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Pyridazines. II.

The Synthesis of Amino-, Azido- and Nitraminopyridazines, Tetrazolo[1,5-b]pyridazines and Related Nitrogen Heterocycles

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The remaining three diaminopyridazines, 3,4,5-triaminopyridazine and several nitraminopyridazines have been prepared. The structure of 3,4,5-triaminopyridazine and the 3,5-diamino-4-nitropyridazine precursor have been established by n.m.r. analysis. In addition 8-amino-6-chloro-, 8-amino-6-hydrazino- and 8-amino-6-azidotetrazolo-[1,5-b]pyridazine has been synthesized along with 4,6-dihydrazino- and 4,6-diazidopyrimidine. Several other chemical transformation of these compounds are described.

Gortinskaya and Shchukina (2) reported the synthesis of 3,6-diaminopyridazine by allowing 3-amino-6-chloropyridazine to react with aqueous ammonia under pressure. The synthesis of the remaining three diaminopyridazines is reported here.

For the synthesis of 3,5-diaminopyridazine (III), 5-amino-4-chloro-3-hydrazinopyridazine (I) (3) served as the starting material. The hydrazino group of I was catalytically cleaved with hydrogen and Raney nickel to give 4-chloro-3,5-diaminopyridazine (II) in 52% yield. 3,5-Diaminopyridazine (III) was obtained readily as the monohydrochloride in good yield by catalytic dechlorination of II in the presence of palladium on charcoal.

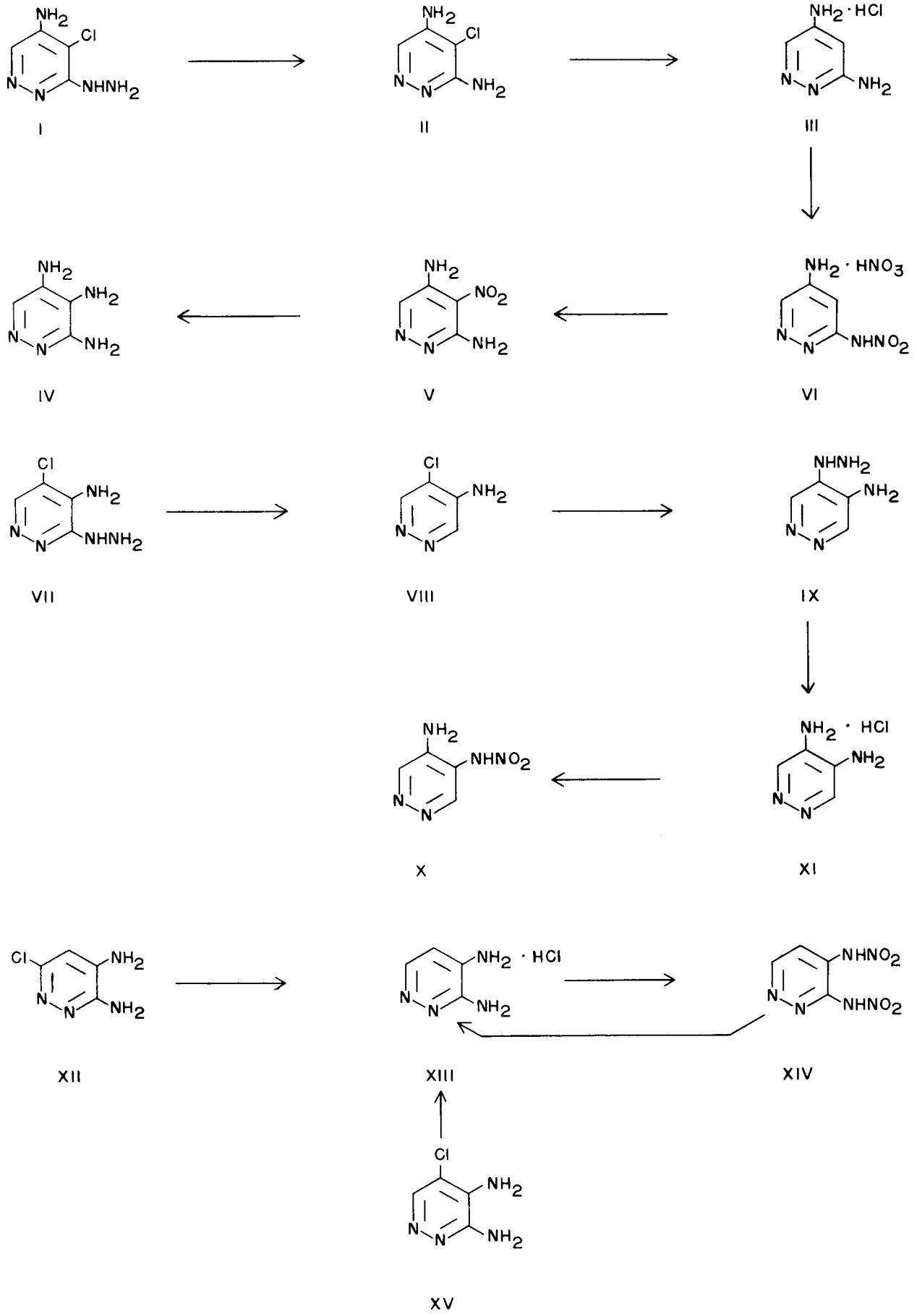
4,5-Diaminopyridazine (XI) was prepared from the key intermediate 4-amino-5-chloropyridazine (VIII) (3) which could be obtained from either 5-amino-4-chloro-3-hydrazinopyridazine (I) or 4-amino-5-chloro-3-hydrazinopyridazine (VII) or from mixtures of I and VII by removal of the hydrazino group in boiling cupric sulfate solution. When VIII was allowed to react with excess hydrazine without other solvent, 4-amino-5-hydrazinopyridazine (IX) was obtained in 47% yield. 4,5-Diaminopyridazine (XI) was obtained as the monohydrochloride by treatment of IX with hydrogen in the presence of Raney nickel in 46% yield.

