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Pyridazines. XXXVIII. Pyrrolo[1,2-*b*]pyridazines and 4*H*-4a,7b-Diazacyclopent[*cd*]indenes

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Pyrrolo[1,2-*b*]pyridazines have been prepared and investigated for electrophilic substitutions. Depending on the electrophile and reaction conditions, mono, di, tri or tetrasubstituted derivatives were formed. Some investigations are reported also for the related 4*H*-4a,7b-diazacyclopent[cd]-indenes.

Our interest in azolopyridazines (1) prompted us to investigate the heteroaromatic pyrrolo[1,2-*b*]pyridazines (2). While our investigations were in progress, a report by Flitsch and Krämer (3,4) describing similar investigations appeared. As it will be shown later, some of their findings are consistent with ours, whereas others do not correlate with physicochemical evidence and therefore structural reassignments have been made.

The synthetic approach most frequently employed to form pyrrolo[1,2-*b*]pyridazines (I) involves the reaction between pyridazines and esters of acetylenedicarboxylic acid (5-7). Pyrrolo[1,2-*b*]pyridazines can also be conveniently prepared from *N*-aminopyrrole and 1,3-dicarbonyl compounds. With acetoacetic ester, ethyl cyclopentan-2-one- or cyclohexan-2-onecarboxylate the corresponding enehydrazines (II, III n = 1,2, respectively) were isolated.

In our attempt to cyclize compound III (n = 1) in polyphosphoric acid, instead of the expected pyrrolo[1,2-*b*]-pyridazine derivative, a cyclopentapyrazolone (IV) was obtained. The structure was ascertained on the basis of its NMR and mass spectrum. This reaction can be explained to proceed by hydrolysis of III followed by condensation of the liberated hydrazine with the β-keto ester to give an intermediate hydrazino derivative, possibly of the type V, which cyclizes subsequently to IV. To get more insight into the above transformation, ethyl cyclopentan-2-onecarboxylate was allowed to react with hydrazine hydrate in the presence of acetic acid and a mixture of V and the cyclopentapyrazolone (VI) was isolated and identified. However, when compound V was heated in polyphosphoric acid the tetracyclic product VII was obtained. NMR and mass spectral data support the proposed structure.

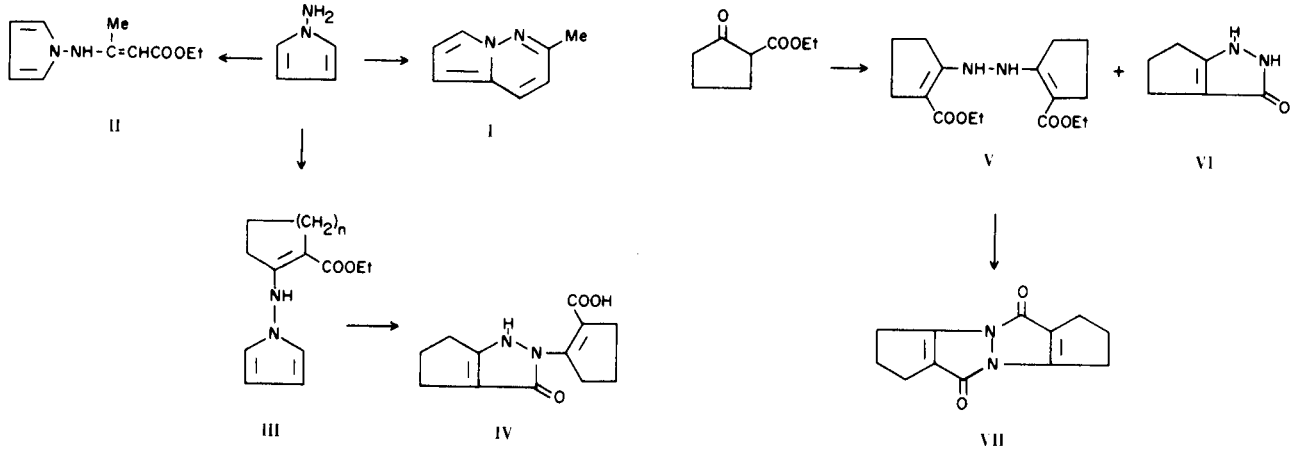
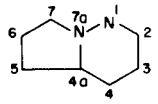


