Department of Chemistry, The University of New Mexico

# The Synthesis of *v*-Triazolo[4,5-c]pyridazines, a New Heterocyclic Ring System as Potential Purine Antagonists

G. Anne Gerhardt (1) and Raymond N. Castle (2)

The free ring system, *v*-triazolo[4, 5-c]pyridazine and several derivatives in this ring system such as the adenine analog, 7-amino-*v*-triazolo[4, 5-c]pyridazine, have been prepared. In addition, the fully aromatic pyrazino[2, 3-c]pyridazine ring system has been prepared for the first time.

This work was undertaken in order to prepare the adenine analog, 7-amino-*v*-triazolo[4,5-c]pyridazine, and the mercapto substituted potential purine antagonists, 7-alkyl- and the 7-substituted benzylthio-*v*-triazolo[4, 5-c]pyridazines.

Kuraishi and Castle (3) have previously prepared 5-chloro-3, 4-diaminopyridazine (I) from 3, 4, 5-trichloropyridazine. For the synthesis of 7-chloro-*v*-triazolo[4, 5-c]pyridazine (II), compound I served as the starting material. When 5-chloro-3, 4-diaminopyridazine (I) was allowed to react with sodium nitrite in the presence of sulfuric acid, 7-chloro-*v*-triazolo[4, 5-c]pyridazine (II) was obtained. Because of the ease with which this compound decomposed, it was difficult to purify and to use in reactions. When compound II was allowed to react with glacial acetic acid a small amount of the 7-hydroxy-*v*-triazolo[4,5-c]pyridazine (IV) was isolated. The unsubstituted ring system was prepared by catalytic dechlorination of II with palladium on charcoal. The assigned structure for *v*-triazolo[4,5-c]-pyridazine (III) was confirmed by elemental analysis. The structural assignment of the *v*-triazolo[4, 5-c]-pyridazine ring system was made by comparing the ultraviolet absorption spectra of *v*-triazolo[4, 5-c]-pyridazine (III) with the spectrum of 8-azapurine (XX) (4). Furthermore, the ultraviolet absorption spectrum of 7-amino-*v*-triazolo[4,5-c]pyridazine (VII) was compared with that of 6-amino-8-azapurine (XXI) (5) and also with that of 7-aminoimidazo[4, 5-c]-pyridazine (XXII) (3). In each instance the spectra of the *v*-triazolo[4,5-c]pyridazines were nearly identical to the spectra of the known 8-azapurines and imidazo[4, 5-c]pyridazines. Small red shifts in the wave length of the absorption maxima were noted in the condensed-ring pyridazines compared to the corresponding condensed-ring pyrimidines. The same shift to longer wave length has been observed when the spectrum of pyridazine (XIX) (6) was compared with the spectrum of pyrimidine (XVIII) (6). Compound II was also readily converted into the *v*-triazolo[4, 5-c]pyridazine-7-thiol (V) by allowing II to react with thiourea in methanol and subsequent decomposition of the intermediate with sodium hydroxide. Since V was difficult to purify it was characterized by conversion into 7-methylthio-*v*-triazolo-[4, 5-c]pyridazine (VI) with methyl iodide in alkaline solution. In similar fashion, by allowing the appropriate benzyl iodide to react with V in aqueous alcoholic solution, the following compounds were prepared: 7-(*p*-chlorobenzylthio)-*v*-triazolo[4, 5-c]-pyridazine (XI), 7-(2, 4-dichlorobenzylthio)-*v*-triazolo[4, 5-c]pyridazine (VIII), 7-(3,4-dichlorobenzylthio)-*v*-triazolo[4,5-c]pyridazine (IX), and 7-(2, 6-dichlorobenzylthio)-*v*-triazolo[4, 5-c]pyridazine (X). These halogenated benzylthio derivatives were prepared for antitumor screening, since compounds such as 5-amino-7-(2,4-dichlorobenzylthio)-*v*-triazolo[d]-pyrimidine (7) and halobenzyl substituted 4-mercaptocinnolines (8) have been shown to have antitumor activity. The adenine analog, 7-amino-*v*-triazolo-[4, 5-c]pyridazine (VII) was prepared from 7-methylthio-*v*-triazolo[4, 5-c]pyridazine (VI) by allowing VI to react with alcoholic ammonia in a rocking autoclave at 120-130° for 8 hours.

