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Antituberculous Compounds. XXV. Some Derivatives of Pyrido[2, 3-*d*]pyridazine

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Attempts to prepare 5, 6-dihydropyrido[2, 3-*d*]pyridazin-8(7H)-one by the hydrogenation of pyrido[2, 3-*d*]pyridazin-8(7H)-one were not successful, but it was found that the hydrogenated compound was 1, 2, 3, 4-tetrahydropyrido[2, 3-*d*]pyridazin-8(7H)-one. The same reaction occurred in the case of pyrido[2, 3-*d*]pyridazin-5(6H)-one and some other derivatives.

In a previous paper,[1] it was reported that an alkyl derivative (2) of isonicotinic acid hydrazide (INH, 1) was more active against tubercle bacilli than the acyl derivative (3) containing the same number of carbon atoms. Although many azaphthalazine derivatives were prepared and tested for their bacteriostatic activities,[2] no effective compound has yet been found.

The constitution of the azaphthalazine (5) is closely related to the acyl derivative of INH, except that the terminal carbonyl group is cyclized to the respective β positions of the pyridine nucleus.

If, however, a methylene group is cyclized to the pyridine nucleus, as in 6, 7, 8 and 9, these compounds will be more effective against tubercle bacilli than azaphthalazine derivatives, since they are similar to the alkyl derivatives of INH.

1) S. Kakimoto and I. Tone, *J. Med. Chem.*, **8**, 868 (1965).

2) E. M. Bavin, D. J. Drain, M. Seiler and D. E. Seymour, *J. Pharmacy Pharmacol.*, **4**, 844 (1952); A. Bernanose, *Bull. Soc. Chim. France Mém.*, **17**, 567 (1950); N. P. Bun-Hoi, M. Welsh, G. De Champs, H. Le Bihan, F. Binon and C. Mentzer, *Compt. Rend. C. R.*, **234**, 1925 (1952); H. Meyer and J. Mally, *Monatsh. Chem.*, **33**, 393 (1912); H. A. Off, W. Siefken and G. Domagk, *Naturwiss.*, **39**, 118 (1952); *Z. Naturforsch.*, **7b**, 446 (1952); J. Shavel, F. Leonhard, F. H. McMillan and J. A. King, *J. Am. Pharm., Assoc., Edit.*, **42**, 402 (1953); H. L. Yale, K. A. Losee, J. Martins, M. Holsing, F. M. Perry and J. Bernstein, *J. Am. Chem. Soc.*, **75**, 1935 (1953).

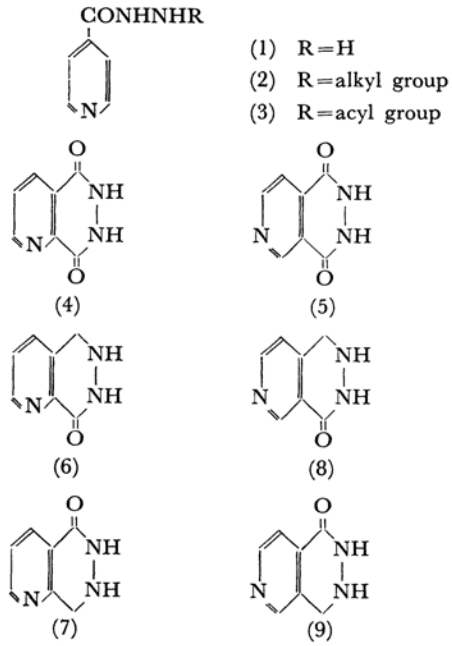


Fig. 1.

Of these compounds, it seems that 9, which is the most similar to the alkyl derivative of INH, will show the best activity towards tubercle bacilli.