TABLE I

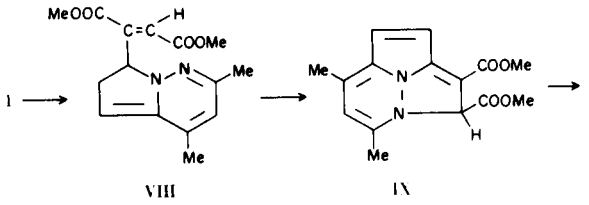
Calculated Electron Densities for Pyrrolo[1,2-*b*]pyridazine



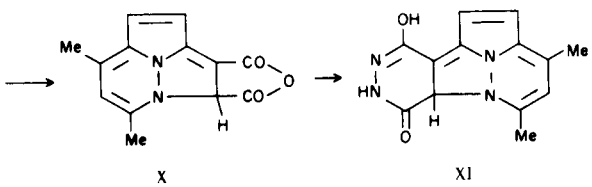
Position	1	2	3	4	4a	5	6	7	7a
A	1.1757	0.9570	1.0155	0.9425	1.0260	1.1292	1.0625	1.0994	1.5922
B	0.1734	0.0094	0.1483	0.0675	0.0757	0.2340	0.0049	0.2638	0.0230

A = total π-electron density. B = frontier electron density.

2,4-Dimethylpyrrolo[1,2-*b*]pyridazine (I, R = Me) added dimethyl acetylenedicarboxylate to afford the substituted fumarate (VIII) which could be cyclized to the tricyclic diazacyclopentindene derivative (IX). A similar reaction with pyrrolo[1,2-*a*]pyridine (indolizine) (8) leads directly to the corresponding tricyclic compound and the reaction is regarded as /8+2/-cycloaddition (9). Saponification and subsequent acidification of the diester (IX) afforded the corresponding anhydride (X) which is formed with unexpected ease and which was characterized by two carbonyl bands in the IR spectrum at 1825 and 1757 cm^{-1} (10) and by its condensation with hydrazine to the condensed pyridazine derivative (XI, or its tautomer). The aforementioned reaction with dimethyl acetylenedicarboxylate indicated a high reactivity at position 7 of the pyrrolo[1,2-*b*]pyridazine ring. Indeed, the calculated total π- and frontier electron densities for the parent system (11) (Table I) suggest that positions 7 and 5 should undergo electrophilic attack most easily. So far, protonation (4) has been observed to take place preferentially at position 7, but to some extent also at position 5. With the 2,4-dimethyl- or 2-methyl-4-phenyl- derivatives an additional activation should be expected at the already somewhat prone position, 3, for electrophilic attack.



VIII IX



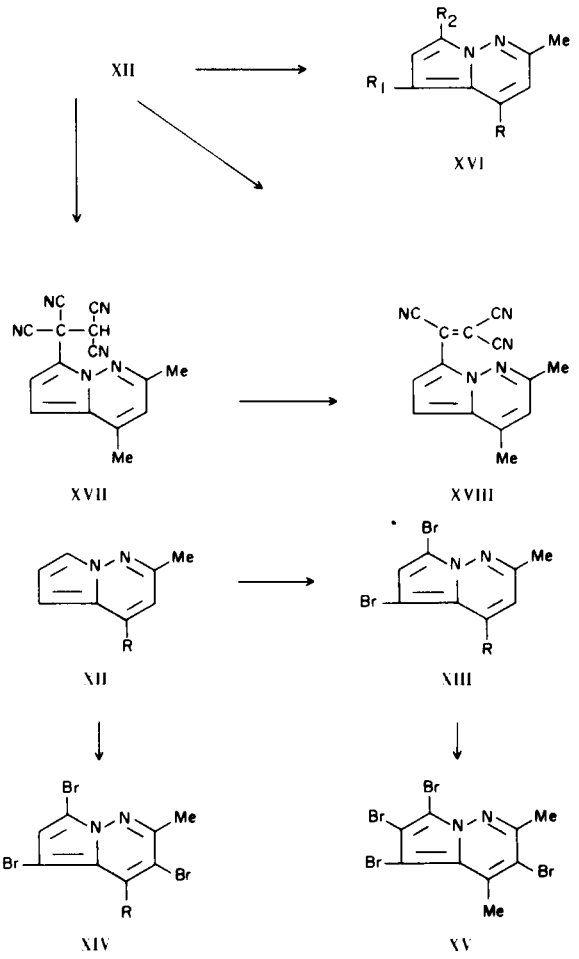
X XI

Thus, bromination with *N*-bromosuccinimide of XII (R = Me or Ph) afforded the dibromo compound XIII (R = Me or Ph), whereas with bromine in glacial acetic acid, in carbon tetrachloride or in chloroform a tribromo compound (XIV, R = Me or Ph) was formed. The structure of this tribromo compound was established on the basis of NMR data correlation with the parent and other brominated products as the 3,5,7-tribromo derivative (XIV, R = Me) and not as the 5,6,7-tribromo derivative as suggested for the product isolated from bromination in chloroform by Flitsch and Krämer (4). Another bromo compound was obtained from bromination of the dibromo product (XIII, R = Me) with bromine in carbon tetrachloride. The product was identified as a tetrabromo derivative and to it, structure XV has been assigned.

