SYNTHESIS AND PROPERTIES OF sym-TRIAZINE DERIVATIVES.

8.* SYNTHESIS OF AMINO AND ALKOXY DERIVATIVES OF sym-TRIAZINE CONTAINING FRAGMENTS OF A STERICALLY-HINDERED PHENOL FROM 2,4-BIS(TRICHLOROMETHYL)-sym-TRIAZINES

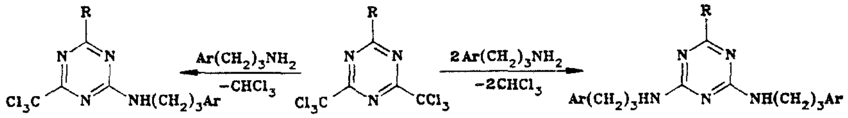
V. I. Kelarev, F. Laauad Yakh'ya, R. A. Karakhanov,
I. A. Golubeva, T. P. Vishnyakova, and O. V. Malova

UDC 547.491.8.04:543.422.4:542.958.3

The reactions of 2,4-bis(trichloromethyl)-6-substituted sym-triazines with several amino and hydroxy derivatives of 2,6-di-tert-butylphenol were studied. It is shown that, depending on the reaction conditions, one or both trichloromethyl groupings in the starting sym-triazines are replaced.

Continuing our research on the synthesis of sym-triazines that include fragments of a sterically-hindered phenol [2-4] in the present paper we report the preparation of compounds of this type from 2,4-bis(trichloromethyl)-6-substituted sym-triazines.

It is known [5-7] that trichloromethyl residues bonded to the sym-triazine ring are activated under the influence of the latter and are readily replaced by various groupings (HO, RO, NH_2, NHR, NR_2, CN, etc.). In the present research we studied the reaction of a number of 2,4-bis(trichloromethyl)-6-R-sym-triazines (Ia-e) with several amino and hydroxy derivatives of a shielded phenol – γ-(4-hydroxy-3,5-di-tert-butylphenyl)propylamine (II), 4-hydroxy-3,5-di-tert-butylbenzyl alcohol (IIIa), and γ-(4-hydroxy-3,5-di-tert-butylphenyl)propyl alcohol (IIIb). Starting triazines Ia-e were synthesized by the joint cyclotrimerization of trichloroacetonitrile with the corresponding nitriles (in a molar ratio of 2:1) in the presence of HCl or $AlBr_3$ + HCl via a previously developed method [8].

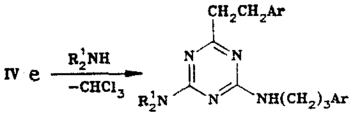


IVa-e Ia-e Va-e

Ar=4-HO-3,5-(*tert*-$C_4H_9)_2C_6H_2$; I, IV, V a R=C_5H_{11}; b R=$C_{10}H_{21}$; c R=C_6H_5; d R=Ar; e R=$ArCH_2CH_2$

sym-Triazines IVa-e were obtained by carrying out the reaction in an inert solvent (benzene or dioxane) at 35-40°C using a small excess (~10%) of amine II. Products of replacement of both Cl_3C groups – Va-e – were synthesized by heating (at 145-150°C) the reagents taken in a molar ratio of 1:2 for several hours in DMF in an inert gas atmosphere.

The same method was used to obtain N-substituted 2,4-diamino-6-R-sym-triazines with mixed structures (VIa, b). For example, 2-amino- (VIa) and 2-dimethylamino-4-[γ-(4-hydroxy-3,5-di-tert-butyl)propylamino]-6-R-sym-triazine (VIb) are formed when a stream of dry ammonia or dimethylamine is passed into a solution of sym-triazine IVe in DMF at 150°C.



