

Air Force Materials Laboratory

s-Triazines. I. Linear, Sulfur Bridged-s-Triazine Oligomers

Gerard A. Loughran, Gerhard F. L. Ehlers and Jerald L. Burkett (1)

A number of new thioether and disulfide oligomers of *s*-triazine have been prepared and identified.

The reactions between 2,4-diphenyl-*s*-triazine-6-thiol and chloro substituted-*s*-triazines are described. A suggested mechanism for the formation of 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) from 2,4-diphenyl-*s*-triazine-6-thiol is discussed.

While the preparation and characterization of a number of aliphatic (2,3,4,5) and aromatic (6,7) thioethers based on thioammeline, dithioammelide, trithiocyanuric acid (3,4,8,9), and aliphatic thioethers of 2,4-diphenyl-substituted-*s*-triazines (10) have been described previously, no instances of the existence of dimeric or trimeric, linear straight chain, or branched tetrameric-*s*-triazinylene thioethers have been reported.

Thus far, the only well characterized sulfur bridged-*s*-triazine derivative reported is 2,2'-dithiobis-(4,6-diamino-*s*-triazine), obtained by Rathke (11) by oxidation of thioammeline with bromine or with nitrous acid.

We now describe the preparation and characterization of a number of new thioether and disulfide oligomers of *s*-triazine. In general the new thioether derivatives of *s*-triazine were prepared by reaction of the appropriate chloro substituted-*s*-triazine with a thiol derivative of *s*-triazine using a suitable acid acceptor. It has been shown by infrared spectra (12) that thiol derivatives of certain alkyl and aryl substituted *s*-triazine actually exist in the solid state as dihydro-*s*-triazinethiones or tetrahydro-*s*-triazine-dithiones. When dissolved in solution, they tautomerize and react as thiols, or dithiols.

When a dioxane solution of 2,4-diphenyl-6-chloro-*s*-triazine (I) was added dropwise to a hot solution of the sodium salt of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) in an alcohol-benzene-acetone mixture, hydrogen sulfide was evident (in small quantities), and both the thioether, 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV), m.p. 225-226.5°, and the disulfide, 2,2'-dithiobis-(4,6-diphenyl-*s*-triazine) (VI), m.p. 275-276° dec., were obtained. The formation of the disulfide (VI) appears to result from an oxidation of the thiol (IIa) since the reaction was not run in an inert atmosphere. The formation of the thioether (IV) seems to indicate that the dehydrohalogenation reaction between I and IIa had occurred. However, loss of hydrogen sulfide suggested the possibility that the thioether (III) may also have been produced simultaneously from the thiol (IIa) by another mechanism. When equimolar quantities

of the chlorotriazine (I) and the thiol (IIa) were heated in boiling pyridine for thirty minutes in a flask a good yield of the thioether (IV) was obtained. Here again, the presence of hydrogen sulfide was detected. None of the disulfide (VI) was isolated, presumably because conditions favoring substantial air oxidation of the thiol (IIa) during the short reaction time were absent. The thioether, 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV) was also prepared in high yield by addition of a methanol solution of sodium sulfide nonahydrate to a dioxane solution of 2,4-diphenyl-6-chloro-*s*-triazine (I) at room temperature. The disulfide, 2,2'-dithiobis-(4,6-diphenyl-*s*-triazine) (VI) was conveniently obtained by nitrous acid oxidation of the thiol (IIa).

An attempt was made to prepare 2,2'-sulfonylbis-(4,6-diphenyl-*s*-triazine), by oxidation of 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV) in glacial acetic

