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SYNTHESIS AND PROPERTIES OF DERIVATIVES OF sym-TRIAZINE.

17.* SYNTHESIS OF 2-METHYL-4,6-DISUBSTITUTED AND 2,4-DIMETHYL-6-SUBSTITUTED sym-TRIAZINES BY REDUCTION OF THE CORRESPONDING TRICHLOROMETHYL DERIVATIVES

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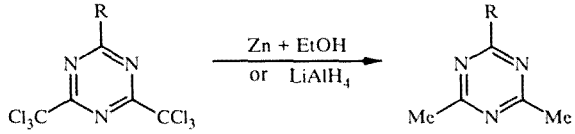
The reduction of trichloromethyl groups in sym-triazine derivatives to methyl groups is studied. It is shown that 2-R-4,6-bis(trichloromethyl)-sym-triazines can be reduced to 2-R-4,6-dimethyl-sym-triazines with zinc dust in ethanol or with lithium aluminum hydride in THF. 2-Amino, N-substituted 2-amino-, and 2-alkoxy-4-trichloromethyl-6-R-sym-triazines are reduced to the corresponding methyl derivatives by boiling with lithium aluminum hydride in dibutyl ether.

Continuing our investigation of the chemical transformations of trichloromethyl derivatives of sym-triazine [1-6], we report here on the preparation of 6-substituted 2,4-dimethyl- and 4,6-disubstituted 2-methyl-sym-triazines by the reduction of the corresponding 2,4-bis(trichloromethyl)- and 2-(trichloromethyl)-sym-triazines. Such sym-triazine derivatives are of definite interest as potentially biologically active substances and also as stabilizers for polymers and for hydrocarbon fuels and lubricating oils.

Up until now, the literature has contained little information concerning the reduction of Cl_3C groups in sym-triazine derivatives. It is known [7, 8] that these substituents can be reduced to methyl groups with zinc powder in alcohol or



Ia-k IIa-k IVa-m VIa-f

Ia, IIa, IVa, VI a,d,eR = C_5H_{11}; Ib, IIbR = $C_{10}H_{21}$; Ic, IIc, IVb,h,VIbR = $C_{12}H_{25}$; Id, IId, IVc,i, VIcR = $C_{17}H_{35}$; Ie, IIeR = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$CH$_2$; If, IIf R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$CH$_2$CH$_2$; Ig, IIg R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$SCH$_2$; Ih, IIhR = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$SCH$_2$CH$_2$; Ii, IIi R = PhCH$_2$S; Ij, IIj, IVg,j,*l* R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$S; Ik, IIk, IV k,m R = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$CH$_2$S; IVr R = furyl-2; IVeR = indolyl-3; IVf R = 1-methylindolyl-3; VIe R = Ph; IV a-g R^1 = H; IV h-k R^1 = Me; IV*l*m R_2^1N = morpholino, VI a-c R^1 = Me; VI d R^1 = Et; VIe,f R^1 = 4-HO-3,5-(*t*-Bu)$_2$C$_6$H$_2$(CH$_2$)$_3$

