tion at 296 nm due to diaminomaleonitrile (1 ml to 10 ml dilution). The presence of urea in this solution was confirmed by paper chromatography using BAW and Ehrlich's reagent.

The degassed solution was opened after 7 months and the pH was found to be 9.36. A uv spectrum (1 ml to 10 ml dilution) had a broad continuum from 200 to 450 nm. The absorption at 296 nm was 0.97 absorbance units but it was impossible from this to say whether diaminomaleonitrile was present. Analysis of the solution for diaminomaleonitrile by paper chromatography using BAW and Folin's reagent did not give a spot corresponding to authentic diaminomaleonitrile. This solution was 1.9×10^{-3} *M* in urea[11] and 0.053 *M* in cyanide.[15]

Portions (15 ml) of the degassed and nondegassed solutions were placed in round-bottom flasks and evaporated to dryness on the rotary evaporator. The two different samples (degassed and nondegassed) were worked up in the same way so as to compare them. The residue in each flask was taken up in 6 *N* hydrochloric acid and the solutions were sealed in vials and heated overnight at 110°. The solutions were concentrated to dryness, and the residues were taken up in 1 ml of water and analyzed for amino acids by paper chromatography using both BAW and PA and using ninhydrin for detection. Both solutions (degassed and nondegassed) gave spots corresponding to authentic glycine, which had also been spotted on the paper. Other ninhydrin-positive materials were also detected. The presence of urea in the degassed solution was confirmed by paper chromatography using BAW and Ehrlich's reagent.

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Registry No.—**3**, 1187-42-4; **4**, 40982-16-9; **5**, 40982-17-0.

Pyridazines. LVIII. Oxidative Transformations of Pyridazinyl Sulfides

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Different oxidizing agents have been employed for conversion of methylthiopyridazines or their *N*-oxides into the corresponding methylsulfinyl or methylsulfonyl derivatives. In some cases, besides S-oxidation, N-oxidation also took place.

It is well known that organic sulfides can be transformed into sulfoxides or sulfones by a variety of oxidizing agents.[1] In the pyridazine series oxidation can, *a priori*, occur at either the sulfur containing side chain(s) or ring nitrogens to give the corresponding *S*-oxides or/and N_1- or N_2-oxides. The reported results on oxidation experiments with some pyridazinyl sulfides are either conflicting with regard to structure assignment or there has been no assignment at all. Pyridazinyl sulfides have been converted into the corresponding sulfones with potassium permanganate or hydrogen peroxide,[2-6] chlorine,[4,7] or sulfur dioxide.[4] For the synthesis of sulfoxides hydrogen peroxide[2,8] or *m*-chloroperoxybenzoic acid[9] was used, but, depending on the quantity of the oxidizing agent and reaction conditions, sometimes a mixture of the corresponding sulfoxides and sulfones resulted.[2,10] Pyridazinyl sulfoxides were transformed into sulfones with potassium permanganate.[11]

An extensive study of oxidative transformations of alkylthiopyridazines with various oxidizing agents was reported by Takahayashi,[12] but the obtained products were mostly designated as monoxides, dioxides, or trioxides. Moreover, he also assumed that in some cases, in addition to the formation of *S*-oxides, N-oxidation took place.[12,13] Moreover, halogens or alkoxy groups bound on the pyridazine ring can suffer hydrolysis and the corresponding pyridazinone derivatives were obtained.[14,15]

We have studied oxidations of pyridazinyl sulfides under differing conditions with different oxidizing agents. We used 70% hydrogen peroxide alone or in admixture with various solvents or in the presence of sodium tungstate, as well as dichloromonoperoxymaleic acid, bromine, potassium permanganate, chromium trioxide, potassium metaperiodate, and ceric ammonium nitrate.

The structures of some products were proved through chemical transformations. In addition, it is possible to distinguish between different oxidation products by nmr and/or ir spectra as well as on hand of color tests.[16-18] Thus, in an analogous series, when observing chemical shifts for a methylthio, methylsulfinyl, and methylsulfonyl group we observed a distinct deshielding effect of approximately 1 τ unit. This is comparable to that observed in 3- or 4-methylthiopyridazines and their oxidation products.[19,20] Infrared spectra are also of diagnostic value since one can

(1) Houben-Weyl, "Methoden der organischen Chemie," Vol. IX, Schwefel-, Selen-, Tellur-Verbindungen, Georg Thieme, Leipzig, 1955, pp 211, 227.

(2) H. Gregory, W. G. Owens, and F. L. Wiggins, *J. Chem. Soc.*, 2066 (1949).

(3) S. Sato, *Yakagaku Zasshi*, **82**, 1085 (1962); *Chem. Abstr.*, **58**, 4558 (1963).

(4) G. B. Barlin and W. V. Brown, *J. Chem. Soc. B*, 648 (1967).

(5) S. Kukolja, Z. Crnić, and D. Kolbah, *Tetrahedron*, **19**, 1153 (1963).

(6) A. Krbavčič and M. Tišler, *Monatsh. Chem.*, **97**, 644 (1966).

(7) W. H. Nyberg and C. C. Cheng, *J. Heterocycl. Chem.*, **1**, 1 (1964).

(8) J. H. M. Hill and J. G. Krause, *J. Org. Chem.*, **29**, 1642 (1964).

(9) G. B. Barlin and M. V. Brown, *J. Chem. Soc. B*, 1435 (1968).