3,4-Diaminopyridazine (XIII) was prepared in 53% yield by catalytic dechlorination of 3,4-diamino-6-chloropyridazine (XII) with hydrogen and palladium on charcoal. 3,4-Diamino-6-chloropyridazine (XII) was prepared by Kuraishi (4) by allowing 4-amino-3,6-dichloropyridazine to react with hydrazine. The resulting 4-amino-6-chloro-3-hydrazinopyridazine (XVIII) was readily cleaved into XII by hydrogenation in the presence of Raney nickel. That XII was correctly formulated, has been demonstrated by cyclization of XII into 6-chloro-*v*-triazolo[4,5-c]-pyridazine (5). Furthermore, XIII has also been prepared by catalytic dechlorination of 5-chloro-3,4-diaminopyridazine (XV) with hydrogen and palladium on charcoal. The constitution of XV has been established by cyclization to 7-chloro-*v*-triazolo[4,5-c]-pyridazine (5).

3,4,5-Triaminopyridazine (IV) has been prepared. The diamine (III) was converted into either 5-amino-3-nitraminopyridazine nitrate (VI) or into the isomeric 3-amino-5-nitraminopyridazine nitrate. Compound VI was readily rearranged into the 3,5-diamino-4-nitropyridazine (V). Compound V was smoothly hydrogenated in quantitative yield to 3,4,5-triaminopyridazine (IV) with Raney nickel. The position of the ring hydrogen in compounds IV and V is readily shown to be the 6-position by n.m.r. analysis. The amino groups attached to the ring causes an upfield shift from $\delta = 9.23$ (6) in unsubstituted pyridazine to $\delta = 8.59$ for V and $\delta = 8.41$ for IV. The hydrogens in the 4,5 positions have a shift of $\delta = 7.62$. It is suggested that VI is 5-amino-3-nitraminopyridazine nitrate since in this instance only the rearrangement product (V) is possible, whereas 3-amino-5-nitraminopyridazine could rearrange into two products, namely V or the isomeric 3,5-diamino-6-nitropyridazine which would have given 3,4,6-triaminopyridazine upon reduction. The fact that only one diaminonitropyridazine was isolated from the rearrangement of VI is taken as circumstantial evidence that VI has been correctly formulated.

When 4,5-diaminopyridazine (XI) was allowed to react with aqueous mixed acids at 0°, 4-amino-5-nitraminopyridazine (X) was obtained. 3,4-Dinitraminopyridazine (XIV) was prepared by allowing the diamine XIII to react with concentrated nitric acid in concentrated sulfuric acid at 0°. Compound XIV was shown to be the dinitramine by conversion of XIV back into XIII with hydrogen and Raney nickel. When 4-aminopyridazine (XVI) (7) was allowed to react with concentrated mixed acid at 5°, 4-nitraminopyridazine (XVII) was obtained in 83% yield. That XVII was a nitramine and not an aminonitropyridazine was established by conversion of XVII into XVI by hydrogenation with Raney nickel.

