ethylbenzamide (16) in 5 ml of glacial acetic acid containing 10 ml of a hot saturated solution of chromium trioxide in glacial acetic acid was allowed to stir for 10 min. The dark green reaction mixture was poured onto ice water and filtered. The residue was washed with water and recrystallized from methanol to give a quantitative yield of dibenzamide as white needles, mp 144–145° (lit.[30] 144°). This material was identified as dibenzamide by a comparison of its infrared spectrum with that of an authentic sample prepared by the method of Lamberton and Standage.[30] A mixture melting point of these two materials was undepressed at 144–145°.

If the oxidation was allowed to proceed for only 2 min a partial oxidation product (17) as well as dibenzamide could be isolated by preparative thick layer chromatography. The structure of this material is assigned as N-1-phenyl-1-phenylglyoxylmethylbenzamide (17), mp 170–171°, on the basis of the following observations.

The infrared spectrum (in a potassium bromide pellet) was characterized by absorptions at 3.02, 5.84, 5.96, 6.06, 6.53, 6.89, 7.48, 7.71, 9.95, 11.82, 12.45, 13.20, 14.06, and 14.50 μ. The mass spectrum (70 eV) exhibited a molecular ion at m/e 343, prominent peaks at 222 (3.0), 221 (16.0), 165 (2.0), 106 (9.0), 105 (100), 52 (2.0), 51 (14.0), 50 (4.0), and had metastable peaks at 56 and 142.

Catalytic Hydrogenation of 1,4-Diphenyl-4-benzoyloxy-2-aza-butadiene (14).—A mixture of 0.08 g of 14 in 200 ml of dry methanol was hydrogenated in a Parr shaker over 0.1 g of 10% palladium on carbon at 50 psig for 3 hr. The catalyst was then removed by filtration and the filtrate concentrated *in vacuo* to leave a white solid, mp 206–208°. The structure of this compound was assigned as the benzylphenethylammonium salt of benzoic acid (19) on the basis of the following observations.

The infrared spectrum of 19 in a potassium bromide pellet showed broad adsorptions at 3.0 to 4.2, 6.3, 6.5, and 7.25 μ all of which are characteristic of benzoic acid salts. Additional bands appeared at 9.4, 9.8, 11.9, 13.3, 13.9, and 14.2 μ.

The structure of 19 was confirmed by generation of benzylphenethylamine from 19. A 0.05-g sample of 19 was dissolved in a 10% sodium carbonate solution and extracted with ether. The ether extracts were washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* gave an oil which was identical in all respects with an authentic sample of benzylphenethylamine.

Alternatively, treatment of 0.1 g of benzylphenethylamine with 0.1 g of benzoic acid in 3 ml of ether afforded a white precipitate. This material, mp 206–208°, was identical in all respects with the material isolated from the catalytic hydrogenation.

Treatment of 1,4-Diphenyl-4-benzoyloxy-2-aza-butadiene (14) with Sodium Methoxide.—A mixture of 0.3 g of 6 was dissolved in 20 ml of a freshly prepared 0.4 N sodium methoxide–methanol solution and was allowed to stir at room temperature for 4 hr. The colored reaction mixture was diluted with water and extracted twice with ether. The ethereal layer was washed with water and dried over anhydrous sodium sulfate. Removal of the solvent *in vacuo* afforded a crude bright yellow solid. Recrystallization from benzene–pentane produced yellow needles, mp 235–237° dec. The structure of this material was assigned as 2,5-dibenzoyl-3,6-diphenyl-1,4-dihydropyrazine (20) on the basis of the following observations.

Anal. Calcd for $C_{30}H_{22}O_2N_2$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.79; H, 5.23; N, 6.08.