(10) T. Takahashi, M. Takaya, and Y. Maki, *Yakugaku Zasshi*, **89**, 1516 (1969); *Chem. Abstr.*, **72**, 55374 (1970).

(11) G. B. Barlin and W. V. Brown, *J. Chem. Soc.*, 921 (1969).

(12) N. Takahayashi, *J. Pharm. Soc. Jap.*, **75**, 1245 (1955); *Chem. Abstr.*, **50**, 8656 (1956).

(13) T. Horie, *Yakugaku Zasshi*, **82**, 627 (1962); *Chem. Abstr.*, **58**, 525 (1963).

(14) N. Takahayashi, *J. Pharm. Soc. Jap.*, **76**, 1293 (1956); *Chem. Abstr.*, **51**, 6645 (1957).

(15) N. Takahayashi and R. Honda, *Chem. Pharm. Bull.*, **6**, 722 (1958); *Chem. Abstr.*, **54**, 17411 (1960).

(16) N. A. Coats and A. R. Katritzky, *J. Org. Chem.*, **24**, 1836 (1959).

(17) A. R. Katritzky and J. M. Lagowski, "Chemistry of the Heterocyclic N-Oxides," Academic Press, New York, N. Y., 1971, p 213.

(18) E. N. Karaulova and G. D. Galpern, *Zh. Obshch. Khim.*, **29**, 3033 (1959); *Chem. Abstr.*, **54**, 12096 (1960).

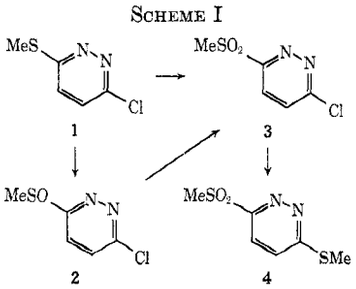
(19) G. B. Barlin and W. V. Brown, *J. Chem. Soc. B*, 648 (1967).

(20) G. B. Barlin and W. V. Brown, *J. Chem. Soc. B*, 1435 (1968).

distinguish between a *N*-oxide and a sulfoxide group. The pyridazine *N*-oxides exhibit a N–O absorption in the 1333–1361-cm^{-1} region, in agreement with previous observations.[21,22] Similarly, all compounds assigned as pyridazine sulfoxides exhibit absorption in the 1042–1066-cm^{-1} region, also in accord with the known data.[23]

3-Chloro-6-methylthiopyridazine (**1**) when oxidized with an equivalent amount of hydrogen peroxide in glacial acetic acid afforded the corresponding sulfoxide (**2**) in good yield (see Scheme I). This compound was

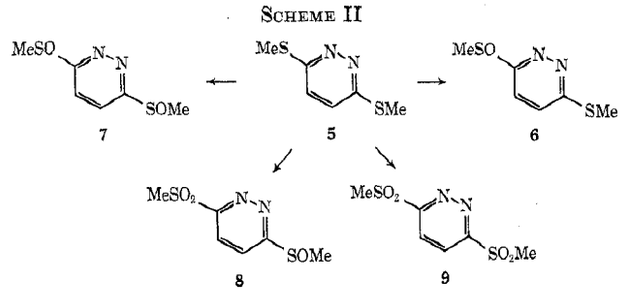
SCHEME I



previously prepared by oxidation with potassium permanganate and described as "monoxide."[12] With excess of peroxide the corresponding sulfone (**3**) was formed in a moderate yield. This compound is most probably identical with a dioxide, obtained by Takahayashi[12] from oxidation with potassium permanganate in acid solution. Furthermore, a second "monoxide" which was obtained by the same author from hydrogen peroxide oxidation in acetic acid was first assumed to be a *N*-oxide,[12] but was later identified[15] as 3-methylsulfonylpyridazin-6(1*H*)-one.

3,6-Bis(methylthio)pyridazine (**5**) could be selectively oxidized with hydrogen peroxide in acetic acid either into the monosulfoxide (**6**), disulfoxide (**7**), sulfoxide–sulfone (**8**), or disulfone (**9**) (Scheme II). The mono-

SCHEME II

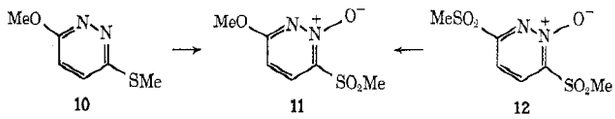


sulfone (**4**) could not be isolated from these experiments but was prepared from 3-chloro-6-methylsulfonylpyridazine and sodium methanethiolate. The monosulfoxide (**6**) could be obtained either from oxidation with bromine or with an equivalent amount of hydrogen peroxide in acetic acid. 3,6-Bis(methylsulfinyl)-pyridazine (**7**) could be prepared from **5** by using only 82% of the required quantity of hydrogen peroxide. If dichloromonoperoxymaleic acid was used, a mixture of **7** and **8** was obtained from **5**. The disulfone (**9**) could be prepared either with dichloromonoperoxymaleic acid or with an excess of 70% hydrogen peroxide in glacial acetic acid or, in the optimum yield, in the presence of a catalytic amount of sodium tungstate. It should be mentioned that tungstate ions are known to be good catalysts for amine oxidations,[24] but also the corresponding sulfone could be obtained from 2-phenylmercaptoethanol in an improved yield in the presence of this catalyst.[25]

Application of other oxidizing agents was less effective since in most cases a mixture of products resulted. The progress of oxidation was followed by tlc. We could thus observe that after 30 min compound **5** was transformed with potassium permanganate in acetic acid at 50° into a mixture of **6**, **7**, **8**, and **9** with some of the starting material remaining unchanged. Oxidation with chromium trioxide in acetic acid at 65° and under controlled addition of the oxidizing agent, could lead to the formation of **6**. The reaction between **5** and potassium metaperiodate proceeded at room temperature very slowly. After 7 days the starting material was transformed completely into a mixture of **6** and **7**.

