Air Force Materials Laboratory

s-Triazines. II. The Synthesis of some New Cyclopoly-s-triazinylene Thioethers and Disulfides

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A number of new cyclopoly-*s*-triazinylene thioethers and disulfides have been prepared in dilute solution. Their structures and methods of formation are discussed. A thermogravimetric analysis of cyclopoly-2-phenyl-*s*-triazinylene-4,6-monosulfide is included.

In a previous paper (2), the preparation of a series of linear triazinylene sulfides in solution was described. Attempts to prepare a linear polytriazinylene sulfide of reasonable molecular weight by melt condensation of equimolar quantities of 2-phenyl-4,6-dichloro-*s*-triazine (I) and 2-phenyl-*s*-triazine-4,6-dithiol (VII) led only to low molecular weight products of low sulfur content (3).

Since reactions in dilute solution between difunctional molecules can be expected to result in formation of cyclic products, it became of interest to study such reactions. Molecular models demonstrate the ease of formation of cyclic structures from *meta* directed aromatic systems. The smallest cyclic molecule of the 2-alkyl- or aryl-substituted-*s*-triazinylene-4,6-monosulfide structure that can form is a cyclic trimer. Cyclic tetramers, pentamers or large ring systems theoretically can exist, however, in dilute solution the formation of cyclic trimers and tetramers appears to be more likely. This has been confirmed by the preparation of a new species of cyclopoly-*s*-triazinylenesulfides with degrees of polymerization in this range. Similarly, oxidation of 2-substituted-*s*-triazine-4,6-dithiols in solution results in formation of cyclopoly-*s*-triazinylene disulfides with degrees of polymerization of the same order.

2-Methyl-*s*-triazine-4,6-dithiol, as one of the starting materials for these studies, was prepared by addition of a dioxane solution of 2-methyl-4,6-dichloro-*s*-triazine to a cold dilute aqueous solution of sodium hydrosulfide. Crystalline 2-methyl-*s*-triazine-4,6-dithiol (from dioxane) has been shown by infrared studies to exist in the thione form in the solid state (4), but tautomerizes in solution. When the mode of addition is reversed, and a dilute aqueous solution of sodium hydrosulfide was added dropwise to a cold dioxane solution of 2-methyl-4,6-dichloro-*s*-triazine, a new compound, $C_4H_3N_3S$, m.p. 212-215° was obtained. Its elementary analysis, molecular weight of 361, and the absence of chlorine end groups indicate that it consists of about three 2-methyl-*s*-triazinylene-4,6-monosulfide units arranged in a cyclic configuration. The corresponding cyclopoly-2-phenyl-*s*-triazinylene-4,6-monosulfide (VIa or VIb) $(C_9H_3N_3S)_n$, m.p. 263.5-264° was prepared by addition of sodium sulfide to a cold or hot dioxane solution of 2-phenyl-4,6-dichloro-*s*-triazine (I). It was free of chlorine and molecular weights on different samples varied from 531 to 643, indicating a degree of polymerization from 2.8 to 3.4.

Fractional recrystallization of this product from dioxane, and subsequently from benzene, gave a small amount of product having a molecular weight of 758 (degree of polymerization, 4.1).

For the reaction between 2-phenyl-4,6-dichloro-*s*-triazine (I) and sodium sulfide, a relatively straightforward reaction scheme (Chart 1) can be postulated which involves the initial formation of 2,2'-thiobis-(4-chloro-6-phenyl-*s*-triazine) (III) (previously reported (2)). Subsequent reaction with sodium sulfide could result in formation of the intermediate linear trimer (IV) and tetramer (V). It can be assumed