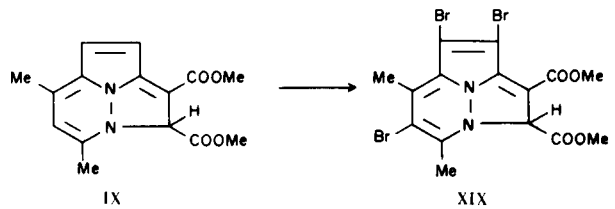
Further studies of electrophilic substitution involved nitration which afforded the 5,7-dinitro compound (XVI, R = Me, $R_1 = R_2 = NO_2$) when starting with the 2,4-dimethyl derivative (XII, R = Me), whereas the 4-phenyl analog (XII, R = Ph) afforded a trinitro derivative with the third nitro group attached to the phenyl substituent (XVI, R = *p*-NO_2-C_6H_4-, $R_1 = R_2 = NO_2$). Less strong electrophiles afforded only monosubstitution products and thus nitrosation, azo coupling or acylation with trifluoroacetic anhydride proceeded at position 7 only (XVI, R = Me, R_1 = H, R_2 = NO or -N = NAr or CF_3CO).

It has also been reported (3,4) that pyrrolo[1,2-*b*]pyridazines react with tetracyanoethylene to form the corresponding tricyanovinyl derivatives of type XVIII. We have found that the reaction proceeds *via* an addition product

XVII. This tetracyanoethane derivative on crystallization or when heated alone eliminates hydrogen cyanide and is transformed into the unsaturated analog XVIII. As already observed, the addition of tetracyanoethylene takes place at position 7.



Finally, it was of interest to examine the tricyclic compound IX for electrophilic substitution. With *N*-bromosuccinimide in carbon tetrachloride or with bromine in glacial acetic acid only the 1,2,6-tribromo derivative (XIX) was formed, demonstrating once again the susceptibility of the six-membered ring for electrophilic attack. The formation of a tetrabromo derivative, which was claimed to result from bromination with bromine in chloroform (4) was not observed.



EXPERIMENTAL (12)

2,4-Dimethylpyrrolo[1,2-*b*]pyridazine (I, R = CH_3).

1-Aminopyrrole (13,14) (1.0 g.), glacial acetic acid (5 ml.) and acetylacetone (1.2 g.) were heated on a water bath for 15 minutes. The cooled solution was neutralized with sodium bicarbonate and extracted with chloroform. After evaporation of the solvent, 1.3 g. (73%) of an oil was obtained, b.p. 72°/0.5 mm (Lit. (3,4) gives b.p. 69°/0.1 mm). NMR spectrum (in deuterioacetone), τ = 3.65 (s, H_3), 3.47 (dd, H_5), 3.18 (dd, H_6), 2.19 (dd, H_7), 7.65 (s, 2-CH_3 and 4-CH_3); $J_{5,6}$ = 4.5, $J_{6,7}$ = 2.7, $J_{5,7}$ = 1.8.

2-Methyl-4-phenylpyrrolo[1,2-*b*]pyridazine (I, R = C_6H_5).

The compound was prepared in a similar manner as above by employing 0.8 g. of *N*-aminopyrrole and 1.6 g. of benzoylacetone. The residual oil after evaporation of chloroform was cooled, filtered and the remaining crystals were dissolved in ethanol. The solution was poured into cold water and acidified with acetic acid (1.2 g. 60%), m.p. 52° (Lit. (3,4) gives m.p. 51°); NMR spectrum (in deuteriochloroform), τ = 3.51 (s, H_3), 3.35 (dd, H_5), 3.15 (dd, H_6), 2.20 (H_7, covered with the multiplet of C_6H_5), 2.3 (m, C_6H_5-), 7.50 (s, CH_3), $J_{5,6}$ = 4.2, $J_{6,7}$ = 2.7, $J_{5,7}$ = 1.5.

Ethyl β-(Pyrroloamino)crotonate (II).