The 6-chloro-*v*-triazolo[4,5-c]pyridazine (XVI) was prepared in several steps from XIII (9) in a manner similar to the preparation of the 7-chloro-*v*-triazolo-[4, 5-c]pyridazine (II). The compound XIII was allowed to react with hydrazine and then this compound, 4-amino-6-chloro-3-hydrazinopyridazine (XIV) (10), was hydrogenated in the presence of Raney nickel to produce the 6-chloro-3,4-diaminopyridazine (XV) by the procedure reported by Kuraishi and Castle (3). The structure of compound XIV had been proven by Yanai and Kinoshita (10). Compound XV was allowed to react with sodium nitrite in the presence of sulfuric acid to produce the 6-chloro-*v*-triazolo-[4,5-c]pyridazine (XVI). This cyclization gave further proof for the structure of the diamine (XV). Although the 6-chloro compound (XVI) was similar to the 7-chloro compound (II), XVI was very much less reactive.

The fully aromatic pyrazino[2,3-c]pyridazine ring system has not been previously reported. This ring was known only as the partially hydrogenated system (11). The 5-chloro-3, 4-diaminopyridazine (I) was allowed to react with benzil to produce a black compound which was shown to be 4-chloro-6, 7-diphenylpyrazino[2,3-c]pyridazine (XII). In a similar fashion 3-chloro-6,7-diphenylpyrazino[2,3-c]pyridazine (XVII) was produced from benzil and 6-chloro-3, 4-diaminopyridazine.

## EXPERIMENTAL (12)

7-Chloro-*v*-triazolo[4,5-c]pyridazine (II).

5-Chloro-3,4-diaminopyridazine (1.01 g., 0.007 mole) was dissolved with warming in 30 ml. of water containing 1 ml. of concentrated sulfuric acid. This solution was cooled to less than 10° and a second solution containing 0.5 g. (0.007 mole) of sodium nitrite in 2 ml. of cold water was added with shaking. The yellow precipitate was collected, rinsed with cold water and dried, yield 0.9 g. (83%), m.p. >260°.

The analytical sample was prepared by suspending the product in ice water to remove inorganic salts, m.p. >300°.

U. V. λ max (95% $C_2H_5OH$): 210 (ε, 15,300); 275 (ε, 8,900); 292 (sh) (ε, 7,020); 305 μ (sh) (ε, 6,440).

Infrared $cm^{-1}$: 3050 (m), 2975 (m), 2800 (s), 2600 (s), 2475 (s), 1825 (w), 1760 (w), 1625 (m), 1540 (m), 1475 (w), 1440 (w), 1350 (s), 1305 (m), 1270 (s), 1250 (s), 1160 (s), 1100 (w), 1030 (s), 980 (w), 940 (s), 885 (s), 680 (s), 610 (w), 537 (w), 500 (m).

*Anal.* Calcd. for $C_4H_2ClN_5$: C, 30.88; H, 1.30; N, 45.03. Found: C, 31.19; H, 1.62; N, 44.93.

7-Hydroxy-*v*-triazolo[4,5-c]pyridazine (IV).

A mixture containing 0.5 g. of 7-chloro-*v*-triazolo[4,5-c]pyridazine and 2 ml. of glacial acetic acid was refluxed for 10 min. The solution was poured onto ice producing a small amount of product. The black residue remaining in the flask was air dried and then extracted with several portions of absolute ethanol. The combined ethanol extracts were filtered and evaporated to dryness, leaving a yellow solid which gave a negative Beilstein test. This solid was recrystallized from water (norite). It darkens above 200° with slow decomposition.

U. V. λ max (95% $C_2H_5OH$): 208 (ε, 15,800); 215 (ε, 15,400); 261 (sh) (ε, 7,370); 278 (ε, 7,870); 327 (sh) (ε, 8,250); 364 mμ (ε, 10,600).

Infrared $cm^{-1}$: 3075 (s), 2925 (s), 1850 (s), 1670 (s), 1625 (s), 1540 (s), 1450 (s), 1350 (s), 1300 (s), 1260 (s), 1200 (w), 1150 (m), 1125 (m), 1090 (m), 1070 (m), 975 (m), 940 (w), 905 (m), 860 (m), 720 (w), 670 (m), 625 (w), 550 (w), 525 (w), 480 (w).

