

SYNTHESIS AND PROPERTIES OF *symm*-TRIAZINE DERIVATIVES.

4.\* SYNTHESIS OF 2,4,6-TRISUBSTITUTED *symm*-TRIAZINES CONTAINING STERICALLY-HINDERED PHENOL FRAGMENTS

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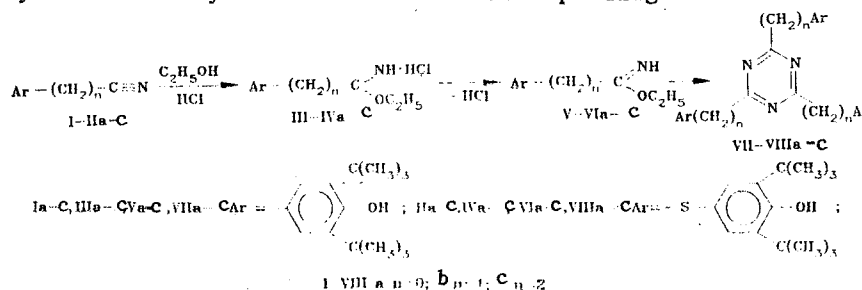
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2,4,6-Trisubstituted *symm*-triazines containing sterically-hindered phenol fragments were synthesized by the cyclotrimerization of ethyl iminoesters. 2,4,6-Trimercapto-*symm*-triazine derivatives containing shielded phenol residues may be formed by the cyclotrimerization of the corresponding thiocyanates in acidic medium.

The introduction of sterically-hindered phenol groups into *symm*-triazines permits the preparation of antioxidants and thermal and light stabilizers for polymer materials and lubricating oils [2-4]. In our previous work [5], we demonstrated the feasibility of preparing such *symm*-triazine derivatives by the reaction of chloro-*symm*-triazines with 4-hydroxy-3,5-di-*tert*-butylaniline. In a continuation of this investigation, we synthesized 2,4,6-trisubstituted *symm*-triazines, in which shielded phenol fragments are attached to the heterocyclic ring by means of C-C or C-S bonds.

Derivatives of *symm*-triazine may be obtained by the cyclotrimerization of the iminoesters of carboxylic esters in the presence of their hydrochloride salts [6, 7] or other acid agents [8, 9]. In the present work, we studied the use of this method for the preparative synthesis of 2,4,6-trisubstituted *symm*-triazines containing 2,6-di-*tert*-butylphenol fragments (VII) and (VIII).

Iminoesters V and VI required for the preparation of this type of heterocyclic compounds were synthesized by the ordinary scheme from the corresponding nitriles I and II.



The hydrochloride salts of ethyl iminoesters III and IV were prepared by the Pinner reaction by passing dry HCl into a mixture of the corresponding nitrile I or II and absolute ethanol in a suitable solvent. In the case of 4-hydroxy-3,5-di-*tert*-butylbenzonitrile (Ia), the reaction was carried out in an excess of ethanol at 10-15°C with subsequent maintenance of the reaction mixture for four days [10]. The iminoester hydrochlorides IIIb, IIIc, and IVa-c were formed in good yield upon carrying out the reaction at 0-5°C using equimolar amounts of the corresponding nitrile and ethanol with subsequent maintenance of the reaction mixture for 10-12 h at 20°C. Iminoester salts III and IV are rather stable compounds and may be stored for prolonged periods avoiding moisture.

\*For communication 3, see [1].

TABLE 1. Characteristic of Ethyl Iminoesters V, VI and Their Hydrochloride Salts III and IV