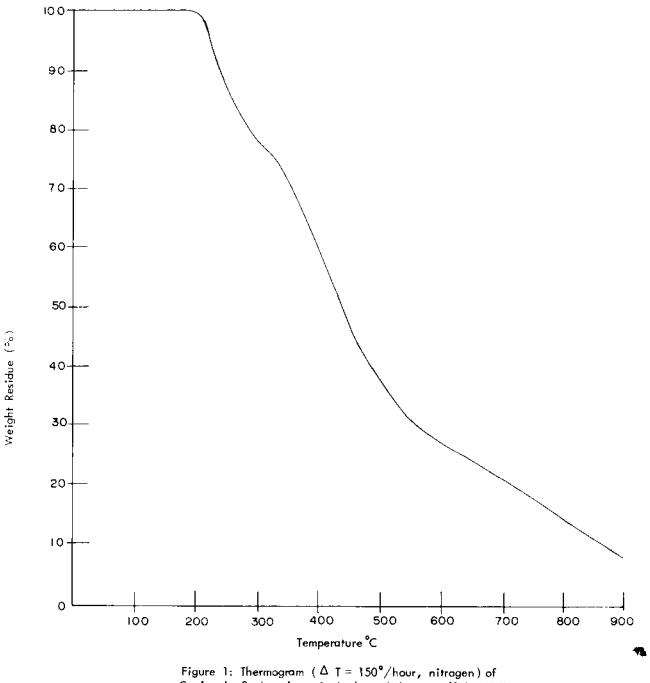


Figure 1: Thermogram (Δ T = 150°/hour, nitrogen) of Cyclopoly-2-phenyl-s-triazinylene-4,6-monosulfide, XIIIa