A suspension of *N*-aminopyrrole (1.0 g.) in glacial acetic acid (5 ml.) was treated with acetoacetic ester (1.0 g.) and the mixture was heated at 60° for 3 hours. Upon cooling the crystals were collected and recrystallized from acetic acid, yield 0.9 g. (38%), m.p. 90° (Lit. (4) gives m.p. 94-96°). NMR spectrum (in deuteriochloroform), τ = 3.48 (m, H_2 and H_5 of pyrrole), 4.00 (m, H_3 and H_4 of pyrrole), -0.1 (broad, NH), 5.37 (s, H_α), 8.34 (s, β-CH_3), 8.80 (t, $COOCH_2CH_3$), 5.95 (q, $COOCH_2CH_3$); J_{COOEt} = 7.0.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.27; N, 14.42. Found: C, 61.90; H, 7.42; N, 14.75.

N-(2′-Carbethoxycyclopent-1′-enylamino)pyrrole (III, n = 1).

To a suspension of *N*-aminopyrrole (1.0 g.) in glacial acetic acid (5 ml.), ethyl cyclopentan-2-onecarboxylate (1.8 g.) was added and the mixture was heated at 40° for 15 minutes. The product was sublimed at 100°/0.1 mm, yield 2.0 g. (74%); m.p. 111-113°; NMR spectrum (in deuteriochloroform), τ 3.25 (m, H_2 and H_5 of pyrrole), 3.85 (m, H_3 and H_4 of pyrrole), + 0.6 (broad, NH), 7.55 (m, 3-CH_2- and 5-CH_2-), 8.16 (m, 4-CH_2-), 8.70 (t, $COOCH_2CH_3$), 5.76 (q, $COOCH_2CH_3$); J_{COOEt} = 7.0.

Anal. Calcd. for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.60; H, 7.08; N, 12.89.

N-(2′-Carboethoxycyclohex-1′-enylamino)pyrrole (III, n = 2).

This compound was prepared in essentially the same manner as the above analog but employing ethyl cyclohexan-2-onecarboxylate (2.0 g.). The product was recrystallized from ethanol (yield 1.2 g., 42%), m.p. 75-76°. NMR spectrum (deuteriochloroform), τ = 3.30 (m, H_2 and H_5 of pyrrole), 3.83 (m, H_3 and H_4 of pyrrole), -0.8 (broad, NH), 8.00 (m, 3-CH_2-), 7.70 (m, 6-CH_2), 8.40 (m, 4-CH_2- and 5-CH_2-), 8.70 (t, $COOCH_2CH_3$), 5.78 (q, $COOCH_2CH_3$); J_{COOEt} = 7.0.

Anal. Calcd. for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 66.34; H, 7.62; N, 11.78.

2-(2′-Carboxycyclopent-1′-enyl)-1,2,3,4,5,6-hexahydrocyclopentapyrazol-3-one (IV).

A mixture of the ester III (n = 1) (1.0 g.) and polyphosphoric acid (30 g., containing 83% phosphorus pentoxide) was heated at 80° for 2 hours. Upon cooling, water (40 ml.) was added, the prod-

uct was filtered off and purified by dissolution in *N,N*-dimethylformamide and pouring the solution in water, yield 150 mg. (28%); m.p. 160° dec.; NMR spectrum (in deuteriochloroform), τ = 8.0 (m, 4-CH_2- and 5-CH_2-), 7.15 (m, -CH_2- at 3,4,5 and 6), 6.15 (broad, COOH or NH).

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.52; H, 6.02; N, 11.96; Found: C, 61.72; H, 6.14; N, 11.88.

N,N'-bis-(2'-carboethoxycyclopent-1'-enyl)hydrazine (V) and 1,2,-3,4,5,6-hexahydrocyclopentapyrazol-3-one (VI).

A mixture of ethyl cyclopentan-2-onecarboxylate (6.24 g.), ethanol (20 ml.), glacial acetic acid (2 ml.) and hydrazine hydrate (1.3 g. of 80%) was heated under reflux for 30 minutes. The product (VI) was filtered off (1.0 g., 13%) and from the filtrate, after cooling, compound V separated (5.0 g., 81%) and was recrystallized from ethanol, m.p. 72.5°; NMR spectrum (in deuteriochloroform), τ = 8.0 (m, 4-CH_2-), 7.50 (m, 3-CH_2- and 5-CH_2), 5.85 (q, $COOCH_2CH_3$), 8.72 (t, $COOCH_2CH_3$); J_{COOEt} = 7.0.

Anal. Calcd. for $C_{16}H_{24}N_2O_4$: C, 62.35; H, 7.85; N, 9.09. Found: C, 62.51; H, 7.63; N, 9.08.

The other compound (VI) had m.p. 295° dec.