Compound	Mp, °C*	R <sub>f</sub> †	Found, %				Chemical formula	Calculated, %				Yield, %
			C	H	N	Cl		C	H	N	Cl	
IIIa	258—260 (260 [21])	—	65,3	8,9	4,6	11,5	C <sub>17</sub> H <sub>27</sub> NO <sub>2</sub> ·HCl	65,1	8,9	4,5	11,3	67
Va	154—155,5	0,42	73,5	9,8	5,2	—	C <sub>17</sub> H <sub>27</sub> NO <sub>2</sub>	73,6	9,7	5,0	—	89
IIIb	172—174	—	66,0	9,1	4,2	11,0	C <sub>18</sub> H <sub>29</sub> NO <sub>2</sub> ·HCl	65,9	9,2	4,3	10,8	74
Vb	80—81	0,30	74,4	9,9	5,0	—	C <sub>18</sub> H <sub>29</sub> NO <sub>2</sub>	74,2	10,0	4,8	—	92
IIIc	116—118	—	66,6	9,3	4,2	10,1	C <sub>19</sub> H <sub>31</sub> NO <sub>2</sub> ·HCl	66,8	9,4	4,1	10,4	93
Vc	Macro	0,25	74,5	10,2	4,8	—	C <sub>19</sub> H <sub>31</sub> NO <sub>2</sub>	74,7	10,2	4,6	—	88
IVa	165—166	—	58,9	8,2	4,2	10,0	C <sub>17</sub> H <sub>27</sub> NO <sub>2</sub> S·HCl	59,0	8,1	4,0	10,3	68
VIa	133—135	0,67	66,2	8,6	4,3	—	C <sub>17</sub> H <sub>27</sub> NO <sub>2</sub> S	66,0	8,7	4,5	—	75
IVb	233—235	—	60,0	8,3	4,0	10,2	C <sub>18</sub> H <sub>29</sub> NO <sub>2</sub> S·HCl	60,1	8,3	3,9	9,9	76
Vib	105—106,5	0,62	57,0	9,1	4,5	—	C <sub>18</sub> H <sub>29</sub> NO <sub>2</sub> S	56,9	9,0	4,3	—	91
IVc	134—136	—	60,8	8,7	3,9	9,3	C <sub>19</sub> H <sub>31</sub> NO <sub>2</sub> S·HCl	61,0	8,6	3,7	9,5	86
VIc	Macro ‡	0,51	67,7	9,2	4,4	—	C <sub>19</sub> H <sub>31</sub> NO <sub>2</sub> S	67,6	9,2	4,2	—	92

\*III and IV were purified by reprecipitation from glacial acetic acid in dry ether, V and VIa were purified by recrystallization from aqueous ethanol, Vb, Vc, Vib, and VIc were purified by chromatography on alumina columns with elution by 10:1 benzene-methanol. Salts IIIa-c and IVa-c melted with decomposition.

†Thin-layer chromatography on alumina with heptane eluent.

‡n<sub>D</sub><sup>20</sup> 1.4864

Ethyl iminoester bases V and VI were obtained by treatment of suspensions of the iminoester salts in ether or methylene chloride at 0-5° by 10% aqueous KOH or saturated aqueous K<sub>2</sub>CO<sub>3</sub>. However, heavy tar formation was noted using this method in the case of iminoesters Vb and VIa and thus, hydrochloride salts IIIb and IVa were converted to the corresponding iminoesters by treatment with triethylamine in dry ether.

The IR spectra of iminoester salts III and IV show strong bands at 1670-1655 cm<sup>-1</sup> characteristic for C=N<sup>+</sup> stretching vibrations [10, 11]. This band in the IR spectra of iminoester bases V and VI appear at lower frequencies (1635-1615 cm<sup>-1</sup>). The C=N<sup>+</sup>-H stretching vibrations in the spectra of salts III and IV are found at 3155-3100 cm<sup>-1</sup>, which is characteristic for NH vibrations in imine salts [12]. The NH group vibrations in the IR spectra of iminoesters V and VI are seen as medium-intensity bands at 3370-3340 cm<sup>-1</sup>.

A study of the cyclotrimerization of ethyl iminoesters V and VI showed that these compounds, with the exception of ethyl iminoester 4-hydroxy-3,5-di-tert-butylbenzoic acid (Va) are smoothly converted to the corresponding 2,4,6-trisubstituted symm-triazines VII and VIII. The cyclotrimerization of iminoesters Vb, Vc and VIa-c was carried out at 90-95°C for 20-25 h in the presence of iminoester hydrochlorides III and IV (3-5 mass % relative to iminoesters V and VI). The yields of symm-triazines VIIb, VIIc, and VIIa-c were 80-88% (Table 2).