a R^1=H; b R^1=CH_3 VIa,b

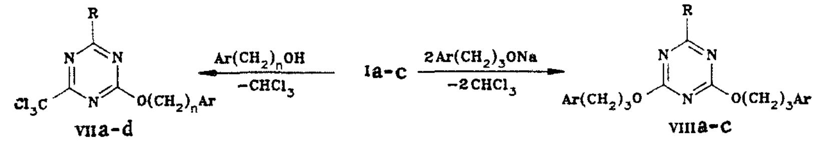
It has been previously shown [6] that the replacement of one Cl_3C group in 2,4-bis(trichloromethyl)-sym-triazines by alkoxy groups occurs readily upon reaction with alcohols in the presence of triethylamine, whereas replacement of both Cl_3C groups occurs on treatment

---

*See [1] for Communication 7.

I. M. Gubkin Moscow Institute of Petroleum and Gas, Moscow 117917. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 681-686, May, 1988. Original article submitted October 21, 1986.

with sodium alkoxides. Taking these data into account we studied the reaction of sym-triazines Ia-c with hydroxy derivatives IIIa, b.



Ar=4-HO-3,5-(*tert*-$C_4H_9)_2C_6H_2$; VIIa,b n=1; VIIc,d n=3; VIIa,c, VIIIa R=C_5H_{11}; VIIb,d, VIIIc R=C_6H_5; VIIb' R=$C_{10}H_{21}$

Monoalkoxy derivatives VIIa-d were obtained by carrying out the reaction in dioxane or 1,2-dimethoxyethane at 60-65°C in the presence of tertiary amines – triethylamine or N-ethylpiperidine – at a sym-triazine Ia, c—IIIa, b—tertiary amine molar ratio of 1:1.2:2.5. It should be noted that the reaction of Ia, c with hydroxy derivatives IIIa under the indicated conditions was accompanied by significant resinification and the formation of a number of side products, among which we isolated and identified 2,6-di-tert-butylphenol and bis(4-hydroxy-3,5-di-tert-butylphenyl)methane. Despite variations in the reaction conditions (the temperature, the reagent ratio, the reaction time, and the nature of the solvent) we were unable to avoid the formation of side compounds and increase the yields of monoalkoxy derivatives VIIa, b.

Dialkoxy derivatives VIIIa-c were synthesized in good yields by heating sym-triazines Ia-c with the sodium alkoxide previously obtained from IIIb at 65-70°C for several hours in an inert solvent – dioxane, THF, or 1,2-dimethoxyethane (the sym-triazine Ia-c—sodium alkoxide molar ratio was 1:2.2).

Absorption maxima with variable intensities at 1525-1560, 1400-1420, 1090-1115, 995-1015, 800-820, and 695-710 cm^{-1}, which are related to stretching, "breathing," and out-of-plane and in-plane deformation vibrations of the sym-triazine ring [2, 4, 9, 10], are observed in the IR spectra of all of the synthesized sym-triazines. In the spectra of sym-triazines IVa-e and VIIa-d these absorption bands are shifted only slightly to the low-frequency region as compared with the spectra of Va-e and VIIIa-c, respectively. In addition to these vibrations, there are also absorption bands due to the residue of the sterically-hindered phenol: a rather narrow band at 3635-3655 cm^{-1}, which is characteristic for a shielded phenol hydroxy group [11]; two bands of medium intensity at 1210-1265 cm^{-1}, which are characteristic for vibrations of Ar—O—H bonds in shielded phenols [12]; two groups of bands at 870-885 cm^{-1} and 815-830 cm^{-1} (out-of-plane deformation vibrations of a 4-substituted benzene ring). The absorption maxima of different intensities at 2970-2985 (ν_{as} CH_3), 2925-2940 (ν_{as} CH_2), 2850-2875 (ν_s CH_3, CH_2), 1435-1470 (δ_{as} CH_3, δ_s CH_2), 1360-1385 (δ_s CH_3), and 725-735 cm^{-1} correspond to stretching and deformation vibrations of C—H bonds in alkyl radicals [13].