*Anal.* Calcd. for $C_4H_3N_5O$: C, 35.04; H, 2.21; N, 51.09. Found: C, 35.18; H, 2.31; N, 50.98.

*v*-Triazolo[4,5-c]pyridazine (III).

A mixture containing 7-chloro-*v*-triazolo[4,5-c]pyridazine (1 g., 0.0065 mole) and approximately 1 g. of 5% palladium on charcoal in 100 ml. of 0.5 N sodium hydroxide was hydrogenated at atmospheric pressure and room temperature. After the theoretical amount of hydrogen was absorbed, the solution was filtered, acidified to *p*H 6-7 with dilute hydrochloric acid and evaporated to dryness leaving a pale colored residue. This residue was suspended in approximately 10 ml. of water and filtered. The remaining precipitate was then crystallized several times from water (norite) giving an analytical sample, m.p. 227-228° dec. A Beilstein test was negative.

U. V. λ max (95% $C_2H_5OH$): 204 (ε, 10,900); 270 (ε, 8,060); 300 mμ (sh) (ε, 2,620).

Infrared $cm^{-1}$: 3450 (w), 3100 (s), 2975 (m), 2850 (m), 2775 (m), 2575 (s), 2450 (s), 1800 (m), 1625 (m), 1550 (m), 1475 (m), 1360 (m), 1310 (s), 1285 (m), 1260 (m), 1170 (m), 1040 (s), 1020 (s), 955 (s), 920 (s), 850 (s), 795 (m), 670 (w), 660 (s), 610 (w), 565 (w), 450 (m).

*Anal.* Calcd. for $C_4H_3N_5$: C, 39.67; H, 2.50; N, 57.84. Found: C, 39.52; H, 2.64; N, 57.99.

7-Methylthio-*v*-triazolo[4,5-c]pyridazine (VI).

7-Chloro-*v*-triazolo[4,5-c]pyridazine (1.1 g., 0.007 mole) was dissolved with warming in 15 ml. of dry methanol, and to this solution was added 1 g. (0.017 mole) of thiourea. The mixture was shaken and kept warm for 10 min. After cooling, the precipitate was collected, washed with dry methanol and allowed to dry.

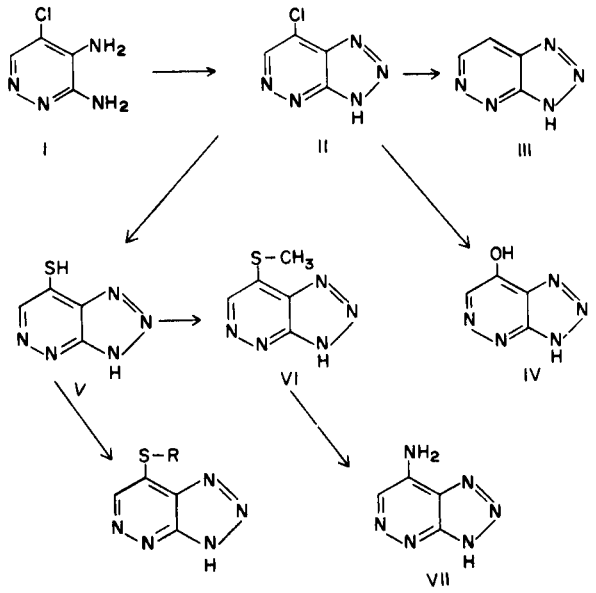
To a solution containing the crude product, prepared as described above, in 25 ml. of 10% sodium hydroxide was added 0.93 g. (0.0065 mole) of iodomethane. This solution was first stirred at room temperature for 1 hr., then heated on the steam bath for an additional 1.5 hrs. After cooling and filtering, the solution was acidified with concentrated hydrochloric acid. The yellow precipitate which gradually formed was collected and dried, yield 0.6 g. (20%) m.p. 218-220° dec., (rapid heating).

The analytical sample was prepared by several recrystallizations from a benzene - absolute ethanol mixture (norite), m.p. 219-220° dec.

