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Studies on Heteroaromatic N-Oxides. IX.[1] The Synthesis and Structure of Benzothiazole N-Oxides

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Several benzothiazole 3-oxides were synthesized by N-oxidation of parent bases with organic peracids. Among the oxidizing reagents, monopermaleic acid gave the best result. On oxidation of 6-substituted benzothiazoles, substituents in the 6-position affect yields of the N-oxides; electrondonating groups caused increase in the yields and electron-attractive groups did decrease. Benzothiazoles bearing a functional group in the 2-position could not be oxidized to the N-oxides only to be hydrolyzed or recovered on the treatment with monopermaleic acid. In order to decide that the oxidized benzothiazoles are N-oxides and not S-oxides, dipole moments were measured.

An interesting reactivity of benzimidazole N-oxides prompted us to compare them with that of benzothiazole N-oxide, very few studies of which have been done.

In contrast with the fact that imidazole N-oxides and benzimidazole N-oxides have never been synthesized by direct oxidation with organic peracid,[3] some thiazole N-oxides were synthesized by this method; Ochiai and Hayashi[4] obtained 4-methylthiazole 3-oxide and 2,4-dimethylthiazole 3-oxide using peracetic acid in yields of 14 and 58%, respectively, and observed formation of ammonium sulfate in the former case. The latter compound was also obtained by oxidation with monoperphthalic acid by Matsumura, *et al.*[5] Liss[6] reported that reductive ring closure of *o*-nitrothiocyanatobenzene gave 2-aminobenzothiazole 3-oxide, and its acetyl derivative was identical with the product obtained by oxidation of 2-acetamidobenzothiazole with trifluoroperacetic acid.

The best synthetic procedure for benzimidazole N-oxides[7] which consists in reductive ring closure of N-substituted N-acetyl-*o*-nitroanilide with sodium borohydride in the presence of a reductive catalyst was applied to the synthesis of benzothiazole N-oxide (II), but only hydrolyzed starting material, *o*-nitrothiophenol was recovered. Reductions either with hydrogen (in the presence of palladium-charcoal and hydrogen chloride or Raney nickel) or with hydrogen sulfide and ammonia resulted in hydrolysis and the N-oxide could not be obtained. Liss' method using trifluoroperacetic acid, which gave a good result in the case of N-oxidation of 2-acetamidobenzothiazole, gave poor results for unsubstituted benzothiazole (III) and 2-chlorobenzothiazole (IV); III was decomposed to many unidentified products as anticipated from analogy of the oxidative degradations of 2-unsubstituted thiazole mentioned above, and 6-unsubstituted pyrimidines.[8] IV was recovered on this reaction.

On the contrary, 2-methylbenzothiazole (V) was readily oxidized to 2-methylbenzothiazole 3-oxide (VI) with various oxidizing agents, although the yields were low in all cases, as shown

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[1] The previous parts of this series were entitled "Benzimidazole N-Oxides." Part VIII: S. Takahashi and H. Kanō, *Chem. Pharm. Bull.* (Tokyo), **16**, 527 (1968).

[2] Location: *Fukushima-ku, Osaka.*

[3] *cf.* R. Kuhn and W. Blau, *Ann.*, **615**, 99 (1958).

[4] E. Ochiai and E. Hayashi, *Yakugaku Zasshi*, **67**, 34 (1947).

[5] E. Matsumura, T. Hirooka and K. Imagawa, *Nippon Kagaku Zasshi*, **82**, 616 (1961).

[6] T.A. Liss, *Chem. Ind.* (London), **1964**, 368.

[7] H. Kanō and S. Takahashi, Japanese Patent applied.

[8] T. Kato, H. Yamanaka and T. Shibata, *Yakugaku Zasshi*, **86**, 1096 (1967).