The cyclotrimerization of iminoester Va proceeded with much more difficulty. Thus, 2,4,6-tris(4-hydroxy-3,5-di-tert-butylphenyl)-symm-triazines (VIIa) was isolated in only 12% yield after carrying out the reaction under the above conditions (90°C, 24 h) and the starting iminoester Va was also isolated. Despite varying the reaction conditions by using other acid catalysts, increasing the reaction time to 100 h and increasing the temperature to 120-125°C, the yield of symm-triazine VIIa could not be markedly increased. We should note that the major reaction products upon carrying out the cyclotrimerization of Va at 145-150°C for 15 h are 4-hydroxy-3,5-di-tert-butylbenzamide and nitrile Ia.

This difference in the behavior of iminoester Va is related to the reduced reactivity of the iminoester group as a consequence of its conjugation with the hydroxy group [10]. In addition, the steric hindrance due to the tert-butyl groups in the vicinity of the reaction site undoubtedly play a definite role.

Dexter et al., [13] have reported the preparation of symm-triazine VIIa by the direct alkylation of 2,6-di-tert-butylphenol with cyanogen chloride (3:1 mole ratio) in the presence of AlCl<sub>3</sub> in tetrachloroethylene. However, all our attempts to reproduce this procedure were unsuccessful and only tar formation was noted; individual compounds could not be isolated.

TABLE 2. Characteristics of 2,4,6-Trisubstituted symm-Triazines VII-VIII and X

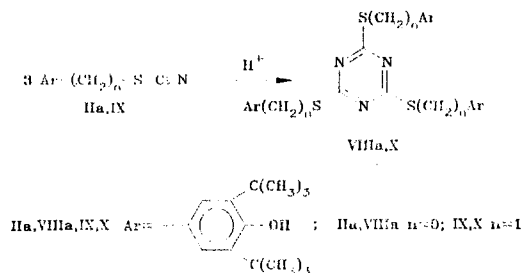
Compound	Mp, °C *	R <sub>f</sub> , †	Found, %				Chemical formula	Calculated, %				Yield, % ‡ (preparative method)
			C	H	N	S		C	H	N	S	
VII a	310—311,5	0,22	78,0	9,0	6,3	—	C <sub>45</sub> H <sub>63</sub> N <sub>3</sub> O <sub>3</sub>	77,9	9,1	6,1	—	15 (A)
VII b	161—162,5	0,54	78,6	9,4	5,0	—	C <sub>48</sub> H <sub>69</sub> N <sub>3</sub> O <sub>3</sub>	78,8	9,4	5,7	—	84 (A)
VII c	209—210	0,46	78,9	9,5	5,6	—	C <sub>51</sub> H <sub>75</sub> N <sub>3</sub> O <sub>3</sub>	78,8	9,6	5,4	—	88 (A)
VIII a	211—212	0,42	58,3	7,9	5,1	12,3	C <sub>45</sub> H <sub>63</sub> N <sub>3</sub> O <sub>3</sub> S <sub>3</sub>	38,4	8,0	5,3	12,2	81 (A), 45 (B), 67 (B)
VIII b	102—104	0,82	39,3	8,3	5,2	11,2	C <sub>48</sub> H <sub>69</sub> N <sub>3</sub> O <sub>3</sub> S <sub>3</sub>	39,4	8,3	5,0	11,5	80 (A)
VIII c	57—59	0,66	70,0	8,7	5,0	10,9	C <sub>51</sub> H <sub>75</sub> N <sub>3</sub> O <sub>3</sub> S <sub>3</sub>	70,1	8,6	4,8	11,0	86 (A)
X	195—196 (197—198 [26])	0,50	59,5	8,4	4,9	11,7	C <sub>48</sub> H <sub>69</sub> N <sub>3</sub> O <sub>3</sub> S <sub>3</sub>	59,4	8,3	5,0	11,5	37 (B), 69 (B)

\*The recrystallization solvents were aqueous DMF (VIIa and VIIb), glacial acetic acid (VIIc), ethanol (VIIIa), aqueous ethanol (VIIIb and VIIIc), and 1:1 toluene-hexane (X).

†In 20:1 benzene-methanol.

