DERIVATIVES OF ISOTRITHIOCYANURIC ACID

D. L. GARMAISE
Research Department, Abbott Laboratories Limited, Montreal, Quebec
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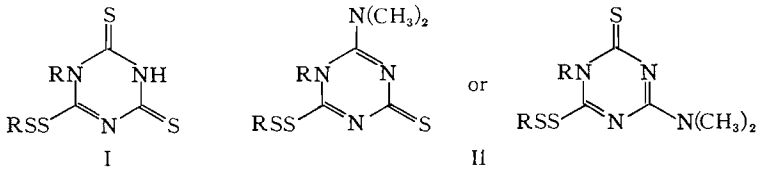
ABSTRACT

A by-product isolated in low yield from the reaction of *p*-chlorobenzyl chloride with potassium thiocyanate and sodium iodide in dimethylformamide was shown to be the isotrithiocyanuric acid derivative I (R = *p*-chlorobenzyl). I gave the isodithiocyanuric acid ester (III) on alkaline hydrolysis, and mono-*p*-chlorobenzyl isotrithiocyanurate (IV) on reduction with sodium hydrosulfite. Treatment of I with sodium hypochlorite in aqueous alcoholic medium resulted in the direct replacement of the sulfhydryl group by an alkoxyl group. The *N,S,S*-triester VIII rearranged, on heating, to the symmetrical *S,S,S*-triester IX; this behavior is opposite to that shown by the oxygen analogues.

During the preparation of *p*-chlorobenzyl isothiocyanate by treatment of *p*-chlorobenzyl chloride with potassium thiocyanate and sodium iodide in dimethylformamide at 150° for 30 min, a mixture of two crystalline by-products separated out in low yield. The major component, which was isolated by extracting the mixture with alcoholic sodium hydroxide and acidifying the alcoholic extract, was a pale-yellow solid with the formula $C_{17}H_{13}Cl_2N_3S_4$. Evidence obtained during this work has led to the assignment of structure I (1-(*p*-chlorobenzyl)-6-(*p*-chlorobenzyldithio)-*s*-triazine-2,4(1*H*,3*H*)-dithione) to this substance. The minor component, which was insoluble in alcoholic sodium hydroxide solution, was an orange-colored substance with the formula $C_{16}H_{12}Cl_2N_2S_4$. When the reaction temperature was maintained at 150° for 3 h instead of 30 min, apparent interaction with dimethylformamide led to the disappearance of I, and a neutral compound (II), which is presumed to have one of the isomeric structures indicated, was isolated.

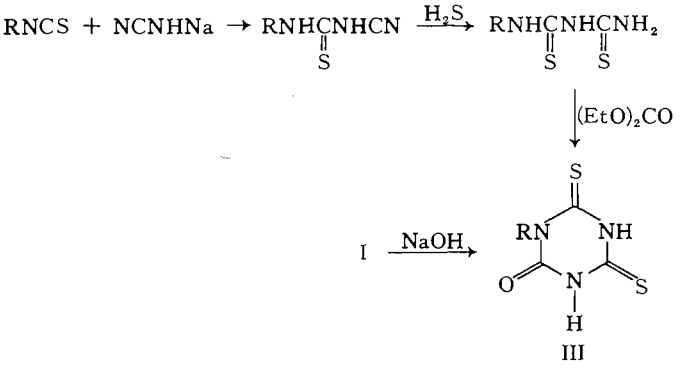


R = *p*-chlorobenzyl throughout

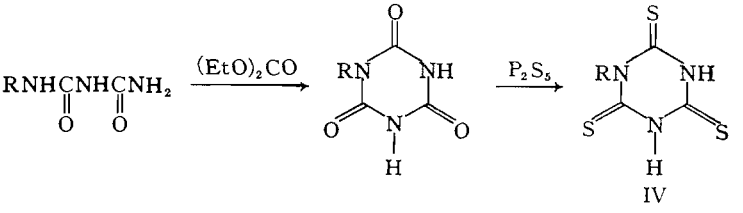
Alkaline hydrolysis of I resulted in the loss of the 4-chlorobenzyldithio group, and the formation of an acidic substance (III) with the formula $C_{10}H_8ClN_3OS_2$. III was shown to be 1-(*p*-chlorobenzyl)-2,4-dithio-*s*-triazine-2,4,6(1*H*,3*H*,5*H*)-trione by synthesis from 1-*p*-chlorobenzyldithiobiuret and diethyl carbonate. The dithiobiuret was prepared by adding *p*-chlorobenzyl isothiocyanate to sodium cyanamide followed by hydrogen sulfide (1).