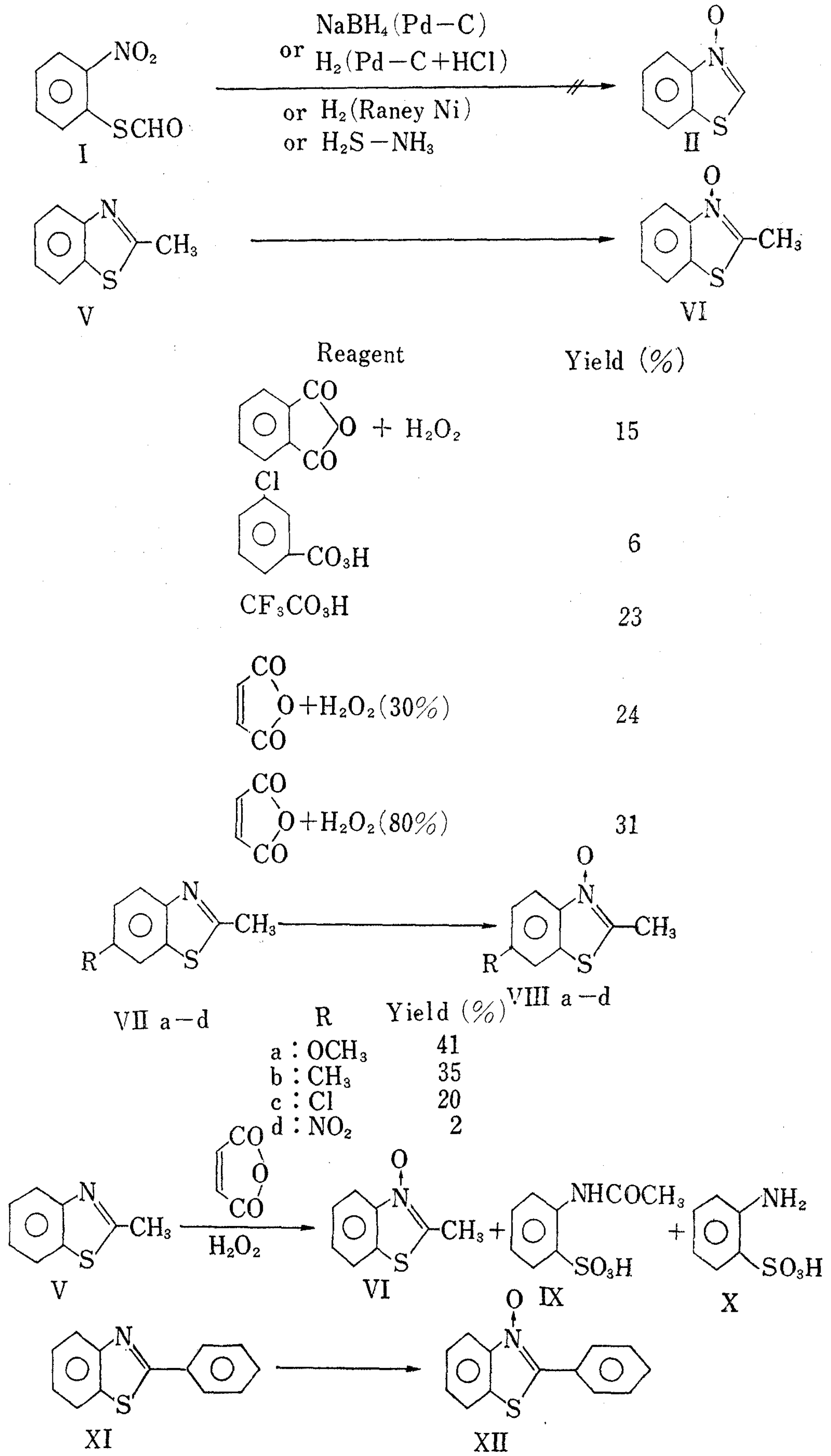

Chart 1

in Chart 1. The use of monopermaleic acid, which was reported to be an effective N-oxidizing reagent by Yamazaki, *et al.*[9] gave VI in the highest yield, on the other hand, the most widely used peracetic acid-oxidation scarcely gave VI.

On the N-oxidation of 6-substituted 2-methylbenzothiazoles (VIIa—d), the substituents of 6-position have a marked influence on the yields of the N-oxides; when the substituent

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9) M. Yamazaki, N. Honjo, K. Noda, Y. Chono and M. Hamana, *Yakugaku Zasshi*, **86**, 749 (1966).

is electrondonating group, the yield is high and when the substituent is electronattracting group, the yield is low (see Chart 1).

Detailed investigation of the oxidation product of V with permaleic acid showed it is a mixture of VI (31%), *o*-acetamidobenzenesulfonic acid (IX) (17%), orthanilic acid (X) (8%), and the recovered starting material V (34%). This result suggests that the thiazole ring of V is susceptible to oxidative ring opening compared with that of 2,4-dimethylthiazole mentioned above, though both thiazoles have a methyl group in the 2-position. In this experiment, neither S-oxide nor S,S-dioxide of V could be detected by infrared or ultraviolet spectroscopy.

N-Oxidation of 2-phenylbenzothiazole (XI) with permaleic acid gave 2-phenylbenzothiazole 3-oxide (XII) in comparable yield to VI.