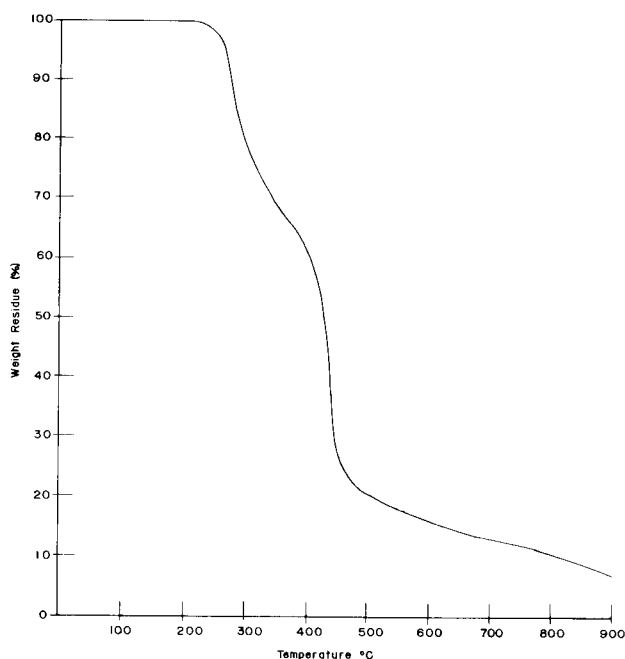


Figure 1: TGA Curve (ΔT: 150 °/hour, under nitrogen) of Compound XIV

CHART I

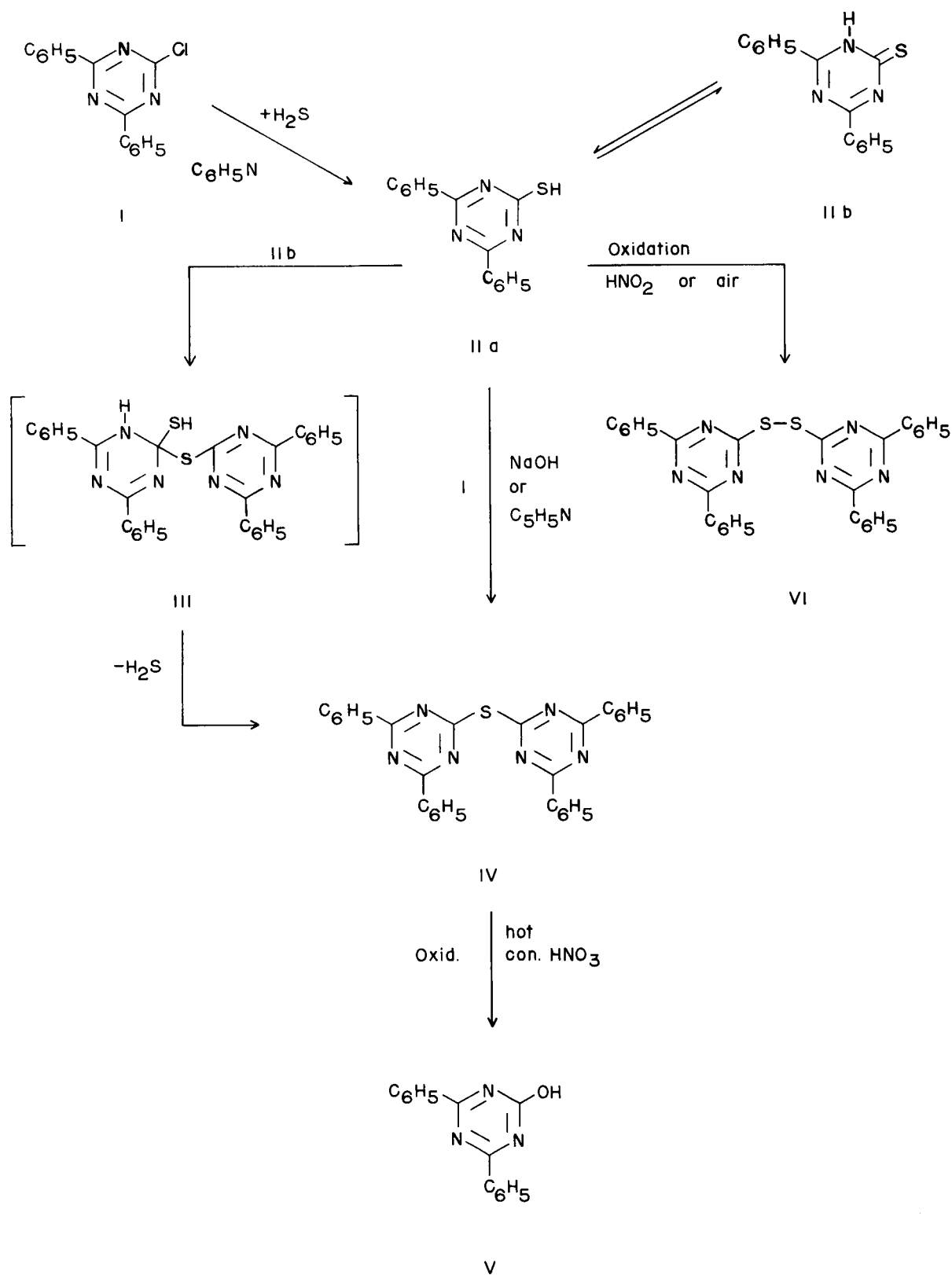
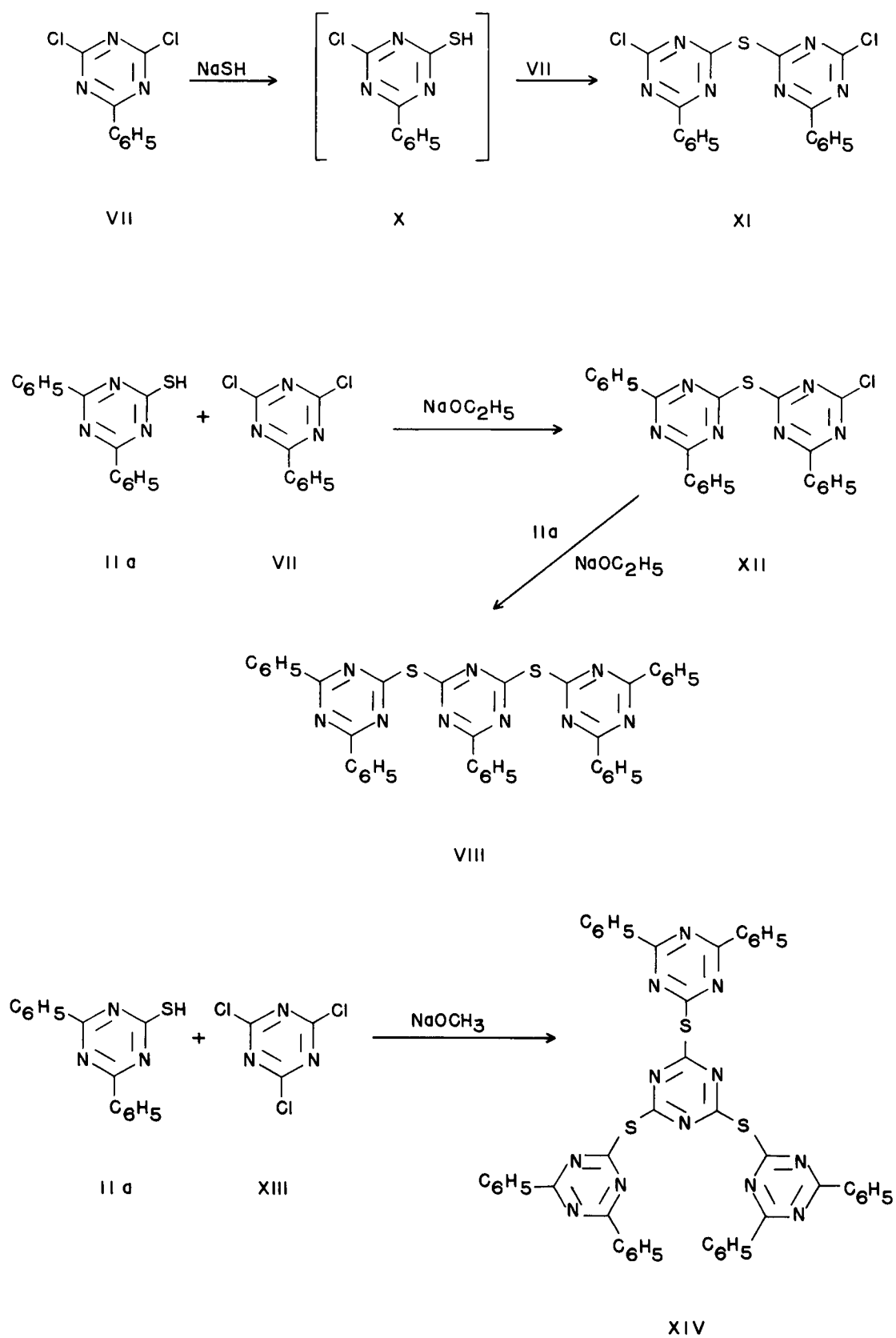