A weak absorption band at 3290-3365 cm^{-1} is observed in the region of NH stretching vibrations in the spectra of sym-triazines IVa-e, Va-e, and VIa. Absorption maxima of medium intensity at 1505-1520 cm^{-1} are characteristic for NH scissors vibrations. A number of bands of medium intensity at 1000-1380 cm^{-1} correspond to stretching vibrations of C—N bonds. According to the data in [14], the absorption maxima at 1345-1380 cm^{-1} should be assigned to stretching vibrations of N—ring bonds, while the absorption frequencies at 1230-1240, 1175-1185, 1130-1135, and 1050-1060 cm^{-1} should be assigned to vibrations of N—alkyl bonds.

Intense narrow absorption bands at 1220-1235 cm^{-1} and several bands of varying intensity at 1025-1080 cm^{-1}, which are related to, respectively, C—O—C asymmetrical and symmetrical stretching vibrations, which is characteristic for alkoxy derivatives of sym-triazine [6], are observed in the spectra of VII and VIII.

The PMR spectra of amino-sym-triazines IV-VI and alkoxy-sym-triazines VII and VIII also confirm the proposed structures quite well. The assignment of the signals in the spectra of these compounds was made taking into account data on the proton spectra of sterically-hindered phenols [11, 15] and sym-triazine derivatives [8, 16, 17]. In the spectra of the synthesized compounds the signals of the hydroxy protons are represented in the form of singlets at 4.80-5.20 ppm, which is characteristic for shielded phenols [11, 15]. Signals of protons of tert-butyl groups are observed in the form of broad singlets at 1.52-1.84 ppm. The singlet signals at 7.08-7.32 ppm correspond to the aromatic protons of hydroxyaryl frag-

TABLE 1. Characteristics of the Synthesized sym-Triazine Derivatives

Compound*	mp,** °C	R_f	Found, %				Empirical formula	Calculated, %				Yield, %
			C	H	Cl	N		C	H	Cl	N	
IVa	67—68	0,74(c)	59,1	7,2	20,3	10,8	$C_{26}H_{39}Cl_3N_4O$	58,9	7,4	20,1	10,6	79
IVb	Oil	0,66(c)	61,8	8,4	17,6	9,1	$C_{31}H_{49}Cl_3N_4O$	62,0	8,2	17,7	9,3	75,5
IVc	128—129	0,88(c)	60,6	6,3	20,1	10,2	$C_{27}H_{33}Cl_3N_4O$	60,5	6,2	19,9	10,4	84
IVd	107—108	0,74(a)	63,4	7,4	16,2	8,2	$C_{35}H_{49}Cl_3N_4O_2$	63,3	7,4	16,0	8,4	76
IVe	68—69,5	0,78(a)	64,3	7,6	15,6	8,0	$C_{37}H_{53}Cl_3N_4O_2$	64,2	7,7	15,4	8,1	80
Va	84—85,5	0,40(a)	74,9	10,2	—	10,7	$C_{42}H_{67}N_5O_2$	74,8	10,0	—	10,4	67
Vb	72,5—73,5	0,32(a)	75,6	10,3	—	9,6	$C_{47}H_{77}N_5O_2$	75,9	10,4	—	9,4	80
Vc	174—176	0,46(a)	75,7	9,1	—	10,5	$C_{43}H_{61}N_5O_2$	76,0	9,0	—	10,3	88 (79)
Vd	124—125	0,45(b)	77,7	7,2	—	9,0	$C_{51}H_{56}N_5O_3$	77,8	7,1	—	8,9	69
Ve	Oil	0,58(b)	78,0	7,3	—	8,8	$C_{53}H_{60}N_5O_3$	78,1	7,4	—	8,6	67
VIa	146—147,5	0,52(a)	73,2	9,2	—	12,1	$C_{36}H_{55}N_5O_2$	73,3	9,3	—	11,3	76
VIb	Oil	0,32(c)	74,0	9,5	—	11,2	$C_{38}H_{59}N_5O_2$	73,9	9,6	—	11,3	82
VIIa	90—91	0,70(c)	51,6	7,6	24,2	9,7	$C_{24}H_{34}Cl_3N_3O_2$	51,5	7,7	24,0	9,5	38
VIIb	129—130	0,77(c)	58,7	5,6	21,1	8,4	$C_{25}H_{28}Cl_3N_3O_2$	59,2	5,5	21,0	8,3	32
VIIc	Oil	0,67(a)	58,7	7,3	19,8	8,2	$C_{26}H_{38}Cl_3N_3O_2$	58,8	7,2	20,0	7,9	78
VIId	54—56	0,84(a)	60,5	5,9	19,6	8,0	$C_{27}H_{32}Cl_3N_3O_2$	60,4	6,0	19,8	7,8	69,5
VIIIa	Oil	0,53(c)	74,8	10,1	—	6,5	$C_{42}H_{65}N_3O_4$	74,6	9,7	—	6,3	80
VIIIb	29—30	0,38(c)	75,8	10,1	—	5,8	$C_{47}H_{75}N_3O_4$	75,7	10,1	—	5,6	68
VIIIc	118—119	0,71(c)	75,9	8,8	—	6,3	$C_{43}H_{59}N_3O_4$	75,7	8,7	—	6,2	85