CHART I

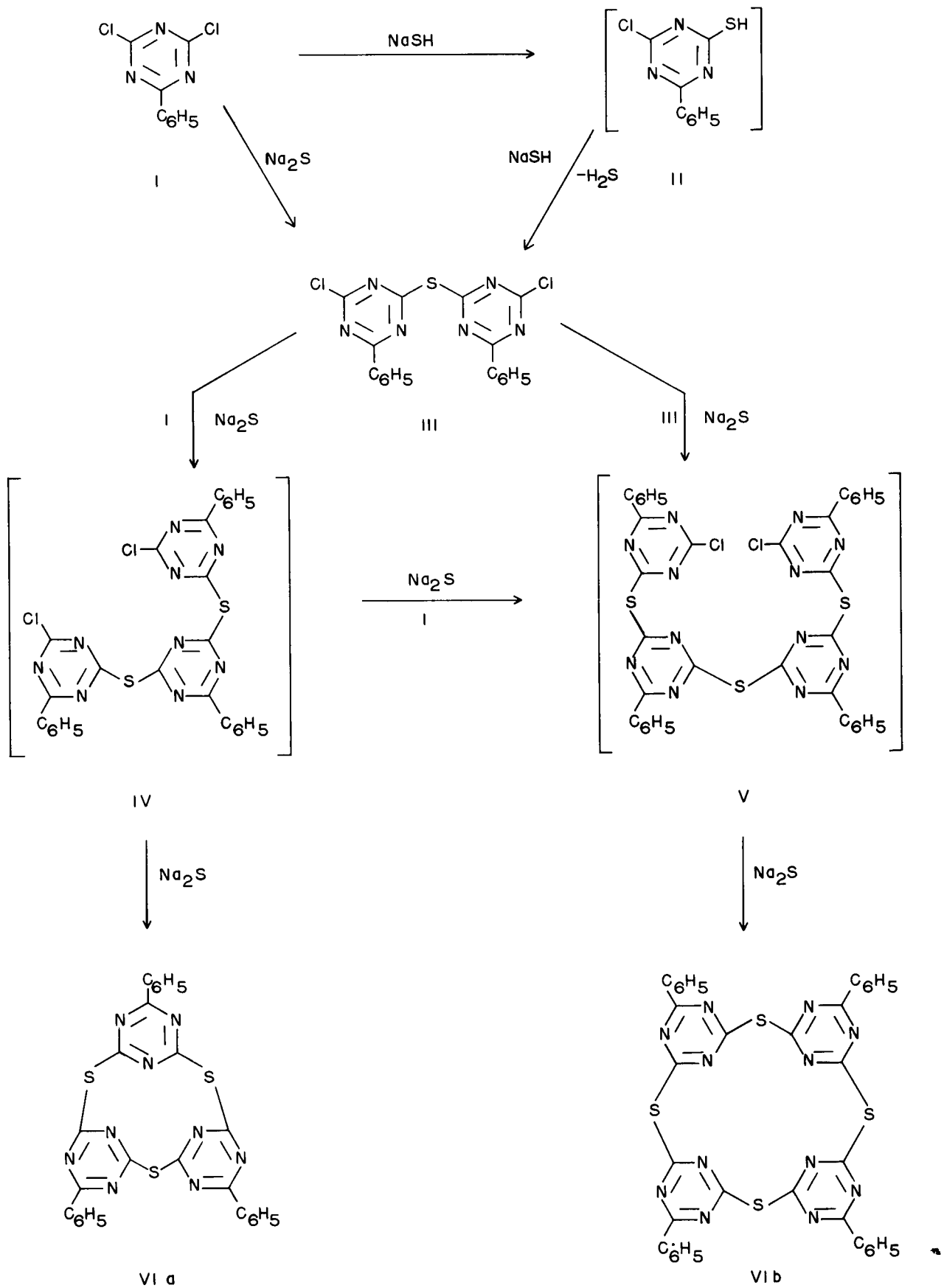

NaSH
Na2S
NaSH
-H2S
I
II
III
I Na2S
III Na2S
Na2S
I
IV
V
Na2S