CHART 2



acid with 30% hydrogen peroxide; it gave only unreacted starting material in spite of the fact that diphenyl sulfide is readily oxidized to diphenyl sulfone by this reagent (13). Attempted oxidation of IV at a higher temperature with cumene hydroperoxide in refluxing xylene also was unsuccessful. More drastic treatment with hot concentrated nitric acid resulted in splitting of the thioether linkage with evolution of sulfur dioxide and formation of 2,4-diphenyl-*s*-triazine-6-ol (V).

It became of interest to explore the reactions involved in the synthesis of higher molecular weight sulfur-bridged *s*-triazine derivatives. Accordingly, the reaction between two moles of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) and one mole of 2-phenyl-4,6-dichloro-*s*-triazine (VII) was investigated. When the reaction was run by addition of a dioxane solution of the dichlorotriazine (VII) to the sodium salt of IIa in a refluxing benzene-alcohol-acetone mixture, three products were isolated: 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV), 2,2'-dithiobis-(4,6-diphenyl-*s*-triazine) (VI) and the linear trimeric monosulfide, 2,4-bis-(2'-thio-4',6'-diphenyl-*s*-triazinylene)-6-phenyl-*s*-triazine (VIII), m.p. 240-243°. As before, some hydrogen sulfide evolution was observed. When the reaction was repeated in boiling pyridine, hydrogen sulfide again was evident, and a mixture of the "dimeric" thioether, 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV) was obtained along with a small amount of the new linear "trimeric" monosulfide (VIII), m.p. 243-244°. Next, an attempt was made to produce the linear "trimeric" monosulfide (VIII) by reaction of two moles of 2,4-diphenyl-6-chloro-*s*-triazine (I) with one mole of 2-phenyl-*s*-triazine-4,6-dithiol (IX) in refluxing pyridine. Here, the chief product isolated from the reaction mixture was 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV) along with a resinous material from which it was not possible to extricate any of the desired trimeric derivative (VIII). The best yield of the "trimeric" thioether (VIII) was obtained by slow addition of a dioxane solution of 2-phenyl-4,6-dichloro-*s*-triazine (VII) to an alcohol solution of the sodium salt of IIa (from IIa and sodium ethylate).