‡A) Cyclotrimerization of iminoesters, B) cyclotrimerization of thiocyanates, C) convergent synthesis.

Martin et al, [14] have reported that 2,4,6-trialkyl- and 2,4,6-triarylthio-symm-triazines may be obtained by the cyclotrimerization of alkyl- and arylthiocyanates in the presence of acids. We attempted to use this method for the synthesis of derivatives of 2,4,6-trimercapto-symm-triazine containing shielded phenol residues. Upon heating in DMF in the presence of catalytic amounts of H<sub>2</sub>SO<sub>4</sub>, 4-hydroxy-3,5-di-tert-butylphenylthiocyanate (IIa) and 4-hydroxy-3,5-di-tert-butylbenzylthiocyanate (IX) were converted in good yield to the corresponding symm-triazines VIIIa and X.



In the present work, 2,4,6-trimercapto-symm-triazine derivatives VIIIa and X were also obtained by convergent synthesis. The condensation of 4-mercapto-2,6-di-tert-butylphenol with cyanogen chloride gave VIIIa, while X was obtained by the reaction of 2,4,6-trimercapto-symm-triazine with 2,6-di-tert-butylphenol and formaldehyde.

The IR spectra of symm-triazines VII, VIII and X have a narrow band at 3650-3635 cm<sup>-1</sup> corresponding to the stretching vibrations of the nonassociated OH group in the hindered phenols [15]. The spectra of these compounds show bands of different intensity characteristic for the stretching and deformation bands of the symm-triazine ring (Table 3) [7, 16-18]. The bands at 885-880 and 825-820 cm<sup>-1</sup> are characteristic for the 4-substituted benzene ring while the two bands at 1265-1210 cm<sup>-1</sup> are characteristic for the Ar-OH bonds [19].

The PMR spectra of symm-triazines VII, VIII and X show signals for the hydroxyl group protons as singlets at 5.12-5.22 ppm, which is characteristic for sterically-hindered phenols [20]. The signals for the tert-butyl group protons are seen as singlets at 1.62-1.75 ppm. The aromatic ring protons give rise to singlets with intensity 2H at 7.14-7.30 ppm.

#### EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer as a suspension in vaseline oil (III and IV), in CCl<sub>4</sub> (V and VI) or in KBr pellets (VII, VIII and X). The PMR spectra were taken on a Tesla BS-487C spectrometer at 80 MHz using the δ scale with HMDS as the internal stand-

TABLE 3. Spectral Data for 2,4,6-Trisubstituted summ-Triazines VII, VIII and X

Compound	IR spectrum, cm <sup>-1</sup>							PMR spectrum, $\delta$ , ppm	
	v <sub>O-H</sub>	v <sub>2</sub> , v <sub>as</sub> C-H (CH <sub>3</sub> , CH <sub>2</sub> )	triazine ring vibrations †				$\delta_s, \delta_{as}$ C-H		v <sub>C-O</sub>
			v	-- ‡	γ	β			
VIIa	3640	2970, 2855	1550, 1525, 1412	1115, 1010	812	685	1475, 1440, 1375	1265, 1228	
VIIb	3650	2975, 2950, 2870, 2840	1555, 1537, 1410	1105, 1012	810	690	1470, 1452, 1360	1260, 1230	1,72 (54H, s, <i>tert</i> -C <sub>4</sub> H <sub>9</sub> ); 3,56 (6H, s, CH <sub>2</sub> ); 5,12 (3H, s, OH); 7,25 (6H, s, arom.protons)
VIIc	3645	2975, 2965, 2860, 2835	1552, 1530, 1415	1112, 1005	815	685	1465, 1445, 1370, 1340	1265, 1235	1,75 (54H, s, <i>tert</i> -C <sub>4</sub> H <sub>9</sub> ); 4,46-4,68 (12H, m, CH <sub>2</sub> -CH <sub>2</sub> ); 5,18 (3H, s, OH); 7,28 (6H, s, arom.protons)
VIIIa	3635	2975, 2858	1550, 1520, 1410	1110, 1015	810	690	1470, 1445, 1365	1260, 1225	
VIIIb	3650	2970, 2955, 2860, 2845	1545, 1530, 1415	1115, 1010	812	685	1465, 1450, 1370, 1355	1265, 1220	1,74 (54H, s, <i>tert</i> -C <sub>4</sub> H <sub>9</sub> ); 4,22 (6H, s, CH <sub>2</sub> ); 5,14 (3H, c, OH); 7,18 (6H, s, arom.protons)
VIIIc	3638	2972, 2960, 2865, 2840	1555, 1535, 1410	1112, 1010	815	590	1470, 1452, 1365	1260, 1225	1,66 (54H, s, <i>tert</i> -C <sub>4</sub> H <sub>9</sub> ); 4,58-4,74 (12H, m, CH <sub>2</sub> -CH <sub>2</sub> ); 5,22 (3H, s, OH); 7,18 (6H, s, arom.protons)
X	3650	2975, 2950, 2875, 2845	1550, 1530, 1412	1115, 1005	810	380	1475, 1455, 1360, 1340	1265, 1232	1,62 (54H, s, <i>tert</i> -C <sub>4</sub> H <sub>9</sub> ); 4,42 (6H, s, CH <sub>2</sub> ); 5,20 (3H, s, OH); 7,14 (6H, s, arom.protons)

