A total of 41 ml (0.40 equiv) of caustic dispersion was added over 7 min to the ketone solution at 45°. Stirring was continued for 20 min, and the mixture was then heated to 86° over 0.5 hr to azeotropically remove additional water. The hot mixture was immediately filtered, using additional ketone to wash the filter cake. Removal of volatile components at pot temperatures up to 108° at 35 mm gave 254 g (85% yield) of low-melting epoxy residue with 1.07% chlorine content and a 122 epoxide equiv wt. Three recrystallizations at 5, 25, and 25° from 20% methanolic solutions gave 77 g of crystalline triglycidyl isocyanurate with a mp 100–104°, a 103 epoxide equiv wt (theory, 99), and a 0.3% chlorine content.

Racemic Modifications of Triglycidyl Isocyanurate.[2]—Extraction of 20 g of the above crystalline product with 80 g of hot methanol permitted separation of the two racemic modifications. The more soluble modification was recrystallized from methanol, and the other from Methyl Cellosolve, to obtain analytical samples for characterization.

The more soluble modification melted at 103–104.5° and had a 99.7 epoxide equiv wt. Its infrared spectrum (mineral oil mull) contained a strong absorption band at 5.90 μ, no band in the region of 6.4 μ, and moderate absorption bands at 10.25, 11.80, 12.55, and 13.10 μ. Infrared data indicated that heating for 6 hr at 160° under nitrogen caused slight decomposition.

Anal. Calcd for $C_{12}H_{15}N_3O_6$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.6, 48.5; H, 4.96, 5.18; N, 13.9, 13.9.

The less soluble modification melted at 156–157.5° and had a 101 epoxide equiv wt. Its infrared spectrum contained a strong absorption band at 5.90 μ, a very minor band (0.03 optical density) at 6.45 μ, and moderate absorption bands at 10.10, 10.75, 11.15, 12.15, 12.70, and 13.25 μ. The infrared spectrum remained unchanged when the modification was held at 165° for 8 hr under nitrogen.

Anal. Found: C, 48.4, 48.4; H, 5.07, 5.01; N, 14.4, 14.7.

Registry No.—I, 2451-62-9.

Studies in the Heterocyclic Series. I. A Novel Diazaphenothiazine System

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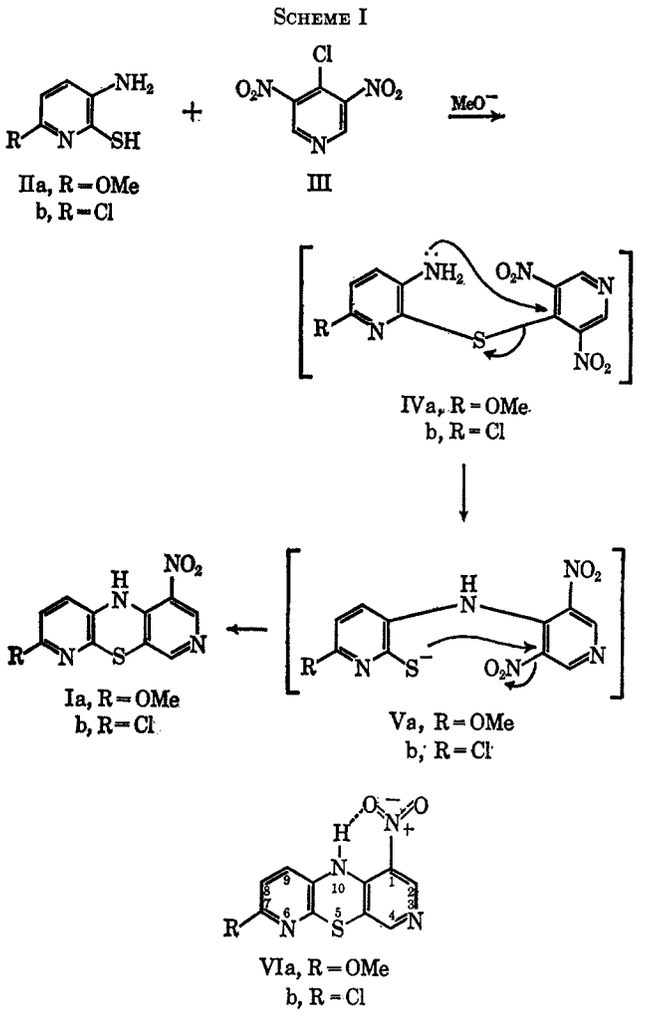
Continued interest in phenothiazines[1] has led to syntheses of 1-aza-,[2] 2-aza-,[3] 3-aza-,[4] 4-aza-,[5] 1,3-diaza-,[6] and 1,6-diazaphenothiazines.[7] In the present paper is reported the synthesis of 3,6-diazaphenothiazines (Ia, R = OMe; Ib, R = Cl) which form another variation of the phenothiazine system. A convenient route to this type of compound involves the condensation of the appropriate 3-amino-2-mercaptopyridine (IIa, R = OMe; IIb, R = Cl) with 3,5-dinitro-4-chloropyridine (III)[8] in the presence of excess base *via* Smiles rearrangement and cyclization. The aminomercaptopyridines were obtained by converting the appropriate aminopyridines to the corresponding 2-aminothiazolo[5,4-*b*]pyridines followed by base-catalyzed hydrolysis.[5] This method is preferred to the alternative method reported which led to a violent explosion during the conversion of nicotinamide to the chloroaminoderivative.[9] Equimolar quantities of the aminomercaptopyridines (IIa, R = OMe; IIb, R = Cl) and III were condensed in methanolic potassium hydroxide to yield the 4′-(3,5-dinitro)pyridyl-3-amino-2-pyridyl sulfides (IVa, R = OMe; IVb, R = Cl). In excess base, the aminodiaryl sulfides IV underwent Smiles rearrangement to the potassium salts of 4′-(3,5-dinitro)pyridyl-2-mercapto-3-aminopyridines (V). The latter products are rather unstable and their instability was used to advantage when they spontaneously cyclized to the more stable 3,6-diazaphenothiazines (Ia, R = OMe; Ib, R = Cl) (Scheme I).