Na2S
VI a
VI b

CHART 2

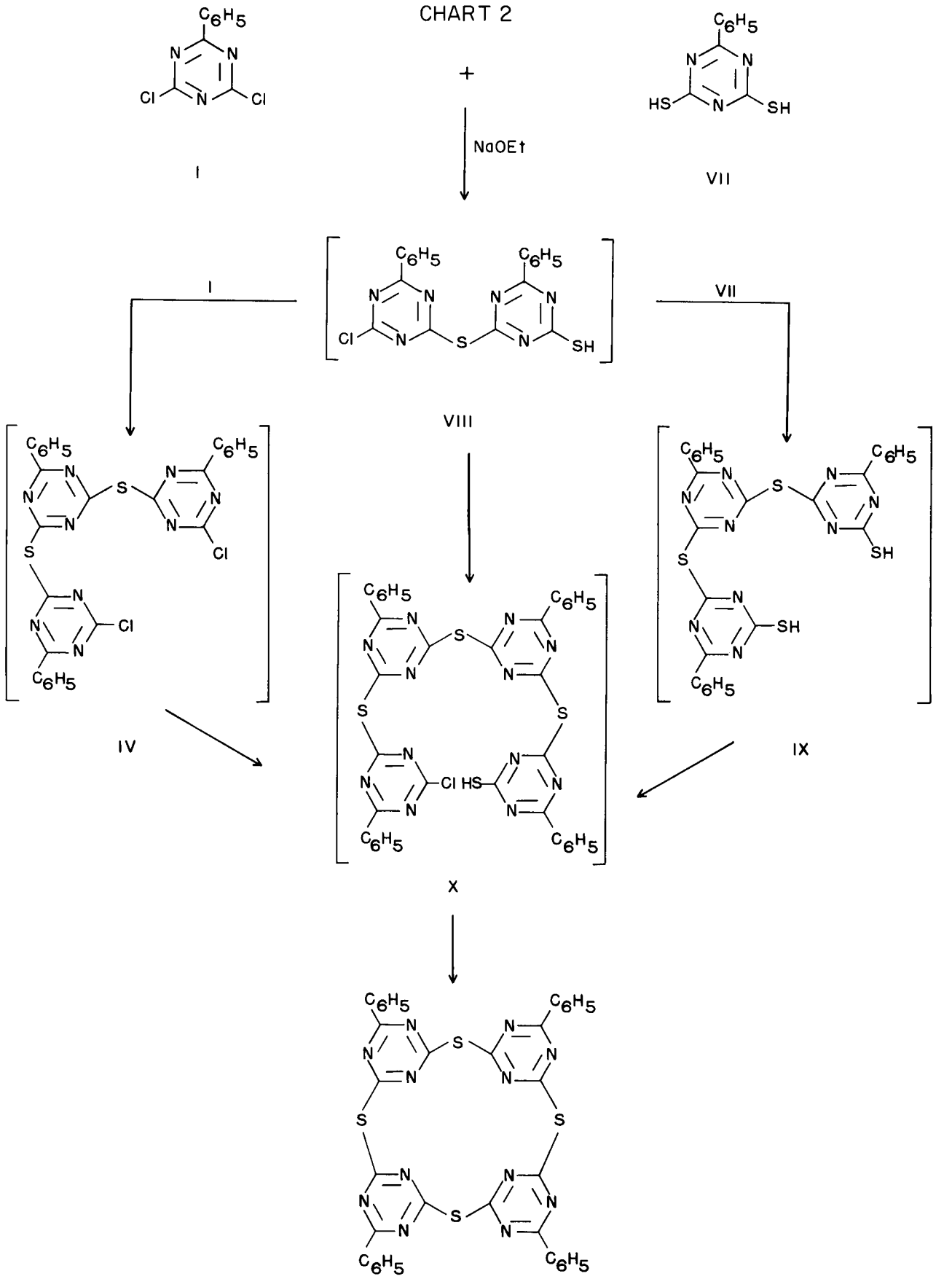
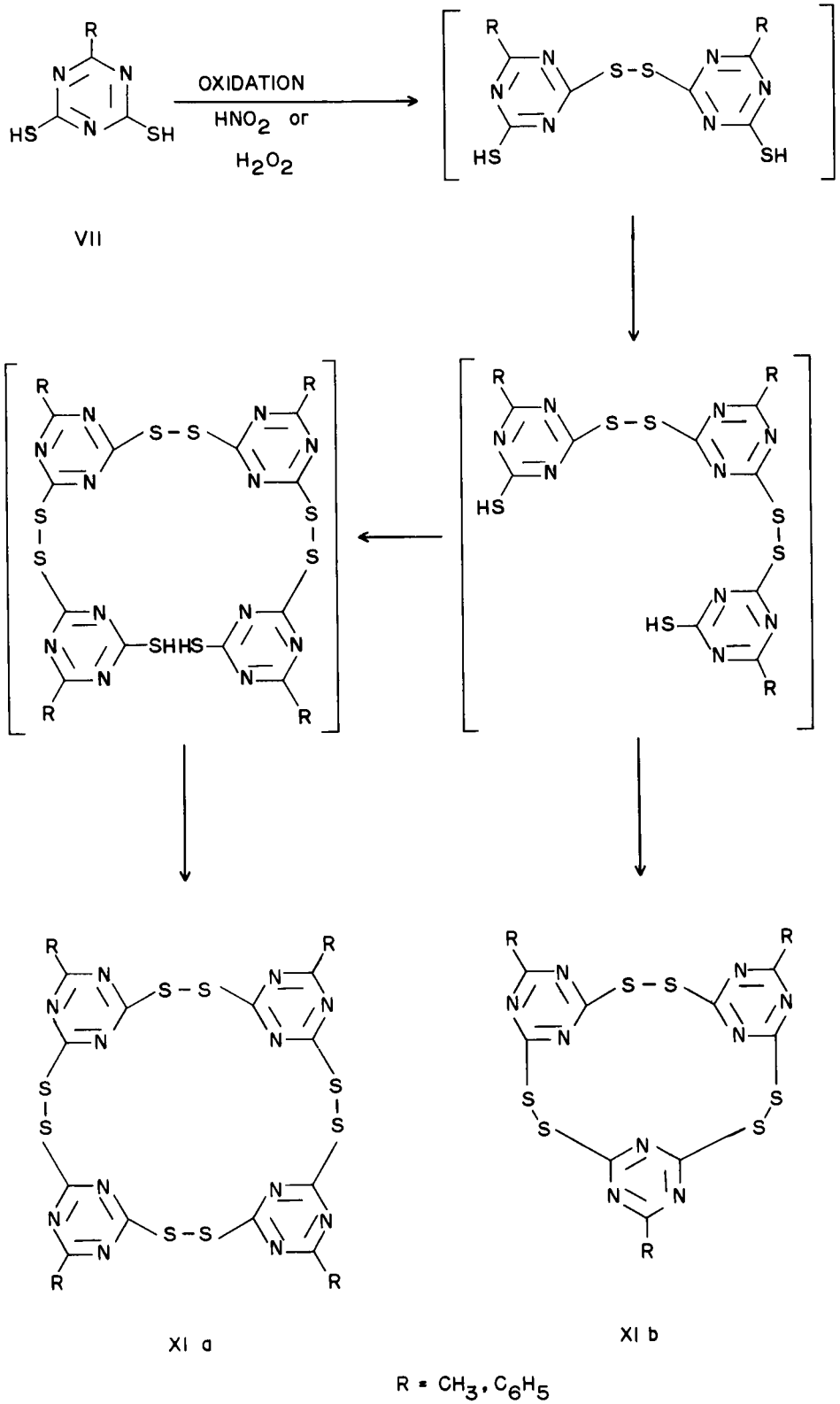