\*The PMR spectra of VIIb, VIIc and X were taken in DMSO-D<sub>6</sub>, while the spectra of VIIIb and VIIIc were taken in deuteromethanol.

†β) In-plane ring deformation vibrations, γ) out-of plane ring deformation vibrations.

‡Ring "breathing" bands.

ard. The reaction was monitored and the purity of the compounds obtained was checked by thin-layer chromatography of Brockman grade II alumina with iodine vapor development or on Silufol UV-254 plates with development in UV light.

4-Hydroxy-3,5-di-*tert*-butylbenzotrile (Ia) [21] and 4-hydroxy-3,5-di-*tert*-butylphenylacetoneitrile (Ib) [22] as well as 4-hydroxy-3,5-di-*tert*-butylphenylthiocyanate (IIa) [23] were obtained according to published procedures.

β-(4-Hydroxy-3,5-di-*tert*-butylphenyl)propionitrile (Ic). A sample of 14.8 g (279 mmoles) freshly prepared acrylonitrile was added dropwise with stirring in an inert gas stream over 10 min to a mixture of 51.0 g (246 mmoles) 2,6-di-*tert*-butylphenol and 6.0 g (120 mmoles) KOH in 150 ml dry DMSO. The reaction mixture was stirred for 8 h at 60-65°C and then DMSO and unreacted 2,6-di-*tert*-butylphenol were removed at reduced pressure. A sample of 15 ml 15% aqueous HCl was added to the residue and the organic layer was extracted with two 150 ml portions of benzene. The benzene solution was washed with 150 ml water, dried over CuSO<sub>4</sub> and evaporated to dryness. The residue was crystallized from hexane to give 19.7 g (13%) nitrile Ic, mp 110-112°C, R<sub>f</sub> 0.95 (20:1 benzene-ethanol), mp 113-114°C [24].

4-Cyanomethylthio-2,6-di-*tert*-butylphenol (IIb). A solution of 3.1 g (55 mmoles) KOH in 45 ml absolute ethanol was added dropwise in an inert gas stream to a stirred solution of 12.9 g (50 mmoles) 4-mercapto-2,6-di-*tert*-butylphenol [25] in 35 ml absolute ethanol at 5-10°C. The reaction mixture was stirred for 30 min at 5°C and then 7.75 g (50 mmoles) chloroacetonitrile was added dropwise in an inert gas stream at 5°C. The mixture was stirred for 3 h at 65-70°C, cooled to 10°C, poured into 200 ml cold water, and acidified by dilute HCl to pH 6.5. The organic layer was extracted with three 50 ml portions of ether. The extract was washed with water, dried over CuSO<sub>4</sub>, and evaporated to dryness. The oil was crystallized from 20:1 hexane-benzene to give 6.57 g (51%) nitrile IIb, mp 60.5-62°C, R<sub>f</sub> 0.18 (heptane). Found: C 73.6%; H 7.0%; N 4.4%; S 10.0%. Calculated for C<sub>20</sub>H<sub>23</sub>NOS: C 73.8; H 7.1; N 4.3; S 9.8%.