4-Amino-6-chloro-3-hydrazinopyridazine (XVIII)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Cl
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I
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NO2
NH2
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NH2
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IV
Cl
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VII
Cl
NH2
VIII
NHNH2
NH2
IX
NH2 · HCl
NH2
XI
NH2
NHNO2
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XIII
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XIV
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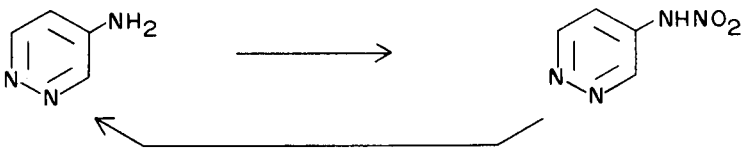
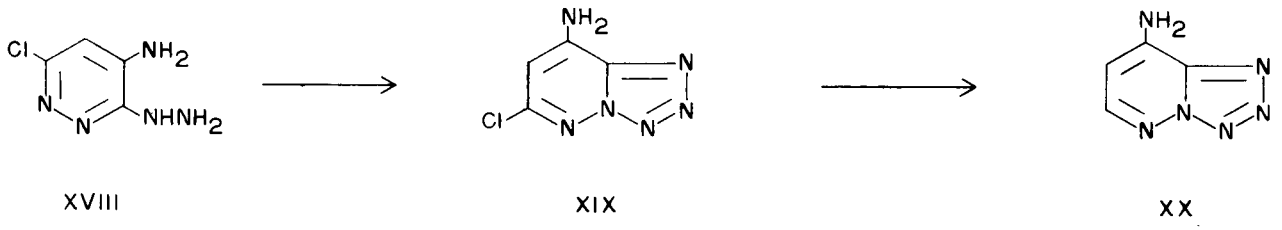
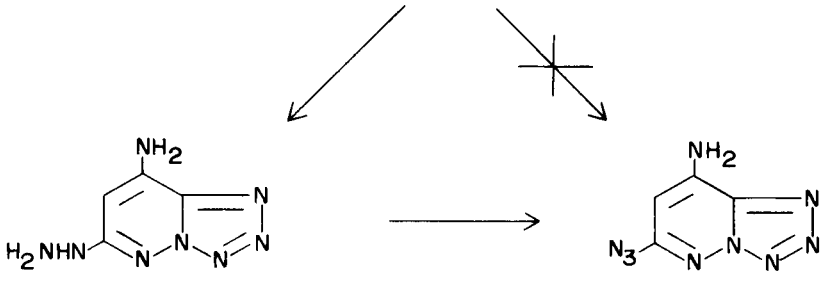
XV



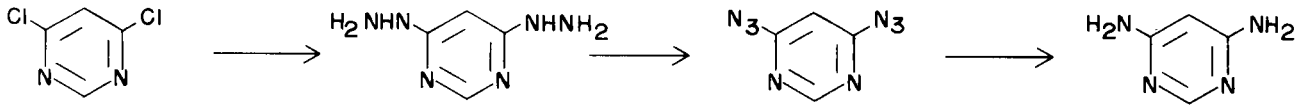
XVI XVII



XVIII XIX XX



XXI XXII



XXIII XXIV XXV XXVI

when allowed to react with nitrous acid at 0° readily produced 8-amino-6-chlorotetrazolo[1,5-b]pyridazine (XIX), isomeric with the 8-amino-6-chlorotetrazolo-[1,5-b]pyridazine previously reported (3). Compound XIX was readily dechlorinated with hydrogen in the presence of palladium on charcoal. The resulting 8-aminotetrazolo[1, 5-b]pyridazine (XX) was identical with that obtained by Kuraishi and Castle (3) from the catalytic dechlorination of 8-amino-7-chloro-tetrazolo[1, 5-b]pyridazine. With excess hydrazine without solvent, XIX was converted into 8-amino-6-hydrazinotetrazolo[1, 5-b]pyridazine (XXI) in 57% yield. Compound XXI was allowed to react with nitrous acid at room temperature, whereupon 6-azido-8-aminotetrazolo[1, 5-b]pyridazine (XXII) was obtained in 76% yield. Compound XXII was not obtained when XIX was allowed to react with ethanolic sodium azide in a sealed tube. Compound XXII was readily characterized by the intense azide absorption band at 2150 cm^{-1} in the infrared spectrum.