CHART 3



that cyclization at an early stage is favored in dilute solution, so, at this point further reaction with sodium sulfide can be expected to result in cyclization to give a mixture of trimeric and tetrameric cyclopoly-2-phenyl-*s*-triazinylene-4,6-monosulfide (VIa and VIb).

In an attempt to isolate and identify some of the proposed -A-B type monomer, 2-phenyl-4-chloro-*s*-triazine-6-thiol (II), a solution of sodium hydrosulfide in dry methanol was added dropwise to a solution of 2-phenyl-4,6-dichloro-*s*-triazine (I) in cold acetone at 0-5°. A mixture of products consisting of cyclopoly-2-phenyl-*s*-triazinylene-4,6-monosulfide (VIa and VIb), 2,2'-thiobis-(4-chloro-6-phenyl-*s*-triazine) (III), 2-phenyl-*s*-triazine-4,6-dithiol (VII) and unreacted 2-phenyl-4,6-dichloro-*s*-triazine (I) were found, but none of the -A-B-type monomer, 2-phenyl-4-chloro-*s*-triazine-6-thiol (II).

The presence of 2,2'-thiobis-(4-chloro-6-phenyl)-*s*-triazine (III) in the reaction mixture suggests that II may have been formed in *situ*, and, because of high reactivity due to the electronegative chlorine substituent in the *meta* position to the sulfhydryl group, reacted immediately with 2-phenyl-4,6-dichloro-*s*-triazine (I) or with itself. Neither the linear trimer (IV) or the linear tetramer (V) could be isolated from the reaction mixture.

An attempt was made to prepare the linear trimer 2-phenyl-*s*-triazinylene-4,6-bis(2'-thio-4'-phenyl-*s*-triazine-6'-thiol) (IX) by reaction of one mole of 2-phenyl-dichloro-*s*-triazine (I) with an excess of two moles of 2-phenyl-*s*-triazine-4,6-dithiol (VII) and two equivalents of sodium ethylate. The chief product of the reaction was again a cyclopoly-2-phenyl-*s*-triazinylene-4,6-monosulfide (VIa, VIb), m.p. 263-264°, having a molecular weight of 688 (D.P. = 3.7) along with unreacted VII. None of the linear trimer (IX) could be found.

One would expect 2-phenyl-4,6-dichloro-*s*-triazine (I) and 2-phenyl-*s*-triazine-4,6-dithiol (VII) to react with each other in a manner as suggested by the scheme depicted in Chart 2 (which excludes cyclotrimer formation) to give a cyclotetramer (VIb). However, insufficient sample of the product of this reaction (D.P.; 3.7) was available for further purification. Nevertheless, it appears to be reasonable to infer that the degree of polymerization of the cyclopoly-2-phenyl-*s*-triazinylene-4,6-monosulfide prepared by the methods described is limited to a maximum of 4.

A thermogravimetric analysis was run on a sample of cyclopoly-2-phenyl-*s*-triazinylene-4,6-monosulfide (VIa, VIb) (Figure 1).

Subsequently, the formation of cyclic triazinylene disulfides by oxidation of 2-methyl-*s*-triazine-4,6-dithiol and 2-phenyl-*s*-triazine-4,6-dithiol was demonstrated. Nitrous acid oxidation of 2-phenyl-*s*-triazine-4,6-dithiol (VII) resulted in formation of a cyclopoly-2-phenyl-*s*-triazinylene-4,6-disulfide (XI), m.p. 282-283° having a degree of polymerization of about 3.5. Its formation is illustrated in Chart 3. The corresponding cyclopoly-2-methyl-*s*-triazinylene-4,6-disulfide, m.p. 300° dec., was obtained by oxidation of 2-methyl-*s*-triazine-4,6-dithiol (II) with hydrogen peroxide.