4-( $\beta$ -Cyanoethyl)thio-2,6-di-tert-butylphenol (IIIc). Three drops of concentrated aqueous KOH was added to a stirred solution of 11.0 g (46 mmoles) 4-mercapto-2,6-di-tert-butylphenol in 60 ml dioxane and then, 7.3 g (138 mmoles) acrylonitrile was added dropwise at 20-25°C. The reaction mixture was stirred at 70°C for 5 h, cooled to 20°C, poured into 200 ml cold water and neutralized with dilute hydrochloric acid to pH 7.0. The organic layers was extracted with three 50-ml portions of ether. The extract was washed with water, dried over CuSO<sub>4</sub> and evaporated to dryness. The residue was crystallized from heptane to yield 10.9 g (70%) nitrile IIc, mp 97-99°C, R<sub>f</sub> 0.24 (heptane). Found: C 74.1; H 7.3; N 4.3; S 93%. Calculated for C<sub>21</sub>H<sub>25</sub>NOS: C 74.3; H 7.4; N 4.1; S 9.4%.

Hydrochloride Salt of the Ethyl Iminoester of 4-Hydroxy-3,5-di-tert-butylbenzoic Acid (IIIa). A stream of dry HCl was passed for 2 h at 10-15°C through a stirred mixture of 4.6 g (12 mmoles) Ia in 40 ml absolute ethanol and 20 ml dry ether. The reaction mixture was maintained for 72 h at 20°C and evaporated to dryness at reduced pressure. The residue was treated with dry ether. The precipitate was filtered and dried in vacuum over KOH.

Hydrochloride Salts of Ethyl Iminoesters IIIb, IIIc, IVa-c. A stream of dry HCl was passed for 1 h through a stirred mixture of 10 mmole nitrile Ib, Ic, IIa-c and 12 mmole absolute ethanol in 30 ml dry ether at 0°C. The reaction mixture was maintained for 4-5 h at 20°C and cooled to -15°C. The hydrochloride precipitate of IIIb, IIIc, IVa-c was filtered off and dried in vacuum over KOH (Table 1).

Ethyl Iminoester of 4-Hydroxy-3,5-di-tert-butylphenylacetic Acid (Vb). A sample of 1.12 g (12 mmoles) triethylamine in 10 ml ether was added dropwise to a stirred suspension of 3.27 g (10 mmoles) hydrochloride IIIb in 120 ml dry ether at 0°C and stirred for 1 h at 0°C. The precipitate was filtered off. The solvent was removed at a water pump and the residue was subjected to chromatography on a 3.5 x 50 cm alumina column with 10:1 benzene-methanol as the eluent.

Ethyl iminoester VIa was obtained analogously. The PMR spectrum of VIa in deuteromethanol: 1.34 (3H, t, CH<sub>3</sub>), 18.2 (18H, s, tert-C<sub>4</sub>H<sub>9</sub>), 4.52 (2H, q, OCH<sub>2</sub>), 5.20 (1H, s, OH), 7.12 (2H, s, aromatic protons), 8.18 ppm (1H, s, NH).

Ethyl Iminoesters of Acids Va, Vc, VIb and VIc. A sample of 35 ml 10% aqueous KOH was added dropwise to a stirred suspension of 25 mmole ethyl iminoester hydrochloride IIa, IIIc, IVb or IVc in 300 ml ether or methylene chloride at 0.5°C. The ethereal layer was separated, washed with 120 ml water and dried over CuSO<sub>4</sub>. The solvent was removed at a water pump. The residue was either crystallized from aqueous ethanol (Va) or subjected to chromatography on a 3.5 x 75 ml alumina column with 10:1 benzene-methanol as eluent (Table 1). PMR spectrum of iminoester Vc (in CCl<sub>4</sub>): 1.22 (3H, t CH<sub>3</sub>), 1.66 (18H, s, tert-C<sub>4</sub>H<sub>9</sub>), 4.24 (2H, q, OCH<sub>2</sub>), 4.48-4.72 (4H, m, CH<sub>2</sub>CH<sub>2</sub>), 5.65 (1H, s, OH), 7.34 (2H, s, aromatic protons), 8.12 ppm (1H, s, NH).