Anal. Calcd. for $C_6H_8N_2O$: C, 58.05; H, 6.50; N, 22.57. Found: C, 57.98; H, 6.48; N, 22.67.

5,10-Dihydrocyclopenta[2,3;6,7]pyrazolo[1,2-*a*]pyrazole-5,10-dione (VII).

The above compound V (1.0 g.) was heated in polyphosphoric acid (25 g.) at 80° for 2 hours. Upon cooling, water (40 ml.) was added and the product was filtered off. Upon recrystallization from ethanol the product (0.4 g., 57%) had m.p. 115°. NMR spectrum (in deuteriochloroform), τ = 7.32 (m, -CH_2-groups).

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.46; H, 5.50; N, 12.89.

Dimethyl (2,4-Dimethylpyrrolo[1,2-*b*]pyridazin-7-yl)fumarate (VIII).

A stirred mixture of I (R = CH_3; 1.0 g.), dimethyl acetylenedicarboxylate (1.0 g.) and ethanol (5 ml.) was treated with acetic acid (1 ml.) and heated on a water bath for 1 hour. Upon cooling the product separated and was recrystallized from ethanol (1.2 g., 61%), m.p. 96° (Lit. (4) gives m.p. 96°); NMR spectrum (in deuteriochloroform), τ = 3.60 (q, H_3), 3.38 (d, H_5), 2.75 (d, H_6), 7.57 (s, 2-CH_3), 7.60 (d, 4-CH_3), 3.10 (s, C=C*H*-COOMe), 6.17 and 6.31 (s, both $COOCH_3$ groups); $J_{5,6}$ = 4.8, $J_{3,4\text{-}CH_3}$ = 1.2.

5,7-Dimethyl-4*H*-4a,7b-diazacyclopent[*cd*]indene (IX).

Compound VIII (1.0 g.) was dissolved in ethanol (15 ml.), concentrated hydrochloric acid (1.0 ml.) was added and the mixture was heated on water bath for 2 hours. Upon cooling, the product was recrystallized from ethanol (0.5 g., 49%), m.p. 135° (Lit. (4) gives m.p. 137°); NMR spectrum (in deuteriochloroform), τ = 3.45 (d, H_1), 3.06 (d, H_2), 2.52 (s, H_4), 3.51 (q, H_6), 7.48 (s, 5-CH_3), 7.57 (d, 7-CH_3), 5.95 (s, 3-$COOCH_3$), 6.15 (s, 4-$COOCH_3$); $J_{1,2}$ = 4.8 $J_{6,7CH_3}$ = 0.75.

5,7-Dimethyl-4*H*-4a,7b-diazacyclopent[*cd*]indene-3,4-dicarboxylic Acid Anhydride (X).

The above diester (IX) (1.0 g.) and a solution of sodium hydroxide (15 ml. of 5%) were heated under reflux for 1.5 hours. The cooled reaction mixture was filtered and acidified with concentrated hydrochloric acid. The crystals were recrystallized from glacial acetic acid (0.7 g., 83%), m.p. 248-250°; NMR spectrum (in deuterio DMSO-d_6 at 100°), τ = 3.19 (d, H_1), 2.28 (d, H_2), 2.60 (s, H_4), 3.14 (q, H_6), 7.45 (s, 5-CH_3), 7.50 (d, 7-CH_3); $J_{1,2}$ = 4.5, $J_{6,7\text{-}CH_3}$ = 0.7.

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.57. Found: C, 64.48; H, 4.11; N, 11.30.

3,5-Dimethyl-9-hydroxy-5b*H*-5a,7,8,9c-tetraazacyclopenta[*jk*]-fluoren-6(7*H*)one (XI).

A solution of the anhydride X (0.5 g.) in glacial acetic acid (5 ml.) was treated with hydrazine hydrate (0.15 g. of 80%) and the mixture was heated under reflux for 3 hours. Upon cooling, the product was collected and sublimed at 250°/0.1 mm (0.3 g., 56%), m.p. 360° dec.

Anal. Calcd. for $C_{13}H_{12}N_4O_2$: C, 60.93; H, 4.72; N, 21.87. Found: C, 61.19; H, 4.70; N, 21.98.

5,7-Dibromo-2,4-dimethylpyrrolo[1,2-*b*]pyridazine (XIII, R = CH_3).

