# REACTION OF AMINOTETRACHLOROPYRIDINES WITH SULFUR CHLORIDES

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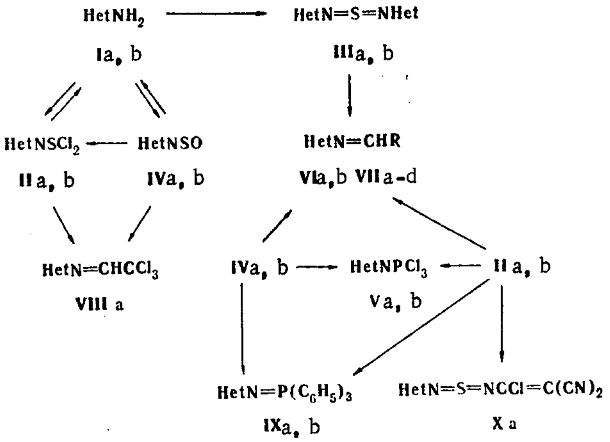
Tetrachloropyridyliminothionyl chlorides and bis(tetrachloropyridyl)diimides of sulfur were obtained by reactions of 2- and 4-aminotetrachloropyridines with sulfur dichloride; tetrachloropyridylthionylimines were obtained in reactions with thionyl chloride. Various aminotetrachloropyridine derivatives were synthesized by reaction of these compounds with aldehydes, phosphorus pentachloride, and triphenylphosphine oxide.

A number of aminotetrachloropyridine derivatives were synthesized in order to search for new plant-growth regulators.

The amino group in aminopolyhalopyridines has low nucleophilicity and does not undergo reaction in most cases. This inertness can usually be overcome by converting the amines to reactive iminothionyl derivatives. We therefore investigated the reactions of aminotetrachloropyridines with sulfur chlorides and also studied some of the properties of the compounds obtained.

2- and 4-Aminotetrachloropyridines (Ia, b) react with sulfur dichloride to give the corresponding imino compounds IIa, b. Sulfur diimides IIIa, b are formed in dichloroethane at a reagent ratio of 2:1. When Ia, b are heated with excess thionyl chloride, they form tetrachloropyridylthionylimines IVa, b in good yields, which are converted by the action of phosphorus pentachloride to iminothionyl chlorides IIa, b. The IR spectra of II-IV contain absorption bands at 1370 $cm^{-1}$ corresponding to vibrations of the N=S bond [1] and absorption bands of the stretching vibrations of the pyridine ring [2] (1570-1590 $cm^{-1}$).



I—VI, VIII—X a Het=tetrachloro-2-pyridyl; b Het=tetrachloro-4-pyridyl, $R=N(CH_3)_2$; VII a Het=tetrachloro-2-pyridyl, $R=C_6H_5$; b. Het=tetrachloro-4-pyridyl, $R=C_6H_5$; c Het=tetrachloro-2-pyridyl, $R=C_6H_5N(CH_3)_2$-*p*; d Het=tetrachloro-4-pyridyl, $R=C_6H_4N(CH_3)_2$-*p*

Tetrachloropyridylimino compounds II-IV are extremely reactive substances and, except for IIIb, are readily hydrolyzed by air moisture to aminopyridines Ia, b. The alkaline hydrolysis of IIIb proceeds similarly. 2- and 4-Trichlorophosphazotetrachloropyridines (Va, b) are formed by the action of phosphorus pentachloride on iminothionyl chlorides II and thionylimines IV. Compounds II-IV react with dimethylformamide (DMF) and aromatic alde-

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TABLE 1. Characteristics of the Synthesized Compounds