In all mentioned cases, no N-oxidation could be observed. However, the formation of a *N*-oxide took place when 3-methylthio-6-methoxypyridazine (**10**) was treated with an excess of hydrogen peroxide in trifluoroacetic acid with the formation of 3-methylsulfonyl-6-methoxypyridazine 2-oxide (**11**). On the other hand, the latter compound could also be obtained from 3,6-bis(methylsulfonyl)pyridazine 2-oxide (**12**) and sodium methylate (Scheme III).

SCHEME III

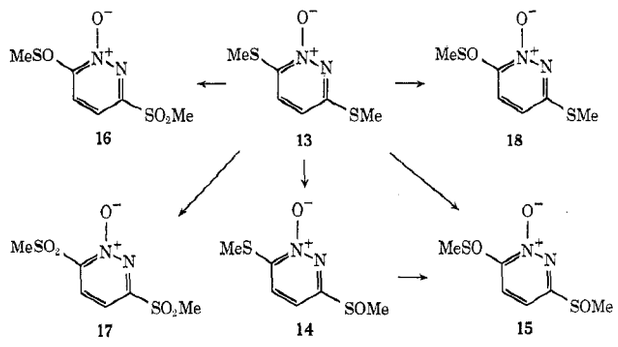


The two methylthio groups of 3,6-bis(methylthio)-pyridazine 1-oxide (**13**) displayed different reactivity. Application of the before-mentioned oxidizing agents revealed the preference for attack at the 3-methylthio group. In this manner, oxidation with bromine gave 3-methylsulfinyl-6-methylthiopyridazine 1-oxide (**14**). Partial oxidation with ceric ammonium nitrate followed with hydrogen peroxide gave the bis sulfoxide (**15**). On the other hand, oxidation with hydrogen peroxide in the presence of sodium tungstate afforded at room temperature a mixture of the bis sulfoxide (**15**) and sulfoxide–sulfone (**16**) in about equal quantity. Both compounds could be separated by tlc on silica. The same reaction, when conducted at 50° gave exclusively 3-methylsulfonyl-6-methylsulfinylpyridazine 1-oxide (**16**). The disulfone 1-oxide (**17**) could be obtained from **13** either with an excess of hydrogen peroxide in the presence of sodium tungstate or in acetic acid or, in moderate yield, with dichloromonoperoxymaleic acid (see Scheme IV).

From the above-described oxidation experiments we were not able to isolate 3-methylthio-6-methylsulfinylpyridazine 1-oxide (**18**). This compound could be obtained from **13** when using ceric ammonium nitrate

(21) M. Ogata and H. Kano, *Chem. Pharm. Bull.*, **11**, 29 (1963).
(22) M. Ogata and H. Kano, *Chem. Pharm. Bull.*, **11**, 35 (1963).
(23) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p 295.
(24) K. Kahr and C. Berther, *Chem. Ber.*, **93**, 132 (1960).
(25) H. S. Schultz, H. B. Freyermuth, and S. R. Buc, *J. Org. Chem.*, **28**, 1140 (1963).

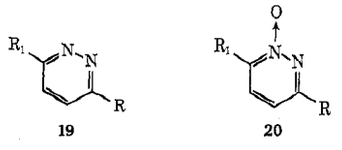
SCHEME IV



in aqueous acetonitrile as the oxidizing agent. Ceric ammonium nitrate, which was recently employed with success for conversion of diaryl sulfides into the corresponding sulfoxides[26] under mild conditions and without overoxidation, reacted in the above case regioselectively. This may be ascribed to the formation of a possible intermediate complex between the *N*-oxide function and the oxidizing agent, similarly as was observed with other substrates.[27]

As judged from experiments, where the progress of oxidation was followed by tlc, use of chromium trioxide in acetic acid is not recommended since a mixture of **14**, **15**, and **18** resulted from **13** at 65° after 1 hr.

Similar stepwise oxidation could be performed with 6-chloro-3-methylthiopyridazine 1-oxide (**20**, R = SMe, R_1 = Cl) and 3-methylthio-6-methoxypyridazine (**10**) to give the corresponding 3-methylsulfinyl (**20**, R = MeSO, R_1 = Cl, or **19**, R = SOMe, R_1 = OMe) or 3-methylsulfonyl analogs (**20**, R = $MeSO_2$,



R_1 = Cl, or **19**, R = SO_2Me, R_1 = OMe). In addition, the latter compound could be transformed into 6-methylsulfonyl-3-methoxypyridazine 1-oxide (**20**, R = OMe, R_1 = $MeSO_2$) with trifluoroperoxyacetic acid. Compound **20** (R = OMe, R_1 = $MeSO_2$) could be also obtained from the nucleophilic replacement of a methylsulfonyl group in 3,6-bis(methylsulfonyl)pyridazine 1-oxide (**17**) with sodium methylate. Other experiments of nucleophilic displacement proceeded similarly and showed that the 3-methylsulfonyl group is displaced preferentially. This parallels the reactivity of 3,6-dichloropyridazine 1-oxide with alkoxides[28] and other nucleophiles.[29,30]

Experimental Section

Melting points were taken on a Kofler micro hot stage. Nmr spectra were recorded on a JEOL JNM-C-60 HL spectrometer (TMS as internal standard) and mass spectra were taken on a Hitachi Perkin-Elmer RMU-6L instrument using direct sample insertion into the ion source. Throughout this paper 70% hydrogen peroxide was used.