The availability of 4, 6-dichloropyrimidine (XXIII) (8) prompted us to prepare 4,6-dihydrazinopyrimidine (XXIV) from XXIII and excess hydrazine without additional solvent. Compound XXIV was converted smoothly into 4, 6-diazidopyrimidine by reaction with nitrous acid at room temperature. Compound XXV was readily characterized by the very strong azide absorption band at 2150 cm^{-1} in the infrared spectrum. To further establish that cyclization to the tetrazolopyrimidine had not occurred as in the pyridazine series, XXV was catalytically reduced with Raney nickel to the known 4,6-diaminopyrimidine (XXVI) (9). In our experience reduction of a tetrazolopyridazine ring has not been observed.

EXPERIMENTAL (10)

4-Chloro-3,5-diaminopyridazine II.

To a suspension of 10 g. (0.063 mole) of 5-amino-4-chloro-3-hydrazinopyridazine in 550 ml. of absolute ethanol was added approximately 8 g. of Raney nickel and the mixture hydrogenated at 55° and at atmospheric pressure. The catalyst was removed and the solution evaporated to dryness under reduced pressure. The residue was extracted with ethyl acetate in a soxhlet extractor yielding 4.7 g. (52%) of white product. The analytical sample was prepared from ethyl acetate (norite), m.p. 198°.

Infrared cm^{-1}: 3440 (s), 3380 (s), 3320 (s), 3270 (s), 3120 (s), 2800 (sh), 2650 (w), 2500 (sh), 2400 (w), 1660 (s), 1630 (s), 1600 (s), 1525 (s), 1500 (s), 1410 (s), 1380 (s), 1275 (m), 1170 (m), 1132 (m), 1031 (s), 853 (s), 825 (m), 750 (s), 730 (s), 646 (m), 630 (s), 575 (s), 540 (s), 520 (s), 470 (s), 450 (s).

Anal. Calcd. for $C_4H_5ClN_4$: C, 33.23; H, 3.49; N, 38.76. Found: C, 33.70; H, 3.88; N, 38.35.

3,5-Diaminopyridazine Hydrochloride III.

A suspension of 9.87 g. (0.0674 mole) of 4-chloro-3,5-diaminopyridazine in 500 ml. of absolute ethanol containing 2.74 g. of sodium hydroxide and 5% palladium on charcoal was hydrogenated at atmospheric pressure. After hydrogen ceased to be absorbed the catalyst was filtered and the solvent removed under reduced pressure. The free base was recrystallized with difficulty from ethanol, therefore isolation as the monohydrochloride was achieved as follows: an absolute ethanol solution of the free base was treated with dry hydrogen chloride gas, chilled and sufficient ether added to precipitate the salt, m.p. 268-269°. The crude free base yield was 7.3 g., 98%.

Infrared cm^{-1} (monohydrochloride): 3400 (s), 3290 (s), 3140 (s), 2930 (s), 2820 (s), 1900 (w), 1680 (s), 1650 (s), 1625 (s), 1610 (s), 1460 (s), 1450 (s), 1435 (s), 1400 (s), 1325 (w), 1260 (s), 1250 (s), 1025 (s), 980 (m), 900 (m), 850 (s), 835 (s), 810 (s), 765 (s), 680 (w), 630 (m), 565 (s), 535 (s), 460 (s), 440 (s).

Anal. Calcd. for $C_4H_7ClN_4$: C, 32.77; H, 4.81; N, 38.23. Found: C, 33.02; H, 5.02; N, 38.48.

3,4,5-Triaminopyridazine IV.

A suspension of 0.46 g. (0.003 mole) of 3,5-diamino-4-nitropyridazine in 200 ml. of absolute ethanol was catalytically hydrogenated (Raney nickel). After hydrogen ceased to be absorbed the catalyst was filtered and the solvent removed under reduced pressure. No suitable recrystallization solvent was found, therefore the compound was isolated as the monohydrochloride in a manner identical to that described for the 3,5-diaminopyridazine monohydrochloride, 0.253 g., 68%, m.p. 214-215°.

Infrared cm^{-1}: 3375 (s), 3300 (s), 3190 (s), 3100 (s), 3045 (s), 2975 (s), 1680 (s), 1630 (s), 1600 (s), 1570 (s), 1500 (m), 1475 (s), 1450 (s), 1400 (s), 1345 (s), 1300 (s), 1275 (m), 885 (s), 760 (s), 720 (s), 685 (m), 580 (s), 550 (s), 520 (s).

Anal. Calcd. for $C_4H_8ClN_5$: C, 29.73; H, 4.99; N, 43.34. Found: C, 29.84; H, 5.39; N, 43.43.

