for 20 min prior to photolysis. The photolysate was analyzed directly by VPC (6 ft column of 3% SE-30 on Chromosorb G, operating between 90 and 120 °C), using dodecane as internal standard. Relative response ratios were obtained from pure authentic samples.

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Registry No.—1, 16536-36-0; 2, 2171-74-6; oxalyl, 79-37-8; catechal, 120-80-9.

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Synthesis and Thermal Decomposition of 1-Methyl-1*H*,3*H*-1,2-benzisothiazole 1-Oxide Hydrochloride[1]

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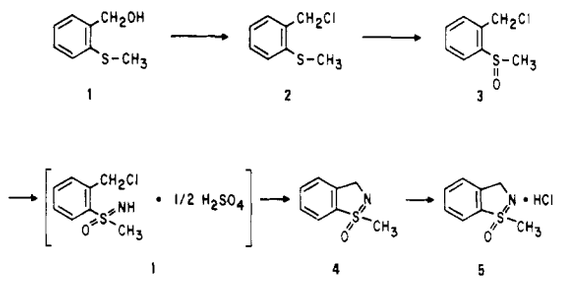
Recently there has been much interest in the sulfoximine function as a synthon and in sulfoximines which possess biological activity.[2] We wish to report the synthesis of a new heterocyclic ring system which contains the sulfoximine function, 1-methyl-1*H*,3*H*-1,2-benzisothiazole 1-oxide hydrochloride, and its thermal decomposition to afford 1,2-benzisothiazole. Experiments pertaining to the mechanism of this thermal decomposition are discussed.

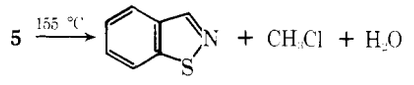
Results and Discussion

The synthesis of 1-methyl-1*H*,3*H*-1,2-benzisothiazole 1-oxide (**4**) and its corresponding hydrochloride (**5**) were accomplished by the sequence of reactions shown in Scheme I. Treatment of *o*-(methylthio)benzyl alcohol (**1**)[3] with thionyl chloride in benzene, according to the procedure of Grice and Owen,[4] afforded *α*-chloro-*o*-tolyl methyl sulfide (**2**) in 73% yield. Oxidation of **2** with *m*-chloroperoxybenzoic acid afforded the corresponding sulfoxide **3** in 54% yield. The conversion of sulfoxide **3** to the sulfoximine proved initially baffling. Treatment of **3** with sodium azide in sulfuric acid and chloroform[5] followed by a basic workup afforded a mixture of the cyclized sulfoximine free base (**4**) and its corresponding hydrochloride (**5**). Isolation of the hydrochloride from a basic workup was confusing. We were subsequently able to isolate the open ring sulfoximine intermediate as the hemi sulfuric acid salt I. Rapid basic treatment of I afforded the hydrochloride **5** in good yield; however, a more prolonged, 20 to 30 min, treatment with base afforded only the free base **4**. This results from the fact that the ring closure of the free base of I in basic medium requires 20 to 30 min for completion. If it is quickly removed from the basic medium, spontaneous ring closure occurs to afford the hydrochloride **5**. The best procedure for the preparation of **4** involves the isolation of I which is subsequently dissolved in water, made basic (pH 12), and stirred at ambient temperature for 0.5 h. Treatment of **4** with ethereal hydrogen chloride afforded the hydrochloride **5**. The structures of **4** and **5** were confirmed by elemental analyses, IR, NMR, and mass spectra (Experimental Section).

Scheme I



When the melting point of **5** was taken, it underwent a smooth gaseous decomposition at ca. 140 °C leaving a clear oil which solidified upon cooling. As a result, this decomposition was carried out on a preparative scale. Compound **5** was heated at 155 °C for 20 min in a small flask to afford a 94% yield of 1,2-benzisothiazole (**6**). 1,2-Benzisothiazole was



identified by elemental analyses, IR, NMR, and mass spectra (Experimental Section). The organic component of the evolved gas was identified as methyl chloride by infrared and the other component was identified as water by NMR. It was found that this reaction also occurred when **5** was heated at reflux in acetonitrile and in Me_2SO at 110 °C.

The demethylation of *S*-methyl sulfoximines represents a unique reaction of the sulfoximine function. Cram and coworkers[6] observed a similar demethylation when (−)-(*R*)-methyl *p*-tolyl *N*-methylsulfoximide was treated with tosyl chloride in pyridine to afford (−)-(*R*)-*N*-methyl-*N*-tosyl-*p*-toluenesulfinamide.