U. V. λ max (95% $C_2H_5OH$): 226 (ε, 15,500); 281 (ε, 6,350); 328 mμ (ε, 14,700).

Infrared $cm^{-1}$: 3075 (s), 2925 (s), 2725 (s), 2600 (s), 1800 (w), 1575 (s), 1425 (m), 1400 (s), 1270 (m), 1250 (m), 1235 (w), 1230 (w), 1205 (w), 1170 (s), 1155 (s), 1105 (s), 1050 (w), 1015 (w), 985 (m), 970 (m), 910 (m), 880 (s), 705 (w), 675 (s), 665 (m), 620 (w), 545 (w), 490 (w).

*Anal.* Calcd. for $C_5H_5N_5S$: C, 35.91; H, 3.01; N, 41.89. Found: C, 36.36; H, 3.23; N, 41.89.

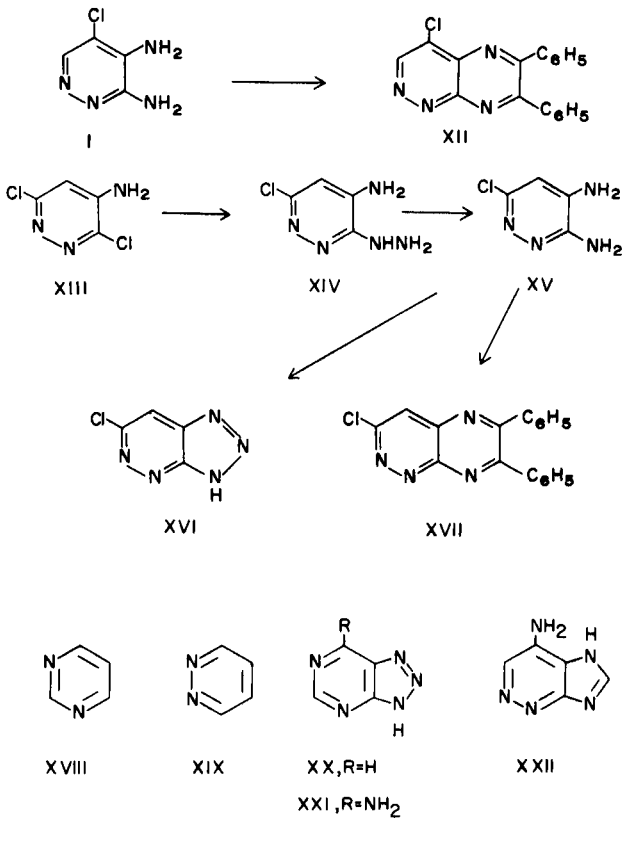



VIII, R = 2,4 - dichlorobenzyl -

IX, R = 3,4 - dichlorobenzyl -

X, R = 2,6 - dichlorobenzyl -

XI, R = p - chlorobenzyl -



7-Amino-*v*-triazolo[4,5-c]pyridazine (VII).

A mixture of 2 g. (0.012 mole) of 7-methylthio-*v*-triazolo[4,5-c]-pyridazine in 200 ml. of absolute ethanol saturated with ammonia at 0-5° was heated in a stainless steel reaction vessel in a rocking autoclave at 120-130° for 8 hrs. After removal of the solvent, the residue was crystallized from water - ethanol (norite). The analytical sample was recrystallized from water, m.p. >300°.

U. V. λ max (95% $C_2H_5OH$): 210 (ε, 17,700); 273 (ε, 12,000); 325 (ε, 16,400); 331 (ε, 16,500); 339 mμ (sh) (ε, 13,700).

Infrared $cm^{-1}$: 3350 (s), 3050 (s), 2700 (s), 1800 (w), 1675 (s), 1625 (s), 1450 (s), 1425 (s), 1370 (m), 1350 (s), 1280 (s), 1220 (w), 1170 (w), 1120 (m), 1070 (s), 1030 (m), 1005 (m), 910 (s), 775 (w), 750 (w), 700 (m), 635 (s), 625 (s), 550 (w), 535 (w), 500 (m), 485 (w).

*Anal.* Calcd. for $C_4H_4N_6$: C, 35.29; H, 2.96; N, 61.75. Found: C, 35.76; H, 2.94; N, 61.51.

7-(2,4-Dichlorobenzylthio)-*v*-triazolo[4,5-c]pyridazine (VIII).