EXPERIMENTAL

Molecular weights were determined by microebullioscopic techniques (5) using benzene, chlorobenzene or dioxane as the solvent, or by thermometric vapor pressure osmometry (6). Thermogravimetric analyses were run by heating 0.2 g. of the compound under nitrogen in a Chevenard type thermobalance (Adamel, Paris, France) to 900° at a heating rate of 150° per hour. Nitrogen values were obtained by the Kjeldahl method.

2-Methyl-4,6-dichloro-*s*-triazine, m.p. 98-100°, b.p. 185-189° was prepared by the Grignard reaction according to the method of Hirt, Nidecker, and Berchtold (7), and 2-phenyl-4,6-dichloro-*s*-triazine (I) was prepared by the Grignard reaction from cyanuric chloride and bromobenzene in 85-95% yield. Ostrogovitch (8) reported a low yield of this compound. 2-Phenyl-*s*-triazine-4,6-dithiol (VII) was prepared by the method of Fairful and Peak (9).

2-Methyl-*s*-Triazine-4,6-dithiol.

A solution of 63.5 g. (0.264 mole) of sodium sulfide nonahydrate was treated in 200 ml. of water with a solution of 15.8 g. (0.264 mole) of glacial acetic acid in 50 ml. of water at 15-20°. This sodium hydrosulfide solution was stirred at room temperature and treated dropwise with a solution of 9.84 g. (0.06 mole) of 2-methyl-4,6-dichloro-*s*-triazine in 300 ml. of dioxane. The green solution was treated with excess cold dilute acetic acid. No precipitation occurred. The reaction mixture was evaporated to dryness in a hood air stream. The light yellow residue, 8.8 g., was stirred into 50 ml. of hot dioxane and the inorganic material was filtered off. A yellow-white granular solid precipitated on cooling, yield 6 g. (64%), m.p. 252-256° dec. Its equivalent weight was determined by electrometric titration to *p*H = 9.2 in alcohol with 0.1 *N* sodium hydroxide solution. Equivalent Weight: Calcd. for $C_4H_5N_3S_2$: 159.2. Found: 157.5.

Anal. Calcd. for $C_4H_5N_3S_2$: C, 30.17; H, 3.16; N, 26.40; S, 40.27; Cl, 0.00. Found: C, 30.11; H, 3.22; N, 26.57; S, 40.15; Cl, 0.00.

Cyclopoly-2-Methyl-*s*-Triazinylene-4,6-Monosulfide.

A sodium hydrosulfide solution was prepared from 14.4 g. (0.06 mole) of sodium sulfide nonahydrate in 100 ml. of water by dropwise treatment in the cold with a solution of 3.6 g. (0.06 mole) of glacial acetic acid in 100 ml. of water. This sodium hydrosulfide solution was added dropwise at room temperature over one and one half hours to a solution of 10.1 g. (0.06 mole) of 2-methyl-4,6-dichloro-*s*-triazine in 250 ml. of dioxane. The yellowish-white residue (14 g.) was extracted with boiling chlorobenzene and 8.5 g. of water soluble material was filtered off. The chlorobenzene was distilled off leaving 6 g. of a yellowish-white residue, yield 80%, m.p. 212-215°.

Molecular weight (ebullioscopic, benzene): Calcd. for $(C_4H_3N_3S)_3$: 375.4. Found: 361 (D.P. = 2.88).

Anal. Calcd. for $(C_4H_3N_3S)_n$: C, 38.39; H, 2.41; N, 33.58; S, 25.62; Cl, 0.00. Found: C, 38.93; H, 2.85; N, 33.20; S, 25.27; Cl, 0.00.

Cyclopoly-2-Phenyl-*s*-Triazinylene-4,6-Monosulfide (VIa, VIb).

(a) By reaction of 2-phenyl-4,6-dichloro-*s*-triazine with sodium sulfide.