The following compounds were prepared according to the procedures described in the literature: 3-Mercaptopyridazine-6(1*H*)-thione,[31] 3,6-bis(methylthio)pyridazine[32] [nmr (DMSO-d_6) τ 2.55 (s, H_4H_5), 7.40 (s, 3- and 6-SMe); nmr ($CDCl_3$) τ 2.92 (s, H_4H_5), 7.30 (s, 3- and 6-SMe)], and 3-chloro-6-methylthiopyridazine.[12]

3-Chloro-6-methylsulfinylpyridazine (**2**).—A warm solution of **1** (1.6 g) in glacial acetic acid (20 ml) was treated with hydrogen peroxide (0.5 g) and the mixture left at 50° for 2.5 hr. The solvent was evaporated *in vacuo*, the residue was treated with water and sodium bicarbonate and extracted with chloroform, and after evaporation of the solvent the product was purified by tlc (on silica, acetone, and ethyl acetate, 2:1 as the mobile phase and methanol for elution). The pure compound (1.6 g, 91%) had mp 74–79° (lit.[12] gives mp 73° for compound, described as "monoxide"); ir 1066 cm^{-1} (SO); nmr ($CDCl_3$) τ 1.68 and 2.08 (d, H_4 and H_5), 6.93 (s, SOMe), $J_{4,5}$ = 9.4 Hz.

Anal. Calcd for $C_5H_5ClN_2OS$: N, 15.86; S, 18.15. Found: N, 16.11; S, 18.30.

3-Chloro-6-methylsulfonylpyridazine (**3**).—A mixture of **1** (3.2 g), glacial acetic acid (40 ml), and hydrogen peroxide (4 g) was heated at 50° for 3 hr. The crystals which separated upon evaporation of the solvent *in vacuo* were washed with ethyl acetate and the product was crystallized from methanol (yield 1.3 g, 34%): mp 122–123° (lit.[12] gives mp 114° for a compound designated as "dioxide"); nmr ($CDCl_3$) τ 1.93 and 2.18 (d, H_4 and H_5), 6.55 (s, SO_2Me), $J_{4,5}$ = 9.5 Hz.

Anal. Calcd for $C_5H_5ClN_2O_2S$: N, 14.54; S, 16.65. Found: N, 14.48; S, 16.40.

3-Methylthio-6-methylsulfonylpyridazine (**4**).—A mixture of **3** (1.9 g), methanol (7 ml), and a solution of potassium methanethiolate (0.01 mol) in methanol was heated under reflux for 3 hr. Upon filtration the filtrate was evaporated to dryness and the product was crystallized from *n*-heptane and ethyl acetate (1:1) (yield 0.7 g, 34%): mp 92–95°: nmr ($CDCl_3$) τ 2.18 (d, H_5), 2.53 (d, H_4), 6.63 (s, SO_2Me), 7.25 (s, SMe), $J_{4,5}$ = 9.0 Hz.

Anal. Calcd for $C_6H_8N_2O_2S_2$: N, 13.72; S, 31.34. Found: N, 14.02; S, 31.10.

3-Methylthio-6-methylsulfinylpyridazine (**6**). **A.**—A warm solution of **5** (1.7 g) in glacial acetic acid (20 ml) was treated with hydrogen peroxide (0.5 g). After 2 hr at 40° the reaction mixture was evaporated *in vacuo;* the residue was neutralized with a solution of sodium bicarbonate and extracted with chloroform. The isolated product, obtained after evaporation of the solvent, was crystallized from ethyl acetate (yield 1.1 g, 59%): mp 118–119°; nmr ($CDCl_3$) τ 2.20 (s, H_5), 2.54 (s, H_4), 7.04 (s, 6-SOMe), 7.26 (s, 3-SMe), $J_{4,5}$ = 9.0 Hz; ir 1058 cm^{-1} (SO).

Anal. Calcd for $C_6H_8N_2OS_2$: N, 14.89; S, 34.11. Found: N, 14.70; S, 33.75.

B.—To a stirred solution of **5** (0.8 g) in dry chloroform (10 ml) a solution of bromine (0.8 g) in chloroform (1 ml) was added. Upon standing on ice, crystals of the bromine complex separated; they were filtered off and washed with *n*-hexane. The crystals were mixed with water and a solution of potassium hydroxide (0.6 g in a minimum amount of water) was added until a pH of 7 was attained. The mixture was extracted with chloroform, and upon evaporation of the solvent the product was found identical with the compound as prepared under A.

3,6-Bis(methylsulfinyl)pyridazine (**7**).—A mixture of **5** (3.5 g), glacial acetic acid (40 ml), and hydrogen peroxide (1.6 g) was heated on a water bath at 50° for 3 hr. Upon evaporation of the solvent *in vacuo*, the oily residue was treated with some water, neutralized with sodium bicarbonate, and extracted with chloroform. The product, obtained upon evaporation of the solvent (2.2 g 54%) was crystallized from methanol: mp 203–204°; ir 1053 cm^{-1} (SO); mass spectrum M^+ 204; nmr ($CDCl_3$) τ 1.58 (s, H_4, H_5), 6.97 (s, 3- and 6-SOMe).