*The compounds were recrystallized: IVa from acetonitrile, IVc, Va, and VIIa, d from aqueous alcohol, IVd and Vd from aqueous DMF, IVe and Vb from aqueous acetone, Vc from benzene—alcohol (3:1), VIa from alcohol, VIIb from benzene—acetone, and VIIIc from aqueous CH_3COOH.

**Compounds IVb, Ve, VIIc, and VIIIa, b were purified with a column packed with Al_2O_3, and VIb was purified with a column packed with silica gel; n_D^{20} 1.4909 (IVb), 1.5154 (VIIc), 1.5218 (VIIIa).

ments [2, 13]. All of the signals of the protons of the secondary amino groups in the spectra of sym-triazines IV-VI are represented in the form of broad singlets at 5.80-6.14 ppm; this is characteristic for amino derivatives of sym-triazine [2, 18].

EXPERIMENTAL

The IR spectra of KBr pellets (for IVa, c-e, Va-d, VIa, VIIa, b, d, and VIIIc) or suspensions in mineral oil (for IVb, Vb, VIb, VIIc, and VIIIa, b) were recorded with a UR-20 spectrometer. The PMR spectra were obtained with a Tesla BS-487C spectrometer (80 MHz) on the δ scale with hexamethyldisiloxane (HMDS) as the internal standard. The course of the reactions and the purity of the compounds obtained were monitored by means of TLC on activity III (Brockmann) Al_2O_3 in benzene—methanol (15:1) (a), benzene—methanol (20:1) (b), and chloroform—methanol (20:1) (c) with development by iodine vapors.

The starting 2,4-bis(trichloromethyl)-6-alkyl-sym-triazines Ia, b [8] and β-(4-hydroxy-3,5-di-tert-butylphenyl)propionitrile [4] were previously synthesized. 2,4-Bis(trichloromethyl)-4-phenyl-sym-triazine (Ic) [19] and 4-hydroxy-3,5-di-tert-butylbenzonitrile [20] were obtained by known methods.