Reduction of I with sodium hydrosulfite in alkaline medium yielded *p*-chloro-α-toluenethiol (isolated as the disulfide) and 1-(*p*-chlorobenzyl)-*s*-triazine-2,4,6(1*H*,3*H*,5*H*)-trithione (IV), along with some III arising from alkaline hydrolysis of I.

The structure of compound IV, which appears to be the first monoester of isotrithiocyanuric acid to have been described, was confirmed by direct synthesis. 1-*p*-Chlorobenzylbiuret was treated with diethyl carbonate (2) to give mono-*p*-chlorobenzyl isocyanurate.

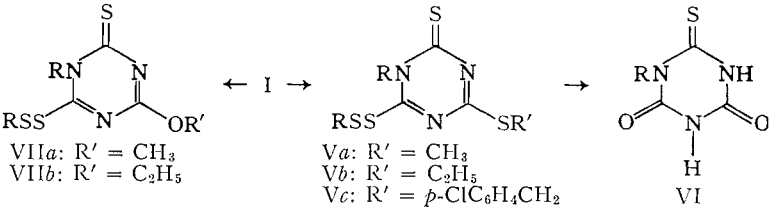


The isocyanurate was not affected by treatment with phosphorus pentasulfide in refluxing pyridine, but fusion with the reagent at 265 °C gave IV in 51% yield.



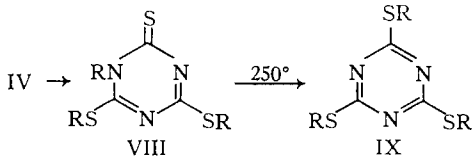
I was readily alkylated in alkaline alcoholic medium to give the neutral esters V*a*–V*c*. When the methyl ester V*a* was treated with hot concentrated sodium hydroxide solution, both the 4-thio and 6-dithio substituents were hydrolyzed, and 1-(*p*-chlorobenzyl)-2-thio-*s*-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (VI) was obtained.

Treatment of I with sodium hypochlorite in aqueous methanol caused the direct replacement of the sulfhydryl group by methoxyl to give VII*a* in good yield; the ethoxy derivative VII*b* was obtained in lower yield by performing the reaction in aqueous ethanol. This rather unexpected replacement reaction is presumed to proceed via the chloro derivative as an intermediate, and its possible application to other thiols is being investigated.



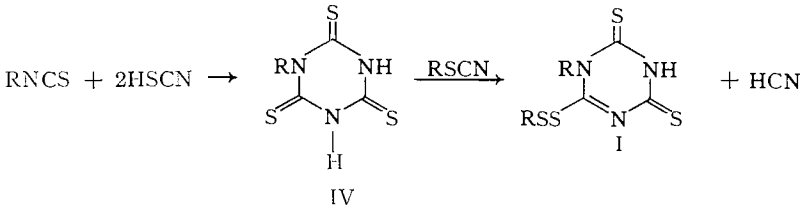
The mixed triester VIII (m.p. 171°), which was prepared by the esterification of IV, rearranged, on heating, to the symmetrical tri-*p*-chlorobenzyl trithiocyanurate (IX), m.p. 122°. The direction of the rearrangement is in interesting contrast to the behavior of the oxygen analogues, since alkyl and aralkyl cyanurates rearrange, on heating, to the isocyanuric acid esters (3, pp. 398–421). The difference in behavior between the thioxo and oxo analogues is consistent with the relative instability of doubly bound sulfur as compared with doubly bound oxygen.

The ultraviolet spectrum of VIII (λ_{max} 288 and 330 mμ) showed peaks at higher wavelengths than that of the normal ester IX (λ_{max} 263 mμ). A similar though smaller difference was observed with mono-*p*-chlorobenzyl isotrithiocyanurate (IV) (λ_{max} 292 mμ) and mono-*p*-chlorobenzyl trithiocyanurate (XII) (λ_{max} 280 mμ).