A solution of 6 g. (0.025 mole) of sodium sulfide nonahydrate in 17 ml. of water was added dropwise to a solution of 5.7 g. (0.026 mole) of 2-phenyl-4,6-dichloro-*s*-triazine (I) in 600 ml. of refluxing dioxane over 75 minutes. The sodium chloride (2.9 g.) was filtered off and the hot filtrate was treated with charcoal, filtered, and cooled. A white fibrous compound precipitated on cooling, yield 5.4 g. (92%), m.p. 263-264° dec.

Molecular weight (V.P.O. benzene): Calcd. for $(C_9H_5N_3S)_3$: 561.1. Found: 638 (D.P. = 3.4).

When the reaction was run at room temperature, VIa, VIb, was obtained in 86% yield, m.p. 263-264° dec.

Molecular weight (ebullioscopic, benzene): Calcd. for $(C_9H_5N_3S)_3$: 561.6. Found: 531 (D.P. = 2.8).

Anal. Calcd. for $(C_9H_5N_3S)_n$: C, 57.74; H, 2.69; N, 22.44; S, 17.13; Cl, 0.00. Found: C, 57.95; H, 2.69; N, 22.28; S, 16.95; Cl, 0.00.

This product (2.1 g.) was fractionally crystallized from dioxane (yield 0.66 g.), then from benzene giving 0.48 g. of white fibrous needles, m.p. 263-264° dec.

Molecular weight (ebullioscopic, benzene): Calcd. for $(C_9H_5N_3S)_4$: 748. Found: 758 (D.P. = 4.1).

Anal. Calcd. for $(C_9H_5N_3S)_n$: C, 57.74; H, 2.69; N, 22.44; S, 17.13. Found: C, 57.70; H, 2.50; N, 22.52; S, 17.09.

(b) By reaction of 2-phenyl-4,6-dichloro-*s*-triazine (I) and 2-phenyl-*s*-triazine-4,6-dithiol (VII) (sodium ethylate as the acid acceptor); 2-phenyl-*s*-triazinylene-4,6-bis-(2'-thio-4'-phenyl-*s*-triazine-6'-thiol (IX) (attempted).

A solution was prepared by the addition of 4.42 g. (0.02 mole) of 2-phenyl-*s*-triazine-4,6-dithiol (VII) to alcoholic sodium ethylate (from 0.46 g. (0.02 eq.) of sodium metal and 300 ml. of alcohol). The solution was stirred at 70° and treated dropwise with 2.26 g. (0.01 mole) of 2-phenyl-4,6-dichloro-*s*-triazine (I) in 100 ml. of dioxane over several hours. Evaporation of the solvents left a yellow residue (7 g.) which was stirred into 200 ml. of hot dioxane. The sodium chloride (1.1 g.) was filtered off and evaporation of the solvent left 6 g. of a yellow residue. This solid was then stirred into 150 ml. of boiling benzene. The yellow benzene insoluble material (2.5 g.) was recrystallized from alcohol and identified as 2-phenyl-*s*-triazine-4,6-dithiol (VII) (2 g., m.p. 245-247°). The benzene solution was treated with charcoal and filtered hot. The filtrate after concentration to 50 ml., and cooling gave 2.0 g. of white fibrous crystalline material, m.p. 263.5-264° dec. (recrystallized once from dioxane and once from benzene).

Molecular weight (ebullioscopic, chlorobenzene): Calcd. for $(C_9H_5N_3S)_3$: 561. Found: 688 (D.P. = 3.7).

Anal. Calcd. for $(C_9H_5N_3S)_n$: C, 57.74; H, 2.69; N, 22.44; S, 17.13; Cl, 0.00. Found: C, 57.70; H, 2.78; N, 22.26; S, 17.06; Cl, 0.00.

2-Phenyl-4-Chloro-*s*-Triazine-6-Thiol (II) (Attempted).