Anal. Calcd for $C_6H_8N_2O_2S_2$: N, 13.72; S, 31.34. Found: N, 13.92; S, 31.40.

3-Methylsulfinyl-6-methylsulfonylpyridazine (**8**).—An ice-cold suspension of dichloromaleic anhydride (28 g) in dry methylene chloride (250 ml) was treated dropwise with hydrogen peroxide (4 g) and stirred 2 hr. Upon addition of **5** (5 g), the mixture was stirred for 1 hr. The separated product and dichloromaleic acid were filtered off, and after washing with water the residue was

(26) T.-L. Ho and C. M. Wong, *Synthesis*, 561 (1972).

(27) K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965, p 243.

(28) M. Tišler and B. Stanovnik, *Advan. Heterocycl. Chem.*, **9**, 211 (1968).

(29) S. Sako, *Chem. Pharm. Bull.*, **10**, 956 (1962).

(30) T. Nakagome, *Yakugaku Zasshi*, **82**, 244 (1962); *Chem. Abstr.*, **58**, 3425 (1963).

(31) A. Pollak, B. Stanovnik, and M. Tišler, *Can. J. Chem.*, **44**, 829 (1966).

(32) J. Druey, K. Meier, and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

neutralized with 10% sodium bicarbonate solution, filtered, and dried. The product was found identical with an authentic specimen of compound **9**. The methylene chloride layer was shaken with a 10% solution of sodium bicarbonate and dried and upon evaporation of the solvent the crude 3-methylsulfinyl-6-methylsulfonylpyridazine was crystallized from ethanol (0.7 g, 11%): mp 184–185°; mass spectrum M^+ 220; ir 1044 cm^{-1} (SO).

Anal. Calcd for $C_6H_8N_2O_3S_2$: N, 12.73; S, 29.07. Found: N, 12.81; S, 29.35.

3,6-Bis(methylsulfonyl)pyridazine (9). A.—A solution of dichloromonoperoxymaleic acid in methylene chloride was prepared exactly as described in the above case (**8**). After addition of **5** (1.7 g) the mixture was stirred for 1 hr. The separated product was filtered off and washed with water. The residue was crystallized from *N*,*N*-dimethylformamide (1.5 g, 64%): mp 278–279°; mass spectrum M^+ 236; nmr (DMSO-d_6) τ 1.35 (s, H_4 H_5), 6.48 (s, 3- and 6-$MeSO_2$).

Anal. Calcd for $C_6H_8N_2O_4S_2$: N, 11.86; S, 27.10. Found: N, 11.94; S, 27.20.

B.—A mixture of **5** (1.7 g), glacial acetic acid (20 ml), and hydrogen peroxide (2.5 g) was heated on water bath at 50°. After 30 min crystals of the disulfone started to separate. The product (1.5 g, 64%) was identical with the compound prepared as described under A.

C.—A mixture of **5** (3.4 g), a few crystals of sodium tungstate, water (40 ml), and hydrogen peroxide (6 g) was heated at 50° for 30 min. The separated product (4.2 g, 89%) was identical with the product obtained as described under A.

3-Methylthio-6-methoxypyridazine (10).—A mixture of **1** (6.5 g) and a solution of sodium methoxide in methanol (prepared from 1 g of sodium and 25 ml of methanol) was heated in an autoclave at 130° for 8 hr. The obtained product was crystallized from *n*-hexane (3.2 g, 50%): mp 88–89°; nmr (DMSO-d_6) τ 2.55 (d, H_4), 3.03 (d, H_5), 7.50 (s, SMe), 6.08 (s, OMe), $J_{4,5}$ = 9.2 Hz.

Anal. Calcd for $C_6H_8N_2OS$: N, 17.94; S, 20.49. Found: N, 17.96; S, 20.10.

3-Methylsulfinyl-6-methoxypyridazine (19, R = SOMe, R_1 = OMe).—The procedure was similar as for preparation of **2**. The product (0.8 g, 73%) was crystallized from *n*-hexane: mp 85–87°; nmr ($CDCl_3$) τ 2.10 (d, H_4), 2.94 (d, H_5), 7.10 (s, SOMe), 5.89 (s, OMe), $J_{4,5}$ = 9.0 Hz; ir 1042 cm^{-1} (SO).

Anal. Calcd for $C_6H_8N_2O_2S$: N, 16.27; S, 18.59. Found: N, 16.45; S, 18.30.

3-Methylsulfonyl-6-methoxypyridazine (19, R = $MeSO_2$, R_1 = OMe). A.—The same procedure as described for the preparation of **3** was followed. The product, obtained in 60% yield, had mp 99–102° (lit.[14] gives mp 99° for a "dioxide" with unspecified structure).

B.—A mixture of **9** (1.2 g) and sodium methoxide in methanol (prepared from 115 mg of sodium and 10 ml of methanol) was heated under reflux for 20 min. The product, obtained after evaporation of the solvent was crystallized from water (0.75 g, 79%), mp 99–102°. The product is identical in all respects with that obtained as described under A: nmr ($CDCl_3$) τ 2.08 (d, H_4), 2.92 (d, H_5), 6.66 (s, SO_2Me), 5.80 (s, OMe), $J_{4,5}$ = 9.0 Hz.

Anal. Calcd for $C_6H_8N_2O_3S$: N, 14.89; S, 17.01. Found: N, 15.34; S, 17.20.