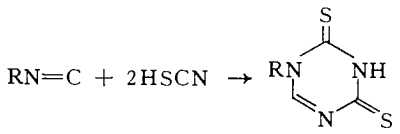


Relatively few derivatives of isotrithiocyanuric acid have been described. Alkyl and aralkyl thiocyanates have long been known to trimerize readily to the normal trithiocyanurates (3, p. 111), but little has been reported on the comparable trimerization of isothiocyanates. In a recent publication (4) it was stated that heating methyl isothiocyanate at 200° in dioxane gave 1,3,5-trimethyl dithioisocyanurate, but the corresponding isotrithiocyanurate has never been described. With respect to monoesters of isotrithiocyanuric acid, no examples could be found in the literature.

The reaction mixture from which I was isolated contains, among other components, *p*-chlorobenzyl isothiocyanate, *p*-chlorobenzyl thiocyanate, and excess thiocyanate ion. The initial reaction in the sequence leading to the formation of I may be the condensation of *p*-chlorobenzyl isothiocyanate with thiocyanic acid to give mono-*p*-chlorobenzyl isotrithiocyanurate (IV), followed by condensation with *p*-chlorobenzyl thiocyanate with the elimination of hydrogen cyanide.



The suggested cyclization reaction is similar to the recently described condensation of isonitriles with thiocyanic acid to give 1-substituted-*s*-triazine-2,4(1*H*,3*H*)-dithiones (5).

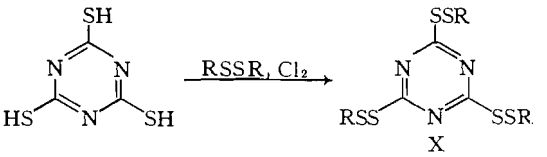


These condensations are stated to occur readily at −20 °C in ether solution, giving the triazine-2,4-dithiones in high yield.

The reaction between thiols and thiocyanates to give disulfides, with the elimination of hydrogen cyanide, has been studied by several investigators (6, 7). This reaction is distinguished from the standard preparation of disulfides by the alkaline hydrolysis of thiocyanates to thiols followed by air oxidation, since it was shown to proceed in a nitrogen atmosphere. Thus, heating *p*-chlorothiophenol and *p*-chlorophenyl thiocyanate at 100° in nitrogen gave a nearly quantitative yield of the disulfide in 8 h.

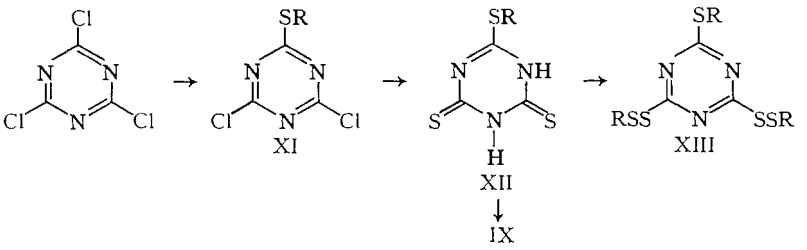
For purposes of comparison with the isotrithiocyanurate I and its derivatives, a number of derivatives of trithiocyanuric acid with *p*-chlorobenzylthio and *p*-chlorobenzyldithio

substituents were synthesized. Some tri(alkyldithio)-*s*-triazines have been prepared (8) by treating alkanethiols with excess chlorine to give the alkylsulfenyl chlorides, which were then allowed to react with trithiocyanuric acid. This procedure did not work with *p*-chloro-α-toluenethiol, but it was found that addition of the calculated amount of chlorine to bis-(*p*-chlorobenzyl) disulfide and trithiocyanuric acid gave 2,4,6-tri-(*p*-chlorobenzyldithio)-*s*-triazine (X) in fair yield.



X

Cyanuric chloride was converted into 2-(*p*-chlorobenzylthio)-4,6-dichloro-*s*-triazine (XI) by treatment with *p*-chloro-α-toluenethiol in the presence of lutidine at −40° by the method of Koopman *et al.* (9).