Although 2-alkyl- and 2-arylbenzothiazoles were oxidized to their N-oxides by treatment with organic peracid as mentioned above, no benzothiazole derivatives possessing a functional group in the 2-position gave the N-oxides; 2-mercaptobenzothiazole (XIII) yielded desulfurized product, benzothiazole III, hydrolyzed product, 2-benzothiazolinone (XIV) and dehydrogenated product, 2,2′-dibenzothiazolyl disulfide (XV). 2-Methylthiobenzothiazole (XVI) yielded 2-methylsulfonylbenzothiazole (XVII). 2-Methoxybenzothiazole (XVIII) yielded hydrolyzed product XIV. Ethyl 2-benzothiazolecarboxylate (XIX) and 2-benzothiazolecarboxamide (XX) were not oxidized on this condition and only the starting materials were recovered.

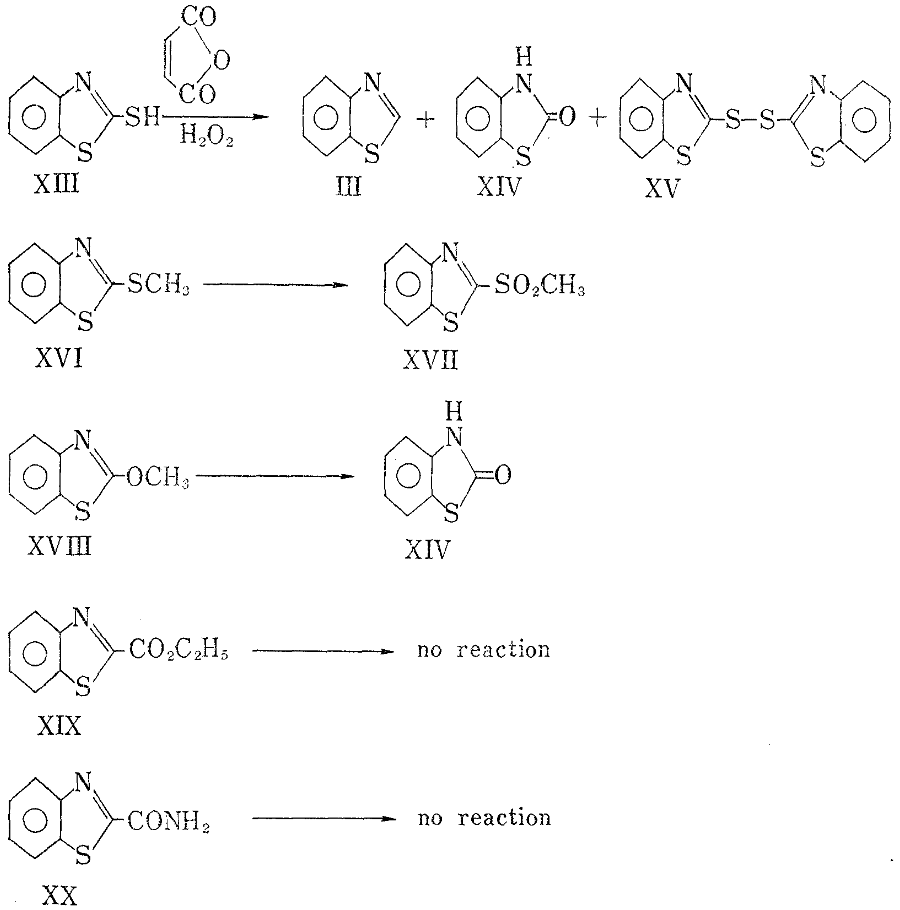

Chart 2

In order to confirm the N-oxide structure assigned, the following experiment has been carried out. Ultraviolet spectra of the above obtained oxidation product VI of 2-methylbenzothiazole shows the typical pattern of blue shift observed in heteroaromatic N-oxides. In infrared spectra of the oxidation products of benzothiazole derivatives mentioned above,

