signals for the protons of these groups appear as two singlets ($\Delta v = 5.5-8.5$ Hz). This may be due to restricted rotation around the C-N bond as a result of the conjugation of the p-electrons of the exocyclic nitrogen atom with the symm-triazine ring [13]. When the spectrum was obtained at a higher temperature ($45^{\circ}C$) these doublets merged into one signal.

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrometer in KBr disks. PMR spectra were obtained on a Tesla BS-487C spectrometer (80 MHz) in DMSO-D₆ and acetone-D₆, with HMDS as internal standard. The course of the reactions and the purity of the products were checked by TLC on grade II (Brockman) alumina in the solvent systems benzene-methanol 20:1 (A) or 10:1 (B), visualized with iodine vapor.

<u>N-Tridecanoylguanidine (VIa)</u>. To a stirred solution of sodium ethoxide, prepared from 2.3 g of sodium and 150 ml of absolute ethanol, was added portionwise at 20°C 9.5 g (0.1 mole) of guanidine hydrochloride. The mixture was stirred for 2 h at 20°C, boiled for 15 min, cooled to 0°C, and the solid (NaCl) which separated was filtered off and washed on the filter with 30 ml of cold ethanol. To the stirred filtrate was added 22.8 g (0.1 mole) of methyl tridecanoate, the mixture boiled for 12 h, and evaporated to dryness under reduced

pressure. The residue was washed with hot hexane (3 × 100 ml), and crystallized from butanol to give 23.3 g (91.5%) of (VIa), mp 82-83°C, R_f 0.81 (A). IR spectrum: 3340, 3300, 3185 (ν_{N-H}), 2960, 2935, 2865 (ν_{C-H}), 1680 (C=0, amide I band), 1665 ($\delta_{s \ NH_2}$), 1635 ($\nu_{C=N}$), 1550 (δ_{N-H} , amide II), 1470, 1445, 1375 ($\delta_{\alpha s}$, $\delta_{s \ C-H}$), 1340, 1250 (ν_{C-N}), 725, 690 cm⁻¹. Found: C 66.0; H 11.4; N 16.3%. C₁₄H₂₉N₃O. Calculated: C 65.9; H 11.4; N 16.5%.

<u>N-Octadecanoylguanidine (VIb)</u> was obtained similarly, from methyl stearate, yield 87%, mp 88-90°C (from butanol), R_f 0.73 (A). IR spectrum: 3355-3320, 3290, 3150 (ν_{N-H}), 2965, 2930, 2865 (ν_{C-H}), 1680 (C=0, amide I), 1650 (δ_{s} NH₂), 1625 (ν_{C-N}), 1562 (ν_{N-H} , amide II), 1465, 1445, 1370 ($\delta_{\alpha s}$, δ_{s} C-H), 1350, 1255 (ν_{C-N}), 725, 685 cm⁻¹. Found: C 70.0; H 12.0; N 12.7%. C₁₉H₃₉N₃O. Calculated: C 70.1; H 12.0; N 12.9%.

<u>2-Amino-4-alkyl-6-trichloromethyl-symm-triazine (IIa, b).</u> A. A suspension of 0.012 mole of the symm-triazine (Ia or b) in 30 ml of 28% aqueous ammonia was stirred for 3 h at 30-35°C. The solid was filtered off, washed on the filter with water, dried, and crystal-lized from aqueous alcohol.

B. A mixture of 0.015 mole of the N-acylguanidine (VIa or b) and 20 ml of trichloroacetonitrile was boiled with stirring until the N-acylguanidine was no longer present in the reaction mixture (18-20 h, followed by TLC), then evaporated to dryness at reduced pressure, and the residue crystallized from aqueous alcohol.

<u>2-Dimethylamino-4-alkyl-6-trichloromethyl-symm-triazine (IIc, d)</u>. These were obtained as for (IIa, b) (method A), from 0.01 mole of the triazine (Ia or b) in 33% aqueous dimethylamine.

<u>2-Propylamino-4-alkyl-6-trichloromethyl-symm-triazines (IIe, f)</u>. To a stirred solution of 0.015 mole of the triazine (Ia or b) in 25 ml of dry benzene was added dropwise at 20°C a solution of 1.06 g (0.018 mole) of propylamine in 8 ml of dry benzene. The mixture was stirred for 4 h at 30-35°C, then evaporated to dryness. The residue was chromatographed on an alumina column (3.5×50 cm) and eluted with a mixture of benzene and methanol (10:1). Removal of the solvent gave the compounds (IIe, f) as viscuous, slightly-colored, uncrystal-lized oils.