Johnson and co-workers[7] reported that the reaction of *N,N*-dimethylaminomethylphenyloxosulfonium fluoroborate with sodium methoxide in refluxing methanol afforded *N,N*-dimethylphenylsulfinamide, presumably by attack of the methoxide on the *S*-methyl or by decomposition of the methylide intermediate. The thermolysis of **5** affords a new and simpler method for the preparation of 1,2-benzisothiazole.[8,9]

In an attempt to elucidate the mechanism of the thermal decomposition of **5**, the following experiments were performed. When the decomposition was terminated at about one-half completion and the reaction mixture was analyzed, only starting material and 1,2-benzisothiazole were present. The reaction was also carried out in Me_2SO-d_6 at 110 °C in an effort to detect any transient intermediate by NMR and TLC; however, none was observed. The thermal decomposition of the deuteriochloride salt of **4** afforded 1,2-benzisothiazole which had incorporated 4 to 5% deuterium at the 3 position (mass spectrum analysis). A kinetic study comparing the relative rates of 1,2-benzisothiazole formation from **5** and the corresponding hydrobromide salt (**5a**) in dimethyl sulfoxide at 110 ± 3 °C showed that the hydrobromide reacted approximately four times more rapidly than did the hydrochloride. These observations are consistent with a mechanism in which the halide ion attacks the methyl group of **4**. The rate-determining step involves the attack of the halide ion on the methyl group of **4**.

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Experimental Section

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were obtained on a Perkin-Elmer Model 421 recording spectrometer in Nujol mulls, the NMR spectra were recorded on a Varian A-60D spectrometer, and the mass spectra were determined on an Atlas CH-4 spectrometer.

α-Chloro-o-tolyl Methyl Sulfoxide (3). *m*-Chloroperoxybenzoic acid (85% pure, 40.1 g; 0.186 mol) in chloroform (400 mL) was added dropwise over a 0.5-h period to a stirred solution of **2**[3] (32 g; 0.186 mol) in chloroform (180 mL) maintained at −20 to −10 °C. Stirring was continued for 1.5 h at −20 to −10 °C and the reaction mixture was allowed to stand at 4 °C for 16 h. The precipitate was removed by filtration and the filtrate was extracted with saturated sodium hydrogen carbonate solution containing sodium sulfite (3 × 200 mL) and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was recrystallized from hexane to afford 18.96 g (54%) of **3**: mp 65–7 °C; IR 665, 690, 745, 780 (aromatic CH/other), 965, 1020, 1060 (S=O), 1645, and 1670 cm^{-1} (C=C); NMR ($CDCl_3$) δ 2.83 (s, 3 H, $SOCH_3$), 4.73 (d of d, 2 H, J = 11 Hz, CH_2Cl), 7.30–7.77 (m, 3 H, aromatic), 7.95–8.17 (m, 1 H, aromatic); mass spectrum *m/e* 188 and 190 (M^+). Anal. Calcd for C_8H_9ClOS: C, 50.93; H, 4.77; Cl, 18.83; S, 16.98. Found: C, 51.05; H, 4.88; Cl, 18.88; S, 17.08.

1-Methyl-1*H*,3*H*-1,2-benzisothiazole 1-Oxide (4) and Its Hydrochloride (5). A mixture of **3** (7.52 g; 0.041 mol), concentrated sulfuric acid (25 mL), and chloroform (170 mL) was heated to 45 °C and sodium azide (13.9 g; 0.212 mol) was added portionwise over a 2-h period with stirring. The mixture was stirred at 45 °C for an additional 16 h and cooled. The precipitate (I) was removed by filtration, dissolved in water (800 mL), and made basic (pH 12) with 6 N sodium hydroxide. The basic solution was stirred at ambient temperature for 0.5 h and extracted with dichloromethane (3 × 500 mL). The combined extracts were dried (Na_2SO_4) and the solvent was removed in vacuo and the residue was recrystallized from ether to afford 4.44 g (65%) of **4**: mp 81–4 °C; IR 790, 785, 765, 760, 750 (ortho CH), 1255, 1225, 1215, 1185, 1170, 1080, 975, 965, 865 (N=S=O/CH), 1595, 1580 (C=C), 3080, 3060 cm^{-1} (=CH); NMR ($CDCl_3$) δ 3.37 (s, 3 H, CH_3), 4.76 (d of d, 2 H, J = 17 Hz, CH_2), 7.30–8.00 (m, 4 H, aromatic); mass spectrum *m/e* 166 and 167 ($M^+ - 1$) and (M^+). Anal. Calcd for C_8H_9NOS: C, 57.48; H, 5.39; N, 8.38; S, 19.16. Found: C, 57.55; H, 5.70; N, 8.44; S, 18.82.