The persistent appearance of hydrogen sulfide during these reactions and the formation of 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV) in reactions of IIa with 2-phenyl-4,6-dichloro-*s*-triazine (VII) suggest that loss of hydrogen sulfide from 2,4-diphenyl-*s*-triazine-6-thiol (IIa) somehow occurs. This was demonstrated by heating IIa for 24 hours in refluxing pyridine. Hydrogen sulfide was evolved, and the chief product was 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV) (accompanied by a small amount of the disulfide (VI) from oxidation of the thiol IIa).

It is known that hydroxy and mercapto derivatives of *s*-triazine exist in the solid state as ones and thiones (12), and tautomerize when brought into solution. It seems conceivable then to suggest a possible mechanism which involves addition of the thiol (IIa) to its thione tautomer (IIb) resulting in formation of a "hemimercaptal" adduct (III) which

in turn splits out hydrogen sulfide to give 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV) (*cf.* Chart 1).

Since 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV) also was produced in the reaction of 2,4-diphenyl-6-chloro-*s*-triazine (I) with 2-phenyl-*s*-triazine-4,6-dithiol (IX) it seems probable that its formation resulted from reaction of the chlorotriazine (I) with hydrogen sulfide (presumably from the dithiol by a scheme similar to that suggested above). Hence, a solution of 2,4-diphenyl-6-chloro-*s*-triazine (I) in refluxing pyridine was treated with hydrogen sulfide over a 6 hour period. The chief product of the reaction was 2,4-diphenyl-*s*-triazine-6-thiol (IIa) accompanied by a small amount of 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV). 2-Phenyl-4,6-dichloro-*s*-triazine (VII) in dioxane was treated with one equivalent of aqueous sodium hydrosulfide at room temperature in an attempt to prepare 2-phenyl-4-chloro-*s*-triazine-6-thiol (X). A new chlorine containing thioether, 2,2'-thiobis-(4-chloro-6-phenyl-*s*-triazine) (XI) m.p. 198-199° was obtained.

Another new dimer, 2-chloro-2',4,4'-triphenyl-6,6'-thiobis-(*s*-triazine) (XII) m.p. 199-200° was obtained when equimolar quantities of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) and 2-phenyl-4,6-dichloro-*s*-triazine (VII) were allowed to react in dioxane in the presence of alcoholic sodium ethylate. This appears to be the precursor of 2,4-bis-(2'-thio-4',6'-diphenyl-*s*-triazinylene)-6-phenyl-*s*-triazine (VIII).

A branched tetramer, tris-(2'-thio-4',6'-diphenyl-*s*-triazinyl)-*s*-triazine (XIV) m.p. 256.5-257° was prepared by reaction of three moles of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) with one mole of cyanuric chloride (XIII) using sodium methylate as acid acceptor. Figure 1 shows its weight loss curve from thermogravimetric analysis.

EXPERIMENTAL

Molecular weights were determined by microbullioscopic techniques (14) using either benzene, chlorobenzene or dioxane as a solvent, or by thermometric vapor pressure osmometry (15).

The nitrogen values reported were obtained by the Kjeldahl method except where indicated with an asterisk (*). Here the Dumas method was employed and usually gave low values with these triazine derivatives.

Thermogravimetric analyses were obtained by heating 0.2-0.3 g. of the compound under nitrogen in a Chevenard type thermobalance (Adamel, Paris, France) to 900° at a heating rate of 150° per hour.

Cyanuric chloride (XIII) was obtained commercially and purified by recrystallization from benzene. 2,4-Diphenyl-6-chloro-*s*-triazine (I) and 2-phenyl-4,6-dichloro-*s*-triazine (VII) were prepared from cyanuric chloride (XIII) and bromobenzene by the Grignard reaction. VII was obtained in 85-95% yield although Ostrovitch (16) reported a low yield for this compound. 2,4-Diphenyl-*s*-triazine-6-thiol (IIa) was prepared by the method of Grundmann (10), and 2-phenyl-*s*-triazine-4,6-dithiol (IX) by the method of Fairful and Peak (17).

2,2'-Thiobis-(4,6-diphenyl-*s*-triazine) (IV).

(1) By reaction of 2,4-diphenyl-6-chloro-*s*-triazine (I) and 2,4-diphenyl-*s*-triazine-6-thiol (IIa) in hot pyridine.

A solution of 1.33 g. (0.005 mole) of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) was mixed with a solution of 1.34 g. (0.005 mole) of 2,4-diphenyl-6-chloro-*s*-triazine (I) in 125 ml. of pyridine and heated for

30 minutes at 100°. The reaction mixture was poured into ice water giving a precipitate of crude 2,2'-thiobis-(4,6-diphenyl-s-triazine) (IV), yield 1.6 g. The product was recrystallized once from cyclohexane, and once from benzene, m.p. 225-226°.

Molecular weight (ebullioscopic, benzene): Calcd. for $C_{30}H_{20}N_6S$ (IV): 496.6. Found: 454.

Anal. Calcd. for $C_{30}H_{20}N_6S$ (IV): C, 72.56; H, 4.06; N, 16.92; S, 6.46. Found: C, 72.53; H, 3.98; N, 16.78; S, 6.51.

(2) By reaction of 2,4-diphenyl-6-chloro-s-triazine (I) with sodium sulfide nonahydrate in methanol.