The infrared spectrum (potassium bromide pellet) was characterized by bands at 3.09, 6.26, 7.06, 7.69, 8.05, 10.93, 11.31, 12.90, 13.47, and 14.25 μ. In order to demonstrate that the band at 3.09 was due to an N–H stretching mode, 0.01 g of 20 was allowed to reflux in methanol-OD for 1 hr. The solvent was removed *in vacuo* and the infrared spectrum revealed that the band at 3.09 μ (N–H) had disappeared and that a new band at 4.08 μ (N–D) had appeared. The nmr spectrum was characterized by a complex multiplet centered at τ 2.42. The mass spectrum (70 eV) had a molecular ion at m/e (relative intensity) 442 (3) and prominent peaks at 41 (37), 43 (62), 44 (40), 55 (38), 56 (16), 57 (80), 69 (30), 71 (50), 77 (68), 85 (33), 105 (100), 323 (35), 338 (40), 349 (30), 426 (60), 427 (20), and 428 (12). The ultraviolet spectrum in cyclohexane exhibited maxima at 235 mμ (ϵ 9100), 259 (6000), and 366 (5450).

Registry No.—1, 24290-58-2; 3, 24807-13-4; 4, 24807-14-5; 5, 24806-70-0; 6, 24807-15-6; 8, 24806-71-7; 13, 23112-19-8; 14, 24294-71-1; 15, 24806-73-3; 16, 24807-17-8; 17, 24807-18-9; 18, 24807-19-0; 19 benzylphenethylammonium salt, 24807-20-3; 20, 24807-21-4.

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Pyridazines. XXXV. Oxidation Products of Some Simple and Bicyclic Pyridazines

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N-Oxides of imidazo[1,2-*b*]pyridazine and *s*-triazolo[4,3-*b*]pyridazine have been obtained by direct oxidation with concentrated hydrogen peroxide in polyphosphoric acid. With several bicyclic compounds further oxidation afforded pyridazine derivatives. 6-Amino bicyclic compounds were resistant toward N-oxidation but afforded the corresponding 6-nitro compounds. Several displacement reactions on substituted pyridazine N-oxides have been performed, and it was also shown that nmr spectral characteristics can be used for distinguishing the site of N-oxidation.

We recently reported[1] the first representative of azoloazine N-oxides with bridgehead nitrogen, *i.e.*, *s*-triazolo[4,3-*b*]pyridazine 5-oxides, which were synthesized by cyclization of the appropriate pyridazine N-oxides since previous direct N-oxidation procedures have failed. We now report the successful direct N-oxidation of such bicyclic systems with concentrated hydrogen peroxide in polyphosphoric acid.

Imidazo[1,2-*b*]pyridazine and 85% hydrogen peroxide in polyphosphoric acid below 40° afforded the 5-oxide (2, X = CH; R = H) in moderate yield. However, with a large excess of the oxidizing agent 3-nitropyridazine 1-oxide was formed by degradative oxidation. A greater tendency toward degradation compared with N-oxidation could be observed with 6-chloro- or 6-methoxyimidazo[1,2-*b*]pyridazine which were transformed into 6-chloro-3-nitropyridazine 1-oxide and 6-methoxy-3-nitropyridazine, respectively. In the last case, the possible alternative structure of the product as a methoxynitrosopyridazine N-oxide could

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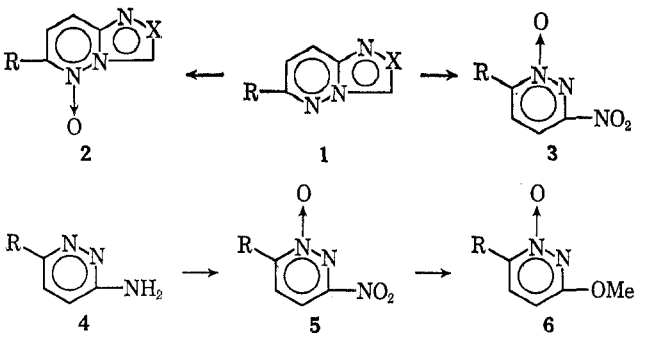

be excluded by the mass spectrum which showed peaks due to M − 30 (NO) and M − 46 (NO_2) loss, a pattern characteristic for organic nitro compounds.[2,3] So far, any variation of the composition of the oxidizing agent, *i.e.*, by employing 85% hydrogen peroxide in acetic, formic, or trifluoroacetic acid, left imidazo[1,2-*b*]-pyridazine unchanged and even traces of the expected 5-oxide could not be detected.