XI XII XIII

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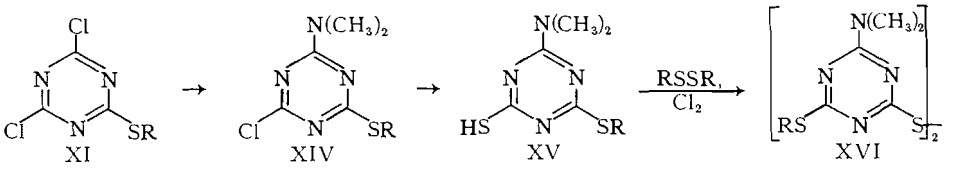
IX

Reaction of XI with sodium hydrosulfide gave mono-(*p*-chlorobenzyl) trithiocyanurate (XII). This monoester melted at a higher temperature than its isomer IV, but was considerably more soluble in ether and ethanol. It was readily esterified to the symmetrical triester (IX) (which could also be prepared from cyanuric chloride and *p*-chloro-α-toluenethiol). Treatment of XII with bis-(*p*-chlorobenzyl) disulfide and chlorine gave the di-disulfide (XIII).



XI XIV XV XVI

In an attempt to prepare a compound containing both a *p*-chlorobenzyldithio and a dimethylamino substituent, as in the by-product II, the dichloro derivative (XI) was first treated with dimethylamine to give XIV, and the remaining chlorine was replaced by a sulfhydryl group to yield the monothiol XV. The reaction of XV with bis-(*p*-chlorobenzyl) disulfide and chlorine, however, yielded the bis-(triazinyl) disulfide (XVI) instead of the desired *p*-chlorobenzyldithio derivative.

EXPERIMENTAL

All melting points are uncorrected. Analytical data were supplied by Dr. C. Daessle, Montreal, Quebec, and by the Microanalytical Department, Abbott Laboratories, North Chicago, Illinois.

1-(p-Chlorobenzyl)-6-(p-chlorobenzyldithio)-s-triazine-2,4(1H,3H)-dithione (I)

p-Chlorobenzyl chloride (500 g, 3.1 moles) was added to a solution of potassium thiocyanate (330 g, 3.4 moles) and sodium iodide (23 g, 0.15 mole) in dimethylformamide (250 ml) at 130° over a period of 15 min.

The temperature was allowed to increase to 150°, and the reaction was maintained at that temperature for 30 min. The hot reaction mixture was poured onto ice, and the mixture was extracted with chloroform (250 ml). The chloroform solution was washed with water and dried. Petroleum ether (500 ml) was added and the solution was allowed to stand at 5° overnight. The precipitated solid (5.7 g, m.p. 190–204°) was extracted with sodium hydroxide (*N*, 30 ml) in ethanol (250 ml), giving an orange-colored residue, yield 0.4 g, m.p. 170–175°. Recrystallization from dimethylformamide raised the melting point to 174–175°.

Anal. Calcd. for $C_{16}H_{12}Cl_2N_2S_4$: C, 44.54; H, 2.81; Cl, 16.44; N, 6.49; S, 29.72. Found: C, 44.50; H, 2.42; Cl, 16.80; N, 6.32; S, 29.70.

Acidification of the alkaline filtrate with 5% hydrochloric acid gave crude I, m.p. 205–206°, yield 5.2 g (0.8%). Recrystallization from dimethylformamide raised the melting point to 207–208°.

Anal. Calcd. for $C_{17}H_{13}Cl_2N_3S_4$: C, 44.53; H, 2.86; Cl, 15.41; N, 9.17; S, 27.97. Found: C, 44.52; H, 2.90; Cl, 15.31; N, 9.19; S, 27.56.

1-(p-Chlorobenzyl)-4(or 2)-dimethylamino-6-(p-chlorobenzyldithio)-s-triazine-2(or 4)(1H)-thione (II)

The reaction was performed as described above, except that the period of heating at 150° was extended to 3 h. The reaction mixture was worked up in the same way, resulting in the isolation of a neutral product, m.p. 225–229°, yield 8.5 g. Recrystallization from dimethylformamide raised the melting point to 232–233°.

Anal. Calcd. for $C_{19}H_{18}Cl_2N_4S_3$: C, 48.61; H, 3.86; Cl, 15.10; N, 11.94; S, 20.49. Found: C, 48.32; H, 4.08; Cl, 15.13; N, 12.08; S, 20.25.

1-(p-Chlorobenzyl)-2,4-dithio-s-triazine-2,4,6(1H,3H,5H)-trione (III)

By Hydrolysis of I

I (1.5 g) was added to a solution of sodium hydroxide (7.5 g) in water (30 ml) and methanol (60 ml), and the mixture was heated on the steam bath for 2 h. The methanol was distilled off slowly as the hydrolysis proceeded. The solution was cooled and acidified, giving the crude product, m.p. 254–262°, yield 0.51 g (51%). Recrystallization from methanol raised the melting point to 280–282 °C.