A solution of 5.28 g. (0.022 mole) of sodium sulfide nonahydrate in 100 ml. of methanol was added dropwise at room temperature to 10.72 g. (0.04 mole) of 2,4-diphenyl-6-chloro-s-triazine (I) in 100 ml. of dioxane. The solvents were distilled off and the residue, 12.3 g. was stirred with 200 ml. of hot benzene and filtered. The benzene filtrate was concentrated to 60 ml. and cooled. The precipitated white fibrous material (IV), 10 g., was recrystallized from toluene, m.p. 222-224°, then from dioxane, m.p. 225-226°.

Anal. Calcd. for $C_{30}H_{20}N_6S$ (IV): C, 72.56; H, 4.06; N, 16.92; S, 6.46. Found: C, 72.55; H, 3.97; N, 16.77; S, 6.57.

(3) By reaction of 2,4-diphenyl-6-chloro-s-triazine (I) and 2,4-diphenyl-s-triazine-6-thiol (IIa) (Sodium hydroxide as acid acceptor).

A solution of 2.68 g. (0.01 mole) of 2,4-diphenyl-6-chloro-s-triazine (I) in 50 ml. of dioxane was added slowly to a solution from 2.65 g. (0.01 mole) of 2,4-diphenyl-s-triazine-6-thiol (IIa) and 0.44 g. of sodium hydroxide in a solvent mixture consisting of 300 ml. of ethanol, 100 ml. of benzene and 100 ml. of acetone at refluxing temperatures. The reaction mixture was refluxed several hours. The solvents were distilled off under reduced pressure and the dry residue was stirred into 200 ml. of boiling benzene. The benzene insoluble material, 2 g., was water soluble. Addition of diluted acetic acid precipitated 0.71 g. of yellow unreacted 2,4-diphenyl-s-triazine-6-thiol, m.p. 197-198° (from ethanol). Evaporation of the benzene gave 2.4 g. of a white solid product. This crude product was recrystallized with a charcoal treatment from 500 ml. of boiling dioxane. Concentration of the solution to 100 ml. gave 0.9 g. of a white crystalline material, m.p. 268-270°. Recrystallization from 80 ml. of benzene gave 0.5 g. of the product, m.p. 275-276°.

Molecular weight (ebullioscopic, benzene): Calcd. for $C_{30}H_{20}N_6S_2$ (VI): 528.6. Found: 527.

Anal. Calcd. for $C_{30}H_{20}N_6S_2$ (VI): C, 68.16; H, 3.81; N, 15.90; S, 12.13. Found: C, 68.28; H, 3.69; N, 16.04; S, 12.32.

Further concentration of the dioxane solution from VI to 25 ml. gave 0.7 g. of a white fibrous material, m.p. 223.5-227°. Recrystallization from 80 ml. of benzene gave 0.22 g. of 2,2'-thiobis-(4,6-diphenyl)-s-triazine (IV) m.p. 225-226°.

Molecular weight (V.P.O., benzene): Calcd. for $C_{30}H_{20}N_6S$ (IV): 496.6. Found: 513.

Anal. Calcd. for $C_{30}H_{20}N_6S$ (IV): C, 72.56; H, 4.06; N, 16.92; S, 6.46. Found: C, 72.20; H, 4.12; N, 16.81; S, 7.30.

2,2'-Dithiobis-4,6-diphenyl-s-triazine (VI).

A solution of 1.06 g. (0.004 mole) of 2,4-diphenyl-s-triazine-6-thiol (IIa) in 150 ml. of dioxane was added slowly to a cold nitrous acid solution from 0.28 g. of sodium nitrite in 50 ml. of dilute hydrochloric acid. A white precipitate formed immediately. It was filtered off and recrystallized from benzene, yield, 0.99 g., m.p. 275-276° dec.

Molecular weight (ebullioscopic, benzene): Calcd. for $C_{30}H_{20}N_6S_2$ (VI): 528.6. Found: 536.

Anal. Calcd. for $C_{30}H_{20}N_6S_2$ (VI): C, 68.16; H, 3.81; N, 15.90; S, 12.13. Found: C, 68.03; H, 3.83; N, 15.69; S, 11.90.

Oxidation of 2,2'-thiobis-(4,6-diphenyl-s-triazine) (IV) with Hot Concentrated Nitric Acid.

To 10 ml. of concentrated nitric acid was added 0.5 g. of solid 2,2'-thiobis-(4,6-diphenyl-s-triazine) (IV). On boiling the compound dissolved. The solution was cooled and poured into 20 ml. of ice water. A white precipitate of 2,4-diphenyl-s-triazine-6-ol (V) precipitated on neutralization with sodium bicarbonate, yield, 0.45 g., m.p. 292-294°.

Anal. Calcd. for $C_{15}H_{11}N_3O$ (V): C, 72.27; H, 4.45; N, 16.85; O, 6.42. Found: C, 72.30; H, 4.57; N, 16.39; O, 6.73 by difference.

2,4-Bis-(2-thio-4',6'-diphenyl-s-triazinylene)-6-phenyl-s-triazine (VIII).