In a similar manner *s*-triazolo[4,3-*b*]pyridazine was oxidized into its 5-oxide (**2**, X = N; R = H) in low yield, a considerable amount of the starting bicyclic compound (**1**, X = N; R = H) remaining unchanged. Resistance toward N-oxidation was observed with 6-amino-*s*-triazolo[4,3-*b*]pyridazine and 6-aminoimidazo-[1,2-*b*]pyridazine, both of which afforded in good yield only the corresponding 6-nitro compounds (**1**, R = NO_2; X = CH or N). It appears that this amino-nitro group transformation greatly decreases the tendency toward N-oxidation and degradative oxidation, an effect undoubtedly due to the electron-withdrawing 6-nitro group.

Application of both polyphosphoric acid and highly concentrated hydrogen peroxide for N-oxidation of these azolopyridazines seems to be responsible for the successful progress of the reaction. Since the basicity of the attacked ring nitrogen is relatively low as judged from the calculated electron densities,[4] this would require a very reactive attacking species. The presence of polyphosphoric acid seems to be important for the uptake of the formed water, rather than acting as a proton donor or Lewis acid.

Since the above experience with the oxidative transformation of an amino group into nitro group could be of synthetic importance for the preparation of not readily accessible 3-nitropyridazine 1-oxides, experiments were extended in this direction.

In this manner 3-aminopyridazine afforded 3-nitropyridazine 1-oxide, and 3-amino-6-chloropyridazine was converted into 6-chloro-3-nitropyridazine 1-oxide. It is well known that 3-amino-6-chloropyridazine can be oxidized with hydrogen peroxide in acetic acid, however, to afford 6-amino-3-chloropyridazine 1-oxide.[5,6] Likewise, other 6-amino-3-substituted pyridazines are transformed into their mono-N-oxides, reaction taking place at the ring nitrogen adjacent to the carbon bearing the amino group[6] and the amino group being left intact in all cases. On the other hand, Koelsch and Gumprecht,[7] who obtained pyridazine N-oxide after treating pyridazine with 30% hydrogen peroxide in acetic acid at room temperature, were not able to nitrate this N-oxide. This was later effected by Itai and Natsume[8] under quite drastic reaction conditions; yet 4-nitropyridazine 1-oxide was formed.

Several displacement reactions have been performed on 6-chloro-3-nitropyridazine 1-oxide (**3**, R = Cl) which reacted with acetyl bromide to give the 6-bromo derivative (**5**, R = Br). Evidently, the displacement of the nitro group common to 3-nitropyridazine 1-oxide[9] and other nitropyridazine N-oxides,[10] under the action of acetyl chloride to give the corresponding chloro compounds, did not take place.

Also, in other nucleophilic displacement reactions the 6-chlorine atom of **3** (R = Cl) was replaced, except when it reacted with sodium methoxide to give 6-chloro-3-methoxypyridazine 1-oxide (**6**, R = Cl). This parallels the reaction of 3,6-dichloropyridazine 1-oxide with alkoxides where 3-alkoxy derivatives are the preponderant products.[10] Other nucleophiles similarly attack preferentially position 3 in 3,6-dichloropyridazine 1-oxide,[11,12] and the position reactivity in halopyridazine 1-oxides, based on kinetic measurements, follows the order 5 > 3 > 6 > 4.[13] Moreover, it has been concluded that the combined effect of a *meta* N-oxide group and an *ortho* nitrogen should be greater than the effect of an *ortho* N-oxide and *meta* nitrogen.

It appears that the above procedure of preparing 6-chloro-3-methoxypyridazine 1-oxide is advantageous of direct oxidation of 6-chloro-3-methoxypyridazine with hydrogen peroxide in acetic acid because, in the last-mentioned reaction, besides the expected N-oxide, also 6-chloro-3(2H)-pyridazinone and 6-methoxy-3-(2H)-pyridazinone are formed.[12,14] Pyridazine itself gave similarly in polyphosphoric acid its N-oxide, free from its 1,2-dioxide which could be obtained in low yield when using 50% hydrogen peroxide in acetic acid.[15]

6-Hydrazino-3-nitropyridazine 1-oxide was converted into the corresponding 6-azido compound **5**, (R = N_3) which, as anticipated, existed completely in the azido form. The destabilization of the otherwise fused tetrazole ring is similar to that of 3-azidopyridazine 1-oxide,[16,17] and the phenomenon of azidotetrazolo valence isomerization associated with fused tetrazolopyridazines has been discussed recently.[17,18]

There are some prominent features of nmr spectra of imidazo[1,2-*b*]pyridazine 5-oxide and *s*-triazolo[4,3-*b*]-pyridazine 5-oxide. Of particular significance is the signal for H_6, being in both cases sharp *vis-à-vis* to the same signal of the parent bicyclic compounds.