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	Molecular formula	T_{bp}, °C (mm Hg) or T_{mp}, °C*	n_D^{20}	R_f (solvent system)	PMR spectra, δ, ppm*2, SSCC, J, Hz	Yield, % (preparative method)
1	2	6	7	8	9	10
IIa	$C_{10}H_{17}N_3$	76...77 (5)	1,4681	0,77 (a)	1,14 (3H, t, Me), 1,26...1,42 (6H, m, 3CH2), 2,44 (6H, s, 2Me), 3,12 (2H, t, CH_2)	74 (A), 85 (B)
IIb	$C_{15}H_{27}N_3$	152...155 (5)	1,4695	0,70 (a)	1,08 (3H, t, Me), 1,32...1,57 (16H, m, 8CH_2), 2,35 (6H, s, 2Me), 3,18 (2H, t, CH_2)	75 (A), 82 (B)
IIc	$C_{17}H_{31}N_3$	133...135 (2)	1,4712	0,64 (a)	1,17 (3H, t, Me), 1,30...1,68 (20H, m, 10CH_2), 2,41 (6H, s, 2Me), 3,34 (2H, t, CH_2)	71 (A), 92 (B)
IId	$C_{22}H_{41}N_3$	177...179 (1); 42...43,5	–	0,58 (a)	1,22 (3H, t, Me), 1,44...1,73 (30H, m, 15CH_2), 2,58 (6H, s, 2Me), 3,05 (2H, t, CH_2)	76 (A)
IIe	$C_{20}H_{29}N_3O$	108...109	–	0,35 (b)	1,58 (18H, ex.b.s, *t*-Bu), 2,30 (6H, s, 2Me), 3,62 (2H, s, CH_2), 5,08 (1H, s, OH), 7,24 (2H, s, H_{Ar})	67 (A), 83 (B)
IIf	$C_{21}H_{31}N_3O$	Oil	1,4832	0,40 (b)	1,50 (18H, ex.b.s, 2*t*-Bu), 2,52 (6H, s, 2Me), 3,96...4,14 (4H, m, 2CH_2), 5,18 (1H, s, OH), 7,35 (2H, s, H_{Ar})	65 (A), 83 (B)
IIg	$C_{20}H_{29}N_3OS$	127...129	–	0,52 (a)	1,72 (18H, ex.b.s, 2*t*-Bu), 2,36 (6H, s, 2Me), 3,85 (2H, s, CH_2), 4,86 (1H, s, OH), 7,32 (2H, s, H_{Ar})	70 (A), 88 (B)
IIh	$C_{21}H_{31}N_3OS$	58...59,5	–	0,44 (a)	1,63 (18H, ex.b.s, 2 *t*-Bu), 2,48 (6H, s, 2Me), 4,02...4,16 (4H, m, 2CH_2), 5,04 (1H, s, OH), 7,18 (2H, s, H_{Ar})	68 (A), 84 (B)
IIi	$C_{12}H_{13}N_3S$	154...156 (2)	1,4757	0,62 (b)	2,52 (6H, s, 2Me), 3,93 (2H, s, CH_2), 6,88...7,04 (5H, m, H_{Ph})	72 (A), 94 (B)
IIj	$C_{19}H_{27}N_3OS$	130...131	–	0,60 (a)	1,68 (18H, ex.b.s, 2*t*-Bu), 2,55 (6H, s, 2Me), 5,10 (1H, s, OH), 7,20 (2H, s, H_{Ar})	70 (A), 85 (B)
IIk	$C_{20}H_{29}N_3OS$	89...91	–	0,30 (b)	1,52 (18H, ex.b.s, 2*t*-Bu), 2,32 (6H, s, 2Me), 3,94 (2H, s, CH_2), 4,90 (1H, s, OH), 7,32 (2H, s, H_{Ar})	75 (A), 89 (B)

TABLE 1. (Continued)