3-Methoxy-6-methylsulfonylpyridazine 1-Oxide (11). A.—A mixture of 3-methoxy-6-methylthiopyridazine (156 mg), trifluoroacetic acid (3 ml), and hydrogen peroxide (0.5 g) was left at room temperature for 24 hr. The solvent was evaporated and the oily residue treated with water. The compound (0.1 g, 49%), mp 193–195°, is identical with the product obtained in B.

B.—A mixture of **12** (1.25 g) and methanolic sodium methoxide (prepared from 115 mg of sodium and 10 ml of methanol) was heated under reflux for 30 min. The separated product was filtered off and crystallized from ethanol (0.7 g, 69%): mp 193°; mass spectrum M^+ 204; nmr ($CDCl_3$) τ 1.75 (d, H_5), 3.20 (d, H_4), 5.86 (s, MeO), 6.53 (s, $MeSO_2$), $J_{4,5}$ = 9.0 Hz; ir 1333 cm^{-1} (N–O).

Anal. Calcd for $C_6H_8N_2O_4S$: N, 13.72; S, 15.67. Found: N, 13.96; S, 16.00.

3,6-Bis(methylthio)pyridazine 1-Oxide (13).—To an ice-cold solution of potassium methanethiolate in ethanol (prepared from 25 ml of methyl mercaptan, 27 g of potassium hydroxide, and 250 ml of ethanol) was added portionwise 3,6-dichloropyridazine 1-oxide[33] (35 g). Temperature was held below 60° and after addition was complete, the mixture was heated at 75° for 3 hr. The product was crystallized from ethanol (yield 34.5 g, 86%): mp 163°; nmr ($CDCl_3$) τ 2.76 (d, H_5), 3.09 (d, H_4), 7.43 (s, 3-SMe), 7.56 (s, 6-SMe), $J_{4,5}$ = 9.0 Hz; ir 1333 cm^{-1} (N–O).

Anal. Calcd for $C_6H_8N_2OS_2$: N, 14.89; S, 34.11. Found: N, 14.82; S, 34.10.

6-Methylthio-3-methylsulfinylpyridazine 1-Oxide (14).—To a stirred solution of **13** (0.9 g) in chloroform (10 ml) a solution of bromine (0.8 g) in chloroform (1 ml) was added dropwise. The separated bromine complex was filtered off and washed with *n*-hexane. It was then suspended in water and a solution of potassium hydroxide was added until pH 7. The mixture was extracted with chloroform and the isolated product was crystallized from a mixture of ethyl acetate and ethanol (yield 0.4 g, 41%): mp 148–151°; mass spectrum M^+ 204; nmr (DMSO-d_6) τ 2.42 (s, H_4), 1.96 (s, H_5), 7.11 (s, 6-SMe), 7.50 (s, 3-SOMe), $J_{4,5}$ = 8.5 Hz; ir 1340 cm^{-1} (N–O).

Anal. Calcd for $C_6H_8N_2O_2S_2$: N, 13.72; S, 31.34. Found: N, 13.92; S, 31.00.

3,6-Bis(methylsulfinyl)pyridazine 1-Oxide (15) and 3-Methylsulfonyl-6-methylsulfinylpyridazine 1-Oxide (16). A.—A stirred suspension of **13** (0.9 g) in acetone (10 ml) was treated with small amount of sodium tungstate in water, and hydrogen peroxide (0.5 g) was added dropwise. After 1 hr a clear solution was obtained and after 65 hr crystals of **16** separated. Upon filtration the filtrate was evaporated to dryness and the residue dissolved in chloroform. The filtered solution was evaporated and the product was purified by tlc (on silica, acetone as mobile phase and methanol for elution). The product, **15**, was crystallized from a mixture of toluene and *N*,*N*-dimethylformamide (yield 0.49 g, 46%): mp 201–202°; mass spectrum M^+ 220; nmr ($CDCl_3$) τ 1.54 (d, H_5), 2.00 (d, H_4), 7.01 (s, 6-SOMe), 6.96 (s, 3-SOMe), $J_{4,5}$ = 9.0 Hz; ir 1351 (N–O), 1058 cm^{-1} (SO).

Anal. Calcd for $C_6H_8N_2O_3S_2$: N, 12.73; S, 29.07. Found: N, 12.32; S, 29.10.

The sulfoxide–sulfone **16** was crystallized from toluene and *N*,*N*-dimethylformamide (yield 0.5 g, 44%): mp 193–195°; mass spectrum M^+ 236; ir 1053 (SO), 1359 cm^{-1} (N–O).

Anal. Calcd for $C_6H_8N_2O_4S_2$: N, 11.86; S, 27.10. Found: N, 12.01; S, 27.45.

B.—A solution of **13** (1.8 g) in aqueous acetonitrile (100 ml of 75%) was treated with ceric ammonium nitrate (11 g) and stirred until complete dissolution. The mixture was left at room temperature overnight, the solvent was evaporated, and the residue was extracted with chloroform. An analysis by tlc revealed that the product is a mixture of isomeric monosulfoxides. Therefore, the product (1.45 g) was dissolved in glacial acetic acid (10 ml), a small amount of sodium tungstate and hydrogen peroxide (0.35 g) was added. After 3 hr at 50°, the solvent was evaporated, the residue neutralized with sodium bicarbonate, and extracted with chloroform. Upon evaporation of the solvent the residue was crystallized from toluene and *N*,*N*-dimethylformamide. The compound was found to be identical in all respects with 3,6-bis(methylsulfinyl)pyridazine 1-oxide obtained as described under A.