| Compound | mp, °C | Found, % | | | Empirical formula | Calc., % | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|
| | | Cl | N | S | | Cl | N | S | |
| IIIa | 131—132[a] | 57,8 | — | 6,5 | $C_{10}Cl_8N_4S$ | 57,7 | — | 6,5 | 81 |
| IIIb | 219—220[b] | — | 11,4 | 6,5 | $C_{10}Cl_8N_4S$ | — | 11,4 | 6,5 | 34 |
| IVa | 58[c] | 51,3 | — | 11,8 | $C_5Cl_4N_2OS$ | 51,0 | — | 11,5 | 92 |
| IVb | 70—72[c] | 51,4 | — | 11,5 | $C_5Cl_4N_2OS$ | 51,0 | — | 11,5 | 68 |
| IIa | 68—69[c] | 63,8 | — | 9,6 | $C_5Cl_6N_2S$ | 63,9 | — | 9,6 | 68 |
| IIb | 117[c] | 63,8 | — | 9,7 | $C_5Cl_6N_2S$ | 63,9 | — | 9,6 | 63 |
| Va | 65—67[c] | 67,3 | 8,3 | — | $C_5Cl_7N_2P$[d] | 67,6 | 8,4 | — | 71 |
| VIa | 97—98[e] | 49,4 | 14,7 | — | $C_8H_7Cl_4N_3$ | 49,3 | 14,6 | — | 87 |
| VIb | 111—112[e] | 49,4 | 14,7 | — | $C_8H_7Cl_4N_3$ | 49,3 | 14,6 | — | 87 |
| VIIa | 70—71[f] | 44,5 | 8,8 | — | $C_{12}H_6Cl_4N_2$ | 44,3 | 8,7 | — | 94 |
| VIIb | 134—135[a] | 44,6 | 8,6 | — | $C_{12}H_6Cl_4N_2$ | 44,3 | 8,7 | — | 81 |
| VIIc | 139—140[g] | 38,9 | 11,6 | — | $C_{14}H_{11}Cl_4N_3$ | 39,1 | 11,6 | — | 83 |
| VIId | 157—158[c] | 39,6 | 11,7 | — | $C_{14}H_{11}Cl_4N_3$ | 39,1 | 11,6 | — | 69 |
| VIII | 145—146[c] | 68,6 | 7,4 | — | $C_7HCl_7N_2$ | 68,7 | 7,7 | — | 97 |
| IXa | 95—96[e] | 28,7 | 5,5 | — | $C_{23}H_{15}Cl_4N_2P$[h] | 28,8 | 5,7 | — | 91 |
| Xa | 119—121[c] | 46,0 | — | 8,4 | $C_9Cl_5N_5S$ | 45,7 | — | 8,3 | 62 |

[a] From cyclohexane. [b] From $CCl_4$. [c] From petroleum ether. [d] Found: P 7.8%. Calculated: P 7.6%. [e] From alcohol. [f] From hexane. [g] From benzene. [h] Found: P 6.2%. Calculated: P 6.3%.

hydes to give formamidines VIa, b and benzylidene derivatives VIIa-d. Chloral reacts with IIa and IVa to give 2-(2,2,2-trichloroethylidene)amino-3,4,5,6-tetrachloropyridine (VIII). Iminothionyl compounds II and IV react with triphenylphosphine oxide to give 2- and 4-triphenylphosphazotetrachloropyridines (IXa, b). Sulfur N-(3,4,5,6-Tetrachloro-2-pyridyl)-N'-(1-chloro-2,2-dicyanovinyl)diimide (Xa) was obtained by reaction of IIa with the sodium salt of tricyanomethane.

## EXPERIMENTAL

The IR spectra of $CCl_4$ solutions or KBr pellets of the compounds were recorded with a UR-20 spectrometer.

The characteristics of the compounds obtained are presented in Table 1.

Sulfur Bis(3,4,5,6-tetrachloro-2-pyridyl)diimide (IIIa). A mixture of 2.32 g (10 mmole) of Ia, 0.5 g (5 mmole) of sulfur dichloride, and 25 ml of dichloroethane was refluxed for 4 h until hydrogen chloride ceased. The solvent was then removed by vacuum evaporation, and the residue (dark-red needles) was crystallized.

Sulfur Bis(2,3,5,6-tetrachloro-4-pyridyl)diimide (IIIb). A) This compound was similarly obtained as yellow prisms form Ib by refluxing the reaction mixture for 8 h.

B) A mixture of 2.32 g (10 mmole) of Ib, and 12 ml of sulfur dichloride was refluxed for 4 h until the solid dissolved completely, after which the mixture was cooled, and the solidified product was crystallized to give 0.96 g (40%) of a product with mp 219-220°C.

3,4,5,6-Tetrachloro-2-pyridylthionylimine (IVa). A mixture of 2.32 g (10 mmole) of Ia and 15 ml of thionyl chloride was refluxed for 3 h until HCl evolution ceased. The excess thionyl chloride was removed by vacuum distillation to give the product in the form of orange crystals.

2,3,5,6-Tetrachloro-4-pyridylthionylimine (IVb). This compound was similarly obtained in the form of yellow crystals from Ib and thionyl chloride by refluxing the mixture for 15 h.