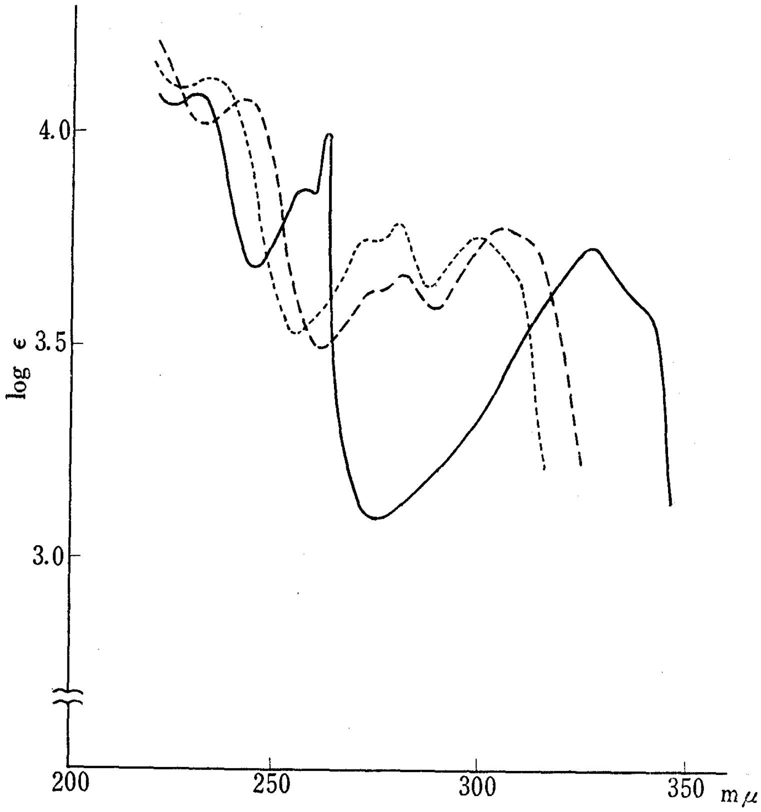

Fig. 1. Ultraviolet Spectra of 2-Methylbenzothiazole 3-Oxide

——: *n*-heptane ------: EtOH ……: H_2O

outstanding absorption bands in a range of 1000—1350 cm^{-1} are as follows (in Nujol Mull); 2-methylbenzothiazole 3-oxide dihydrate, 1109 (s), 1133 (s), 1203 (m) and 1307 (s), VIIIa, 1054 (m), 1140 (s), 1252 (s) and 1310 (m), VIIIb, 1146 (s) and 1310 (m), VIIIc, 1145 (s), 1306 (s) and 1328 (m), and VIIId, 1148 (s), 1311 (s) and 1340 (s).

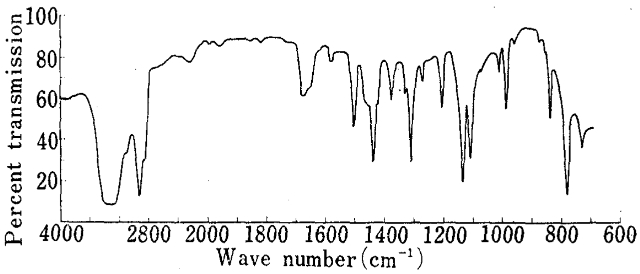

Fig. 2. Infrared Spectrum of 2-Methylbenzothiazole 3-Oxide

Table I. Dipole Moments of Benzothiazoles

Compounds	Calculated value (D)	Observed value (D)
5-Chloro-2-methylbenzothiazole	2.15	2.56
6-Chloro-2-methylbenzothiazole	0.64	1.76
5-Chloro-2-methylbenzothiazole N-oxide	4.05	4.44
5-Chloro-2-methylbenzothiazole S-oxide	2.32	—
6-Chloro-2-methylbenzothiazole N-oxide	2.67	3.06
6-Chloro-2-methylbenzothiazole S-oxide	3.11	—

Because of these spectral data do not necessarily exclude the possibility that the compounds are benzothiazole S-oxides, dipole moments of some oxidized products together with their parent bases were measured to get decisive evidence. The results were listed in Table I. The calculated values were roughly estimated on the basis of the following assumptions; benzene and thiazole rings of the benzothiazoles are regular hexagonal and regular pentagonal, respectively and values of group moments may be used those of thiophen (0.52 D), pyridine (2.20 D), pyridine N-oxide (4.24 D), thiophen oxide (3.9 D) and chlorobenzene (1.55 D), and the effect of methyl group is neglected. The agreement between the calculated and observed value is not so good, but this data are enough to decide that the oxidized benzothiazoles must be benzothiazole N-oxides.

Experimental[10]

***o*-Nitroformylthiophenol (I)**——*o*-Nitrothiophenol (7.0 g) was added to AcOCHO,[11] prepared from Ac_2O (19.0 ml) and HCOOH (98%, 8.0 ml). After standing overnight at room temperature, the resulting slightly yellow solution was evaporated and the residue was dissolved in $CHCl_3$, then neutralized with aq. $NaHCO_3$ solution. The $CHCl_3$ layer was separated and evaporated. Distillation of the residue gave pale yellow oil (6.0 g), bp 113° (0.10 mmHg). *Anal.* Calcd. for $C_7H_5O_3NS$: C, 45.91; H, 2.75; N, 7.65. Found: C, 46.21; H, 3.01; N, 7.54.