2,4-Bis(trichloromethyl)-6-(4-hydroxy-3,5-di-tert-butylphenyl)-sym-triazine (Id). A stream of dry HCl was passed for 2 h at —10°C into a stirred mixture of 5.77 g (25 mmoles) of 4-hydroxy-3,5-di-tert-butylbenzonitrile, 7.22 g (50 mmoles) of trichloroacetonitrile, and 0.67 g (2.5 mmoles) of $AlBr_3$ in 50 ml of dry ether, after which the reaction mixture was maintained for 12 h at 20°C. The solvent and excess HCl were removed at reduced pressure, and the residue was heated for 12 h at 145°C. The resulting dark mass was washed successively with 3% $NaHCO_3$ solution (three 50 ml portions) and water (two 30 ml portions) and extracted with hot acetonitrile (three 70 ml portions). The extract was dried over $CuSO_4$, concentrated to a volume of 15-18 ml, and chromatographed with a column (4.5 by 90 cm) packed with Al_2O_3. Initial elution with benzene—acetone (30:1) gave 0.76 g of the starting nitrile (mp 145-146°C; mp 147°C [20]). Subsequent elution with benzene—methanol (20:1) gave 3.51 g (27%) of Id with mp 208-210°C (from aqueous Methyl Cellosolve) and R_f 0.64 (a). PMR spectrum [$CDCl_3$—d_6-DMSO (1:4)]: 1.68 (18H, s, tert-C_4H_9), 4.88 (1H, s, OH), 7.20 ppm (2H, s, aromatic). Found: C 45.9; H 4.0; Cl 41.2; N 8.0%. $C_{19}H_{21}Cl_6N_3O$. Calculated: C 43.8; H 3.9; Cl 40.9; N 8.1%. Elution with benzene—methanol (5:1) gave 3.25 (45% based on trichloroacetonitrile) of 2,4,6-tris(trichloromethyl)-sym-triazine with mp 93-94°C (from alcohol) and R_f 0.77 (b) (mp 94-95°C [8]).

2,4-Bis(trichloromethyl)-6-[β-(4-hydroxy-3,5-di-tert-butylphenyl)ethyl]-sym-triazine (Ie). A stream of dry HCl was passed for 2 h at —5°C into a stirred solution of 3.88 g (15 mmole) of β-(4-hydroxy-3,5-di-tert-butyphenyl)propionitrile and 3.25 g (22.5 mmole) of trichloroacetonitrile in 35 ml of dry chloroform, after which the reaction mixture was maintained for 12 h at 20°C. The solvent and excess HCl were removed at reduced pressure, and the residue was heated for 2 h at 100°C. The reaction mixture was cooled and extracted with ether (four 60-ml portions), and the extract was washed successively with 3% $NaHCO_3$ solution (two 75-ml portions) and water (two 100-ml portions) and dried over $CuSO_4$. The solvent was removed at reduced pressure, and the residual oil was chromatographed with a column (4.5 × 75 cm) packed with Al_2O_3. Initial elution with benzene—hexane (5:1) gave a small amount of the starting nitrile, and subsequent elution with benzene—methanol (20:1) gave 5.75 g (70%) of the Ie in the form of light-yellow oil with n_D^{20} 1.4805 and R_f 0.49 (b). It was additionally purified by chromatography with a column packed with silica gel using chloroform—acetone (30:1) as the eluent. PMR spectrum ($CDCl_3$): 1.60 (18H, s, tert-C_4H_9), 4.02-4.14 (4H, m, CH_2CH_2), 5.10 (1H, s, OH), 7.18 ppm (2H, s, aromatic). Found: C 45.9; H 4.5; Cl 39.2; N 7.4%. $C_{21}H_{25}Cl_6N_3O$. Calculated: C 46.0; H 4.6; Cl 38.9; N 7.6%. Elution with benzene—methanol (5:1) gave 0.48 g (15% based on trichloroacetonitrile) of 2,4,6-tris(trichloromethyl)-syn-triazine.