Anal. Calcd. for $C_{10}H_8ClN_3OS_2$: C, 42.03; H, 2.82; Cl, 12.41; N, 14.70; mol. wt. 285.76. Found: C, 42.34; H, 3.31; Cl, 12.69; N, 14.16; mol. wt. 283.

Via 1-p-Chlorobenzyldithiobiuret

Cyanamide (2.1 g, 0.05 mole) was added to a solution of sodium methoxide (prepared from 1.15 g sodium) in ethanol (20 ml). *p*-Chlorobenzyl isothiocyanate (9.1 g, 0.05 mole) was added and the solution was refluxed for 30 min. The solution was evaporated to dryness and the solid residue was dissolved in 75 ml H_2O, to which was added 2.4 g ammonium chloride and 8.0 ml concentrated ammonium hydroxide. Hydrogen sulfide was bubbled through the solution at 90° for 6 h, giving the crude dithiobiuret, m.p. 160–165°, yield 8.1 g (62%). Recrystallization from methanol raised the melting point to 167–169 °C.

Anal. Calcd. for $C_9H_{10}ClN_3S_2$: C, 41.61; H, 3.88; Cl, 13.65; N, 16.18; S, 24.68. Found: C, 41.75; H, 3.96; Cl, 13.84; N, 16.14; S, 24.47.

Sodium (0.23 g) was dissolved in 10 ml ethanol, and diethyl carbonate (1.2 g, 0.1 mole) and 1-*p*-chlorobenzyldithiobiuret (1.3 g, 0.05 mole) were added. The solution was refluxed for 40 min and then evaporated to dryness. The residue was dissolved in water (100 ml) and the solution was washed with ether to remove the unreacted diethyl carbonate. Acidification of the aqueous solution gave a precipitate which was extracted with chloroform (100 ml) and recrystallized from ethanol to give the pure product, m.p. 270–272°, yield 0.25 g (18%). There was no melting point depression on admixture with the product obtained from I, and the ultraviolet and infrared spectra were identical.

1-(p-Chlorobenzyl)-s-triazine-2,4,6(1H,3H,5H)-trithione (Mono-p-chlorobenzyl Isotrithiocyanurate) (IV)

By Reduction of I

Sodium hydrosulfite (17.4 g, 0.1 mole) was added to a solution of I (2.5 g, 0.0055 mole) in 50% methanol (300 ml) containing sodium hydroxide (1.2 g, 0.03 mole). The solution was refluxed for 2 h, and *N* sodium hydroxide was added continuously to maintain a pH of 8. After being allowed to stand overnight, the solution deposited crystals of bis-(*p*-chlorobenzyl) disulfide (10), m.p. 58°. Acidification of the filtrate gave a mixture (2.1 g) of compounds I, III, and IV. The mixture was extracted with boiling absolute ethanol (100 ml), in which only the isodithiocyanurate III was soluble. The residue, consisting of I and IV, was suspended in 20 ml *N* aqueous sodium hydroxide, and the insoluble sodium salt of I was removed by filtration. Acidification of the alkaline filtrate gave pure IV, m.p. 320° (decomp.) (crystal change at 275°), yield 0.26 g (16%).

Anal. Calcd. for $C_{10}H_8ClN_3S_3$: C, 39.79; H, 2.67; Cl, 11.75; N, 13.92; S, 31.87. Found: C, 40.05; H, 2.86; Cl, 11.66; N, 13.74; S, 31.71.

From Mono-p-chlorobenzyl Isocyanurate

p-Chlorobenzylamine (24 g, 0.17 mole) and nitrobiuret (25 g, 0.17 mole) were heated in 150 ml water at 95° for 1 h. Filtration of the hot solution gave 1-(*p*-chlorobenzyl)-biuret, m.p. 190–192°.

Anal. Calcd. for $C_9H_{10}ClN_3O_2$: C, 47.48; H, 4.43; Cl, 15.58. Found: C, 47.55; H, 4.58; Cl, 15.71.