Because of the proximity of the N-10 proton to the 1-nitro group, it is possible that a six-membered chelate

SCHEME I



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of high stability may be formed through strong NHO hydrogen bonding[10] (VIa, R = OMe; VIb, R = Cl). Evidence for this chelation is found in the infrared spectrum of Ia, in which the single NH-stretching frequency is shifted from 3500–3310 to 3295 cm^{-1}. The shift in the N=O frequency[11] from 1340 to 1316 cm^{-1} confirms the chelation and the assigned structure.

Experimental Section

Melting points were determined in capillary tubes on an electrothermal apparatus and were corrected. Although not usually specified, infrared spectra were taken of all compounds using Perkin-Elmer Model 237 spectrophotometer. Unless specified, the spectra were taken in Nujol mulls and were used in conjunction with melting points and analyses to determine the structures of the products.

2-Aminothiazolo[5,4-*b*]pyridines.—These compounds were prepared as described in the literature[12] but with some modifications. During the addition of bromine in glacial acetic acid, the temperature was never allowed to exceed −20°. The orange residue on filtering was extracted with boiling acetone. The acetone extract was concentrated *in vacuo* leaving the acetic acid salt which was neutralized with dilute sodium hydroxide to give the desired product. More of this thiazolopyridine was obtained upon neutralizing the original filtrate with sodium carbonate (to pH 5.5) as reported. This technique led to increased yields (83–90.5%) compared with 50–60% yields if these compounds were prepared as reported.[12]

3-Amino-2-mercaptopyridines.—The compounds II were obtained from 2-aminothiazolo[5,4-*b*]pyridines as described in the literature[5a] except that the reflux time was increased from 1 to 3 hr to avoid partial hydrolysis which was observed with 2-amino-5-methoxythiazolo[5,4-*b*]pyridine.

3,5-Dinitro-4-hydroxypyridine.—The preparation of 3,5-dinitro-4-hydroxypyridine from 4-hydroxypyridine has been reported.[8a] Its preparation from 3-nitro-4-hydroxypyridine is therefore described. 4-Hydroxypyridine (mp 146–147°, lit.[13] mp 147–151°) was prepared from pyridine and converted to 3-nitro-4-hydroxypyridine (mp 278–279°, lit.[8b] mp 278–279°). To a cooled (0°) and well-stirred mixture of fuming nitric acid (225 ml) and 30% oleum (200 ml) was added 3-nitro-4-hydroxypyridine (140 g, 1.0 mole) at such a rate that the temperature never exceeded 50°. After the addition, the ice bath was removed and the mixture was stirred below 100° for 24 hr and at 140° for another 24-hr period. The mixture was cooled, poured into ice, and partially neutralized with concentrated ammonia solution. The product was collected and recrystallized from hot water giving light yellow platelets of 3,5-dinitro-4-hydroxypyridine (170.2 g, 92%): mp >300°; ν_{max} 1950, 1830, 1650, 1605, 1545, 1525, 1345, 1240, 1190, 1155, 1105, 1060, 980, 952, 920, 875, 827, 788, 758, and 703 cm^{-1}.