Attempted Reductive Ring Closure of I to Benzothiazole N-Oxide (II)——A) $NaBH_4$: To a solution of $NaBH_4$ (1.50 g) in H_2O (10 ml) was added a suspension of Pd–C (5%, 0.30 g) in H_2O (5 ml) with stirring and cooling in an ice–water bath. To this suspension was added a solution of I (0.90 g) in dioxane (10 ml) dropwise during *ca.* 0.5 hr with stirring at room temperature. The catalyst and solvent were removed and the residue was dissolved into H_2O and acidified with 6N HCl to give yellow oil, which was extracted with ether. The oil (0.60 g) was identified with *o*-nitrothiophenol. The acidified H_2O layer was neutralized with aq. $NaHCO_3$ solution, evaporated and the residue was extracted with abs. EtOH, but nothing was obtained.

B) H_2(Pd–C+HCl): A solution of I (0.60 g) in EtOH (10 ml) containing conc. HCl (0.30 ml) was shaken in H_2 atmosphere over Pd–C (5%, 0.20 g). No H_2 was absorbed during 5 hr. Working up gave *o*-nitrothiophenol (0.50 g).

C) H_2 (Raney Ni): A solution of I (0.60 g) in EtOH (10 ml) was shaken in H_2 atmosphere over Raney Ni (W–5 from 0.50 g alloy). H_2 of calculated amount being absorbed during *ca.* 10 hr, but removal of the catalyst and solvent gave yellow oil (0.50 g) which was identified with *o*-nitrothiophenol.

D) H_2S–NH_3: H_2S gas was passed through a solution of I (1.00 g) in EtOH (10 ml) and EtOH–NH_3 (saturated at 0°, 5.0 ml) for 1 hr. After standing at room temperature for an additional 3 hr, the resulting solution was evaporated and the residue was extracted with *n*-hexane. From the hexane solution, a yellow oil (0.40 g) was obtained which was identified with *o*-nitrothiophenol. The residue was washed with MeOH to give yellow crystals (0.40 g), mp 192—194°, which was identified with di-*o*-nitrophenyl disulfide.[12]

Oxidation of Benzothiazole (III) with Trifluoroperacetic Acid——To a suspension of III (0.68 g) and Na_2CO_3 (5.0 g) in CH_2Cl_2 (10 ml) was added a solution of CF_3CO_3H in CH_2Cl_2,[13] prepared from $(CF_3CO)_2O$ (2.50 g), H_2O_2 (90%, 0.38 g) in CH_2Cl_2 (5.0 ml), dropwise with stirring and heating under reflux. After stirring and heating for an additional 2.5 hr, further CF_3CO_3H solution and Na_2CO_3 (the same amounts mentioned above) were added and the reaction was allowed to proceed for further 2 hr. At this time, starch–iodide paper showed that the oxidizing reagent had been consumed perfectly.

To the reaction mixture was added H_2O to dissolve the inorganic salt and the H_2O layer was extracted with $CHCl_3$. The $CHCl_3$ solution was evaporated and the residue (0.55 g) was chromatographed to give the colorless oil (0.49 g), which was identified with III, and several minor unidentified products.

Oxidation of 2-Chlorobenzothiazole (IV) with Trifluoroperacetic Acid——To a suspension of IV (0.85 g) and Na_2CO_3 (5.0 g) in CH_2Cl_2 (10 ml) was added a solution of CF_3CO_3H in CH_2Cl_2, prepared from $(CF_3CO)_2O$ (2.50 g), H_2O_2 (90%, 0.38 g) in CH_2Cl_2 (5.0 ml), dropwise with stirring and heating under reflux. After the addition, the mixture was heated under reflux for 3 hr and then cooled. To the resulting mixture was added

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10) All melting points were taken on a Kofler hot-stage and are uncorrected. Solvents were removed under reduced pressure using a rotary evaporator. Each identification was made by comparison of the infrared spectrum with that of a sample prepared by an unequivocal route and if the sample had a melting point, it was also compared by mixed fusion. Infrared spectra were recorded with a Jasco Model IR–S Infrared Spectrophotometer. The measurements of the dielectric constants were carried out in benzene at a low concentration at 25° by means of a heterodyne beat apparatus provided with a platinium cell. For each solute, determinations were made with a solution at four different concentrations appropriately chosen below 1.5 weight percent. The deformation polarization of each compound was assumed to be 1.05 times as much as the molar refraction approximated with the sum of atomic refractions for the D line.