Hydrogen sulfide gas (1 ml.) was condensed in a trap in a dry ice-acetone bath, then warmed slightly and allowed to bubble through a fritted glass gas dispersion tube into a sodium methylate solution from 0.575 g. (0.025 eq.) of sodium metal and 100 ml. of reagent grade methanol. The resulting methanolic sodium hydrosulfide was added dropwise to a solution of 5.26 g. (0.023 mole) of 2-phenyl-4,6-dichloro-*s*-triazine (III) in 100 ml. of reagent grade acetone at 0-5° over one hour. The solvents were evaporated off at room temperature and the residue (6.2 g.) was dried *in vacuo*. The dry residue was dissolved in 150 ml. of acetone. The inorganic material (1.1 g.) was insoluble in acetone and was filtered off. It was water soluble and gave a positive test for chloride ion. The acetone soluble product (5.1 g.) was partly soluble in hot benzene (150 ml.); 1.9 g. of insoluble material was filtered off. The benzene solution was treated with charcoal, filtered and concentrated to 50 ml. On cooling, 3.0 g. of a white fibrous material precipitated, m.p. 263.5-264° dec.

Anal. Calcd. for $(C_9H_5N_3S)_n$: C, 57.74; H, 2.69; N, 22.44; S, 17.13; Cl, 0.00. Found: C, 57.88; H, 2.99; N, 22.24; S, 16.96; Cl, 0.00.

Evaporation of the benzene filtrate to dryness left 0.8 g. of a white residue which was extracted with eight 50 ml. portions of petroleum ether. The insoluble material (0.3 g.), m.p. 196-198° was identified as 2,2'-thiobis-(4-chloro-6-phenyl)-*s*-triazine (III) (2).

Anal. Calcd. for $C_{18}H_{10}Cl_2N_6S$: C, 52.30; H, 2.44; N, 20.33; S, 7.76; Cl, 17.17. Found: C, 52.69; H, 2.79; N, 19.98; S, 7.84; Cl, 16.03.

The benzene insoluble material (1.9 g.) was a yellow solid, which was taken up in 50 ml. of water treated with charcoal, and filtered. The filtrate was poured into dilute acetic acid giving a precipitate (0.8 g.), m.p. 245-247°, identified as 2-phenyl-*s*-triazine-4,6-dithiol (VII).

The petroleum ether extracts on evaporation to dryness left 0.4 g. of unreacted 2-phenyl-4,6-dichloro-*s*-triazine (I), m.p. 116-119°.

Cyclopoly-2-Methyl-*s*-Triazinylene-4,6-Disulfide.

A solution was prepared from 3.4 g. (0.02 mole) of 2-methyl-*s*-triazine-4,6-dithiol and 1.6 g. (0.02 mole) of sodium hydroxide in 150 ml. of water. The *p*H was adjusted to 7.0 with dilute acetic acid and 23 ml. of 3% hydrogen peroxide was added dropwise with stirring. A white precipitate formed. This was filtered off, washed with water, and oven dried at 120°, yield 1 g. The filtrate was treated with more hydrogen peroxide until no more precipitation occurred, total yield, 2.9 g. (92%). The product was insoluble in known solvents.

Anal. Calcd. for $(C_4H_3N_3S_2)_n$: C, 30.56; H, 1.92; N, 26.73; S, 40.79. Found: C, 30.61; H, 1.98; N, 26.57; S, 40.55.

Cyclopoly-2-phenyl-*s*-Triazinylene-4,6-Disulfide (XI).

A solution was prepared from 6.6 g. (0.03 mole) of 2-phenyl-*s*-triazine-4,6-dithiol (VII) and 2.4 g. (0.06 mole) of sodium hydroxide in 100 ml. of water. The slightly opalescent solution was treated with charcoal and filtered. Sodium nitrite (4.2 g., 0.06 mole) was added to the clear filtrate and this solution was added dropwise to a solution of 7.8 g. (0.13 mole) of glacial acetic acid in 242 ml. of water at 50°. The temperature rose to 90° during the addition. The white precipitate was filtered off, washed with water and dried at 140°, yield 6.3 g. (96%). It was recrystallized from chlorobenzene, m.p. 263-266°. After extraction with cold benzene and subsequent recrystallization from dioxane, a pure product was obtained, m.p. 282-283° dec.

Molecular weight (ebullioscopic, benzene): Calcd. for $(C_9H_5N_3S_2)_3$: 657.8. Found: 770 (D.P. = 3.52).

Anal. Calcd. for $(C_9H_5N_3S_2)_n$: C, 49.29; H, 2.30; N, 19.17; S, 29.24. Found: C, 49.43; H, 2.52; N, 18.89; S, 28.99.

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