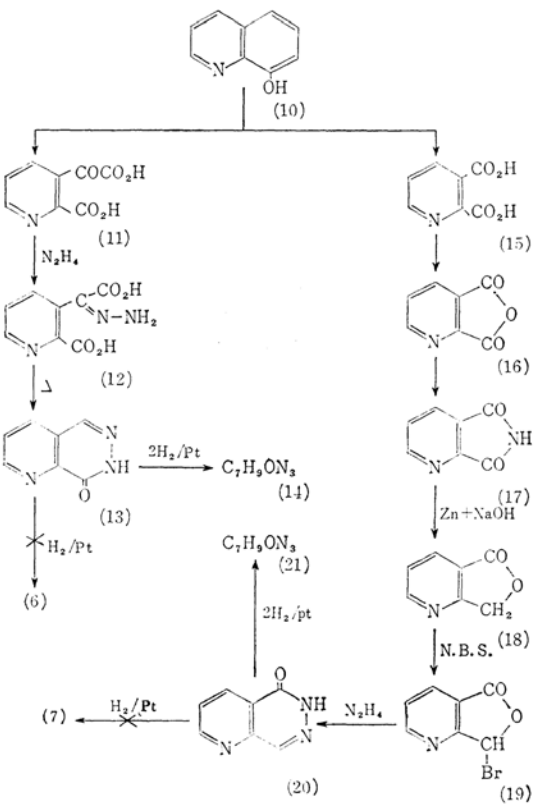


Fig. 2.

Initially, in order to test this assumption, syntheses of compounds 6 and 7 were attempted, as is shown in Fig. 2.[3]

Carboni and Bottari[4] have oxidized 8-hydroxyquinoline with nitric acid to yield 2-carboxy-3-pyridine glyoxalic acid (11) and quinolinic acid (15), and pyrido[2, 3-*d*]pyridazin-8(7H)-one (13) has been prepared by the vacuum sublimation of the hydrazone of the keto acid (11). The lactone of 2-hydroxymethylnicotinic acid (18) has been prepared from quinolinic acid amide (17).[5]

The lactone (18) was brominated with *N*-bromosuccinimide to yield the bromolactone (19), which was then treated with hydrazine hydrate to give pyrido[2, 3-*d*]pyridazin-5(6H)-one (20).

It was expected that each pyridopyridazinone would be reduced by catalytic hydrogenation to give the compounds 6 and 7, but they continuously absorbed 2 mol of hydrogen and were converted to the tetrahydro compounds $C_7H_9ON_3$ (14 and 21) in a theoretical yield. When the reduction was terminated after 1 mol of hydrogen had been consumed, the reaction mixture consisted of 50% of the tetrahydro compound and 50% of the unreacted starting material.

Recently, Nitta *et al.*[6] have reported that 5-chloropyrido[2, 3-*d*]pyridazin-8-ol and pyrido-[2, 3-*d*]pyridazin-8-ol were hydrogenated to give a compound, $C_7H_9ON_3$, which, it was suggested without further investigation, was 1, 2, 3, 4-tetrahydropyrido[2, 3-*d*]pyridazin-8-ol.

The compound 14 crystallized from water as its monohydrate, which gave the anhydrous substance on sublimation. The infrared spectrum showed a strong band at 3300 cm^{-1} (secondary amino group) which was not observed in the original compound, 13. The presence of a secondary amino group in 14 was also indicated from the NMR spectrum (broad signal at τ 3.57). The tetrahydro compound, 14, afforded a nitroso compound, 22, in good yield when treated with nitrous acid. As the nitroso compound did not exhibit a band at 3300 cm^{-1}, it was concluded that the nitrosation took place on the secondary amino group. If any kind of ring opening on the pyridazine nucleus occurred by hydrogenation, the amino group would be split off by nitrous acid.

The tetrahydro compound, 14, was oxidized by chromic anhydride in acetic acid to give the original compound, 13. When half an equivalent of oxygen was used in this oxidation, the yield

3) The syntheses of the compounds 8 and 9 will be reported in other report.

4) S. Carboni, *Gazz. Chim. Ital.*, **85**, 1194 (1955); F. Bottari and S. Carboni, *ibid.*, **86**, 990 (1956).

5) J. H. Gardner and C. A. Nayler, "Organic Syntheses," Coll. Vol. II, p. 526 (1943).