Compound	Molecular formula	T_{bp}, °C(mm Hg) or T_{mp}, °C*	n_D^{20}	R_f (solvent system)	PMR spectra, δ, ppm*[2], SSCC, J, Hz	Yield, % (preparative method)
1	2	6	7	8	9	10
IVa	$C_{49}H_{16}N_4$	137...138	—	0,74 (c)	1,15 (3H, t, Me), 1,54...1,87 (6H, m, $3CH_2$), 2,56 (3H, s, Me), 3,34 (2H, t, CH_2), 5,88 (2H, ex.b.s, NH_2)	72(C)
IVb	$C_{16}H_{30}N_4$	119...120	—	0,60 (a)	1,27 (3H, t, Me), 1,84...2,12 (20H, m, $10CH_2$), 2,45 (3H, s, Me), 3,05 (2H, t, CH_2), 6,10 (2H, ex.b.s, NH_2)	77 (C)
IVc	$C_{21}H_{40}N_4$	131...132 (129...130 [19])	—	0,52 (a)	1,13 (3H, t, Me), 1,37...1,55 (30H, m, $15CH_2$), 2,40 (3H, s, Me), 2,80 (2H, t, CH_2), 6,22 (2H, ex.b.s, NH_2)	69 (C)
IVd	$C_8H_8N_4O$	229...230 (230...231 [20])	—	0,70 (c)	2,47 (3H, s, Me), 5,78 (2H, ex.b.s, NH_2), 6,18 (1H, d.d, 3-H_{Het}, J_{35} = 0,8), 6,63 (1H, d.d, 4-H_{Het}, J_{34} = 3,4), 7,37 (1H, d.d, 5-H_{Het}, J_{45} = 1,8)	81 (C)
IVe	$C_{12}H_{11}N_5$	144...145 (decomp.)	—	0,58 (c)	2,32 (3H, s, Me), 5,94 (2H, ex.b.s, NH_2), 7,10...7,25 (2H, m, 5- and 6-H_{Het}), 7,35 (1H, d, 7-H_{Het}, J_{67} = 7,3), 7,60 (1H, d, 4-H_{Het}, J_{45} = 7,3), 7,72 (1H, d, 2-H_{Het}, J_{12} = 2,7), 8,14 (1H, ex.b.s, NH)	70 (C)
IVf	$C_{13}H_{13}N_5$	100...102	—	0,64 (a)	2,54 (3H, s, Me), 3,38 (3H, s, N—Me), 6,05 (2H, ex.b.s, NH_2), 7,15...7,29 (2H, m, 5-and 6-H_{Het}), 7,45 (1H, d, 7-H_{Het}, J_{67} = 7,1), 7,60 (1H, d, 4-H_{Het}, J_{45} = 7,1), 7,76 (1H, s, 2-H_{Het})	66(C)
IVg	$C_{18}H_{26}N_4OS$	138...140	—	0,48 (c)	1,68 (18H, ex.b.s, 2*t*-Bu), 2,38 (3H, s, Me), 4,97 (1H, s, OH), 6,20 (2H, ex.b.s, NH_2), 7,12 (2H, s, H_{Ar})	75(C)
IVh	$C_{18}H_{34}N_4$	57...58	—	0,60 (a)	1,17 (3H, t, Me), 1,45...1,74 (20H, m, $10CH_2$), 2,30 (3H, s, Me), 2,95 (2H, t, CH_2), 3,28 (6H, ex.b.s, NMe_2)	73(C)
IVi	$C_{23}H_{44}N_4$	Oil	1,4774	0,44 (a)	1,10 (3H, t, Me), 1,32...1,50 (30H, m, 15CH2), 2,47 (3H, s, Me), 3,04 (2H, t, CH_2), 3,37 (6H, ex.b.s, NMe_2)	70(C)
IVj	$C_{20}H_{30}N_4OS$	67...69	—	0,60 (b)	1,63 (18H, ex.b.s, 2 *t*-Bu), 2,53 (3H, s, Me), 3,12 (6H, s, NMe_2), 5,08 (1H, s, OH), 7,34 (2H, s, H_{Ar})	79 (C)
IVk	$C_{21}H_{32}N_4OS$	Oil	1,4729	0,52 (b)	1,55 (18H, ex.b.s, 2 *t*-Bu), 2,46 (3H, s, Me), 3,28 (6H, s, NMe_2), 3,92 (2H, s, CH_2S), 5,05 (1H, s, OH), 7,22 (2H, s, H_{Ar})	72(C)
IV*l*	$C_{22}H_{34}N_4O_2S$	94...95	—	0,57 (a)	1,61 (18H, ex.b.s, 2*t*-Bu), 2,33 (3H, s, Me), 2,54...2,72 (4H, m, $2NCH_2$), 3,42...3,60 (4H, m, $2OCH_2$), 4,95 (1H, s, OH), 7,16 (2H, s, H_{Ar})	68(C)

TABLE 1. (Continued)