3,5-Diamino-4-nitropyridazine V.

The crude product (1.0 g.) obtained from the nitration of 3,5-diaminopyridazine monohydrochloride was added slowly to 6 ml. of concentrated sulfuric acid at 5° with stirring and allowed to come to room temperature followed by warming at 50-55° for 3 hours. This solution was then poured slowly on ice and neutralized with sodium bicarbonate. The resulting yellow solid was collected and washed with water. The filtrate was extracted three times with ethyl acetate, the extracts dried (anhydrous magnesium sulfate) and evaporated to dryness under reduced pressure. The additional yellow solid was combined with that obtained above and recrystallized from water, m.p. 291°.

Infrared cm^{-1}: 3475 (s), 3450 (s), 3425 (s), 3400 (s), 3325 (s), 3280 (s), 3120 (s), 3050 (s), 3000 (s), 2950 (s), 2810 (m), 2640 (m), 1625 (s), 1600 (s), 1530 (s), 1510 (s), 1480 (s), 1420 (s), 1400 (s), 1290 (s), 1270 (s), 1180 (m), 1160 (s), 1140 (s), 1100 (s), 1030 (s), 1020 (s), 860 (s), 795 (s), 780 (s), 720 (m), 660 (m), 640 (s), 620 (s), 585 (s), 560 (m), 475 (s), 430 (s), 415 (s).

Anal. Calcd. for $C_4H_5N_5O_2$: C, 30.97; H, 3.25; N, 45.15. Found: C, 31.38; H, 3.53; N, 45.30.

5-Amino-3-nitraminopyridazine Mononitrate VI.

To 5 ml. of concentrated sulfuric acid at 5° was added slowly 2 g. (0.0137 mole) of 3,5-diaminopyridazine monohydrochloride with stirring followed by dropwise addition of 2.5 ml. of concentrated nitric acid. This was allowed to come to room temperature and to stand for 30 minutes after solution was complete. This was then poured on ice and adjusted to *p*H 5.5 with sodium bicarbonate. The resulting yellow solid was collected, washed with cold water, boiled in ethanol and filtered to remove a small amount of insoluble yellow solid. The filtrate was evaporated to dryness under reduced pressure and recrystallized from water, 2.42 g., 81%, m.p. 259-260°.

Infrared cm^{-1}: 3500 (s), 3200 (s), 2170 (w), 1680 (m), 1600 (s), 1575 (s), 1500 (m), 1450 (s), 1420 (s), 1380 (s), 1350 (s), 1300 (s), 1290 (s), 1205 (s), 1170 (s), 1100 (s), 1045 (s), 1025 (m), 1010 (m), 955 (w), 945 (w), 910 (s), 865 (m), 830 (s), 775 (s), 770 (s), 750 (m), 720 (w), 695 (s), 660 (m), 555 (m), 480 (m), 430 (m).

Anal. Calcd. for $C_4H_6N_6O_5$: C, 22.02; H, 2.77; N, 38.53. Found: C, 21.99; H, 2.89; N, 38.83.

4-Amino-5-hydrazinopyridazine IX.

A mixture of 1.6 g. (0.0124 mole) of 4-amino-5-chloropyridazine and 6.5 ml. of 95% hydrazine was refluxed 3 hours. After cooling in ice, 8 ml. of water was added and the mixture cooled further and stirred. The resulting solid was collected, washed with cold water and recrystallized from water, 0.72 g., 47%, m.p. 150-150.5°.

Anal. Calcd. for $C_4H_7N_5$: C, 38.39; H, 5.64; N, 55.97. Found: C, 38.28; H, 5.95; N, 55.83.

5-Amino-4-nitraminopyridazine X.

To a solution of 3 ml. of concentrated sulfuric acid and 3 ml. of water at 0° was added slowly 0.5 g. (0.0025 mole) of XII. Upon solution, 3 ml. of a 1:1 mixture of concentrated sulfuric and nitric acids was added and the mixture allowed to stand at 0° for 15 minutes. The mixture was poured on ice and neutralized to *p*H 7 with sodium bicarbonate to precipitate 0.3 g. of crude product. The analytical sample was prepared from absolute ethanol. Compound X darkened at 250-270° and melted with decomposition above 400°.