To a solution of 1.0 g. (0.0065 mole) of 7-chloro-*v*-triazolo[4,5-c]-pyridazine in 15 ml. of dry methanol was added 1 g. of thiourea and the solution was kept warm for 10 min. After cooling, the solid which separated was dissolved in 10% sodium hydroxide solution and an ethanol solution containing 1.87 g. (0.0065 mole) of 2,4-dichlorobenzyl iodide was added. The mixture was stirred at room temperature for 1 hr. and then heated on the steam bath for 1.5 hrs. The solution was acidified with concentrated hydrochloric acid and cooled. The reaction yielded 1.4 g. (69%) of product, m.p. 195-197° dec. An analytical sample was prepared by several recrystallizations from absolute ethanol (norite), m.p. 204-205° dec.

U. V. λ max (95% $C_2H_5OH$): 206 (ε, 29,300); 224 (ε, 24,400); 281 (ε, 7,660); 329 mμ (ε, 16,300).

Infrared $cm^{-1}$: 3450 (w), 3075 (m), 2975 (m), 2925 (m), 2875 (m), 2850 (m), 2775 (m), 1600 (s), 1560 (m), 1500 (m), 1475 (s), 1425 (m), 1400 (w), 1375 (m), 1320 (w), 1310 (w), 1280 (w), 1265 (w), 1245 (w), 1230 (s), 1195 (w), 1165 (w), 1150 (m), 1130 (w), 1095 (m), 1040 (s), 1015 (w), 975 (w), 955 (w), 870 (s), 850 (m), 840 (m), 755 (w), 720 (w), 685 (w), 660 (w), 650 (w), 620 (w), 560 (w), 475 (m), 465 (w), 455 (w), 430 (m).

*Anal.* Calcd. for $C_{11}H_7Cl_2N_5S$: C, 42.32; H, 2.26; N, 22.44. Found: C, 42.44; H, 2.30; N, 22.20.

7-(3,4-Dichlorobenzylthio)-*v*-triazolo[4,5-c]pyridazine (IX).

Compound IX was prepared in 59% yield [1.2 g., m.p. 190-194° dec. (fast)] from 7-chloro-*v*-triazolo[4,5-c]pyridazine via the intermediate thiol and 3,4-dichlorobenzyl iodide by a procedure similar to that described for VIII. This product was recrystallized from absolute ethanol, m.p. 197-198° dec.

U. V. λ max (95% $C_2H_5OH$): 205 (ε, 28,900); 220 (sh) (ε, 24,200); 280 (ε, 7,040); 328 mμ (ε, 15,600).

Infrared $cm^{-1}$: 3425 (w), 3050 (m), 2975 (m), 2925 (m), 2800 (m), 1600 (m), 1560 (m), 1525 (w), 1490 (w), 1475 (s), 1425 (w), 1400 (m), 1320 (w), 1270 (w), 1230 (m), 1200 (w), 1160 (m), 1150 (m), 1130 (m), 1090 (m), 1040 (m), 1030 (m), 975 (w), 875 (m), 825 (m), 735 (w), 685 (w), 655 (w), 615 (w), 565 (w), 540 (w), 505 (w), 480 (w), 470 (w), 440 (w).

*Anal.* Calcd. for $C_{11}H_7Cl_2N_5S$: C, 42.32; H, 2.26; N, 22.44. Found: C, 42.71; H, 2.43; N, 22.80.

7-(2,6-Dichlorobenzylthio)-*v*-triazolo[4,5-c]pyridazine (X).

This compound was obtained as described above, from 7-chloro-*v*-triazolo[4,5-c]pyridazine and 2,6-dichlorobenzyl iodide. It was recrystallized from 95% ethanol, m.p. 176-177° dec.

U. V. λ max (95% $C_2H_5OH$): 206 (ε, 23,800); 220 (sh) (ε, 21,800); 280 (ε, 9,160); 329 mμ (ε, 15,700).

Infrared $cm^{-1}$: 3450 (w), 3075 (m), 2975 (m), 2925 (m), 2800 (m), 2600 (m), 1560 (s), 1525 (m), 1440 (s), 1360 (w), 1290 (w), 1270 (m), 1235 (m), 1205 (w), 1165 (m), 1090 (m), 1035 (m), 1015 (m), 970 (m), 870 (m), 780 (m), 760 (m), 685 (w), 665 (w), 630 (w), 610 (w), 540 (w), 510 (w), 500 (w), 490 (w).