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(3) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 512.
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(16) T. Itai and S. Kamiya, *Chem. Pharm. Bull.* (Tokyo), **11**, 348 (1963).
(17) B. Stanovnik, M. Tišler, M. Ceglar, and V. Bah, *J. Org. Chem.*, **35**, 1138 (1970).
(18) B. Stanovnik and M. Tišler, *Tetrahedron*, **25**, 3313 (1969).

Here, the signal for H_6 is broad owing to the electric quadrupole moment of the neighboring nitrogen. This observation can be of diagnostic value in connection with the assignment of the N-oxidation site.

The same phenomenon is observed also with simple pyridazines. Here, because of the unsymmetrical structure with respect to the position of the N-oxide group, two positional isomers can exist. Application of nmr spectroscopy for determination of the position of N–O group in pyridazine N-oxides was based mainly on the position of chemical shifts. Thus, it was established that the signal of a proton attached to the carbon atom adjacent to the N-oxide group appears at a higher field than that of the proton attached to the carbon atom adjacent to the ring nitrogen.[19] Now, a comparison of the shape of such signals with those of the deoxygenated pyridazine allows an assignment of the N-oxidation site.

Experimental Section

Melting points were determined on a Kofler micro hot stage and are corrected. Infrared spectra were recorded on a Perkin-Elmer 137 Infracord as KBr disks and nmr spectra were recorded on a JEOL JNM-60HL spectrometer using tetramethylsilane as internal standard. All mass spectra were recorded at a resolution of approximately 1000 on a CEC 21-110C instrument using direct sample insertion into the ion source which was operating at temperature of 170°. The ionization voltage was 70 V and the emission current 100 μA. Throughout this paper polyphosphoric acid Fluka, containing 83% P_2O_5, was used.

Imidazo[1,2-*b*]pyridazine 5-Oxide (2, X = CH; R = H).—A solution of imidazo[1,2-*b*]pyridazine (4.8 g) in polyphosphoric acid (100 g) was prepared at 60° and then cooled to 30°. Under stirring, hydrogen peroxide (6.0 g of 85%) was added during 2 hr in such a manner that the temperature did not surpass 40°. After the addition was complete, the mixture was left to stand at room temperature and in the dark for 48 hr. Upon dilution with water (200 ml), neutralization with sodium carbonate to pH 6, and extraction with four portions of 50 ml of chloroform, the combined extracts were dried and evaporated *in vacuo*. The yellow residue (2.9 g, 54%) was recrystallized from ethyl acetate to afford colorless crystals: mp 175–176°; nmr ($CDCl_3$) τ 1.80 (dd, H_3), 2.34 (d, H_2), 2.18 (dd, H_6), 3.00 (dd, H_7), 2.42 (ddd, H_8) ($J_{2,3}$ = 0.6, $J_{6,7}$ = 5.7, $J_{7,8}$ = 10.0, $J_{6,8}$ = 0.45 $J_{3,8}$ = ~0.2 cps).

Anal. Calcd for $C_6H_5N_3O$: C, 53.33; H, 3.73; N, 31.10. Found: C, 53.37; N, 3.95; H, 31.24.

Oxidation of 6-Chloroimidazo[1,2-*b*]pyridazine.—A stirred solution of 6-chloroimidazo[1,2-*d*]pyridazine (3.0 g) in polyphosphoric acid (50 g) was treated with hydrogen peroxide (1.0 g of 85%), and the mixture was left to stand at room temperature for 48 hr. After dilution with water (70 ml) and neutralization with sodium bicarbonate to pH 5, the mixture was extracted with chloroform (four portions of 30 ml) and the combined extracts were dried and evaporated to dryness. A thin layer chromatographic examination on silica gel, using commercially available plates (DC-Fertigplatten Kieselgel F 254, Merck) and developing them with ethyl acetate, revealed that the product is a mixture of the starting compound (R_f = 0.6) and another nonfluorescent compound (R_f = 0.8). The crude product (100 mg) was separated on a larger scale by thin layer chromatography and there were obtained 13 mg of the compound with an R_f value of 0.8. Upon recrystallization from ethyl acetate there were obtained yellow needles of mp 164–165°. The compound was found to be identical by undepressed mixture melting point and identical ir spectrum with 6-chloro-3-nitropyridazine 1-oxide (3, R = Cl).