Infrared cm^{-1}: 3360 (s), 3320 (s), 3150 (s), 3050 (sh), 2940 (s), 1880 (w), 1770 (w), 1660 (s), 1575 (s), 1540 (s), 1470 (m), 1390 (s), 1350 (s), 1285 (s), 1250 (s), 1195 (s), 1057 (w), 1020 (m), 947 (w), 907 (w), 900 (sh), 866 (m), 857 (s), 763 (m), 742 (m), 672 (s), 660 (sh), 580 (m), 490 (w), 480 (w), 469 (w).

Anal. Calcd. for $C_4H_5N_5O_2$: C, 30.97; H, 3.25; N, 45.15. Found: C, 31.33; H, 3.75; N, 44.74.

4,5-Diaminopyridazine Hydrochloride XI.

To 3.7 g. (0.03 mole) of IX in 300 ml. of absolute ethanol was added 4 g. of Raney nickel. The mixture was hydrogenated under atmospheric pressure and at room temperature until 420 ml. of hydrogen had been absorbed. The solution was filtered, acidified with hydrogen chloride gas and the volume reduced under diminished pressure to 150 ml. Dry ether was added to precipitate the diamine hydrochloride. The crude product was recrystallized from the absolute ethanol - dry ether solvent pair yielding 2.0 g. (46%) of XI, m.p. 234-235°.

Infrared cm^{-1}: 3460 (s), 3300 (s), 3170 (s), 3100 (sh), 3000 (s), 1820 (w), 1740 (w), 1675 (s), 1640 (s), 1620 (s), 1570 (s), 1480 (s), 1410 (s), 1380 (s), 1340 (m), 1245 (m), 1042 (s), 920 (m), 898 (m), 835 (s), 792 (w), 735 (w), 620 (w), 595 (w), 538 (s), 512 (s), 437 (m).

Anal. Calcd. for $C_4H_7ClN_4$: C, 32.77; H, 4.81; N, 38.22. Found: C, 32.97; H, 4.75; N, 38.10.

3,4-Diaminopyridazine hydrochloride XIII. Method I.

A solution containing 6.1 g. (0.042 mole) of 6-chloro-3,4-diaminopyridazine, 1.6 g. of sodium hydroxide pellets and approximately 1 g. of 5% palladium on charcoal in 300 ml. of 95% ethanol was hydrogenated until 1 l. of hydrogen had been absorbed. The solution was filtered and evaporated to dryness under reduced pressure. The residue was dissolved in absolute ethanol (norite), filtered, and acidified with hydrogen chloride gas. The solution was cooled and the product precipitated by the addition of dry ether to yield 3.3 g. (53%) of the diamine hydrochloride, m.p. 200.5-201.5°.

Infrared cm^{-1}: 3360 (sh), 3320 (sh), 3280 (s), 3080 (s), 3000 (s), 1670 (s), 1640 (s), 1570 (s), 1540 (s), 1510 (s), 1440 (s), 1375 (w), 1330 (w), 1280 (w), 1155 (m), 1130 (m), 1070 (w), 1020 (w), 965 (w), 915 (w), 810 (s), 760 (s), 700 (w), 614 (m), 564 (m), 530 (m), 482 (s).

Anal. Calcd. for $C_4H_7ClN_4$: C, 32.77; H, 4.81; N, 38.22. Found: C, 33.12; H, 4.46; N, 38.30.

Method II.

To 250 ml. of absolute alcohol was added 1.0 g. (0.0069 mole) of XV, 0.28 g. (0.0069 mole) of sodium hydroxide pellets and approximately 1 g. of 5% palladium on charcoal. The mixture was hydrogenated at atmospheric pressure until 180 ml. of hydrogen had been absorbed. The solution was acidified with concentrated hydrochloric acid and 0.7 g. (69%) of XV precipitated by the addition of ether, m.p. 195-196°. A mixed melting point determination with XIII prepared by method I gave a melting point of 199-200°.

Method III.

In order to establish that XIV was the 3,4-dinitraminopyridazine,

0.5 g. (0.0025 mole) of XIV was placed in 300 ml. of absolute ethanol, approximately 4 g. of Raney nickel added and the mixture hydrogenated at atmospheric pressure until 400 ml. of hydrogen had been absorbed. The catalyst was removed, the solution evaporated to 75 ml. under reduced pressure, acidified with hydrogen chloride gas, and the product precipitated by the addition of ether. A mixed melting point determination with XIII prepared by method I gave a melting point of 200-203°.

3,4-Dinitraminopyridazine XIV.