2,4-Diamino-6-alkyl-symm-triazines (IIIa, b). A. Into a stirred solution of 0.01 mole of the triazine (Ia or b) in 25 ml of dry DMF was passed a stream of dry ammonia at 150-155°C for 2 h. The mixture was cooled to 20°C and poured into 150 ml of water, and the solid which separated was filtered off, washed with water, dried, and crystallized.

B. To a stirred mixture of 0.02 mole of the appropriate nitrile and 0.22 g (0.004 mole) of finely-ground KOH in 80 ml of ethylcellosolve (2-ethoxyethanol) was added portionwise over 2 h 2.0 g (0.024 mole) of dicyandiamide. The reaction mixture was stirred for 1 h at 145-150°C, cooled to 20°C, and neutralized with glacial acetic acid. The solvent was removed in vacuo, and the residue crystallized with the addition of activated charcoal.

<u>2,4-Bis(dimethylamino-6-alkyl-symm-triazines (IIIc, d)</u>. These were obtained as for (IIIa, b) (method A). The triazines (IIIc, d) were isolated as dark-colored oils, which were extracted with ether. The ether extracts were washed with water, dried over CuSO₄, and evaporated to dryness in vacuo. The residue was chromatographed on a column of alumina $(3.5 \times 50 \text{ cm})$, and eluted with a mixture of benzene and methanol (5:1). Removal of the sol-vent gave (IIIc) as a viscous, pale yellow oil, and (IIId) as a crystalline solid.

<u>2,4-Bis(propylamino)-6-alkyl-symm-triazines (IIIe, f).</u> A solution of 0.01 mole of the triazine (Ia or b) and 4.13 g (0.07 mole) of propylamine in 25 ml of dry dioxane was heated in a sealed ampul for 5 h at 135-140°C. The contents of the ampul were cooled to 20°C, and poured into 150 ml of cold water. The oil which separated was extracted with ether $(3 \times 30 \text{ ml})$, and the extracts washed with water, dried over CuSO₄, evaporated until the volume reached 5-8 ml, and chromatographed on a column of alumina $(3.5 \times 30 \text{ cm})$. Elution with a mixture of benzene and acetone (5:1) and removal of the solvents gave the triazines (IIIe, f) as viscous, dark yellow oils, which crystallized on storage at -10°C for 24 h.

<u>2-Amino-4-dimethylamino-6-alkyl-symm-triazines (IIIg, h).</u> A. A stream of dry ammonia was passed into a stirred solution of 0.07 mole of the symm-triazine (IIc or d) in 20 ml of dry DMF at 150-155°C for 1 h. The mixture was then cooled to 20°C, poured into 100 ml of water, and the solid which separated was filtered off, washed with water, and dried.

Compounds (IIg, h) were obtained similarly from the triazines (IIa, b) and gaseous dimethylamine.

B. To a stirred solution of sodium ethoxide, obtained from 1.40 g (0.061 mole) of sodium and 100 ml of absolute ethanol, was added portionwise at 0-5°C 9.93 g (0.06 mole) of NNdimethylbiguanide hydrochloride. The mixture was stirred for 20 min at 20°C, and the NaCl which separated was filtered off and washed on the filter with 10 ml of absolute ethanol. To the resulting solution of the biguanide free base was added dropwise with stirring a solution of 0.06 mole of the methyl ester of the appropriate acid in 20 ml of absolute ethanol. The mixture was boiled with stirring for 18 h, then evaporated to dryness under reduced pressure. The residue was washed with hot hexane $(3 \times 30 \text{ ml})$, and crystallized.

2-Oxo-4-amino-6-alkyl-1(3)H-symm-triazines (Va, b). A mixture of 0.01 mole of the triazine (Ia or b) and 35 ml of 28% aqueous ammonia was heated in a sealed ampul for 6 h at 95-105°C (bath temperature). After cooling to 20°C, the contents of the ampul were poured into 100 ml of cold water, and the solid which separated was filtered off, washed with water, and dried.

Compounds (Va, b) were obtained similarly from the symm-triazines (IIa, b).

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