Anal. Calcd for $C_4H_2ClN_3O_3$: C, 27.39; H, 1.15; N, 23.96. Found: C, 27.49; H, 1.46; N, 24.18.

6-Nitroimidazo[1,2-*b*]pyridazine (1, X = CH; R = NO_2).—6-Aminoimidazo[1,2-*b*]pyridazine (2.0 g) was treated in the same manner as above with hydrogen peroxide (3.0 g of 85%) and using 50 g of polyphosphoric acid. After 24 hr crushed ice was added (50 g) to the reaction mixture which was then neutralized with $NaHCO_3$ to pH 5. The obtained product (1.8 g, 73%) was recrystallized from ethyl acetate, mp 145–146°.

Anal. Calcd for $C_6H_4N_4O_2$: C, 43.91; H, 2.46; N, 34.14. Found: C, 44.22; H, 2.62; N, 34.25.

In the mass spectrum, besides the peak for molecular ion (164) there is a peak of very low intensity at M − 30 (loss of NO) and an intense peak at M − 46 (loss of NO_2). Further fragmentation process involves loss of HCN (*m/e* 91 and 64).

6-Methoxy-3-nitropyridazine from 6-Methoxyimidazo[1,2-*b*]pyridazine.—The method to obtain 6-nitroimidazo[1,2-*b*]pyridazine was followed, starting with 6-methoxyimidazo[1,2-*b*]pyridazine (1.5 g). For analysis the crude product (1.1 g, 70%) was sublimed at 130° (0.01 mm), mp 143–144° (lit.[20] mp 142–143°).

Anal. Calcd for $C_5H_5N_3O_3$: C, 38.71; H, 3.25; N, 27.09. Found: C, 39.01; H, 3.59; H, 27.02.

3-Nitropyridazine 1-Oxide (3, R = H). A.—A solution of imidazo[1,2-*b*]pyridazine (1.2 g) in polyphosphoric acid (50 g) was treated with hydrogen peroxide (4.0 g of 85%) at such a rate as to keep the temperature of the reaction mixture between 35 and 40°. After addition was complete, the mixture was left to stand in the dark at room temperature for 24 hr, after which hydrogen peroxide (2.0 g) was added. After 48 hr at room temperature, water (60 ml) was added, and the mixture was neutralized with sodium carbonate and extracted with chloroform (four times with 30 ml). After the solvent was removed the residue (0.4 g, 29%) was crystallized from ethyl acetate to give yellow crystals with mp 164–165°. There was no depression in melting point on admixture with the product prepared as described in section B and ir spectra were identical.

B.—3-Aminopyridazine (1.9 g) was dissolved in polyphosphoric acid (50 g) at 100° and after the solution was cooled to 30°, under stirring, hydrogen peroxide (4.0 g of 85%) was added dropwise at such a rate as to keep the temperature in the range of 30–40° (about 3 hr). After 24 hr, water (50 ml) was added, the mixture neutralized with sodium carbonate to pH 6, and the yellow precipitate collected. Upon recrystallization from ethyl acetate yellow crystals (1.8 g, 65%) of mp 165–166° (lit.[9] mp 166°) were obtained. The compound was identical with the product prepared as described in section A. Nmr ($CDCl_3$)-τ 1.81 (d, H_4), 1.30 (dd, H_5), 1.86 (d, H_6) ($J_{4,5}$ = 6.0, $J_{5,6}$ = 1.3 cps, $J_{4,6}$ is not observed).