(1) By reaction of 2 moles of the sodium salt of 2,4-diphenyl-s-triazine-6-thiol (IIa) in alcohol and one mole of 2-phenyl-4,6-dichloro-s-triazine (VII) in dioxane.

A solution was prepared from 0.46 g. (0.02 g. atom) of sodium metal and 5.5 g. (0.02 mole) of 2,4-diphenyl-s-triazine-6-thiol (IIa)

in 250 ml. of ethanol. This solution was gently refluxed while a solution of 2.2 g. (0.01 mole) of 2-phenyl-4,6-dichloro-s-triazine (VII) in 50 ml. of dioxane was added dropwise. After refluxing for one hour, followed by cooling, a yellowish-white precipitate formed. It weighed 6 g. (88%) after drying at 120° and was recrystallized once from benzene after Norite treatment. Further recrystallization from dioxane, then again from benzene gave 3.4 g. of product, m.p. 243-244°.

Molecular weight (ebullioscopic, benzene): Calcd. for $C_{39}H_{25}N_9S_2$ (VIII): 684. Found: 732, 593, Average 662.

Anal. Calcd. for $C_{39}H_{25}N_9S_2$ (VIII): C, 68.50; H, 3.68; N, 18.44; S, 9.38. Found: C, 68.26; H, 3.78; N, 18.33; S, 8.95.

(2) By reaction of 2 moles of 2,4-diphenyl-s-triazine-6-thiol (IIa) with one mole of 2-phenyl-4,6-dichloro-s-triazine (VII) with sodium hydroxide as the acid acceptor.

2,4-Diphenyl-s-triazine-6-thiol (IIa) (2.65 g., 0.01 mole) was dissolved in a solvent mixture from 200 ml. of benzene, 300 ml. of alcohol, and 50 ml. of acetone. Then a solution containing 0.44 g. of sodium hydroxide in 50 ml. of alcohol was added. The solution was refluxed at 66° and a solution of 1.13 g. (0.005 mole) of 2-phenyl-4,6-dichloro-s-triazine (VII) in 50 ml. of dioxane was added dropwise over one hour. The mixture was refluxed for three hours after which the solvents were distilled off leaving behind a yellowish white residue, yield 4 g. The crude product was dissolved in 200 ml. of boiling benzene. The insoluble inorganic material (1 g.) was filtered off. It was soluble in water and gave a yellow precipitate of starting material (IIa), m.p. 196-198°, on acidification, yield 0.3 g. The benzene filtrate on concentration to 75 ml. gave 1.8 g. of crude crystalline product (A), m.p. 225-275°. Recrystallization of this crude material from cyclohexane, then benzene and finally fractionally crystallized from dioxane gave 0.2 g. of 2,2'-dithiobis-(4,6-diphenyl-s-triazine) (VI), m.p. 273-275° dec.

Anal. Calcd. for $C_{30}H_{20}N_6S_2$ (VI): C, 68.16; H, 3.81; N, 15.90; S, 12.13. Found: C, 67.79; H, 3.99; N, 15.88; S, 11.73.

Further concentration of the benzene filtrate from crude VI gave 0.8 g. of crystalline product B, m.p. 233-235°, which was recrystallized twice more from benzene with charcoal treatment, m.p. 240-243°.

Anal. Calcd. for $C_{39}H_{25}N_9S_2$ (VIII): C, 68.50; H, 3.68; N, 18.44; S, 9.38. Found: C, 68.74; H, 3.64; N*, 17.40; S, 9.53.

The benzene filtrate from crude product B was concentrated to 25 ml. to give 0.66 g. of a white product, m.p. 203-205°. Recrystallization once from dioxane and twice from benzene with charcoal treatment gave 0.2 g. of 2,2'-thiobis-(4,6-diphenyl-s-triazine) (IV), m.p. 223-225°.

(3) Reaction between 2,4-diphenyl-s-triazine-6-thiol (IIa), and 2-phenyl-4,6-dichloro-s-triazine (VII) (pyridine as the acid acceptor).

A solution of 1.13 g. (0.005 mole) of 2-phenyl-4,6-dichloro-s-triazine (VII) in 60 ml. of dioxane was mixed with a solution of 2.92 g. (0.011 mole) of 2,4-diphenyl-s-triazine-6-thiol (IIa) and the mixture was refluxed for three hours. A lavender precipitate formed on pouring into one liter of ice water. The material (3.2 g.) was extracted with hot alcohol, then dissolved in 50 ml. of hot dioxane, filtered, and cooled, giving a white precipitate (1.7 g.). This solid was dissolved in 100 ml. of boiling benzene. Fractional crystallization gave 0.9 g. of 2,2'-thiobis-(4,6-diphenyl-s-triazine) (IV), m.p. 224-225° (identical with a previous sample of IV), and 0.7 g. of the linear trimer, 2,4-bis-(2'-thio-4',6'-diphenyl-s-triazinylene)-6-phenyl-s-triazine (VIII), m.p. 243-244°.