2,4,6-Trisubstituted symm-Triazines (VIIa-c, VIIIa-c). A mixture of 30 mmoles ethyl iminoester Va-c or VIa-c and 3 mmoles of the corresponding iminoester hydrochloride was heated at 90-95°C for 20-25 h with protection from atmospheric moisture. The reaction mixture was maintained for 1 h in vacuum created by a water pump on a steam bath. The residue was subjected to chromatography on a 3.5 x 80 ml alumina column with 30:1 benzene-methanol as the eluent (Table 2).

4-Hydroxy-3,5-di-tert-butylbenzylthiocyanate (IX). A solution of 34.3 g (135 mmoles) 4-hydroxy-3,5-di-tert-butylbenzyl chloride in 50 ml ethanol was added dropwise to a stirred suspension of 19.4 g (200 mmoles) potassium thiocyanate in 100 ml ethanol. The reaction mixture was heated at reflux with stirring for 2 h and then, 80-85 ml solvent was distilled off. A sample of 150 ml cold water was added to the residue. The organic layer was extracted with three 75 ml portions of ether. The extract was washed with 100 ml water, dried over CaCl<sub>2</sub> and evaporated to dryness. The residue was crystallized from aqueous ethanol with activated charcoal to yield 20.2 g (54%) thiocyanate IX, mp 42-43.5°C, R<sub>f</sub> 0.52 (20:1 benzene-methanol). Found: C 69.2; H 8.2; N 4.9; S 11.7%. Calculated for C<sub>16</sub>H<sub>23</sub>NOS: C 69.3; H 8.3; N 5.0; S 11.5%.

2,4,6-Tris(4-hydroxy-3,5-di-tert-butylphenylthio)-symm-triazine (VIIIa). B. Five drops of concentrated sulfuric acid was heated to a solution of 4.0 g (15 mmoles) thiocyanate IIa in 15 ml dry DMF and heated at reflux for 8 h. The reaction mixture was cooled to 20°C and poured into 100 ml cold water. The dark oil isolated was extracted with 100 ml ether. The extract was washed with 50 ml water, dried over CuSO<sub>4</sub>, and evaporated in vacuum.

The residue was subjected to chromatography on a 3.5 × 50 ml alumina column with 10:1 benzene-methanol as eluent to yield 1.8 g (45%) symm-triazine VIIIA, mp 210-211°C (from ethanol).

C. An ethanolic solution of potassium mercaptide obtained from 8.14 g (30 mmoles) 4-mercapto-2,6-di-tert-butylphenol and 1.68 g (30 mmoles) KOH in 30 ml absolute ethanol was added dropwise to a solution of 1.84 g (10 mmoles) cyanogen chloride in 25 ml acetone. The reaction mixture was heated at reflux for 3 h, cooled to 10°C, and the KCl formed was filtered off. The filtrate was poured into 100 ml water. The organic layer was extracted with three 50 ml portions of ether and dried over CuSO<sub>4</sub>. The solvent was distilled off and the residue was crystallized from ethanol to yield 5.2 g (67%) symm-triazine VIIIA.

2,4,6-Tris(4-Hydroxy-3,5-di-tert-butylbenzylthio)-symm-triazine (X). B. This compound was obtained by analogy to symm-triazine VIIIA from thiocyanate IX in 37% yield, mp 195-196°C.

C. A solution of 27.8 (130 mmoles) 2,6-di-tert-butylphenol in 80 ml glacial acetic acid was added with stirring to a suspension of 7.14 g (40 mmoles) 2,4,6-trimercapto-symm-triazine and 7.25 paraformaldehyde in 30 ml glacial acetic acid, and then 13 ml 20% hydrochloric acid was added. The reaction mixture was stirred for 6 h at 45°C. The precipitate was filtered off, washed with 150 ml water and then with 100 ml 2:1 ethanol-acetone to yield 23.1 g (69.5%) symm-triazine X, mp 194-195°C.

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