***s*-Triazolo[4,3-*b*]pyridazine 5-Oxide (2, X = N; R = H).**—A solution of *s*-triazolo[4,3-*b*]pyridazine (2.4 g) in polyphosphoric acid (60 g) was prepared at 100°, cooled to 30°, and, with stirring, treated at once with hydrogen peroxide (2.0 g of 85%). After 24 hr at room temperature, the mixture was treated again with the same quantity of hydrogen peroxide and left to stand for 48 hr. Thereafter, the reaction mixture was diluted with water (150 ml) and neutralized with sodium carbonate to pH 6. After extraction with chloroform (four portions of 40 ml) and evaporation of the solvent, there were obtained 1.3 g of the crude product. Thin layer chromatographic analysis, using commercially available plates (DC-Fertigplatten Kieselgel F 254, Merck, and ethyl acetate for developing), revealed that the product consisted of the unreacted starting compound and its N-oxide. The first compound was removed by sublimation *in vacuo* at 130° (0.01 mm) and the remaining N-oxide (0.5 g, 18%) was recrystallized from ethanol to give colorless crystals: mp 243–244°; a mixture melting point with an authentic specimen[1] showed no depression and ir spectra were identical; nmr ($CDCl_3$) τ 0.26 (d, H_3), 1.65 (d, H_6), 2.54 (dd, H_7), 1.96 (dd, H_8), ($J_{6,7}$ = 5.6, $J_{7,8}$ = 9.5; $J_{3,8}$ = 0.8, $J_{6,8}$ = ~0.1 cps).

Anal. Calcd for $C_5H_4N_4O$: C, 44.12; H, 2.96; N, 41.17. Found: C, 44.25; H, 2.71; N, 41.30.

6-Nitro-*s*-triazolo[4,3-*b*]pyridazine (1, X = N; R = NO_2).—The procedure as described for the preparation of 6-nitroimidazo-[1,2-*b*]pyridazine was followed. There were employed 6-amino-*s*-triazolo[4,3-*b*]pyridazine (1.35 g), polyphosphoric acid (40 g), and hydrogen peroxide (2.0 g of 85%). After 24 hr the mixture was diluted with water (50 ml) and neutralized with sodium carbonate to pH 6; the product was filtered off, washed with water, and dried *in vacuo*. The crude product (1.1 g, 67%)

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was (for analysis) recrystallized from ethanol to give yellow needles with mp 200–201°.

Anal. Calcd for $C_5H_3N_5O_2$: C, 36.37; H, 1.83; N, 42.42. Found: C, 36.15; H, 1.95; N, 42.25.

Pyridazine 1-Oxide.—A stirred solution of pyridazine (1.6 g) in polyphosphoric acid (40 g) and hydrogen peroxide (1.6 g, 85%) was added in one portion and the mixture was left to stand for 24 hr. After dilution with water (100 ml), neutralization with sodium carbonate, and extraction (four 30-ml portions of chloroform), the extracts were concentrated *in vacuo*. The crude product (1.6 g, 84%) was (for analysis) purified by distillation under high vacuum: mp 38–39° (lit.[7] mp 38–39°); nmr ($CDCl_3$) τ 1.70 (m, H_3), 3.00 (ddd, H_4), 2.43 (ddd, H_5), 1.92 (ddd, H_6) ($J_{4,5} = 7.5$, $J_{5,6} = 6.0$, $J_{4,6} = 1.0$, $J_{3,5} = 2.4$, $J_{3,6} = 0.6$ cps).

The crude product was examined by thin layer chromatography, but no traces of eventually present 1,2-dioxide could be detected.

6-Chloro-3-nitropyridazine 1-Oxide (3, R = Cl) was obtained from 3-amino-6-chloropyridazine (4.0 g) in essentially the same way as pyridazine 1-oxide with the exception that initial heating was necessary to dissolve the compound in polyphosphoric acid and then the solution was cooled to 35°. There were employed 6.0 g of 85% hydrogen peroxide and 50 g of polyphosphoric acid. The crude product was recrystallized from ethyl acetate to give yellow needles (3.0 g, 57%) with mp 164–165°.

Anal. Calcd for $C_4H_2ClN_3O_3$: C, 27.39; H, 1.15; N, 23.96. Found: C, 27.48; H, 1.45; N, 23.74.

6-Chloro-3-methoxypyridazine 1-Oxide (6, R = Cl).—Compound **3** (R = Cl; 1.75 g) and a solution of sodium methoxide (prepared from 0.25 g of sodium and 15 ml of absolute methanol) were left to stand at room temperature for 24 hr. The residue, obtained from concentration of the reaction mixture *in vacuo*, was crystallized twice from ethyl acetate to give colorless crystals, mp 160–162° (lit.[14] mp 159–161°).