11) C.W. Huffman, *J. Org. Chem.*, 23, 727 (1958).

12) M.T. Bogert and A. Stull, "Organic Syntheses," Coll. Vol. I ed. by A.H. Blatt, John Wiley and Sons Inc., New York, N.Y., 1948 p. 220.

13) W.D. Emmons and A.S. Pagano *J. Am. Chem. Soc.*, 77, 89 (1955).

H_2O and extracted with $CHCl_3$. The $CHCl_3$ solution was concentrated and chromatographed on Al_2O_3 with $CHCl_3$ gave colorless oil (0.82 g), which was identified with IV.

Detailed Investigation of N-Oxidation of 2-Methylbenzothiazole (V)——To a solution of V (0.050 mole, 7.50 g) in CH_2Cl_2 (10 ml) was added a solution of permaleic acid in CH_2Cl_2, prepared from maleic anhydride (0.065 mole, 6.10 g) and H_2O_2 (80%, 0.065 mole, 2.80 g) in CH_2Cl_2 (30 ml), dropwise with stirring and heating under reflux. After the addition, the stirring and heating were continued for an additional 2 hr. In the course of this time, a crystalline product, maleic acid, precipitated. The reaction mixture was cooled for a time and the precipitated maleic acid was filtered off and washed with CH_2Cl_2. The combined filtrate and washings was extracted with 2N HCl. The HCl-solution was evaporated and the residue was triturated with AcOEt. The AcOEt solution was evaporated, neutralized with aq. NH_3 solution and extracted with CH_2Cl_2 to remove maleic acid. The CH_2Cl_2 solution was chromatographed on Al_2O_3 (containing H_2O 3%) with benzene to give colorless oil, V (2.50 g, 33%) and then with MeOH–CH_2Cl_2 (1:15) to give slightly reddish brown tar (2.60 g, 31%), which was crystallized by addition of H_2O–acetone (0.3—1.0 ml) with scratching and recrystallized from AcOMe or ether to give colorless prisms, mp 46—48°. *Anal.* Calcd. for $C_8H_7ONS \cdot 2H_2O$ (2-methylbenzothiazole 3-oxide dihydrate): C, 47.76; H, 5.51; N, 6.96. Found: C, 48.01; H, 5.38; N, 7.04.

The hemihydroperchlorate of VI was obtained by addition of perchloric acid to the aqueous solution of VI. Recrystallization from H_2O or EtOH gave colorless needles, mp 202° (decomp.). *Anal.* Calcd. for $C_8H_7ONS \cdot 1/2\ HClO_4$: C, 44.60; H, 3.52; N, 6.50. Found: C, 44.63; H, 3.51; N, 6.46.

The neutralized aqueous solution was evaporated and the residue was triturated with abs. EtOH gave ammonium salt of *o*-acetamidobenzenesulfonic acid (2.0 g, 17%), as colorless prisms, mp 252—254° (decomp.).

The residue triturated with AcOEt was then triturated with abs. EtOH. Removal of the solvent gave orthanilic acid (0.65 g, 8%) as colorless scales, mp >250°.

These two compounds were identified with authentic specimens, respectively.

Oxidation of V with Monoperphthalic Acid——To a mixture of V (5.00 g) and H_2O_2 (30%, 1.14 g) was added phthalic anhydride (3.80 g) with stirring and cooling and the resulting mixture was stand overnight in a refrigerator. The mixture was extracted with $CHCl_3$ and the $CHCl_3$ solution was concentrated and chromatographed by the same procedure as mentioned above to give V (4.00 g) and VI (0.82 g, 15%).

Oxidation of V with *m*-Chloroperbenzoic Acid——A solution of V (0.75 g) and *m*-chloroperbenzoic acid (purity 85%, 1.30 g) in benzene (20 ml) was stand in a refrigerator for a week. The resulting solution was evaporated and the residue was triturated with $CHCl_3$. The $CHCl_3$ solution was concentrated and chromatographed by the same procedure as for the oxidation with monopermaleic acid to give V (0.50 g) and VI (0.05 g, 6%).

Oxidation of V with Trifluoroperacetic Acid——To a suspension of V (0.75 g) and Na_2CO_3 (3.0 g) in CH_2Cl_2 (20 ml) was added a solution of CF_3CO_3H in CH_2Cl_2, prepared from $(CF_3CO)_2O$ (2.50 g), H_2O_2 (90%, 0.38 g) in CH_2Cl_2 (5.0 ml), dropwise with stirring and heating under reflux. After stirring and heating for an additional 0.5 hr, the reaction mixture was evaporated, H_2O (20 ml) was added to the residue and the solution was extracted with $CHCl_3$. The $CHCl_3$ solution was concentrated and chromatographed by the same procedure as for the oxidation with monopermaleic acid to give V (0.40 g) and VI (0.19 g, 23%).