*Anal.* Calcd. for $C_{11}H_7Cl_2N_5S$: C, 42.32; H, 2.26; N, 22.44. Found: C, 42.39; H, 2.51; N, 22.33.

7-(*p*-Chlorobenzylthio)-*v*-triazolo[4,5-c]pyridazine (XI).

This compound was prepared similarly from 7-chloro-*v*-triazolo-[4,5-c]pyridazine and *p*-chlorobenzyl iodide, yielding 1.1 g. (54%) of product, m.p. 194-195° dec. after recrystallization from absolute ethanol (norite). The analytical sample was purified by crystallization from 95% ethanol, m.p. 198-198.5° dec.

U. V. λ max (95% $C_2H_5OH$): 203 (ε, 18,200); 223 (ε, 18,900); 280 (ε, 7,900); 328 mμ (ε, 14,400).

Infrared $cm^{-1}$: 3050 (m), 2925 (m), 2775 (m), 1900 (w), 1575 (m), 1490 (s), 1410 (m), 1375 (m), 1270 (m), 1255 (w), 1230 (m), 1195 (w), 1170 (s), 1145 (m), 1095 (s), 1015 (m), 975 (m), 885 (m), 875 (m), 840 (m), 805 (w), 740 (m), 690 (w), 670 (w), 655 (w), 610 (w), 535 (w), 510 (m), 490 (w), 435 (w).

*Anal.* Calcd. for $C_{11}H_8ClN_5S$: C, 47.57; H, 2.90; N, 25.22. Found: C, 47.75; H, 3.30; N, 25.20.

4-Chloro-6,7-diphenylpyrazino[2,3-c]pyridazine (XII).

5-Chloro-3,4-diaminopyridazine (1 g., 0.007 mole) was mixed with benzil (1.45 g., 0.007 mole). The mixture was heated for 15 min. between 160-175°. The black gummy residue was removed from the test tube by treatment with ethanol. The ethanol was evaporated and the solid which remained after the treatment with hot cyclohexane was recrystallized from pyridine - water (norite), slow decomposition above 300°.

U. V. λ max (95% $C_2H_5OH$): 207 (ε, 21,500); 233 (ε, 19,450); 274 (sh) (ε, 15,500); 372 mμ (ε, 11,900).

Infrared $cm^{-1}$: 3375 (m), 3050 (m), 1600 (m), 1550 (s), 1475 (m), 1450 (m), 1385 (s), 1365 (s), 1335 (m), 1280 (m), 1235 (m), 1190 (m), 1120 (m), 1075 (m), 1055 (m), 1020 (m), 1000 (w), 985 (w), 895 (w), 830 (w), 790 (w), 770 (m), 695 (s), 615 (w), 605 (w), 535 (w).

*Anal.* Calcd. for $C_{18}H_{11}ClN_4$: C, 67.82; H, 3.48; N, 17.58. Found: C, 67.80; H, 3.57; N, 17.67.

4-Amino-3,6-dichloropyridazine (XIII) (9).

The procedure of Kuraishi (9) was modified and scaled up. A stainless steel reaction vessel of 1.7 l. capacity was charged with 86 g. (0.47 mole) of 3,4,6-trichloropyridazine and 1.25 l. of absolute ethanol saturated with ammonia at 0°. The reaction mixture was heated at 125° in a rocking autoclave for 7 hrs. The crude reaction product was recrystallized from water (norite), yielding 46.5 g. (61%), m.p. 203°.

4-Amino-6-chloro-3-hydrazinopyridazine (XIV) (10).

4-Amino-3,6-dichloropyridazine (46.5 g., 0.285 mole) and anhydrous hydrazine (151 ml.) were heated on the steam bath for 3 hrs. After the addition of 500 ml. of water and cooling, the crystals were collected, washed well with water and dried under reduced pressure, m.p. 209°.

6-Chloro-3,4-diaminopyridazine (XV).