Anal. Calcd for $C_5H_5ClN_2O_2$: C, 37.42; H, 3.14; N, 17.45. Found: C, 37.74; H, 3.01; N, 17.62.

6-Bromo-3-nitropyridazine 1-Oxide (5, R = Br).—A mixture of **3** (R = Cl, 0.5 g) and acetyl bromide (15 ml) was heated under reflux for 3 hr to obtain a solution. Excess of acetyl bromide was removed *in vacuo;* the residue was treated with ice (10 g) and neutralized with sodium bicarbonate. The crude product (0.4 g, 65%) was purified by recrystallization from ethyl acetate, mp 184–185°.

Anal. Calcd for $C_4H_2BrN_3O_3$: C, 21.85; H, 0.92; N, 19.11. Found: C, 22.25; H, 1.27; N, 18.92.

6-Anilino-3-nitropyridazine 1-Oxide (5, R = NHC_6H_5).—A suspension of 6-chloro-3-nitropyridazine 1-oxide (0.35 g) in ethanol (5 ml) and aniline (0.2 g) was heated under reflux for 3 hr. The obtained product was recrystallized from ethanol to give orange needles of mp 186–187° (yield 67%).

Anal. Calcd for $C_{10}H_8N_4O_3$: C, 51.72; H, 3.47; N, 24.13. Found: C, 51.77; H, 3.78; N, 23.86.

In essentially the same way **6-morpholino-3-nitropyridazine 1-oxide** was obtained in 64% yield, mp 214–215° (from ethanol).

Anal. Calcd for $C_8H_{10}N_4O_4$: C, 42.48; H, 4.46; N, 24.77. Found: C, 42.49; H, 4.73; N, 24.69.

6-Hydrazino-3-nitropyridazine 1-Oxide (5, R = $NHNH_2$).—A suspension of compound **3** (R = Cl, 1.75 g) in methanol (30 ml) was treated with hydrazine hydrate (1.0 g of 100%). The The resulting dark mixture was stirred at room temperature for 6 hr and the yellow needles which formed were filtered off and washed with methanol. Upon recrystallization from dilute methanol the pure compound melted at 187–188°.

Anal. Calcd for $C_4H_5N_5O_3$: C, 28.07; H, 2.95; N, 40.93. Found: C, 28.35; H, 2.55; N, 40.82.

The benzylidene derivative was prepared in the usual way and had mp 199–200°.

Anal. Calcd for $C_{11}H_9N_5O_3$: C, 50.96; H, 3.50; N, 27.02. Found: C, 51.11; H, 3.80; N, 27.06.

6-Azido-3-nitropyridazine 1-Oxide (5, R = N_3).—The above hydrazino compound (0.34 g) was dissolved in hydrochloric acid (5 ml of 5%) and the solution was cooled to 0°. Under stirring, a solution of sodium nitrite (0.14 g in 1 ml of water) was added dropwise and, after addition was complete, stirring was continued for 10 min. The separated product was recrystallized from ethyl acetate and, *n*-hexane to give (0.2 g, 55%) pale yellow plates of mp 119–120°, ir, in KBr, 2119 cm^{-1} (N_3).

Anal. Calcd for $C_4H_2N_6O_3$: C, 26.38; H, 1.11; N, 46.15. Found: C, 26.70; H, 1.36; N, 46.44.

Registry No.—**1** (X = CH; R = NO_2), 24716-49-2; **1** (X = N; R = NO_2), 24716-50-5; **2** (X = CH; R = H), 24716-51-6; **2** (X = N; R = H), 20552-65-2; **3** (R = Cl), 24716-53-8; **3** (R = H), 24716-54-9; **5** (R = Br), 24710-95-0; **5** (R = NHC_6H_5), 24704-30-1; **5** (R = $NHNH_2$), 24704-31-2; benzylidene derivative of **5** (R = $NHNH_2$), 24710-96-1; **5** (R = N_3), 24710-97-2; **6** (R = Cl), 14634-52-7; pyridazine 1-oxide, 1457-42-7; 6-morpholino-3-nitropyridazine 1-oxide, 24711-00-0.

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