6) Y. Nitta, I. Matsu-ura and F. Yoneda, *Chem. Pharm. Bull.*, **13**, 586 (1965).

was 50% less, but no dihydro compound was obtained.

Upon acetylation with acetic anhydride, the tetrahydro compound, 14, gave an *O*-acetyl compound (IR 1290 cm^{-1}). With phosphorus pentasulfide, compounds 13 and 14 were converted to a thioamide. These reactions are shown in Fig. 3.

In order to investigate the unexpected hydrogenation further, 7-phenyl-, 7-methyl- and 1-methyl derivatives were prepared as is shown in Fig. 4.

The 7-phenyl- (26) and 7-methyl (28) derivatives were prepared by the method used for the compound 13, except that phenylhydrazine and methylhydrazine, respectively, were used instead of hydrazine. They were then converted to the tetrahydro compounds (27, 29) by catalytic hydrogenation. The bands corresponding to the secondary amino group appeared at 3340 cm^{-1} for 27 and at 3280 cm^{-1} for 29. The compound, however, does not show this band; this indicates that compounds 27 and 29 have undergone hydrogenation at the pyridine nucleus as well.

The color reaction of 8-hydroxyquinoline with ferric chloride is well known. The compound 13 did not give this color reaction, whereas the compound 14 did. This is because the enol form predominates, in contrast to the case of compound 13. The tetrahydro 7-phenyl and 7-methyl compounds cannot exist in the enol form; therefore, they do not show the color reaction. On the other hand, the compound 30, which was prepared by the direct *N*-methylation of the compound 14, gave the color reaction, although it was much weaker than 14; moreover, it did not exhibit a band in the infrared spectrum corresponding to a secondary amino group.

Pyrido[2, 3-*d*]pyridazin-5(6H)-one (20) was also treated in the same way as pyrido[2, 3-*d*]pyridazin-8(7H)-one (13), as is shown in Fig. 5.

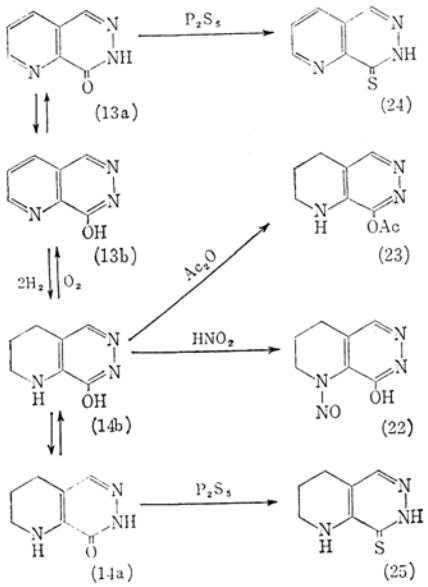


Fig. 3.

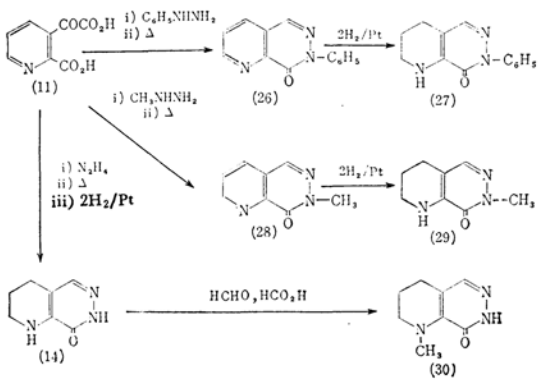


Fig. 4.