Compound	Molecular formula	T_{bp}, °C (mm Hg) or T_{mp}, °C*	n_D^{20}	R_f (solvent system)	PMR spectra, δ, ppm*[2], SSCC, J, Hz	Yield, % (preparative method)
1	2	6	7	8	9	10
IVm	$C_{23}H_{36}N_4O_2S$	50...52	–	0,42 (a)	1,67 (18H, ex.b.s, 2 *t*-Bu), 2,37 (3H, s, Me), 2,50...2,74 (4H, m, $2NCH_2$), 3,37...3,55 (4H, m, $2OCH_2$), 3,88 (2H, s, CH_2S), 5,16 (1H, s, OH), 7,30 (2H, s, H_{Ar})	77 (C)
VIa	$C_{10}H_{17}N_3O$	107...109 (2)	1,4818	0,81 (a)	1,16 (3H, t, Me), 1,28...1,67 (6H, m, $3CH_2$), 2,40 (3H, s, Me), 2,89 (2H, m, CH_2), 3,68 (3H, s, OMe)	38 (D), 75 (C)
VIb	$C_{17}H_{31}N_3O$	144...145 (1)	1,4841	0,70 (a)	1,10 (3H, t, Me), 1,22...1,76 (20H, m, $10CH_2$), 2,52 (3H, s, Me), 3,04 (2H, t, CH_2), 3,74 (3H, s, OMe)	34 (D), 78 (C)
VIc	$C_{22}H_{41}N_3O$	59...61	–	0,54 (a)	1,17 (3H, t, Me), 1,30...1,88 (30H, m, $15CH_2$), 2,43 (3H, s, Me), 3,21 (2H, s, CH_2), 3,80 (3H, s, OMe)	35 (D), 84 (C)
VId	$C_{11}H_{19}N_3O$	128...130 (2)	1,4830	0,76 (a)	1,12 (3H, t, Me), 1,20 (3H, t, Me), 1,34...1,70 (6H, m, $3CH_2$), 2,37 (3H, s, Me), 2,94 (2H, t, CH_2), 4,12 (2H, q, CH_2O)	37 (D), 80 (C)
VIe	$C_{26}H_{38}N_3O_2$	Oil	1,4837	0,72 (в)	1,15 (3H, s, Me), 1,26...1,51 (6H, m, 3CH2), 1,67 (18H, ex.b.s, 2*t*-Bu), 2,15...2,32 (4H, m, $2CH_2$), 2,58 (3H, s, Me), 3,24 (2H, t, CH_2), 4,40 (2H, t, CH_2O), 4,92 (1H, s, OH), 7,24 (2H, s, H_{Ar})	82 (C)
VIf	$C_{27}H_{35}N_3O_2$	112...114	–	0,57 (a)	1,54 (18H, ex.b.s, 2 *t*-Bu), 2,10...2,35 (4H, m, $2CH_2$), 2,54 (3H, s, Me), 4,18 (2H, t, CH_2O), 5,15 (1H, s, OH), 6,89...7,11 (5H, m, $H_{P\,h}$), 7,33 (2H, s, H_{Ar})	74 (C)

*Compounds IIe, g, h, k, IVa-c, f, h, j, *l*, m, and VIc were recrystallized from aqueous ethanol; IIj, IVe, and VIf, from dioxane/cyclohexane mixture; and IVd, g, from aqueous DMFA.

*[2]The spectra of compounds IIa-f, j, k, IVa-g, and VIa-d were recorded in DMSO-D_6; of IIg-i, IVh-k, and VIe, f, in acetone-D_6; and of IV*l*, m, in CD_3OD.

formamide. In the present work we have shown that this method can be used for the reduction of 6-alkyl-2,4-bis(trichloromethyl)- (Ia-h) and 6-benzyl(aryl)thio-2,4-bis(trichloromethyl)-sym-triazines (IIa-k) are formed in yields of 65-76% by boiling (25-30 h) compounds Ia-h with a 5-6-fold excess of activated zinc dust in absolute ethanol (method A).

It is known [9, 10] that aliphatic halogen derivatives can be reduced with lithium aluminum hydride. We have shown that Cl_3C groups in sym-triazines Ia-k can also be reduced to methyl groups with lithium aluminum hydride. When compounds Ia-k are boiled (3-4 h) with $LiAlH_4$ (1:6-1:7 mole ratio) in THF, the desired 2,4-dimethyl-sym-triazines IIa-k are formed in yields of 83-94% (method B).

6-Substituted 2-amino- (IIIa-g), 2-dimethylamino- (IIIa-k), and 2-morpholino-4-trichloromethyl-sym-triazines (IIIm, n) resisted reduction with zinc dust in boiling ethanol or formamide. Even after the reactants had undergone prolonged boiling (20-25 h) in formamide, only the starting materials were isolated from the reaction mixture. We established that Cl_3C groups in sym-triazines of this type are easily reduced with lithium aluminum hydride (1:3 mole ratio) in dibutyl ether (boiling, 3-4 h), and that the desired 6-substituted 2-amino-4-methyl-symtriazines (IVa-m) are formed in 68-81% yields (method C).

Heating 6-alkyl(phenyl)-2-alkoxy-4-trichloromethyl-sym-triazines (Va-f) with zinc dust in formamide leads to tar formation. It was possible, by means of preparative TLC, to isolate the corresponding 4-methyl derivatives (VIa-f) from the reaction mass, but in yields not exceeding 34-40% (method D). At the same time, when compounds Va-f are reduced by method C with lithium aluminum hydride in dibutyl ether, products VIa-f are formed in 75-84% yields.

The compositions and structures of the synthesized 6-substituted 2,4-dimethyl(IIa-k), 2-amino-4-methyl- (IVa-m), and 2-alkoxy-4-methyl-sym-triazines (VIa-f) are in good accord with the elemental analyses and the PMR and IR spectral data.