2-[γ-(4-Hydroxy-3,5-di-tert-butylphenyl)propylamino]-4-trichloromethyl-6-substituted sym-Triazines IVa-e. A mixture of 15 mmoles of sym-triazines Ia-e and 4.33 g (16.5 mmoles) of amine II in 30 ml of dry benzene or dioxane was stirred for 4 h at 30-35°C in a nitrogen atmosphere, after which the reaction mixture was evaporated at reduced pressure, and the resulting sym-triazines were purified either by recrystallization (for IVa, c-e) or by chromatography with a column packed with Al_2O_3 (for IVb) by elution with benzene—methanol (20:1). PMR spectrum of sym-triazine IVa (CD_3OD): 1.12 (3H, t, CH_3), 1.62 (18H, s, tert-C_4H_9), 1.90-2.32 (10H, m, CH_2), 3.34 (2H, q, CH_2—N), 5.12 (1H, s, OH), 5.88 (1H, s, NH), 7.18 ppm (2H, s, aromatic). PMR spectrum of sym-triazine IVd (d_6-acetone): 1.56 (18H, s, tert-

C_4H_9), 1.72 (18H, s, tert-C_4H_9), 3.64-3.88 (6H, m, CH_3), 5.02 (1H, s, OH), 5.13 (1H, s, OH), 6.02 (1H, s, NH), 7.14 (2H, s, aromatic), 7.22 ppm (2H, s, aromatic).

2,4-Bis[γ-(4-hydroxy-3,5-di-tert-butylphenyl)propylamino]-6-substituted sym-Triazines Va-e. A mixture of 15 mmoles of sym-triazines Ia-e and 7.89 g (30 mmoles) of amine II in 50 ml of dry DMF was stirred for 5 h at 145°C in a nitrogen atmosphere, after which the reaction mixture was cooled to 20°C and poured into 300 ml of cold water. sym-Triazines Va-e were extracted with ether or methylene chloride (three 100-ml portions), and the extracts were washed with water (two 100-ml portions), dried over $CuSO_4$, and evaporated to dryness at reduced pressure. The residue was chromatographed with a column (4.5 × 80 cm) packed with Al_2O_3 by elution with benzene—methanol (15:1). The solvents were removed at reduced pressure, and the compounds obtained were purified either by recrystallization from a suitable solvent (for Va-d) or by repeated chromatography with a column packed with Al_2O_3 (for Ve) by elution with benzene—methanol (20:1). PMR spectrum of sym-triazine Vd (CCl_4—d_6-DMSO (2:1)]: 1.52 (18H, s, tert-C_4H_9), 1.77 (36H, broad s, tert-C_4H_9), 3.60-3.94 (12H, m, CH_2), 4.82 (1H, s, OH), 5.04 (2H, s, OH), 6.02 (2H, broad s, NH), 7.12 (2H, s, aromatic), 7.28 ppm (4H, s, aromatic). PMR spectrum of sym-triazine Ve (d_6-acetone): 1.58 (18H, s, tert-C_4H_9), 1.78 (36H, broad s, tert-C_4H_9), 3.70-4.12 (16H, m, CH_2), 4.88 (1H, s, OH), 5.04 (2H, s, OH), 6.08 (2H, broad s, NH), 7.16 (2H, s, aromatic), 7.26 ppm (4H, s, aromatic).

2-Amino-4-[γ-(4-hydroxy-3,5-di-tert-butylphenyl)propylamino]-6-[β-(4-hydroxy-3,5-di-tert-butylphenyl)ethyl]-sym-triazine (VIa). A stream of dry ammonia was passed for 2 h at 145-150°C into a stirred solution of 3.44 g (5 mmoles) of sym-triazine IVe in 30 ml of dry DMF, after which the reaction mixture was stirred for 1 h at 150°C. It was then cooled to 20°C and poured into 100 ml of cold water, and the resulting precipitate was removed by filtration, washed on the filter with water, dried, and crystallized.