Compound **4** (3.95 g; 0.0235 mol) was dissolved in ether and treated with ethereal hydrogen chloride. The precipitate was recrystallized from ethanol–ether to afford 4.08 g (85%) of **5**: mp 138–141 °C dec; IR 760 (ortho CH), 990, 1050, 1250 (N=S=O), 1580, 1600 cm^{-1} (C=C); NMR (Me_2SO-d_6) δ 4.32 (s, 3 H, CH_3), 4.95 (s, 2 H, CH_2), 7.76–8.17 (m, 3 H, aromatic), 8.38–8.63 (m, 1 H, aromatic); mass spectrum *m/e* 166 and 167 ($M^+ - 1$) and (M^+) for free base; high resolution mass spectrum *m/e* 167.0409, Calcd for C_8H_9NOS *m/e* 167.0405. Anal. Calcd for $C_8H_{10}ClNOS$: C, 47.17; H, 4.91; Cl, 17.44; N, 6.88; S, 15.72. Found: C, 47.13; H, 5.20; Cl, 17.59; N, 7.04; S, 15.86.

Thermolysis of 5. Compound **5** (1 g; 4.9 mmol) was heated at 155 °C for a period of 20 min to afford 0.62 g (94%) of 1,2-benzisothiazole (**6**). The analytical sample was recrystallized from pentane to afford colorless crystals: mp 34.5–35.5 °C (lit.[9] mp 37 °C); NMR ($CDCl_3$) δ 7.27–7.72 (m, 2 H), 7.87–8.23 (m, 2 H), 8.94 (s, 1 H); mass spectrum *m/e* 135 (M^+);[10] high resolution mass spectrum *m/e* 135.0136, Calcd for C_7H_5NS *m/e* 135.0143. Anal. Calcd for C_7H_5NS: C, 62.22; H, 3.70; N, 10.37; S, 23.70. Found: C, 62.09; H, 3.78; N, 10.52; S, 23.33.

Compound **5** was heated at ca. 150 °C and the gaseous material was analyzed by IR. The IR spectrum consisted of absorptions characteristic of methyl chloride; however, technical difficulties precluded the positive identification of water. Water was identified as a product when **5** was heated at 150 °C in a small flask equipped with a condenser. The liquid which collected in the condenser was identified as water by NMR (neat).

Kinetic Study for Conversion of 5 and 5a to 6. Compounds **5** (1.30 g; 6.40 mmol) and the corresponding hydrobromide (**5a**) (1.59 g; 6.40 mmol) were separately dissolved in Me_2SO (28 mL) and heated at 110 ± 3 °C. At timed intervals aliquots (2.00 mL) were removed and added to water (10 mL) and extracted with dichloromethane (2 × 5 mL). The combined extracts were washed with water (15 mL) and dried (Na_2SO_4). The solvent was removed in vacuo and the residues were dissolved in acetone (0.25 mL). GC analyses of 2.0-μL aliquots were performed on a Hewlett Packard Model 5700A gas chromatograph with a Supelco 3 ft 3% OV-225 on 80/100 Supelcoport column. The instrument was previously calibrated with known amounts of 1,2-benzisothiazole. Least-squares analyses of the data showed that **5a** decomposed ca. 4 times more rapidly than did **5**.

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Base-Catalyzed Cis–Trans Isomerization of Bis(4-benzylideneaminocyclohexyl)methane

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Exhaustive hydrogenation of bis(4-aminophenyl)methane (**1**) to bis(4-aminocyclohexyl)methane (**2**) in the presence of noble metal catalysts under mild conditions produces predominately the kinetically favored cis,cis isomer **2a.**[1] This is in contrast to the hydrogenation run using cobalt or nickel (or its compounds) as catalyst at high temperature (above 200 °C) and high pressures (above 130 atm) of hydrogen which yields an amine mixture containing larger amounts of the thermodynamically favored cis,trans and trans,trans isomers **2b** and **2c,** respectively.[2,3]

Since an isomer mixture enriched in *trans,trans*-**2c** is a major component of several novel polyamide fibers, attempts have been made to convert cis,cis- and cis,trans-rich isomer mixtures into **2c.** Most processes involve heating of cis-rich products with metal (predominately from group 8) catalysts in the presence of hydrogen but the degree of isomerization to **2c** seldom exceeds 50%.[4] Consequently, hydrogenating **1** in the presence of ruthenium catalysts at high temperature and pressure leads directly to trans-rich mixtures of **2.**[5] In addition, several patented processes deal with the separation of the trans,trans isomer from crude hydrogenation mixtures.[6]

We have found a method to isomerize the bis(benzaldimines) **3a** and **3b** of **2a** and **2b** into *trans,trans*-**3c** on treatment with base under very mild conditions. Deprotonation on C-4 and C-4′ of the cyclohexane rings adjacent to the CN double bonds (giving **4a**) will lead to a partial charge distribution over the C–N–C unit with formation of an isomeric azaallylic carbanion **5** and eventually will result in an enrichment of the thermodynamically favored trans,trans-imine **3c** via **4b.**[7] (See Scheme II.)

Thus greater than 90% yield of **3c** is realized on stirring a suspension of **3a** in 1,2-dimethoxyethane (DME) in the presence of 20 wt % of potassium *tert*-butoxide at room temperature for 60–70 h. No significant amounts of by-products

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