In the IR spectra of these compounds one finds absorption maxima of various intensities characteristic of stretching (1570-1550, 1540-1530, and 1430-1415 cm^{-1}), breathing (1125-1105, and 1015-1000 cm^{-1}), out-of-plane (825-805 cm^{-1}), and in-plane (720-695 cm^{-1}) vibrational modes of the sym-triazine ring [1-6, 11, 12]. These absorption bands are shifted to higher frequencies compared to the spectra of the starting triazines, Ia-k, IIIa-m, Va-f. Note that in the spectra of methyl-substituted IIa-k, IVa-m, and VIa-f, the intense absorption bands at 785-770 cm^{-1} that are characteristic of the C–Cl stretching modes in trichloromethyl-sym-triazines [4, 13] are absent.

The spectra of compounds IIe-h, IVg, j-m, and VIe, f also contain absorption bands due to a sterically hindered phenol residue: a narrow band at 3655-3640 cm^{-1} characteristic of a screened hydroxyl [14]; two bands of medium intensity in the 1265-1210 cm^{-1} region arising from vibrations of the Ar–OH bond in screened phenols [15]; and two groups of bands at 885-870 and 830-820 cm^{-1} (out-of-plane bending vibrations of a tetrasubstituted benzene ring).

In the PMR spectra of the synthesized sym-triazines (Table 1), the proton signals of the methyl groups appear as singlets with intensities of six (compounds IIa-k) or three proton units (compounds IVa-i and VIa-f) in the 2.30-2.58 ppm range. In the spectra of alkyl substituted products IIa-d, IVa-c, h, i, and VIa-e, three groups of signals are found arising from protons of the alkyl radicals and differing in intensity and chemical shift. The methyl group proton signals from a symmetric triplet at 1.08-1.27 ppm. The complex multiplets in the 1.26-2.12 ppm range must be attributed to protons of the methylene links, and the weak field, unsymmetrical triplets (2.80-3.34 ppm) to CH_2 groups bound to the triazine ring [2, 3].

In the spectra of compounds IIe-h, IVg, j-m, and VIe, f, the signals of the hydroxyl protons appear as singlets in the 4.86-5.18 ppm range, which is characteristic of screened phenols [14, 16]. Signals of the tert-butyl group protons are found as singlets in the 1.50-1.72 ppm range. Two magnetically equivalent protons of the hydroxyaryl residues are responsible for singlets at 7.12-7.35 ppm [1, 5, 16].

In the spectra of 2-amino-4-methyl-sym-triazines IVa-g, the signals of the amine group protons appear as broadened singlets with an intensity of two proton units in the 5.78-6.22 ppm range [1-3, 5, 6].

EXPERIMENTAL

The IR spectra were taken on a Bruker IFS-48 instrument in KBr tablets or mineral oil suspension. The PMR spectra were recorded on Bruker WP-100 SY (100 MHz) and Bruker WM-250 (250 MHz) instruments, TMS internal standard. The course of the reactions and the purity of the compounds obtained were monitored by means of TLC on Al_2O_3 (III degree Brockman activity) in 20:1 benzene/methanol (a), 30:1 benzene/methanol (b), and 15:1 CCl_4/methanol (c) solvent systems, developed with iodine vapor.

The elementary analyses for C, H, and N agree with the calculated values (see Table 1).

The starting 6-alkyl- (Ia-d) [17], 6-[(4-hydroxy-3,5-di-tert-butylphenyl)methyl]- (Ie) [13], 6[2-(4-hydroxy-3,5-di-tert-butylphenyl)ethyl]- (If) [13], 6-[(4-hydroxy-3,5-di-tert-butylphenylthio)methyl]- (Ig) [13], 6-[2-(4-hydroxy-3,5-di-tert-butylphenylthio)ethyl]- (Ih) [13], 6-benzylthio- (Ii) [18], 6-(4-hydroxy-3,5-di-tert-butylphenylthio)- (Ij) [13], and 6-[(4-hydroxy-3,5-di-tert-butylphenyl)methylthio]-2,4-bis(trichloromethyl)-sym-triazine (Ik) [13], as well as 2-amino-4-alkyl- (IIIa-c) [19], 2-amino-4-(furyl-2)- (Id) [20], 2-amino-4-(indolyl-3)- (IIIe) [6], 2-amino-4-(1-methylindolyl-3)- (IIIf) [6], 2-amino-4-(4-hydroxy-3,5-di-tert-butylphenylthio)- (IIIg) [1], 2-alkyl-4-dimethylamino- (IIIh, i) [3], 2-(4-hydroxy-3,5-di-tert-butylphenylthio)-4-dimethylamino-(IIIj)[1],2-[4-hydroxy-3,5-di-tert-butylphenyl)methylthio]-4-dimethylamino-(IIIk)[1],2-(4-hydroxy-3,5-di-tert-butylphenylthio)-4-morpholino- (III*l*) [1], 2-[(4-hydroxy-3,5-di-tert-butylphenyl)methylthio]-4-morpholino- (IIIm) [1], 2-alkoxy-4-alkyl- (Va-d) [2], 2-[3-(4-hydroxy-3,5-di-tert-butylphenyl)propoxy]-4-pentyl- (Ve) [5], and 2[3-(4-hydroxy-3,5-di-tert-butylphenyl)propoxy]-4-phenyl-6-trichloromethyl-sym-triazine (Vf) [5] were prepared by the known methods cited above.