Anal. Calcd. for $C_{39}H_{25}N_9S_2$ (VIII): C, 68.50; H, 3.68; N, 18.44; S, 9.38. Found: C, 68.61; H, 3.87; N, 18.12; S, 9.00.

(4) Reaction between 2,4-diphenyl-6-chloro-s-triazine (I) (2 moles) and 2-phenyl-s-triazine-4,6-dithiol (IX) (1 mole) (pyridine as the acid acceptor).

A solution of 5.35 g. (0.02 mole) of 2,4-diphenyl-6-chloro-s-triazine (I) and 1.9 g. (0.01 mole) of 2-phenyl-s-triazine-4,6-dithiol (IX) in 150 ml. of pyridine was heated at 90° for 90 minutes, then poured into ice water. The lavender precipitate (4.6 g.) was recrystallized from 300 ml. of boiling cyclohexane, giving 2 g. of white 2,2'-thiobis-(4,6-diphenyl-s-triazine) (IV), m.p. 223-224°.

Anal. Calcd. for $C_{30}H_{20}N_6S$ (IV): C, 72.56; H, 4.06; N, 16.92; S, 6.46. Found: C, 72.52; H, 3.98; N, 16.75; S, 6.51.

The cyclohexane filtrate on evaporation left 2.1 g. of a white residue which on recrystallization from dioxane gave an additional 1.2 g. of product. Evaporation of the dioxane filtrate left 0.9 g. of an amber resinous material. None of the trimer (VIII) could be found.

2,2'-Thiobis-(4-chloro-6-phenyl-s-triazine) (XI).

A solution of sodium hydrosulfide was prepared from 3 g. (0.05 mole) of glacial acetic acid and 12 g. (0.05 mole) of sodium sulfide nonahydrate in 100 ml. of cold water. The solution was added slowly

from a dropping funnel over two hours to a solution of 22.6 g. (0.10 mole) of 2-phenyl-4,6-dichloro-*s*-triazine (VII) in 300 ml. of dioxane at room temperature. After removal of the dioxane, the residue was stirred with 50 ml. of boiling toluene, and the insoluble inorganic material was filtered off. Evaporation of the toluene left 20.1 g. of a yellowish-white residue. Crystallization from 200 ml. of hot benzene gave 8 g. of finely divided, yellowish-white XI, m.p. 189-191°. The benzene mother liquors were evaporated to dryness, and the residue was crystallized from 200 ml. of dioxane giving 1.4 g. of a more pure sample of XI, m.p. 198-200°. Concentration of the dioxane filtrate deposited 5.1 g. of yellow 2-phenyl-*s*-triazine-4,6-dithiol (IX). Both crops of XI were combined and recrystallized from dioxane, then twice more from benzene, m.p. 199-200°.

Molecular weight (ebullioscopic, benzene): Calcd. for $C_{18}H_{10}Cl_2N_6S$: 413.4. Found: 438.

Anal. Calcd. for $C_{18}H_{10}Cl_2N_6S$ (XI): C, 52.30; H, 2.44; N, 20.33; S, 7.76; Cl, 17.17. Found: C, 52.88; H, 2.61; N, 19.88; S, 7.95; Cl, 17.04.

2-Chloro-2',4,4'-triphenyl-6,6'-thiobis-(*s*-triazine) (XII).

A warm solution of 5.3 g. (0.02 mole) of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) in 100 ml. of alcohol was added to a sodium ethylate solution of 0.46 g. (0.02 g. atom) of sodium metal in 200 ml. of alcohol. Then a solution of 4.5 g. (0.02 mole) of 2-phenyl-4,6-dichloro-*s*-triazine (VII) in 200 ml. of dioxane was added dropwise. A white precipitate (8.3 g.) was filtered off and recrystallized from 400 ml. of benzene. A small amount of (0.9 g.) of 2,4-bis-(2'-thio-4',6'-diphenyl-*s*-triazinylene)-6-phenyl-*s*-triazine (VIII), m.p. 243-244° separated first from the warm solution. The filtrate was concentrated to 50 ml. giving 6.9 g. of a white crystalline compound (XII), m.p. 198-199°.

Molecular weight (ebullioscopic, benzene): Calcd. for $C_{24}H_{15}ClN_6S$ (XII): 455. Found: 435.

Anal. Calcd. for $C_{24}H_{15}ClN_6S$ (XII): C, 63.35; H, 3.32; N, 18.47; S, 7.05; Cl, 7.81. Found: C, 63.66; H, 3.58; N, 18.18; S, 7.01; Cl, 7.40.

Decomposition of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) in Boiling Pyridine.

A solution of 2.65 g. (0.01 mole) of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) and 50 ml. of pyridine was refluxed for 24 hours. Slow evolution of hydrogen sulfide was noticeable. The reaction mixture was poured into ice cold dilute hydrochloric acid giving a lavender precipitate which was filtered off and oven dried at 120°, yield 2.3 g. The solid was stirred in 100 ml. of hot benzene and filtered. The benzene insoluble material was recrystallized from hot methanol, m.p. 194-197° dec., and identified as starting material (IIa). Yellowish-white fibrous crystals precipitated from the benzene solution, yield 0.8 g.