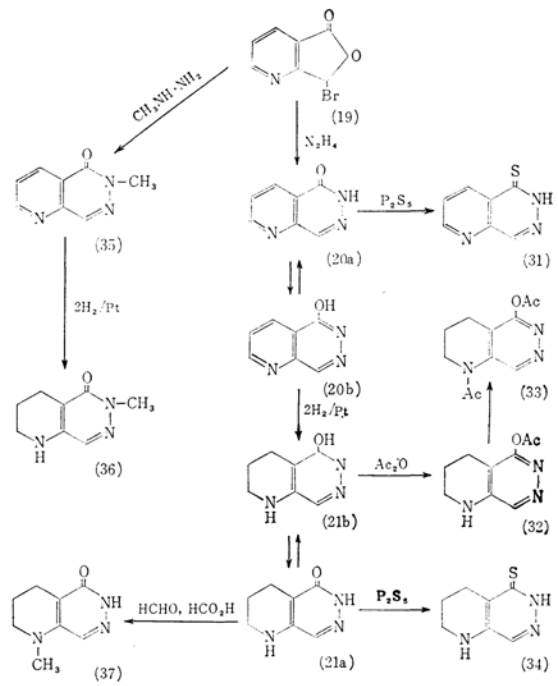


Fig. 5.

It was found that tetrahydropyrido[2, 3-*d*]-pyridazin-5(6H)-one (21) had a secondary amino group in the same way as has been shown in the case of the compound 14, and when it was directly methylated, the band at 3300 cm^{-1} disappeared. The isomeric 5-methyl tetrahydro compound (36), which was prepared from the compound 35, has the absorption band. All reactions of compound 21 are the same as those of compound 14 except for acetylation, in which the *O*-acetyl compound (32) and the diacetyl compound (33) were obtained.

TABLE 1. MAJOR ABSORPTION BANDS IN INFRARED SPECTRA IN cm^{-1}

	Amino group	Carbonyl group and others
Pyrido[2, 3-*d*]pyridazin-8(7H)-one (13)	3225(w), 3105(w)	1695, 1677
Tetrahydro compound of 13 (14)	3300(s), 3105(w)	1640, 1603
7-Methyl compound of 13 (28)	—	1658, 1592
7-Methyl tetrahydro comp. (29)	3278(s)	1626, 1600
1-Methyl tetrahydro comp. (30)	—	1623, 1587
O-Acetyl tetrahydro comp. (23)	3300(s)	1664, 1647, 1574, 1261 (-O-C)
1-Nitroso tetrahydro comp. (22)	3155(w)	1655, 1600, 1438 (N-NO)
7-Phenyl compound of 13 (26)	—	1743, 1672
7-Phenyl tetrahydro comp. (27)	3344(s)	1640, 1610
S-Compound of 13 (24)	3155(w), 3100(w)	1025 (C=S)
S-Comp. of tetrahydro comp. (25)	3311(s), 3175(w), 3058(w)	1020 (C=S)
Pyrido[2, 3-*d*]pyridazin-5(6H)-one (20)	3215(w), 3100(w)	1675, 1665
Tetrahydro compound of 20 (21)	3310(s), 3105(w)	1640, 1598
6-Methyl comp. of 20 (35)	—	1660, 1595
6-Methyl tetrahydro comp. (36)	3210(s)	1620, 1585
1-Methyl tetrahydro comp. (37)	—	1618, 1590
O-Acetyl tetrahydro comp. (32)	3250(s)	1666, 1635, 1602, 1243 (-O-C)
Diacetyl tetrahydro comp. (33)	3160(w)	1735, 1675, 1615, 1255 (-O-C)
S-Compound of 20 (31)	3150(w), 3075(s)	1020 (C=S)
S-comp. of tetrahydro comp. (34)	3310(s), 3190(w), 3075(w)	1030 (C=S)
Pyrido[2, 3-*d*]pyridazin-5, 8(6H, 7H)-dione (38)	3190(w), 3095(w)	1690, 1635
Tetrahydro compound of 38 (39)	3250(s), 3110(w), 3075(w)	1640, 1600
O-Acetyl tetrahydro comp. (40)	3205(s)	1665, 1642, 1600, 1247 (-O-C)
Diacetyl tetrahydro comp. (41)	3110(w)	1770, 1680, 1635, 1241 (-O-C)

The infrared absorption data for the above compounds are shown in Table 1.