2,4-Dimethyl-6-R-sym-triazines (IIa-k).

A. A mixture of 15 mmoles of 6-R-2,4-bis(trichloromethyl)-sym-triazine (Ia-k) and 5.9 g (90 mmoles) of zinc dust (first activated with dilute HNO_3) in 100 ml of absolute ethanol is boiled while stirred for 25-30 h until there is no more starting sym-triazine 1 in the reaction mixture (by TLC). The reaction mixture is cooled to 20°C and filtered. The filtrate is evaporated under reduced pressure and the remaining oil washed with 5% HCl (2 × 20 ml) and extracted with ether or methylene dichloride. The extract is dried over Na_2SO_4, the solvent removed under reduced pressure, and the residue either vacuum distilled in a stream of inert gas (to obtain product IIa-d, i), or crystallized from an appropriate solvent (see Table 1) (to obtain products IIe, g, h, j, k). In the case of triazine IIf, however, the residue is chromatographed on an Al_2O_3 column (90 × 4.5 cm) and eluted with a 10:1 chloroform/acetone mixture.

B. A solution of 12 mmoles of triazine Ia-c, e-k in 20 ml of anhydrous THF is added dropwise to a boiling suspension of 3.2 g (84 mmoles) of lithium aluminum hydride in 120 ml of anhydrous THF with stirring over 0.5 h. The reaction mixture is stirred and boiled for 4 h, cooled to 0°C, 150 ml of ether is added, and then 10% H_2SO_4 is added dropwise with stirring until the solid matter is completely dissolved (~50-55 ml). The organic layer is separated, washed with water, and dried over Na_2SO_4. The solvent is removed under reduced pressure and the residue treated as described above to obtain products IIa-c, e-k.

2-Amino-(IVa-g), 2-Dimethylamino- (IVh-k), 2-Morpholino- (IV*l*, m), and 2-Alkoxy-4-methyl-6-R-sym-triazines (VIa-f) (general method).

C. A solution of 10 mmoles of 4-trichloromethyl-substituted sym-triazine IIIa-k, Va-f in 20 ml of anhydrous dibutyl ether or dioxane is added dropwise to a stirred suspension of 1.1 g (30 mmoles) of lithium aluminum hydride in 100 ml of anhydrous dibutyl ether at 50-55°C. The reaction mixture is boiled and stirred for 3 h, cooled to 0°C, and 10% H_2SO_4 is added dropwise with stirring until the solid matter is completely dissolved (~30-35 ml). The organic layer is separated, washed with water, dried over Na_2SO_4 and the solvent removed under reduced pressure. Products IVa-h, k, *l*, m and VIc, f are isolated from the residue by crystallization from an appropriate solvent with activated charcoal (see Table 1), and products IVi, k and VIe, by chromatography on an Al_2O_3 column (85 × 4.5 cm) with a 10:1 benzene/methanol or 15:1 chloroform/acetone eluting agent. Products VIa, b, d are obtained by the vacuum distillation of the residue in a stream of inert gas.

2-Methoxy-4-methyl-6-dodecyl-sym-triazine (VIb).

D. A mixture of 1.59 g (6 mmoles) of triazine Vb and 2.36 g (36 mmoles) of zinc dust in 50 ml of formamide is boiled with stirring for 25 h. The reaction mixture is cooled to 20°C, filtered, and the filtrate evaporated under reduced pressure. The residue is chromatographed on a plate with Al_2O_3 (55 × 105 cm) in solvent system *a*, and the zone with R_f 0.64-0.76 is extracted with acetone to give 0.61 g of product VIb.

Products VIa, c, d are obtained in similar fashion.

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