2-Dimethylamino-4-[γ-(4-hydroxy-3,5-di-tert-butylphenyl)propylamino]-6-[β-(4-hydroxy-3,5-di-tert-butylphenyl)ethyl]-sym-triazine (VIb). This compound was similarly obtained in the form of a viscous colored oil, which was purified by chromatography with a column packed with silica gel by elution with hexane—benzene (5:1). PMR spectrum of sym-triazine VIb (d_6-acetone): 1.74 (18H, s, tert-C_4H_9), 1.82 (18H, s, tert-C_4H_9), 3.08 (6H, d, N—CH_3), 3.26-3.98 (10H, m, CH_2), 4.96 (1H, s, OH), 5.05 (1H, s, OH), 6.05 (1H, s, NH), 7.26 (2H, s, aromatic), 7.32 ppm (2H, s, aromatic).

2-(4-Hydroxy-3,5-di-tert-butylbenzyloxy)-4-trichloromethyl-6-substituted sym-Triazines VIIa, b. A solution of 3.4 g (14 mmoles) of IIIa in 25 ml of anhydrous dioxane was added at 60°C in the course of 1 h to a stirred solution of 12 mmoles of sym-triazine Ia, c and 3.8 g (36 mmoles) of dry triethylamine in 35 ml of anhydrous dioxane, after which the reaction mixture was stirred for 3 h at 60°C. It was then evaporated to dryness at reduced pressure, and the residue was chromatographed with a column (4.5 × 100 cm) packed with Al_2O_3. Elution with hexane—benzene (15:1) gave 0.55 g of 2,6-di-tert-butylphenol with mp 36°C (from hexane) and R_f 0.89 (c) (mp 36.5°C [11]). Subsequent elution with benzene—methanol (50:1) gave 0.35 g of bis(4-hydroxy-3,5-di-tert-butylphenyl)methane with mp 153-154°C (from aqueous acetone) and R_f 0.54 (b) (mp 155°C [11]). Further elution with benzene—methanol (20:1) gave sym-triazines VIIa, b. After removal of the solvents, the compounds obtained were crystallized from suitable solvents. PMR spectrum of sym-triazine VIIa (d_6-DMSO): 1.14 (3H, t, CH_3), 1.70 (18H, s, tert-C_4H_9), 1.84-2.06 (6H, m, CH_2), 2.92 (2H, t, ring CH_2), 4.22 (2H, s, CH_2—O), 5.10 (1H, s, OH), 7.20 ppm (2H, s, aromatic).

2-[γ-(4-Hydroxy-3,5-di-tert-butylphenyl)propyloxy]-4-trichloromethyl-6-substituted sym-Triazines VIIc, d. A mixture of 10 mmoles of sym-triazine Ia, c, 3.27 g (30 mmoles) of dry triethylamine, and 3.32 g (12 mmoles) of IIIb in 45 ml of anhydrous dioxane was stirred for 6 h at 60-65°C, after which the reaction mixture was evaporated to dryness at reduced pressure. The residue was chromatographed with a column (4.5 × 70 cm) packed with Al_2O_3 by elution with benzene—methanol (15:1). After removal of the solvents, VIIc was obtained in the form of a viscous uncrystallizable oil, whereas VIId was obtained in the form of a solid substance, which was purified by recrystallization. PMR spectrum of sym-triazine VIId (d_6-DMSO): 1.67 (18H, s, tert-C_4H_9), 2.22-2.64 (4H, m, CH_2), 4.10 (2H, t, CH_2—O), 4.96 (1H, s, OH), 7.12 (2H, s, aromatic), 7.25-7.43 ppm (5H, m, aromatic).