Oxidation of V with Monopermaleic Acid——To a solution of V (7.50 g) and maleic anhydride (6.10 g) in CH_2Cl_2 (25 ml) was added H_2O_2 (30%, 6.35 g) dropwise with stirring and heating under reflux. After the addition, stirring and heating were continued for an additional 1 hr, then the reaction mixture was cooled in an ice–water bath. A resulting precipitated product, maleic acid, was filtered off and washed with CH_2Cl_2. The combined filtrate and washings was concentrated and chromatographed by the same procedure mentioned above to give V (3.5 g) and VI (2.00 g, 24%).

Oxidation of V with Peracetic Acid——To a solution of V (0.50 g) in AcOH (5.0 ml) was added H_2O_2 (30%, 1.5 ml) and the solution was warmed at 60° for 3 hr, then further H_2O_2 (30%, 1.5 ml) was added and the solution was warmed at 60° for an additional 5 hr. The solution was evaporated and the residue was basified by the addition of $NaHCO_3$ and extracted with $CHCl_3$. The $CHCl_3$ solution was concentrated and chromatographed by the same procedure mentioned above to give V (0.40 g) and VI (*ca.* 5 mg).

6-Methoxy-2-methylbenzothiazole 3-Oxide (VIIIa)——To a solution of VIIa[14] (1.79 g) and maleic anhydride (4.00 g) in CH_2Cl_2 (10 ml) was added H_2O_2 (30%, 4.0 ml) dropwise with stirring and heating under reflux. Working up by the same procedure as for the oxidation of V with monopermaleic acid gave VIIa (0.08 g) and VIIIa (0.80 g). Recrystallization from AcOEt gave colorless prisms, mp 139—141° (decomp.). *Anal.* Calcd. for $C_9H_9O_2NS$: C, 55.38; H, 4.65; N, 7.18. Found: C, 55.41; H, 4.64; N, 7.18.

2,6-Dimethylbenzothiazole 3-Oxide (VIIIb)——This reaction was carried out by the same procedure as for the oxidation of V with monopermaleic acid. The cooled reaction mixture, prepared from VIIb[14] (0.80 g), maleic anhydride (2.0 g), H_2O_2 (30%, 2.0 ml) and CH_2Cl_2 (5.0 ml), was filtered and a crystalline product was washed with CH_2Cl_2. The combined filtrate and washings was concentrated and chromatographed on Al_2O_3 (containing H_2O 3%) with CH_2Cl_2 gave VIIb (0.10 g), *p*-acetotoluide (0.07 g), mp 152—153° then

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14) Y. Mizuno and K. Adachi, *Ann. Rept. Fac. Pharm. Kanazawa Univ.*, 1, 8 (1951).

VIIIb (0.28 g). Recrystallization of VIIIb from AcOEt gave colorless plates, mp 112—114°. *Anal.* Calcd. for C_9H_9ONS: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.23; H, 5.21; N, 8.00.

6-Chloro-2-methylbenzothiazole 3-Oxide (VIIIc)——This reaction was carried out by the same procedure as for the oxidation of VIIb. From VIIc[14] (0.92 g), maleic anhydride (2.0 g), H_2O_2 (30%, 2.0 ml) and CH_2Cl_2 (5.0 ml), VIIIc (0.20 g) was obtained accompanied with VIIc (0.36 g). Recrystallization of VIIIc from C_6H_6-*n*-hexane or AcOEt gave colorless scales or prisms, mp 132—133° (decomp.). *Anal.* Calcd. for C_8H_6ONClS: C, 48.11; H, 3.03; N, 7.04. Found: C, 47.85; H, 3.10; N, 7.29.

6-Nitro-2-methylbenzothiazole 3-Oxide (VIIId)——This reaction was carried out by the same procedure as for the oxidation of VIIb. From VIId[15] (1.95 g), maleic anhydride (2.00 g) H_2O_2 (30%, 2.0 ml) and CH_2Cl_2 (10 ml), VIIId (0.035 g) was obtained accompanied with VIId (0.75 g). Recrystallization from acetone gave yellow prisms or plates, mp 201—203° (turn brown above 185°). *Anal.* Calcd. for $C_8H_6O_3N_2S$: C, 45.72; H, 2.88; N, 13.33. Found: C, 45.63; H, 2.82; N, 13.41.