The biuret (22.8 g, 0.1 mole) and diethyl carbonate (23.6 g, 0.2 mole) were added to a solution of sodium methoxide (0.2 mole) in methanol (200 ml), and the solution was refluxed for 2 h. The precipitated solid was

filtered off and extracted with 600 ml water; acidification of the filtrate gave mono-*p*-chlorobenzyl isocyanurate, m.p. 249–251°.

Anal. Calcd. for $C_{10}H_8ClN_3O_3$: C, 47.35; H, 3.18; Cl, 13.98; N, 16.57. Found: C, 47.47; H, 3.20; Cl, 13.70; N, 16.49.

A mixture of mono-*p*-chlorobenzyl isocyanurate (8.8 g, 0.035 mole) and phosphorus pentasulfide (8.0 g, 0.036 mole) was heated at 255–265° for 20 min. Water (50 ml) was added, and the suspension was boiled for 10 min and filtered. The precipitate was extracted with 4% sodium hydroxide (300 ml) and the alkaline extract was acidified to give the product (8.8 g, 83%), m.p. 295–300°. Recrystallization from dimethylformamide–methanol raised the melting point to 320°; the ultraviolet and infrared spectra were identical with those of the product obtained by reduction of I.

1-(p-Chlorobenzyl)-4-methylthio-6-(p-chlorobenzyldithio)-s-triazine-2(1H)-thione (Va)

I (498 mg, 1.09 mmoles) was dissolved in a solution of sodium hydroxide (*N*, 1.8 ml) in methanol (40 ml), and methyl iodide (1.0 ml) was added at 0°. The product separated out immediately, giving 425 mg (82%), m.p. 163–165°. Recrystallization from dimethylformamide raised the melting point to 169–170°.

Anal. Calcd. for $C_{18}H_{15}Cl_2N_3S_4$: C, 45.75; H, 3.20; Cl, 15.01; N, 8.89; S, 27.14. Found: C, 45.73; H, 3.72; Cl, 14.88; N, 9.08; S, 26.94.

1-(*p*-Chlorobenzyl)-4-ethylthio-6-(*p*-chlorobenzyldithio)-*s*-triazine-2(1*H*)-thione (V*b*), prepared in the same way with ethyl iodide, melted at 115–116° after recrystallization from methanol.

Anal. Calcd. for $C_{19}H_{17}Cl_2N_3S_4$: C, 46.90; H, 3.52; Cl, 14.58; N, 8.64. Found: C, 47.09; H, 3.77; Cl, 14.91; N, 8.89.

1-(*p*-Chlorobenzyl)-4-(*p*-chlorobenzylthio)-6-(*p*-chlorobenzyldithio)-*s*-triazine-2(1*H*)-thione (V*c*), m.p. 120–122°, was obtained in 87% yield.

Anal. Calcd. for $C_{24}H_{18}Cl_3N_3S_4$: C, 49.44; H, 3.11; Cl, 18.24; N, 7.21; S, 22.00. Found: C, 49.82; H, 3.17; Cl, 17.79; N, 6.90; S, 21.64.

1-(p-Chlorobenzyl)-2-thio-s-triazine-2,4,6(1H,3H,5H)-trione (VI)

A suspension of the methyl derivative V*a* (730 mg) in methanol (50 ml) and 50% sodium hydroxide solution (16 g) was heated on the steam bath for 2 h, and the methanol was evaporated. The alkaline solution was diluted with water (150 ml) and filtered, and the filtrate was acidified. The crude precipitate (185 mg) was recrystallized from glacial acetic acid to a constant melting point of 279–281°, yield 132 mg (32%).

Anal. Calcd. for $C_{10}H_8ClN_3O_2S$: C, 44.53; H, 2.99; Cl, 13.15; N, 15.58; S, 11.89. Found: C, 44.54; H, 3.05; Cl, 13.19; N, 15.55; S, 11.76.

1-(p-Chlorobenzyl)-4-methoxy-6-(p-chlorobenzyldithio)-s-triazine-2(1H)-thione (VIIa)

I (0.68 g, 1.48 mmoles) was dissolved in methanol (60 ml) containing 3.4 ml of aqueous *N* sodium hydroxide, and sodium hypochlorite solution (9 ml, available chlorine 5%) was added. The suspension was stirred at room temperature for 2 days. The precipitated product (0.51 g, 75%) melted at 142–143° after recrystallization from methanol.