2,4-Bis[γ-(4-hydroxy-3,5-di-tert-butylphenyl)propyloxy]-6-substituted sym-Triazines VIIIa-c. A 0.39 g (17 mmoles) sample of sodium was added in small portions at 12-15°C to a stirred solution of 4.2 g (16 mmoles) of IIIb in 50 ml of dry 1,2-dimethoxyethane, after which the reaction mixture was stirred for 1.5 h at 35°C. The resulting suspension of the alcoholate was added to a stirred solution of 7 mmoles of sym-triazines Ia-c in 30 ml of dry 1,2-dimethoxyethane, and the mixture was stirred for 8 h at 75°C, cooled to 20°C, and poured into 250 ml of water. sym-Triazines VIIIa-c were extracted with dichloromethane (three 80 ml portions), and the extracts were washed with water (two 100 ml portions), dried over $CuSO_4$, and evaporated to dryness. The residue was chromatographed with a column (4.5 × 70 cm) packed with Al_2O_3 by elution with chloroform—methanol (20:1). After removal of the solvents, dialkoxy derivatives VIIIa, b were obtained in the form of viscous oils, which were purified by repeated chromatography with a column packed with Al_2O_3 by elution with chloroform—methanol (20:1). PMR spectrum of sym-triazine VIIIb (d_6-acetone): 1.14 (3H, t, CH_3), 1.70-1.74 (36H, broad s, tert-C_4H_9), 1.90-2.32 (24H, m, CH_2), 2.88 (2H, t, ring CH_2), 4.42 (4H, t, CH_2—O), 5.08 (2H, s, OH), 7.24 ppm (4H, s, aromatic).

LITERATURE CITED

1. V. I. Kelarev, R. A. Karakhanov, M. Bellul', R. L. Ushakova, and A. I. Mikaya, Khim. Geterotsikl. Soedin., No. 5, 674 (1988).
2. O. V. Malova, T. P. Vishnyakova, I. A. Golubeva, V. I. Kelarev, and A. F. Lunin, Khim. Geterotsikl. Soedin., No. 12, 1678 (1984).
3. O. V. Malova, V. I. Kelarev, I. A. Golubeva, T. P. Vishnyakova, and A. F. Lunin, Zh. Vses. Khim. Obshch., 29, 462 (1984).
4. V. V. Kelarev, F. Laauad Yakh'ya, R. A. Karakhanov, A. F. Lunin, and O. V. Malova, Khim. Geterotsikl. Soedin., No. 1, 107 (1986).
5. A. Kreutzberger, Adv. Chem. Soc., 34, 208 (1962).
6. V. I. Kelarev, Dibi Ammar, and A. F. Lunin, Khim. Geterotsikl. Soedin., No. 12, 1674 (1984).
7. V. I. Kelarev, Dibi Ammar, and A. F. Lunin, Khim. Geterotsikl. Soedin., No. 11, 1557 (1985).
8. V. I. Kelarev, Dibi Ammar, and A. F. Lunin, and O. V. Malova, Zh. Org. Khim., 21, 1306 (1985).
9. A. I. Finkel'shtein and E. N. Boitsov, Usp. Khim., 31, 1496 (1962).
10. A. R. Katritzky (ed.), Physical Methods in Heterocyclic Chemistry, Academic Press, New York (1963).
11. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, Sterically-Hindered Phenols [in Russian], Khimiya, Moscow (1972), p. 38.
12. M. Avram and G. Hattcescu, Infrared Spectroscopy, Wiley—Interscience, New York (1970), p. 527.
13. R. Silverstein, H. Bassler, and T. Morril, Spectrometric Identification of Organic Compounds, 3rd edn., Wiley, New York (1974).
14. A. R. Katritzky and R. A. Jones, J. Chem. Soc., 3674 (1959).
15. T. N. Pliev, Zh. Prikl. Spektrosk., 13, 124 (1970).
16. K. Wakabayashi, M. Tsunoda, and Y. Suzuki, J. Synth. Org. Chem. Jpn., 28, 252 (1970).
17. P. Haque and S. Lilley, Appl. Spectrosc., 26, 309 (1972).
18. O. P. Shkurko, L. R. Roitman, and V. P. Mamaev, Zh. Org. Khim., 9, 1012 (1973).
19. K. Wakabayashi, M. Tsunoda, and M. Suzuki, Bull. Chem. Soc. Jpn., 42, 2924 (1969).
20. L. A. Cohen, J. Org. Chem., 22, 1333 (1957).