To 4 ml. of concentrated sulfuric acid at 0° was slowly added with stirring 1 g. (0.0068 mole) of XIII. When all of the diamine hydrochloride was in solution, 1 ml. of concentrated nitric acid was added slowly. The mixture was allowed to stand at 0° with occasional stirring for one half hour; at the end of this time, the mixture was poured on ice. The resulting precipitate was collected, washed with water, dried, and recrystallized (norite) from benzene yielding 1.05 g. (77%) of the dinitramine, m.p. 144° dec.

Infrared cm^{-1}: 3200 (s), 3100 (s), 3075 (s), 1980 (w), 1630 (s), 1620 (sh), 1575 (s), 1530 (s), 1475 (s), 1390 (s), 1360 (sh), 1325 (s), 1270 (s), 1230 (s), 1155 (s), 1134 (s), 1067 (m), 995 (s), 893 (m), 866 (s), 850 (s), 820 (m), 804 (m), 788 (sh), 774 (s), 758 (m), 747 (m), 690 (s), 633 (m), 592 (w), 470 (w), 455 (w).

Anal. Calcd. for $C_4H_4N_6O_4$: C, 24.00; H, 2.01; N, 42.00. Found: C, 23.65; H, 2.46; N, 42.06.

4-Nitraminopyridazine XVII.

To 11.5 ml. of concentrated sulfuric acid at 10° was added slowly 3.7 g. (0.039 mole) of 4-aminopyridazine with stirring followed by the dropwise addition of 16 ml. of a 1:1 mixture of concentrated sulfuric acid and concentrated nitric acid. Stirring was continued until solution was complete. The solution was allowed to stand at room temperature for 30 minutes then poured on ice. The resulting yellow solid was collected and washed with water. The filtrate was adjusted to *p*H 4.6-4.8 with sodium bicarbonate and an additional amount of crude product collected and added to that obtained above. This yellow solid recrystallized from methanol as heavy amber needles, 4.5 g., 83%, m.p. 185° dec.

Infrared cm^{-1}: 3160 (s), 3120 (s), 3050 (s), 1600 (m), 1555 (s), 1480 (s), 1460 (s), 1400 (s), 1355 (m), 1320 (m), 1280 (s), 1260 (s), 1210 (s), 1150 (m), 1100 (s), 1040 (s), 1020 (s), 995 (w), 985 (w), 930 (m), 895 (s), 850 (s), 775 (s), 760 (w), 730 (w), 685 (m), 640 (s), 440 (s), 420 (s).

Anal. Calcd. for $C_4H_4N_4O_2$: C, 34.29; H, 2.88; N, 39.99. Found: C, 34.38; H, 3.30; N, 39.70.

8-Amino-6-chlorotetrazolo[1,5-b]pyridazine XIX.

To 140 ml. of water containing 9 ml. of concentrated hydrochloric acid was added 7.6 g. (0.0578 mole) of 4-amino-6-chloro-3-hydrazinopyridazine. This was warmed to complete solution of the solid and cooled to room temperature. Sodium nitrate (3.5 g.) in 25 ml. of water was added dropwise with stirring. The resulting solid was collected and the filtrate neutralized with sodium bicarbonate to yield additional solid which was added to that obtained above and recrystallized from water, 5.5 g., 68%, m.p. 284-285°. This compound was catalytically dechlorinated (5% palladium on charcoal) to the 8-aminotetrazolo[1,5-b]pyridazine. The structure of XX was established by Kuraishi and Castle (3). A mixed melting point with their compound showed no depression.

Infrared cm^{-1}: 3365 (s), 3340 (s), 3230 (m), 3195 (s), 3080 (s), 2710 (w), 1660 (s), 1575 (s), 1460 (m), 1450 (s), 1400 (s), 1390 (s), 1375 (m), 1275 (s), 1230 (m), 1160 (m), 1140 (s), 1100 (m), 1055 (m), 1005 (m), 940 (s), 855 (m), 795 (w), 760 (w), 635 (w), 570 (m), 520 (w).

Anal. Calcd. for $C_4H_3ClN_6$: C, 28.22; H, 1.77; N, 49.39. Found: C 28.10; H, 2.15; N, 48.96.

8-Amino-6-hydrazinotetrazolo[1,5-b]pyridazine XXI.

A suspension of 0.2 g. (0.0012 mole) of 8-amino-6-chlorotetrazolo-[1,5-b]pyridazine in 4 ml. of 95% hydrazine was refluxed 45 minutes. This was then chilled in ice and 10 ml. of water added with stirring. The resulting yellow solid was collected, washed with cold water and recrystallized from water, 0.11 g., 57%, m.p. 309-310°.