Anal. Calcd for $C_5H_3N_3O_5$: C, 32.44; H, 1.63; N, 22.70. Found: C, 32.31; H, 1.73; N, 22.61.

4-Chloro-3,5-dinitropyridine (III).—A mixture of 3,5-dinitro-4-hydroxypyridine (18.5 g, 0.1 mole), phosphorus pentachloride (38 g, 0.156 mole), and phosphoryl chloride (5.0 ml) was refluxed on an oil bath at 140–150° for 3 hr. The phosphorus halides were removed by distillation and the dark residue was extracted with five successive 100-ml portions of boiling light petroleum ether (bp 60–80°). The solvent was removed by distillation leaving a brown solid (16 g, 78.5%) which was used in the next stage of the synthesis without further purification, mp 236–239°.

1-Nitro-7-methoxy-3,6-diazaphenothiazine (Ia).—3,5-Dinitro-4-chloropyridine (III, 12.3 g, 0.06 mole) was added a little at a time to a stirred mixture of 6-methoxy-3-amino-2-mercaptopyridine (7.0 g, 0.045 mole) and 85% potassium hydroxide (6.6 g, 0.1 mole) in anhydrous methanol. The pH of the solution was measured from time to time and more methanolic potassium hydroxide was added to ensure that the solution remained basic (pH 8.5). The 4′-(3,5-dinitro)pyridyl-3-amino-6-methoxy-2-pyridyl sulfide (IVa, R = OMe) formed, rearranged to the diarylamine (Va, R = OMe), which, in the presence of excess base, cyclized to the desired product. The dark purple mixture was stirred for 3 hr at room temperature and filtered. The residue was washed with cold water to remove potassium salts. On filtering, a deep purple product was collected. The original dark purple filtrate was concentrated *in vacuo* to near dryness and, on mixing with water and filtering, another fraction of the product was collected. The combined product was recrystallized from acetone–ethanol mixture (1:1) after treatment with activated carbon giving 1-nitro-7-methoxy-3,6 diazaphenothiazine (Ia, 7.6 g, 61.3%) as deep, glistening, bluish purple platelets: mp 267–268° dec; ν_{max} 3295, 3025, 1605, 1570, 1510, 1440, 1425, 1395, 1316, 1300, 1275, 1250, 1225, 1195, 1175, 1150, 1130, 1100, 1025, 906, 880, 835, 820, 763, and 740 cm^{-1}.

Anal. Calcd for $C_{11}H_8N_4SO_3$: C, 47.82; H, 2.92; N, 20.28; S, 11.61. Found: C, 47.64; H, 3.00; N, 20.23; S, 11.70.

1-Nitro-7-chloro-3,6-diazaphenothiazine (Ib).—This compound was prepared from 3,5-dinitro-4-chloropyridine (III, 6.1 g, 0.03 mole), 3-amino-6-chloro-2-mercaptopyridine (IIb, 3.22 g, 0.02 mole), and 85% potassium hydroxide (3.3 g, 0.05 mole) in a manner similar to that described for 1-nitro-7-methoxy-3,6-diazaphenothiazine (Ia). A 2.9-g yield (52%) of the glistening platelets (Ib) was obtained: mp 294–295° dec; ν_{max} 3270, 3030, 1590, 1575, 1545, 1506, 1326, 1280, 1234, 1182, 1135, 1095, 920, 905, 860, and 766 cm^{-1}.

Anal. Calcd for $C_{10}H_5ClN_4O_2S$: C, 42.78; H, 1.78; Cl, 12.66; N, 19.96; S, 11.41. Found: C, 42.65; H, 1.82; Cl, 12.62; N, 19.86; S, 11.52.

Registry No.—Ia, 10425-68-0; Ib, 10425-69-1; III, 10425-70-4; 3,5-dinitro-4-hydroxypyridine, 10425-71-5.

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The Reaction of Trichloromethyl Aromatic Compounds with Triethyl Phosphite

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Recent publications[1,2] describing the synthesis and the polymerization of $\alpha,\alpha,\alpha',\alpha'$-tetrachloro-*p*-xylylene prompt us to record some observations made during an investigation into the chemistry of aromatic trichloromethyl compounds. When $\alpha,\alpha,\alpha,\alpha',\alpha',\alpha'$-hexachloro-*p*-xylene (I) is heated with triethyl phosphite (II) in homogeneous solution above 100°, an extremely exothermic reaction occurs with evolution of a gas and copious precipitation of a white solid. The gaseous product was collected in a cold trap and identified as ethyl chloride (IV) by its infrared spectrum[3] and by elemental analysis. The colorless, solid product is an intractable material, insoluble in all solvents including hot, concentrated sulfuric acid; this product believed to

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