From these experiments on the two series of compounds, it was concluded that the hydrogenation of the pyridopyridazinone system occurs, unexpectedly, at the pyridine nucleus and not at the pyridazinone nucleus. In confirmation of this conclusion, several of the NMR signals observed are shown in Table 2.

Pyrido[2, 3-*d*]pyridazin-5, 8(6H, 7H)-dione (38) was hydrogenated by the same method as was used for the two series. The reaction product, (39), was shown to be 1, 2, 3, 4-tetrahydropyrido-[2, 3-*d*]pyridazin-5, 8(6H, 7H)-dione from a study of its infrared and NMR spectra. Benzo[*d*]-pyridazin-1, 4(2H, 3H)-dione was not hydrogenated under the same conditions.

A compound 39 was acetylated to give an *O*-acetyl compound, 40, and diacetyl compound, 41. Compound 39 has a color reaction with ferric chloride, but compounds 40 and 41 do not; therefore, the *O*-acetyl compound must be an 8-acetyl derivative. The observation of the infrared absorption spectrum confirms this.

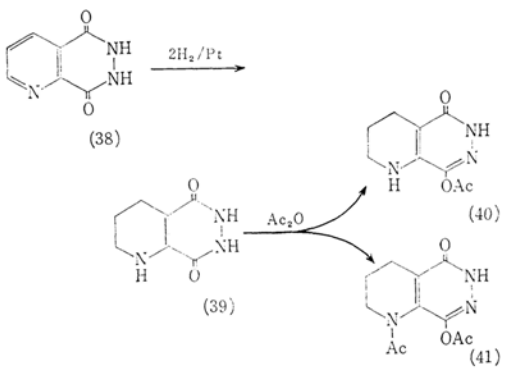


Fig. 6.

Experimental

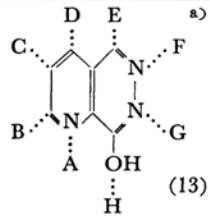
1, 2, 3, 4-Tetrahydropyrido[2, 3-*d*]pyridazin-8-(7H)-one (14). Compound 13 (2.5 g) was hydrogenated under atmospheric pressure at room temperature over a platinum catalyst (0.3 g of $PtO_2 \cdot H_2O$) in 50 m*l* of acetic acid until absorption had ceased. About 860 m*l* of hydrogen was absorbed during 3 hr. The reaction mixture was then evaporated to dryness under reduced pressure. The crystalline residue was recrystallized from water to give colorless prisms, mp 223°C; yield 2.5 g.

Found: C, 50.05; H, 6.64%. Calcd for $C_7H_9ON_3 \cdot H_2O$: C, 49.69; H, 6.55%.

The anhydrous substance was obtained by the vacuum sublimation of the monohydrate.

Found: C, 55.68; H, 6.12%. Calcd for $C_7H_9ON_3$: C, 55.61; H, 6.00%.

TABLE 2. τ VALUE OF NMR SPECTRA

	A	B	C	D	E	F	G	H
 (13) [a]	—	0.62(q) (1H)	2.17(q) (1H)	1.05(q) (1H)	1.62(s) (1H)	—	—	6.75(s) (1H)
		J_{BC}=4.5, J_{CD}=8.0, J_{BD}=2.0 (cps)						
(14)[a]	3.57(br) (1H)	6.75(t) (2H)	8.11(m) (2H)	7.45(t) (2H)	2.65(s) (1H)	—	−2.27(br) (1H)	—
(28)[b]	—	0.88(q) (1H)	2.28(q) (1H)	1.88(q) (1H)	1.82(s) (1H)	—	6.11(s) (3H)	—
		J_{BC}=4.5, J_{CD}=9.0, J_{BD}=2.0 (cps)						
(29)[b]	4.90(br) (1H)	6.60(t) (2H)	8.20(m) (2H)	7.50(t) (2H)	2.63(s) (1H)	—	6.31(s) (3H)	—
(30)[b]	6.51(s) (3H)	6.78(br) (2H)	8.10(br) (2H)	7.45(br) (2H)	2.65(s) (1H)	—		
(20)[a]	—	0.90(q) (1H)	2.18(q) (1H)	1.43(q) (1H)	6.75(s) (1H)	—	—	1.63(s) (1H)
		J_{BC}=4.5, J_{CD}=8.0, J_{BD}=2.0 (cps)						
(21)[a]	3.30(br) (1H)	6.80(br) (2H)	8.25(br) (2H)	7.62(br) (2H)	—	−1.93(br) (1H)	—	2.67(s) (1H)
(35)[b]	—	0.95(q) (1H)	2.37(q) (1H)	1.30(q) (1H)	—	6.15(s) (3H)	—	1.60(s) (1H)
		J_{BC}=4.5, J_{CD}=8.5, J_{BD}=2.0 (cps)						
(36)[b]	5.10(br) (1H)	6.70(t) (2H)	8.15(m) (2H)	7.45(t) (2H)	—	6.32(s) (3H)	—	2.63(s) (1H)
(39)[a]	3.75(br) (1H)	6.75(br) (2H)	8.21(br) (2H)	7.63(br) (2H)	—			—