C.—If a suspension of **13** (0.9 g) in water (10 ml) was treated with hydrogen peroxide (0.5 g) in the presence of a small quantity of sodium tungstate at 50°, the separated product was found to be **16** (0.25 g, 45%), identical with the product obtained as described under A.

3,6-Bis(methylsulfonyl)pyridazine 1-Oxide (17). A.—A mixture of **13** (0.9 g), water (10 ml), and hydrogen peroxide (1.5 g) was heated in the presence of a small amount of sodium tungstate at 50° for 1 hr. The separated product was crystallized from glacial acetic acid (yield 1.1 g, 92%): mp 262°; mass spectrum M^+ 252; nmr (DMSO-d_6) τ 1.28 (d, H_5), 1.98 (d, H_4), 6.45 (s, 3-SO_2Me), 6.55 (s, 6-SO_2Me), $J_{4,5}$ = 8.5 Hz.

Anal. Calcd for $C_6H_8N_2O_5S_2$: N, 11.11; S, 25.38. Found: N, 11.47; S, 25.40.

B.—Compound **13** (0.9 g) in glacial acetic acid (10 ml) was treated with hydrogen peroxide (2 g) at 50° for 3 hr. The product was found to be identical in all respects with that described under A (yield 0.9 g, 75%).

C.—Compound **13** (0.9 g) was treated with a solution of dichloromonoperoxymaleic acid (prepared from 8.0 g of dichloromaleic anhydride in 70 ml of methylene chloride and 3.0 g of hydrogen peroxide) for 1 hr. The product (0.75 g, 62%) was identical with that described under A.

3-Methylthio-6-methylsulfinylpyridazine 1-Oxide (18).—To a stirred solution of **13** (0.9 g) in aqueous acetonitrile (50 ml of 75%)

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ceric ammonium nitrate (5.5 g) was added and the mixture was left at room temperature overnight. The solvent was evaporated, the residue was extracted with chloroform, and upon evaporation of the solvent the product was crystallized from methanol (yield 0.85 g, 88%): mp 143–145°; nmr ($CDCl_3$) τ 2.19 (d, H_5), 2.86 (d, H_4), 7.00 (s, 6-SOMe), 7.40 (s, 3-SMe), $J_{4,5}$ = 8.5 Hz; ir 1049 (SO), 1332 cm^{-1} (N–O).

Anal. Calcd for $C_6H_8N_2O_2S_2$: N, 13.72; S, 31.34. Found: N, 13.65; S, 31.20.

6-Chloro-3-methylthiopyridazine 1-Oxide (20, R = SMe, R_1 = Cl).—To a stirred solution of 3,6-dichloropyridazine 1-oxide (33 g) in toluene (200 ml) at 70–85° was added dropwise an equivalent amount of potassium methanethiolate in methanol. After 5 hr the solvent was evaporated to dryness. The residue was treated with water and recrystallized from methanol (yield 10 g, 28%): mp 192–193°; mass spectrum M^+ 176; nmr ($CDCl_3$) τ 2.65 (d, H_5), 2.93 (d, H_4), 7.53 (s, SMe), $J_{4,5}$ = 9.0 Hz; ir 1340 cm^{-1} (N–O).

Anal. Calcd for $C_5H_5ClN_2OS$: N, 15.86; S, 18.15. Found: N, 15.74; S, 18.30.

6-Chloro-3-methylsulfinylpyridazine 1-Oxide (20, R = MeSO, R_1 = Cl).—A mixture of the above compound (0.9 g), glacial acetic acid (10 ml), hydrogen peroxide (0.25 g), and a small amount of sodium tungstate was left at room temperature. The separated crystals were crystallized from *n*-hexane and ethyl acetate (1:1) (yield 0.9 g, 92%): mp 131–132°; nmr ($CDCl_3$) τ 1.93 (d, H_5), 2.60 (d, H_4), 6.95 (s, SOMe), $J_{4,5}$ = 9.0 Hz; ir 1359 cm^{-1} (N–O), 1063 cm^{-1} (SO).

Anal. Calcd for $C_5H_5ClN_2O_2S$: N, 14.54; S, 16.64. Found: N, 14.44; S, 16.40.

6-Chloro-3-methylsulfonylpyridazine 1-Oxide (20, R = $MeSO_2$, R_1 = Cl).—The procedure was as described in the above case, except that the amount of hydrogen peroxide was greater (1.0 g) and reaction temperature 50° (1 hr). The product, obtained after evaporation of the solvent, was crystallized from *n*-hexane and ethyl acetate (1:1) (yield 0.6 g, 57%): mp 152°; mass spectrum M^+ 208; nmr ($CDCl_3$) τ 1.67 and 2.68 (d, H_4 and H_5), 6.55 (s, SO_2Me), $J_{4,5}$ = 9.0 Hz.

3-Hydrazino-6-methylsulfonylpyridazine (19, R = $NHNH_2$, R_1 = $MeSO_2$).—A suspension of **9** (1.2 g) in ethanol (7 ml) was treated with hydrazine hydrate (0.5 g of 100%), and the mixture was heated under reflux for 2 hr. Upon cooling on ice, the separated product was filtered and crystallized from ethanol (yield 0.85 g, 84%): mp 178–179°; nmr (DMSO-d_6) τ 2.87 (d, H_4), 2.22 (d, H_5), 6.73 (s, SO_2Me), 1.05 (broad, $NHNH_2$), 5.45 (broad, $NHNH_2$), $J_{4,5}$ = 9.0 Hz.