Anal. Calcd. for $C_{18}H_{15}Cl_2N_3OS_3$: C, 47.36; H, 3.31; Cl, 15.54; N, 9.21; S, 21.07. Found: C, 47.11; H, 3.43; Cl, 15.35; N, 9.07; S, 21.25.

1-(p-Chlorobenzyl)-4-ethoxy-6-(p-chlorobenzyldithio)-s-triazine-2(1H)-thione (VIIb)

Sodium hypochlorite (10 ml, available chlorine 5%) was added to a solution of I (458 mg, 1 mmole) and aqueous sodium hydroxide (*N*, 1.5 ml) in ethanol (50 ml). After being allowed to stand for 1 day, the reaction solution was evaporated, and the residue was extracted with chloroform (50 ml). The chloroform was washed with water, dried, and evaporated, and the residue was crystallized from ethanol to give the product, m.p. 130–131°, yield 108 mg (23%).

Anal. Calcd. for $C_{19}H_{17}Cl_2N_3OS_3$: C, 48.51; H, 3.64; Cl, 15.07; N, 8.93; S, 20.44. Found: C, 48.27; H, 3.65; Cl, 15.21; N, 9.04; S, 20.23.

1-p-Chlorobenzyl-4,6-di-(p-chlorobenzylthio)-s-triazine-2(1H)-thione (VIII)

A solution of III (91 mg, 0.3 mmole) in 0.66 ml of *N* sodium hydroxide (0.66 mmole) was added to *p*-chlorobenzyl chloride (106 mg, 0.66 mmole) in ethanol (6 ml). The product separated out after the solution had stood for 12 h, yield 166 mg (70%), m.p. 172–174° after recrystallization from methanol.

Anal. Calcd. for $C_{24}H_{18}Cl_3N_3S_3$: C, 52.32; H, 3.29; N, 7.63; S, 17.46. Found: C, 52.01; H, 3.30; N, 8.04; S, 17.89.

Rearrangement of VIII to 2,4,6-Tri-(p-chlorobenzylthio)-s-triazine (IX)

A sample of VIII (m.p. 174°) (10 mg) was heated in a tube sealed *in vacuo* at 250° for 1 h. The product was crystallized from ether–alcohol, m.p. 117 °C. The product was identical with the triester prepared by esterification of either trithiocyanuric acid or the monoester XI with *p*-chlorobenzyl chloride. The analytical sample melted at 120–122°.

Anal. Calcd. for $C_{24}H_{18}Cl_3N_3S_3$: C, 52.32; H, 3.29; Cl, 19.31; N, 7.63; S, 17.46. Found: C, 52.26; H, 3.23; Cl, 19.70; N, 7.80; S, 17.59.

2,4,6-Tri-(p-chlorobenzyldithio)-s-triazine (X)

Chlorine (0.55 ml, 0.025 mole) was added to bis-(*p*-chlorobenzyl) disulfide (7.89 g, 0.025 mole) in carbon tetrachloride (20 ml) at −8° to −10° over a period of 25 min. This solution was added to trithiocyanuric acid (0.7 g, 0.004 mole) suspended in a mixture of carbon tetrachloride (20 ml) and chloroform (10 ml) at −10° with stirring, and the stirring was continued for 1 h at 10°. The solution was evaporated at room temperature and the residue was crystallized from ethanol, giving 1.2 g (46%), m.p. 119–120°.

Anal. Calcd. for $C_{24}H_{18}Cl_3N_3S_6$: C, 44.54; H, 2.80; Cl, 16.44; N, 6.49; S, 29.73. Found: C, 44.04; H, 2.79; Cl, 16.61; N, 6.50; S, 29.79.

2-(p-Chlorobenzylthio)-4,6-dichloro-s-triazine (XI)

To a stirred solution of cyanuric chloride (29.1 g, 0.158 mole) in acetone (200 ml) was added dropwise a mixture of *p*-chloro-α-toluenethiol (25 g, 0.158 mole) and lutidine (20 ml) at −40° over a 15 min period. The stirring was continued at −25° for a further 2 h. The reaction mixture was poured into ice water (1 000 ml) and the precipitated solid was recrystallized from heptane, giving 21.0 g (38%), m.p. 72–75 °C. The analytical sample melted at 75–77 °C.