Solvent: s: singlet, t: triplet, q: quartet, m: multiplet, br: broad.
a) $(CD_3)_2SO$
b) $CDCl_3$

The Oxidation of Compound 14 to Compound 13. Compound 14 (0.30 g) was dissolved in 20 m*l* of acetic acid; then 40 m*l* of a 1/5 N chromic oxide solution in acetic acid was added to the solution, and it was allowed to stand 3 hr. The acetic acid was then evaporated under reduced pressure. The residue was treated with water, and the crystals were recrystallized from water; mp 305°C; yield, 0.25 g. Its identity as compound 13 was established by measuring its infrared spectrum and melting point.

***O* - Acetyl - 1, 2, 3, 4 - tetrahydropyrido [2, 3 - *d*] - pyridazin-8-ol (23).** Compound 14 (0.3 g) was refluxed with 3 m*l* of acetic anhydride for 3 hr. The reaction mixture was evaporated to dryness under reduced pressure, and the residue was treated with water to afford a crude crystalline mass, which was then recrystallized from alcohol to give colorless prisms 0.2 g; mp 172°C.

Found: C, 56.12; H, 5.62%. Calcd for $C_9H_{11}O_2N_3$: C, 56.16; H, 5.57%.

1- Nitroso - 1, 2, 3, 4 - tetrahydropyrido [2, 3 - *d*] - pyridazin-8(7H)-one (22). Compound 14 (0.2 g) was dissolved in 10 m*l* of N hydrochloric acid, and the solution was cooled to 0°C. A solution of 0.3 g of sodium nitrite in 10 m*l* of water was added, drop by drop, to the cooled solution, and the mixture was kept at 0—3°C for 1/2 hr. The mixture was then stirred for 1 hr at room temperature. The resultant clear solution was kept in an ice chamber overnight to afford yellow needles without recrystallization; mp 159°C; yield, 0.17 g.

Found: C, 46.47; H, 4.80%. Calcd for $C_7H_9O_2N_4$: C, 46.66; H, 4.48%.

Pyrido[2, 3-*d*]pyridazin-8(7H)-thione (24). Compound 13 (1.8 g) was refluxed with 4 g of phosphorus pentasulfide in 50 m*l* of pyridine. The reaction mixture was then dried on a steam bath. The residue was triturated with water, and the crystalline mass was recrystallized from pyridine-water as yellow needles, mp 212°C; yield, 1 g. The needles contained one mole of the water of crystallization.

Found: C, 46.65; H, 3.97; H_2O, 10.11%. Calcd for $C_7H_5SN_3 \cdot H_2O$: C, 46.39; H, 3.89; H_2O, 9.94%.

1, 2, 3, 4 - Tetrahydropyrido [2, 3 - *d*] pyridazin-8-(7H)-thione (25). Compound 14 was treated in the manner described above to give yellow prisms, mp 182°C.

Found: C, 50.01; H, 5.42%. Calcd for $C_7H_9SN_3$: C, 50.27; H, 5.42%.