Anal. Calcd for $C_5H_8N_4O_2S$: N, 29.78; S, 17.01. Found: N, 29.75; S, 17.40.

6-Methylsulfonyl-3-piperidinopyridazine (19, R = $N(CH_2)_5$, R_1 = $MeSO_2$) was prepared in a similar way, except that *N*,*N*-dimethylformamide was used as solvent (at 60°). After addition of water the product separated and was crystallized from *n*-hexane and ethyl acetate (1:1) (yield 1.1 g, 90%): mp 124–125°; nmr ($CDCl_3$) τ 3.00 (d, H_4), 2.20 (d, H_5), 6.65 (s, SO_2Me), 6.20 and 8.25 (m, piperidine part), $J_{4,5}$ = 9.4 Hz.

Anal. Calcd for $C_{10}H_{15}N_3O_2S$: N, 17.42; S, 13.26. Found: N, 17.62; S, 13.26.

3-Hydrazino-6-methylsulfonylpyridazine 1-Oxide (20, R = $NHNH_2$, R_1 = $MeSO_2$).—The procedure was the same as in the case of the deoxygenated analog and 3,6-bis(methylsulfonyl)-pyridazine 1-oxide was used as starting material: mp 190–192° (from water, yield 83%); mass spectrum M^+ 204.

6-Methylsulfonyl-3-piperidinopyridazine 1-Oxide (20, R = $N(CH_2)_5$, R_1 = $MeSO_2$).—The compound was synthesized from 3,6-bis(methylsulfonyl)pyridazine 1-oxide in the same manner as described for the deoxygenated analog: mp 163–165° (from *n*-hexane and ethyl acetate (1:1), 71% yield); nmr (DMSO-d_6) τ 2.20 (d, H_5), 2.53 (d, H_4), 6.65 (s, 6-SO_2Me), 6.40, and 8.35 (m, piperidine part), $J_{4,5}$ = 9.2 Hz; ir 1361 cm^{-1} (N–O).

Anal. Calcd for $C_{10}H_{15}N_3O_3S$: N, 16.33; S, 12.44. Found: N, 16.61; S, 12.60.

Registry No.—**1**, 7145-61-1; **2**, 40953-86-4; **3**, 7145-62-2; **4**, 40953-88-6; **5**, 37813-54-0; **6**, 40953-90-0; **7**, 40953-91-1; **8**, 40953-92-2; **9**, 40953-93-3; **10**, 40953-94-4; **11**, 40953-95-5; **12**, 40953-96-6; **13**, 40953-97-7; **14**, 40953-98-8; **15**, 40953-99-9; **16**, 40954-00-5; **17**, 40953-96-6; **18**, 40954-02-7; **19** (R = SOMe, R_1 = OMe), 40954-03-8; **19** (R = $MeSO_2$, R_1 = OMe), 40954-04-9; **19** (R = $NHNH_2$, R_1 = $MeSO_2$), 40954-05-0; **19** (R = $N(CH_2)_5$, R_1 = $MeSO_2$), 40954-06-1; **20** (R = SMe, R_1 = Cl), 40954-07-2; **20** (R = MeSO, R_1 = Cl), 40954-08-3; **20** (R = $MeSO_2$, R_1 = Cl), 40954-09-4; **20** (R = $NHNH_2$, R_1 = $MeSO_2$), 40954-10-7; **20** [R = $N(CH_2)_5$, R_1 = $MeSO_2$], 40954-11-8; potassium methanethiolate, 26385-24-0; sodium methoxide, 124-41-4; 3,6-dichloropyridazine, 25974-26-9.

Photolysis and Spectral Properties of Some *N*-Sulfonyliminopyridinium Ylides

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The photolyses of the title compounds have been studied at different wavelengths and in different solvent systems. The main products are either the 1-sulfonyl-1,2-diazepine or the sulfonamide, depending on the reaction conditions. In no case was any evidence obtained for the formation of singlet sulfonyl nitrenes, although the sulfonamides may arise from triplet nitrene. The uv, nmr, and mass spectra of some of the compounds studied are reported and discussed briefly.

Sulfonyl nitrenes are almost always generated by the thermolysis of sulfonyl azides at 120° or higher.[1] In view of the observation that *N*-sulfonylazepines are the products of kinetic control of the reaction of singlet sulfonyl nitrenes with aromatic substrates while the *N*-phenylsulfonamides are the products of thermodynamic control,[2] it was desirable to develop a method of generating sulfonyl nitrenes at low (preferably ambient, or below) temperatures.

Of the various possible methods considered, photolysis of sulfonyl azides appeared the most obvious. Unfortunately, photolysis of aliphatic and aromatic sulfonyl azides in nonprotic, nonpolar solvents such as benzene or cyclohexane, or in a polar solvent such as pyridine, produces insoluble high-melting materials that have not been characterized.[3-5] When, however, the photolysis of methanesulfonyl azide was carried out in benzene at 25° such that the walls of the photolysis apparatus were not coated with tar, a very small amount of *N*-mesylazepine was isolated.[4] The only sulfonyl azide known to photolyze smoothly under these conditions is ferrocenylsulfonyl azide.[6] On the other hand, it has been reported that a number of nitrene derivatives can be produced by the photolysis of appro-

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