3,4,5,6-Tetrachloro-2-pyridyliminothionyl Chloride (IIa). A) A mixture of 2.32 g (10 mmole) of Ia and 12 ml of sulfur dichloride was refluxed for 2 h until HCl evolution ceased and the solid dissolved completely, after which the excess sulfur dichloride was removed in vacuo to give the product in the form of yellow crystals.

B) A mixture of 2.78 g (10 mmole) of IVa, 2.08 g (10 mmole) of phosphorus pentachloride, and 15 ml of $CCl_4$ was refluxed for 6 h, after which the solvent was removed in vacuo, and the residue was crystallized to give 1.2 g (36%) of a product with mp 67-68°C.

2,3,5,6-Tetrachloro-4-pyridyliminothionyl Chloride (IIb). A) This compound was similarly obtained in the form of yellow crystals by refluxing Ib with sulfur dichlroide for 8 h.

B) This compound [1 g (30%)], with mp 116-117°C, was similarly obtained from IVb.

2-Amino-3,4,5,6-tetrachloropyridine (Ia). A) Water (50 ml) was added to a solution of 2.46 g (5 mmole) of IIIa in 5 ml of dioxane, and the resulting precipitate was removed by filtration and washed with water to give the product, with mp 172-173°C (from methanol) (mp 174-175°C [3]), in quantitative yield. No melting-point depression was observed for a mixture of this product with a genuine sample.

B) This compound was similarly obtained in quantitative yield from IVa (95%) and IIa.

4-Amino-2,3,5,6-tetrachloropyridine (Ib). A) A total of 3 ml of 30% KOH was added to a solution of 2.46 g (5 mmole) of IIIb in 20 ml of dioxane, and the mixture was shaken and treated with 100 ml of water. The reaction product was removed by filtration and washed with water to give 2 g (86%) of a product with mp 211-212°C (from acetone–heptane) (mp 214-215°C [4]).

B) This compound was similarly obtained in quantitative yield from IVb (78%) and IIb.

2-Trichlorophosphazo-3,4,5,6-tetrachloropyridine (Va). A) A mixture of 2.78 g (10 mmole) of IVa and 4.16 g (20 mmole) of ground $PCl_5$ was heated at 150°C for 30 min, after which the excess $PCl_5$ was removed in vacuo, and the solidified mass was recrystallized from petroleum ether.

B) This compound was similarly obtained in 74% yield from IIa and had mp 66°C.

4-Trichlorophosphazo-2,3,5,6-tetrachloropyridine (Vb). This compound was similarly obtained from IIb (79%) and IVb (68%) and had mp 86-87°C [5].

N,N-Dimethyl-N'-(3,4,5,6-tetrachloro-2-pyridyl)formamidine (VIa). Dimethylformamide (5 ml) was added to 0.49 g (1 mmole) of IIIa, and the mixture was refluxed for 2 h. It was then cooled and treated with 20 ml of water, and the resulting precipitate was removed by filtration, washed with water, and dried.

B) This compound was similarly obtained from IVa (90%) and IIa (70%) and had mp 97-98°C.

N,N-Dimethyl-N'-(2,3,5,6-tetrachloro-4-pyridyl)formamidine (VIb). This compound was similarly obtained from IIb, IIIb, and IVb. The yields were 9.41 g (72%) and 0.51 g (89%).

2-Benzylideneamino-3,4,5,6-tetrachloropyridine (VIIa) and 4-Benzylideneamino-2,3,5,6-tetrachloropyridine (VIIb). A) A mixture of 2.46 g (5 mmole) of IIIa or IIIb, 1.1 g (10 mmole) of benzaldehyde, and 10 ml of benzene was refluxed for 4 h until sulfur dioxide evolution ceased, after which the benzene was removed in vacuo.

B) These compounds can also be synthesized from II or IV.

2-(p-Dimethylaminobenzylideneamino)-3,4,5,6-tetrachloropyridine (VIIc) and 4-(p-Dimethylaminobenzylideneamino)-2,3,5,6-tetrachloropyridine (VIId). A) A mixture of 0.56 g (2 mmole) of IVa or IVb, 0.3 g (2 mmole) of p-dimethylaminobenzaldehyde, and 5 ml of benzene was refluxed for 4 h, after which the solvent was removed in vacuo, and the residue was crystallized to give the product in the form of orange needles.

B) These compounds were similarly obtained from IIa, b.

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