A mixture of compound XII (R = CH_3, 1.0 g.), carbon tetrachloride (15 ml.) and *N*-bromosuccinimide (1.2 g.) was heated under reflux for 1 hour. Upon cooling and filtration the filtrate was neutralized with sodium bicarbonate and the mixture filtered again. The carbon tetrachloride layer was dried (magnesium sulfate) and the solvent evaporated *in vacuo* to dryness. The pasty residue was recrystallized from methanol-ethanol (1:1) (0.8 g., 37% yield), m.p. 104-106°. NMR spectrum (in deuteriochloroform), τ = 3.70 (q, H_3), 3.16 (s, H_6), 7.54 (s, 2-CH_3), 7.30 (d, 4-CH_3); $J_{3,4\text{-}CH_3}$ = 0.9.

Anal. Calcd. for $C_9H_8Br_2N_2$: C, 35.56; H, 2.65; N, 9.25. Found: C, 35.42; H, 2.64; N, 9.36.

5,7-Dibromo-2-methyl-4-phenylpyrrolo[1,2-*b*]pyridazine (XIII, R = C_6H_5).

The compound was prepared as above and the product was recrystallized from methanol-ethanol (1:1) (0.8 g., 44% yield), m.p. 133-135°. NMR spectrum (in deuteriochlorofrom), τ = 2.50 (H_3, partially covered with the phenyl multiplet), 3.13 (s, H_6), 7.27 (s, 2-CH_3), 2.55 (m, 4-C_6H_5).

Anal. Calcd. for $C_{14}H_{10}Br_2N_2$: C, 45.94; H, 2.75; N, 7.65. Found: C, 46.12; H, 2.98; N, 7.65.

2,4-Dimethyl-3,5,7-tribromopyrrolo[1,2-*b*]pyridazine (XIV), R = CH_3).

A stirred mixture of compound XII (R = CH_3, 1.0 g.) and glacial acetic acid (5 ml.) was treated dropwise with a solution of bromine (3.3 g.) in glacial acetic acid (5 ml.). After the addition was complete stirring was continued for 15 minutes at room temperature, the crystals were separated and washed with glacial acetic acid. The product was purified by sublimation at 160° (1.6 g., 61%), m.p. 183° (Lit. (4) gives m.p. 160-180° but designates the compound as the 5,6,7-tribromo derivative, *i.e.* as 1,2,3-tribromo-6,8-dimethyl-5-azaindolizine); NMR spectrum (in deuteriochloroform, τ = 3.18 (s, H_6), 7.13 (s) and 7.34 (s) for 2-CH_3 and 4-CH_3.

Anal. Calcd. for $C_9H_7Br_3N_2$: C, 28.23; H, 1.84; N, 7.31. Found: C, 28.06; H, 2.05; N, 6.99.

2-Methyl-4-phenyl-3,5,7-tribromopyrrolo[1,2-*b*]pyridazine (XIV, R = C_6H_5).

It was obtained in the same way as the above methyl analog in 46% yield, m.p. 115° (from methanol-ethanol, 1:1); NMR spectrum (in deuteriochlorofrom), τ = 3.13 (s, H_6), 7.26 (s, 2-CH_3), 2.50 (m, 4-C_6H_5).

Anal. Calcd. for $C_{14}H_9Br_3N_2$: C, 37.79; H, 2.04; N, 6.29. Found: C, 37.91; H, 2.26; N, 6.22.

2,4-Dimethyl-3,5,6,7-tetrabromopyrrolo[1,2-*b*]pyridazine (XV).

The 5,7-dibromo compound (XIII, R = CH_3; 1.0 g.) was dissolved in carbon tetrachloride (10 ml.) and bromine (1.5 ml.) was added with stirring. The product (1.3 g., 85%) had m.p. 140°; NMR spectrum (in deuteriochloroform), τ = 7.17 and 7.37 (s, 2-CH_3 and 4-CH_3).

Anal. Calcd. for $C_9H_6Br_4N_2$: C, 23.41; H, 1.37; N, 6.07. Found: C, 23.57; H, 1.33; N, 6.03.

2,4-Dimethyl-7-nitrosopyrrolo[1,2-*b*]pyridazine (XVI, R = CH_3. R_1 = H, R_2 = NO).

A suspension of compound XII (R = CH_3; 0.5 g.) in hydrochloric acid (5 ml. of 2*N*) was treated portionwise with sodium nitrite (0.23 g.). Thereafter the mixture was heated on water bath for 15 minutes, neutralized with sodium carbonate, the product was collected and recrystallized from ethanol (yield 0.25 g., 41%); m.p. 160°; NMR spectrum (in deuteriochloroform), τ = 2.87 (q, H_3), 3.35 (degenerated dd, H_5,H_6), 7.25 (2-CH_3, s), 7.42 (d, 4-CH_3); $J_{5,6}$ = 4.8, $J_{3,4\text{-}CH_3}$ = 1.2.