Infrared cm^{-1}: 3360 (s), 3325 (s), 3150 (s), 1680 (s), 1630 (s), 1610 (s), 1600 (s), 1550 (s), 1500 (s), 1420 (w), 1400 (m), 1380 (m), 1270 (s), 1250 (s), 1220 (s), 1120 (m), 1080 (m), 1025 (m), 1010 (m), 925 (m), 865 (w), 830 (s), 755 (m), 720 (m), 705 (m), 625 (m), 605 (m), 550 (s).

Anal. Calcd. for $C_4H_6N_8$: C, 28.91; H, 3.64; N, 67.45. Found: C, 29.15; H, 3.64; N, 67.05.

8-Amino-6-azidotetrazolo[1,5-b]pyridazine XXII.

To 45 ml. of 5% hydrochloric acid was added 2.2 g. (0.0133 mole) of 8-amino-6-hydrazinotetrazolo[1,5-b]pyridazine. This was warmed gently to effect solution and cooled to room temperature. This was followed by the dropwise addition of sodium nitrite (1.2 g.) in 10 ml. of water with stirring. The resulting solid was collected, washed with cold water and recrystallized from ethanol, 1.78 g., 76%, m.p. 244° dec.

Infrared cm^{-1}: 3370 (s), 3330 (s), 3230 (m), 3190 (s), 3070 (s), 3020 (w), 2750 (w), 2700 (w), 2360 (w), 2230 (m), 2150 (s), 2110 (s), 1660 (s), 1590 (s), 1500 (w), 1475 (s), 1445 (s), 1430 (s), 1400 (s), 1380 (s), 1285 (s), 1250 (s), 1230 (s), 1130 (m), 1100 (m), 1060 (s), 1005 (m), 980 (s), 870 (s), 845 (s), 760 (m), 720 (m), 705 (m), 680 (m), 640 (m), 605 (w), 585 (s), 550 (s), 535 (s), 510 (m), 445 (w).

Anal. Calcd. for $C_4H_3N_9$: C, 27.12; H, 1.71; N, 71.17. Found: C, 27.50; H, 1.69; N, 71.22.

4,6-Dihydrazinopyrimidine XXIV.

A solution of 1.2 g. (0.0081 mole) of 4,6-dichloropyrimidine in 10 ml. of ethanol and 5 ml. of 95% hydrazine was refluxed one hour. A partial precipitation of the product occurred during the reflux period. After cooling in ice, a white solid was collected and recrystallized from ethanol, 1.0 g., 89%, m.p. 223-224° dec. During recrystallization from water the product decomposed slightly.

Infrared cm^{-1}: 3320 (s), 3250 (s), 3200 (s), 3070 (s), 3000 (s), 2960 (s), 1640 (s), 1600 (s), 1520 (s), 1450 (s), 1430 (s), 1420 (s), 1350 (s), 1260 (m), 1240 (m), 1140 (m), 1100 (s), 1000 (s), 980 (s), 960 (s), 810 (s), 760 (m), 685 (m), 630 (m), 510 (w), 460 (m), 410 (m).

Anal. Calcd. for $C_4H_8N_6$: C, 34.28; H, 5.75; N, 59.97. Found: C, 33.85; H, 6.08; N, 59.85.

4,6-Diazidopyrimidine XXV.

To 0.8 g. (0.0057 mole) of 4,6-dihydrazinopyrimidine in 20 ml. of 5% hydrochloric acid at room temperature, sodium nitrite (0.8 g.) in 5 ml. of water was added dropwise with stirring. The resulting solid was collected, washed with water and dried in air. This was sublimed at 80-85° and 20 mm., 0.72 g., 77%, m.p. 106-107°.

Infrared cm^{-1}: 3100 (m), 3050 (m), 2400 (m), 2350 (m), 2255 (m), 2240 (m), 2150 (s), 2070 (m), 1930 (w), 1750 (w), 1720 (w), 1600 (s), 1580 (s), 1540 (s), 1450 (s), 1375 (s), 1330 (m), 1275 (m), 1260 (s), 1250 (s), 1220 (s), 1190 (s), 1155 (s), 1100 (w), 985 (s), 970 (m), 920 (s), 855 (s), 835 (s), 760 (m), 740 (s), 540 (m), 460 (m).

Anal. Calcd. for $C_4H_2N_8$: C, 29.63; H, 1.24; N, 69.13. Found: C, 29.93; H, 1.34; N, 69.16.

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