A mixture of 7 g. (0.044 mole) of dry 4-amino-6-chloro-3-hydrazinopyridazine and 3 g. of freshly prepared Raney nickel catalyst in 800 ml. of absolute ethanol was hydrogenated at atmospheric pressure and room temperature. After removal of the catalyst, the filtrate was evaporated at room temperature under a stream of compressed air. The residue was recrystallized from a small amount of water (norite), 3.7 g. (53%), m.p. 186-187°. The analytical sample was recrystallized from water (norite), m.p. 186-187°.

U. V. λ max (95% $C_2H_5OH$): 210 (ε, 19,200); 226 (ε, 18,200); 262 (ε, 13,000); 303 mμ (ε, 13,900).

Infrared $cm^{-1}$: 3425 (s), 3350 (s), 3175 (s), 2725 (m), 1675 (s), 1625 (s), 1560 (s), 1460 (s), 1340 (s), 1310 (m), 1180 (s), 1120 (m), 1095 (m), 1055 (m), 960 (s), 855 (m), 780 (m), 760 (m), 680 (s), 620 (m), 550 (m).

*Anal.* Calcd. for $C_4H_5ClN_4$: C, 33.21; H, 3.46; N, 38.76. Found: C, 33.63; H, 3.04; N, 38.61.

6-Chloro-*v*-triazolo[4,5-c]pyridazine (XVI).

6-Chloro-3,4-diaminopyridazine (3.2 g., 0.022 mole) was dissolved in 80 ml. of water and 4.3 ml. of concentrated sulfuric acid. The solution was cooled in ice and a cold water solution containing 1.76 g. (0.025 mole) of sodium nitrite was added. After standing in an ice-bath for 20 min., the yellow solid was collected, washed with cold water and air dried, yielding 1.6 g. (47%) m.p. 217° dec. The analytical sample was recrystallized from 95% ethanol (norite), m.p. 218° dec.

U. V. λ max (95% $C_2H_5OH$): 209 (ε, 20,620); 280 (ε, 4,220); 316 mμ (sh) (ε, 1,500).

Infrared $cm^{-1}$: 3100 (m), 3050 (s), 3000 (s), 2875 (s), 2800 (s), 2700 (s), 2625 (s), 1700 (w), 1625 (s), 1550 (m), 1475 (w), 1400 (s), 1375 (s), 1290 (m), 1240 (w), 1145 (m), 1075 (s), 1020 (m), 965 (s), 905 (m), 875 (w), 810 (m), 790 (w), 735 (s), 620 (w), 480 (m).

*Anal.* Calcd. for $C_4H_2ClN_5$: C, 30.88; H, 1.30; N, 45.03. Found: C, 30.81; H, 1.22; N, 44.89.

3-Chloro-6,7-diphenylpyrazino[2,3-c]pyridazine (XVII).

A mixture of 1 g. (0.007 mole) of 6-chloro-3,4-diaminopyridazine and 1.45 g. (0.007 mole) of benzil was heated in an oil bath between 160-175° for 15 min. After cooling to room temperature, the solid was dissolved in several portions of 95% ethanol and the combined portions of ethanol evaporated to dryness. The residue was treated with two 50 ml. portions of cyclohexane and filtered hot. The insoluble material was collected and dried. Recrystallization from pyridine - water (norite) gave a pure product, m.p. 185° dec.

U. V. λ max (95% $C_2H_5OH$): 208 (ε, 29,100); 230 (sh) (ε, 24,800); 242 (ε, 26,600); 260 (sh) (ε, 17,500); 385 mμ (ε, 10,400).

Infrared $cm^{-1}$: 3400 (w), 3050 (w), 1675 (w), 1600 (m), 1550 (m),

1485 (m), 1450 (s), 1385 (m), 1360 (s), 1305 (w), 1285 (w), 1240 (m), 1175 (m), 1155 (w), 1100 (m), 1075 (m), 1045 (s), 1020 (s), 1000 (w), 985 (m), 955 (w), 920 (w), 870 (w), 845 (w), 795 (w), 770 (m), 745 (w), 730 (w), 695 (s), 675 (w), 605 (w), 535 (w).

*Anal.* Calcd. for $C_{18}H_{11}ClN_4$: C, 67.82; H, 3.48; N, 17.58. Found: C, 67.67; H, 3.73; N, 18.06.

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