Anal. Calcd. for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.48; H, 5.23; N, 23.58.

2,4-Dimethyl-7-trifluoroacetylpyrrolo[1,2-*b*]pyridazine (XVI, R = CH_3, R_1 = H, R_2 = CF_3CO).

Compound XII (R = CH_3; 1.0 g.) was carefully introduced into trifluoroacetic anhydride (10 ml.). The solution was then heated under reflux for 15 hours. The cooled solution was left in an open vessel in a hood at room temperature for 12 hours and thereafter poured into water. The product (0.9 g., 45%) had m.p. 149-152°; NMR spectrum (in deuteriochloroform), τ = 3.26 (q, H_3), 3.45 (d, H_5), 2.45 (dq, H_6), 7.39 (s, 2-CH_3), 7.48 (d, 4-CH_3); $J_{5,6}$ = 4.8; $J_{3,4\text{-}CH_3}$ = 0.9, $J_{6,COCF_3}$ = 2.4.

Anal. Calcd. for $C_{11}H_9F_3N_2O$: C, 54.51; H, 3.74; N, 11.56. Found: C, 54.44; H, 3.76; N, 11.38.

2,4-Dimethyl-7-(*p*-nitrophenylazo)pyrrolo[1,2-*b*]pyridazine (XVI, R = CH_3, R_1 = H, R_2 = *p*-$NO_2C_6H_4$-N=N-).

The dimethyl compound XII (R = CH_3; 1.0 g.) in methanol (5 ml.) was treated dropwise with a solution of diazotized *p*-nitroaniline. The separated product was recrystallized from methanol-ethanol (1:1) (0.8 g., 40%), m.p. 180°.

Anal. Calcd. for $C_{15}H_{13}N_5O_2$: C, 61.01; H, 4.44; N, 23.72. Found: C, 61.12; H, 4.55; N, 23.82.

2,4-Dimethyl-7-phenylazopyrrolo[1,2-*b*]pyridazine Hydrochloride (XVI, R = CH_3, R_1 = H, R_2 = C_6H_5N=N-).

This compound was obtained in the same manner as the above analog in 53% yield, m.p. 178-180°; NMR spectrum (in deuterio DMSO-d_6 at 67°), τ = 3.25 (q, H_3), 3.25 (d, H_5), 2.87 (d, H_6), 7.50 (s, 2-CH_3), 7.55 (d, 4-CH_3), 2.40 (m, C_6H_5-); $J_{5,6}$ = 4.9; $J_{3,4\text{-}CH_3}$ = 0.9.

Anal. Calcd. for $C_{15}H_{15}ClN_4$: C, 62.82; H, 5.28; N, 19.54. Found: C, 62.88; H, 5.29; N, 19.87.

2,4-Dimethyl-5,7-dinitropyrrolo[1,2-*b*]pyridazine (XVI, R = CH_3, R_1 = R_2 = NO_2).

To an ice cold solution of compound XII (R = CH_3, 1.0 g.) in concentrated sulfuric acid (5 ml.) and nitric acid (0.34 ml. of d = 1.5) was added dropwise. After addition was complete, the mixture was left to stand at room temperature for 30 minutes, poured on ice and the product was collected; yield 0.5 g., 31%, m.p. 137° (from methanol-ethanol, 1:1); NMR spectrum (in deuteriochloroform), τ = 3.03 (q, H_3), 1.90 (s, H_6), 7.37 (s, 2-CH_3), 7.19 (d, 4-CH_3); $J_{3,4\text{-}CH_3}$ = 0.9.

Anal. Calcd. for $C_9H_8N_4O_4$: C, 45.76; H, 3.41; N, 23.72. Found: C, 45.55; H, 3.41; N, 23.48.

5,7-Dinitro-2-methyl-4-(*p*-nitrophenyl)pyrrolo[1,2-*b*]pyridazine (XVI, R = *p*-$NO_2C_6H_4$-, R_1 = R_2 = NO_2).

The compound was prepared in the same manner as the above dinitro compound, but employing 1.0 g. of compound XII (R = C_6H_5), 10 ml. of sulfuric acid and 0.29 ml. of nitric acid (d = 1.5); yield 0.2 g., 12%, m.p. 92° (from methanol-ethanol, 1:1). NMR spectrum (in deuteriochloroform), τ = 2.67 (s, H_3), 1.62 (s, H_6), 7.17 (s, 2-CH_3), 1.60 and 2.35 (*m*, *p*-$NO_2C_6H_4$).