7-Methyl-pyrido[2, 3-*d*]pyridazin-8(7H)-one (28).

Compound 11 (5 g) was heated with 6 g of monomethyl hydrazine on a steam bath for 6 hr, and then the reaction mixture was dried on a steam bath. The residue was slightly acidified with dilute hydrochloric acid, and the crystals were sublimed in a vacuum to give 28 (1.4 g; mp 192°C).

Found: C, 59.46; H, 4.36%. Calcd for $C_8H_7ON_3$: C, 59.62; H, 4.38%.

7-Methyl-1, 2, 3, 4-tetrahydropyrido[2, 3-*d*]pyridazin-8(7H)-one (29). Compound 28 was hydrogenated in the manner described in the case of 14 to give 29, mp 115°C.

Found: C, 58.13; H, 6.70%. Calcd for $C_8H_{11}ON_3$: C, 58.16; H, 6.71%.

7-Phenyl-pyrido[2, 3-*d*]pyridazin-8(7H)-one (26). Compound 11 was treated with phenylhydrazine in the manner described in the case of 28 to give 26, mp 199°C.

Found: C, 69.84; H, 4.18%. Calcd for $C_{13}H_9ON_3$: C, 69.94; H, 4.06%.

7-Phenyl-1, 2, 3, 4-tetrahydropyrido[2, 3-*d*]-pyridazin-8(7H)-one (27). Compound 26 was hydrogenated in the manner described in the case of 14 to give 27, mp 120°C.

Found: C, 68.61; H, 6.04%. Calcd for $C_{13}H_{13}ON_3$: C, 68.70; H, 5.77%.

1-Methyl-1, 2, 3, 4-tetrahydro[2, 3-*d*]pyridazin-8-(7H)-one (30). Compound 14 (0.2 g) was dissolved in 1.5 g of 90% formic acid, and then 3 m*l* of 35% formaldehyde solution was added to the solution. The mixture was heated for 6 hr on a steam bath and dried. After acidification with hydrochloric acid, the reaction mixture was dried. The residue was treated with a small amount of dilute ammonium hydroxide to give colorless crystals, which were then recrystallized from ethanol, mp 147°C.

Found: C, 58.13; H, 6.70%. Calcd for $C_8H_{11}ON_3$: C, 58,16; H, 6.71%.

Pyrido[2, 3-*d*]pyridazin-5(6H)-one (20). To a solution of 0.2 g of 18[7] in 30 m*l* of carbon tetrachloride, 0.28 g of *N*-bromosuccinimide and 0.1 g of benzoyl peroxide were added; after the mixture had been refluxed on a water bath for 2.5 hr, the succinimide isolated from the solution was filtered off. The filtrate was treated with a 5% sodium bisulfite solution to remove free bromine, washed with water, dried with calcium chloride, and then evaporated. The residue was dissolved in 10 m*l* of ethanol, and 0.3 g of hydrazine hydrate was added to the solution. It was refluxed on a water bath for 1 hr. After cooling, the crystalline mass was recrystallized from ethanol; mp 261—263°C; yield, 0.11 g.

Found: C, 56.87; H, 3.41%. Calcd for $C_7H_5ON_3$: C, 57.14; H, 3.43%.

1, 2, 3, 4-Tetrahydropyrido[2, 3-*d*]pyridazin-5-(6H)-one (21). Compound 20 (1.5 g) was dissolved in 60 m*l* of acetic acid and hydrogenated by the method mentioned above. Colorless plates were obtained by recrystallization from ethanol; mp 241—243°C; yield, 1.2 g.

Found: C, 55.36; H, 6.15%. Calcd for $C_7H_9ON_3$: C, 55.61; H, 6.00%.

7) H. J. Rimek, *Ann.*, **670**, 69 (1963).

The Acetylation of Compound 21. A solution of 0.4 g of 21 in 5 m*l* of acetic anhydride was refluxed for 3 hr. When it was cooled for 12 hr, crude crystals of the diacetyl compound 33, mp 220—221°C (decomp.), separated from the solution.