2-Phenylbenzothiazole 3-Oxide (XII)——This compound (0.22 g) was obtained from 2-phenylbenzothiazole (1.05 g), maleic anhydride (2.00 g), H_2O_2 (30%, 2.0 ml) and CH_2Cl_2 (5.0 ml) by the same procedure as for the oxidation of V with monopermaleic acid mentioned above. Recrystallization from AcOEt gave colorless plates, mp 150—151°. *Anal.* Calcd. for $C_{13}H_9ONS$: C, 68.72; H, 3.99; N, 6.17. Found: C, 68.70; H, 4.02; N, 6.09.

Oxidation of 2-Mercaptobenzothiazole (XIII)——To a suspension of XIII (1.67 g) and maleic anhydride (1.92 g) in CH_2Cl_2 (20 ml) was added H_2O_2 (30%, 3.0 ml) dropwise with stirring and heating under reflux. After a few minutes, the starting material was dissolved into the solution and then a crystalline product precipitated, which dissolved again into the solution. After stirring and heating for 1 hr, H_2O (5 ml) was added to the reaction mixture and shaking. The H_2O-layer was separated, evaporated and the residue was extracted with acetone. The acetone solution was evaporated to give colorless crystals (0.01 g), mp 135—136°, which was identified with 2-benzothiazolinone.[16] The CH_2Cl_2-layer was evaporated and the residue was extracted with ether. The ether solution was evaporated to give a colorless oil (0.60 g) which was identified with benzothiazole. Identification of benzothiazole was made by comparison of the retention time of G.L.C. with that of the authentic specimen (Apparatus: Varian Aerograph Model 1520-1B. Column: each stainless steel 5′×1/8″ O.D., 5% liquid phase on Chromosorb W (60—80 mesh). Temperature: injector 200°, column 145°, detector (FID) 200°, Carrier Gas: N_2 20 ml/min. Retention Time (adjusted): SE-52 2.85 min, PDEAS 1.50 min). The residue extracted with ether was recrystallized from AcOEt to give colorless scales (0.40 g), mp 184—186°, which was identified with an authentic specimen of 2,2′-dibenzothiazolyl disulfide.[17]

Oxidation of 2-Methylthiobenzothiazole (XVI)——To a solution of XVI (1.00 g) and maleic anhydride (2.0 g) in CH_2Cl_2 (5.0 ml) was added H_2O_2 (30%, 2.0 ml) dropwise with stirring and heating under reflux. After the addition, stirring and heating were continued for an additional 1 hr. The resulting precipitated crystals were filtered off and washed with CH_2Cl_2. The combined filtrate and washings was concentrated and chromatographed on Al_2O_3 with CH_2Cl_2 to give colorless crystals (1.10 g), mp 92—93°, which was identified with an authentic specimen of 2-methylsulfonylbenzothiazole.[18]

Attempted Oxidation of 2-Methoxybenzothiazole (XVIII)——This reaction was carried out by the same procedure as for the oxidation of XVI. From XVIII (1.20 g), maleic anhydride (2.0 g),H_2O_2 (30 %, 2.0 ml) and CH_2Cl_2 (5.0 ml), 2-benzothiazolinone[16] (20%) was obtained accompanied with XVIII (0.60 g).

Attempted Oxidation of Ethyl 2-Benzothiazolcarboxylate (XIX)——A solution of XIX (2.2 g), maleic anhydride (2.0 g), H_2O_2 (30%, 2.0 ml) in CH_2Cl_2 (5 ml) was treated by the same procedure as for the oxidation of XVI, and only the starting material, XIX (2.0 g) was recovered.

Attempted Oxidation of 2-Benzothiazolecarboxamide (XX)——A mixture of XX (1.9 g), maleic anhydride (2.0 g), H_2O_2 (30%, 2.0 ml) in CH_2Cl_2 (10 ml) was treated by the same procedure as for the oxidation of XVI, and only the starting material, XX (1.7 g) was recovered.

5-Chloro-2-methylbenzothiazole 3-Oxide——This compound was obtained from 5-chloro-2-methylbenzothiazole[14] by the same procedure as for the oxidation of VIIc in yield of 20%. Recrystallization from *n*-hexane or AcOEt gave colorless short prisms, mp 124—126° (turn brown). *Anal.* Calcd. for C_8H_6ONClS: C, 48.11; H, 3.03; N, 7.04. Found: C, 48.24; H, 3.04; N, 7.05.

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