The benzene filtrate was evaporated to dryness leaving a yellowish-white residue (0.7 g.) which was combined with the 0.8 g. of crystalline material above and boiled with 50 ml. of alcohol for 30 minutes. After cooling the whiter insoluble material was filtered off from the yellow alcohol solution and recrystallized as pure white crystals from 300 ml. of dioxane, yield 0.5 g., m.p. 252-265°. A second recrystallization from 250 ml. of benzene gave 0.15 g. of pure white product, m.p. 273.5-274.5°.

Anal. Calcd. for $C_3H_2N_2S_2$ (VI): C, 68.16; H, 3.81; N, 15.90; S, 12.13. Found: C, 68.33; H, 3.93; N, 15.80; S, 12.09.

Concentration of the dioxane from crude VI to 20 ml. gave white

fibrous crystals of 2,2'-thiobis-4,6-diphenyl-*s*-triazine (IV), m.p. 224-225°, yield 0.5 g.

Evaporation of the alcohol filtrate gave 0.5 g. of unreacted IIa.

Reaction between 2,4-diphenyl-6-chloro-*s*-triazine (I) and Hydrogen Sulfide in Hot Pyridine.

Liquid hydrogen sulfide (0.68 g., 1 ml.) condensed in a trap was allowed to evaporate and bubble through a refluxing solution of 2.67 g. (0.01 mole) of 2,4-diphenyl-6-chloro-*s*-triazine (I) in 50 ml. of pyridine. After 6 hours the solution was poured into cold dilute hydrochloric acid solution and the gray precipitate (2.6 g.) was filtered off, oven dried at 120° and boiled with 100 ml. of benzene. The benzene insoluble portion (2.2 g.) was recrystallized from alcohol and identified as 2,4-diphenyl-*s*-triazine-6-thiol (IIa), m.p. 195-198°. The benzene filtrate left a residue of 0.38 g., which consisted mostly of 2,2'-thiobis-(4,6-diphenyl-*s*-triazine) (IV), m.p. 225-226° along with 0.04 g. of 2,4-diphenyl-*s*-triazine-6-ol (V), m.p. 290°.

Tris-(2'-thio-4',6'-diphenyl-*s*-triazinyl)-*s*-triazine (XIV).

A solution of 4.15 g. (0.0155 mole) of 2,4-diphenyl-*s*-triazine-6-thiol (IIa) and 189 ml. of 0.82 *N* sodium methylate solution in 300 ml. of methanol was refluxed and stirred and a solution of 0.625 g. (0.0038 mole) of cyanuric chloride (XIII) in 100 ml. of benzene was added dropwise. The solvent was distilled off and the residue was taken up in hot chlorobenzene and filtered. The filtrate on cooling gave a 1.67 g. of a white precipitate. Recrystallization of the product from one liter of dioxane gave 1.05 g. of product, m.p. 256.5-257.5°. Concentration of the filtrate gave additional quantities of the branched triazinylene sulfide tetramer.

Molecular weight (V.P.O., chlorobenzene, 100°): Calcd. for $C_{48}H_{30}N_{12}S_3$: 871. Found: 733.

Anal. Calcd. for $C_{48}H_{30}N_{12}S_3$ (XIV): C, 66.19; H, 3.47; N, 19.30; S, 11.04. Found: C, 66.07; H, 3.65; N, 19.22; S, 10.88.

REFERENCES

- (1) University of Dayton Research Institute, Dayton, Ohio.
- (2) G. D'Alelio and J. Underwood, U. S. Patent 2,324,285.
- (3) A. Hoffman, *Ber.*, 18, 2196 (1885).
- (4) P. Klason, *J. Prakt. Chem.*, (2), 33, 131 (1886).
- (5) W. Terweck and I. Goffey, U. S. Patent 2,267,068.
- (6) E. Friedheim, U. S. Patent 2,391,452.
- (7) E. Friedheim, U. S. Patent 2,415,556.
- (8) G. A. Loughran and E. O. Hook, U. S. Patent 2,676,151.
- (9) J. Gillis, *Chem. Wæckblad.*, 15, 73 (1918).
- (10) C. Grundmann, H. Ulrick, and A. Kreutzberger, *Chem. Ber.*, 86, 181 (1953).
- (11) B. Rathke, *Ber.*, 1675 (1890).
- (12) G. A. Loughran, G. F. L. Ehlers, W. J. Crawford, J. L. Burkett, and J. D. Ray, *Appl. Spectry.*, 18, 129 (1964).
- (13) O. Hinsberg, *Ber.*, 43, 289 (1910).
- (14) M. Dimbat and F. H. Stross, *Anal. Chem.*, 29, 1517 (1957).
- (15) J. J. Neumayer, *Anal. Chim. Acta*, 20, 519 (1959).
- (16) A. Ostrogovitch, *Chemiker Z.*, 36, 739 (1912).
- (17) A. E. S. Fairful and D. A. Peak, *J. Chem. Soc.*, 803 (1955).

Received (Revised) February 15, 1966

Wright-Patterson Air Force Base, Ohio 45433