Found: C, 56.41; H, 5.72; $COCH_3$, 35.2%. Calcd for $C_7H_8ON_3 \cdot 2(COCH_3)$: C, 56.16; H, 5.57; $COCH_3$, 36.6%.

The filtrate was dried, and the residue was recrystallized from ethanol to give 0.17 g of the *O*-acetyl compound 32, mp 204°C.

Found: C, 56.00; H, 5.78; $COCH_3$, 23.1%. Calcd for $C_7H_8ON_3 \cdot COCH_3$: C, 55.95; H, 5.74; $COCH_3$; 22.3%.

Pyrido[2, 3-*d*]pyridazin-5(6H)-thione (31). To a solution of 0.5 g of 20 in pyridine, 1 g of phosphorus pentasulfide was added; the solution was then refluxed for 10 hr and dried on a water bath. The residue was recrystallized from water-pyridine to give yellow needles, mp 205—207°C.

Found: C, 51.46; H, 3.34. Calcd for $C_7H_5SN_3$: C, 51.53; H, 3.09%.

1, 2, 3, 4-Tetrahydropyrido[2, 3-*d*]pyridazin-5-(6H)-thione (34). This compound was obtained from 21 by the method described for 25, mp 180—182°C.

Found: C, 50.46; H, 5.66. Calcd for $C_7H_9SN_3$: C, 50.27; H, 5.42%.

6-Methyl-pyrido[2, 3-*d*]pyridazin-5(6H)-one (35). Compound 18 (1.5 g) was brominated by the method described for 20, and then to its solution in 10 m*l* of ethanol, 1.9 g of monomethyl hydrazine sulfate and 1.1 g of sodium hydroxide were added and the mixture was refluxed for 2.5 hr. After cooling, sodium sulfate was filtered off, and the filtrate was evaporated to dryness. The residue was triturated with acetone to afford a crystalline mass, which was recrystallized from ethanol to give 0.45 g of 35, mp 110—112°C.

Found: C, 59.61; H, 4.56%. Calcd for $C_8H_7ON_3$: C, 59.62; H, 4.38%.

6-Methyl-1, 2, 3, 4-tetrahydropyrido[2, 3-*d*]pyridazin-5(6H)-one (36). This compound was prepared by the method described for 14, mp 172—174°C.

Found: C, 57.91; H, 6.69%. Calcd for $C_8H_{11}ON_3$: C, 58.16; H, 6.71%.

1-Methyl-1, 2, 3, 4-tetrahydropyrido[2, 3-*d*]pyridazin-5(6H)-one (37). This compound was prepared by the method described for 30, mp 212—214°C.

Found: C, 58.15; H, 6.65%. Calcd for $C_8H_{11}ON_3$: C, 58.16; H, 6.71%.

1, 2, 3, 4-Tetrahydropyrido[2, 3-*d*]pyridazin-5, 8-(6H, 7H)-dione (39). Compound 38 was hydrogenated in the manner described in the case of 14 to give 39 mp 291—293°C.

Found: C, 50.80; H, 5.65%. Calcd for $C_7H_9O_2N_3$: C, 50.29; H, 5.43%.

The Acetylation of 1, 2, 3, 4-Tetrahydropyrido-[2, 3-*d*]pyridazin-5, 8(6H, 7H)-dione. Compound 39 (1.0 g) was acetylated with 10 m*l* of acetic anhydride by the method used in the case of 11 to give 0.35 g of the diacetyl compound 41, mp 159—161°C and 0.25 g of the monoacetyl compound 40, mp 196—198°C.

Found: C, 52.74; H, 5.32; $COCH_3$, 33.1%. Calcd

for $C_7H_5O_2N_3 \cdot 2(COCH_3)$: C, 52.58; H, 5.22; $COCH_3$, 34.2%. $C_7H_8O_2N_3 \cdot COCH_3$: C, 51.67; H, 5.30; $COCH_3$, 20.6%.

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