Anal. Calcd. for $C_{14}H_9N_5O_6$: C, 48.98; H, 2.64; N, 20.40. Found: C, 48.65; H, 2.97; N, 20.27.

[2,4-Dimethylpyrrolo[1,2-*b*]pyridazin-7-yl]tetracyanoethane (XVII).

To a solution of compound XII (R = CH_3, 1.0 g.) in acetone (5 ml.), tetracyanoethylene (0.8 g.) was added and the solution was set aside at room temperature for 2 hours. Thereafter it was poured in petroleum ether (40 ml.) and the product collected (0.9 g., 48%), m.p. 122-125°; NMR spectrum (in deuterio DMSO-d_6), τ = 2.82 (q, H_3), 2.98 (d, H_5), 2.22 (d, H_6), 7.47 (2-CH_3 and 4-CH_3, partially covered with the peak of DMSO); $J_{5,6}$ = 4.5; $J_{3,4\text{-}CH_4}$ = 1.0, τ = 3.87 (s, -*CH*$(CN)_2$).

Anal. Calcd. for $C_{15}H_{10}N_6$: C, 65.68; H, 3.68; N, 30.64. Found: C, 65.34; H, 3.93; N, 30.87.

[2,4-Dimethylpyrrolo[1,2-*b*]pyridazin-7-yl]tricyanoethylene (XVIII).

(a) Compound XII (R = CH_3, 1.0 g.) was treated portionwise while stirring with tetracyanoethylene (0.8 g.); thereafter acetone (5 ml.) was added and the mixture was poured into ice water (20 ml.). After standing on ice for 30 minutes, the separated crystals were collected and washed with cold water. The product was recrystallized from chloroform and petroleum ether (1:1). Yield 0.6 g. (36%); m.p. 204-205° (Lit. (4) gives m.p. 204°). NMR spectrum (in deuterio DMSO-d_6): τ = 2.82 (q, H_3), 2.94 (d, H_5), 2.18 (d, H_6), 7.47 (2-CH_3 and 4-CH_3, partially covered with DMSO); $J_{5,6}$ = 4.5; $J_{3,4\text{-}CH_3}$ = 1.0.

Anal. Calcd. for $C_{14}H_9N_5$: C, 68.00; H, 3.67; N, 28.33. Found: C, 67.81; H, 3.83; N, 28.45.

(b) Compound XVII (0.2 g.) was heated at 130° to melt and upon cooling the product was dissolved in acetone and poured into petroleum ether (yield 0.1 g., 55%); m.p. 204-205°. The compound was found to be identical in all respects with the product obtained as described under (a).

3,4-Dicarbomethoxy-5,7-dimethyl-1,2,6-tribromo-4*H*-4a,7b-diazacyclopent[*cd*]indene (XIX).

(a) A mixture of compound IX (0.5 g.), carbon tetrachloride (7 ml.) and *N*-bromosuccinimide (0.9 g.) was heated under reflux for 1 hour. The cooled mixture was filtered, neutralized with sodium bicarbonate, filtered again and the carbon tetrachloride layer dried (magnesium sulfate) and evaporated to dryness. The pasty residue was recrystallized from ethanol (0.3 g., 33%); m.p. 178°. NMR spectrum (in deuteriochloroform): τ = 2.62 (s, H_4), 7.47 (s, 5-CH_3), 7.12 (s, 7-CH_3), 6.08 (s, 3-$COOCH_3$), 6.20 (s, 4-$COOCH_3$).

Anal. Calcd. for $C_{15}H_{13}Br_3N_2O_4$: C, 34.31; H, 2.49; N, 5.34. Found: C, 34.71; H, 2.57; N, 5.30.

(b) To a warm solution of compound IX (1.0 g.) in glacial acetic acid (25 ml.) under stirring a solution of bromine (3.0 g.) in glacial acetic acid (5 ml.) was added dropwise. The separated product was recrystallized from glacial acetic acid (yield 0.4 g.)

and on the basis of its m.p., mixed m.p. and NMR spectrum it was found identical with the above tribromo compound, prepared as described under (a).

From the filtrate, when poured into water, a product separated (0.3 g., 14%) which was recrystallized from glacial acetic acid and had m.p. 120-130°. On the basis of its analysis, the product is a complex of the tribromo compound with ½ Br_2.

Anal. Calcd. for $C_{15}H_{13}Br_3N_2O_4 \cdot 1/2Br_2$: C, 29.71; H, 2.17; N, 4.63. Found: C, 29.35; H, 2.35; N, 4.49.

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