Anal. Calcd. for $C_{10}H_6Cl_3N_3S$: C, 39.17; H, 1.97; Cl, 34.69; N, 13.71; S, 10.46. Found: C, 39.08; H, 1.89; Cl, 34.83; N, 13.81; S, 10.77.

2-(p-Chlorobenzylthio)-s-triazine-4,6(3H,5H)-dithione (XII)

A solution of XI (13.0 g, 0.0424 mole) in dioxane (20 ml) was added to aqueous sodium hydrosulfide (50%, 20 ml) in methanol (40 ml). The solution was boiled briefly, cooled, and acidified, and the precipitated product was recrystallized from dimethylformamide, yield 8.4 g (65%). The purified product underwent a crystal change at 239–240°, and did not melt below 330 °C.

Anal. Calcd. for $C_{10}H_8ClN_3S_3$: C, 39.79; H, 2.67; Cl, 11.75; N, 13.92; S, 31.87. Found: C, 39.91; H, 2.75; Cl, 11.89; N, 13.77; S, 32.18.

2-(p-Chlorobenzylthio)-4,6-di-(p-chlorobenzyldithio)-s-triazine (XIII)

A solution of chlorine (0.11 ml, 5 mmoles) and bis-(*p*-chlorobenzyl) disulfide (1.58 g, 5 mmoles) in carbon tetrachloride (4 ml) was prepared at −10 °C. A suspension of XII (0.245 g, 0.81 mmole) in carbon tetrachloride (10 ml) was added at the same temperature, and the clear solution was allowed to stand at 10° for 30 min. The solution was evaporated and the residue was crystallized from petroleum ether to give the product, m.p. 93–95°, yield 85 mg (17%).

Anal. Calcd. for $C_{24}H_{18}Cl_3N_3S_5$: C, 46.86; H, 2.95; Cl, 17.29; N, 6.83; S, 26.07. Found: C, 46.88; H, 2.99; Cl, 17.64; N, 6.73; S, 26.38.

2-Chloro-4-(p-Chlorobenzylthio)-6-dimethylamino-s-triazine (XIV)

To a solution of X (3.07 g, 0.01 mole) in acetone (350 ml), aqueous dimethylamine solution (1.43 *N*, 70 ml, 0.01 mole) and 60 ml of aqueous sodium bicarbonate (1.18 g, 0.02 mole) were added at 25–35° over 1 h. The pH of the reaction mixture was kept at 8–8.5. The reaction temperature was allowed to rise to 35–40° for 10 min. Water (300 ml) was added to precipitate the product, yield 2.65 g (84%), m.p. 128–130°. The analytical sample was recrystallized from methanol, m.p. 129–130°.

Anal. Calcd. for $C_{12}H_{12}Cl_2N_4S$: C, 45.72; H, 3.83; Cl, 22.50; N, 17.77; S, 10.17. Found: C, 45.58; H, 3.77; Cl, 22.86; N, 17.55; S, 10.12.

4-(p-Chlorobenzylthio)-6-dimethylamino-s-triazine-2(1H)-thione (XV)

A solution of XIV (2.3 g) in dioxane (50 ml) was added to sodium hydrosulfide (0.84 g) in water (25 ml), and the reaction mixture was boiled for 5 min. The solution was cooled and acidified, and the product was purified by crystallization from chloroform, yield 1.5 g (66%), m.p. 250–253°.

Anal. Calcd. for $C_{13}H_{13}ClN_4S_2$: C, 46.07; H, 4.18; Cl, 11.33; N, 17.91; S, 20.50. Found: C, 45.71; H, 4.00; Cl, 11.62; N, 18.04; S, 20.61.

2,2'-Dithiobis-(4-(p-chlorobenzylthio)-6-dimethylamino-s-triazine) (XVI)

Treatment of XV with bis-(*p*-chlorobenzyl) disulfide and chlorine as described for the preparation of XII and XIII gave the ditriazinyl disulfide, yield 88%, m.p. 183–184° after crystallization from dimethylformamide.

Anal. Calcd. for $C_{24}H_{24}Cl_2N_8S_4$: C, 46.21; H, 3.88; Cl, 11.37; N, 17.97; S, 20.57. Found: C, 45.98; H, 3.98; Cl, 11.63; N, 17.76; S, 21.00.

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