(7), 352 (100), 333 (7), 178 (12), 161 (11), 149 (9).

***cis*-2,3-Methylenedioxy-10,11-dimethoxy-13-(acetoxymethyl)tetrahydroprotoberberine (8).** A solution prepared by dissolving the cis amino alcohol **7** (400 mg, 1.08 mmol) in acetic anhydride (1 mL) was stirred at room temperature for 1 h. After addition of ice and ammonium hydroxide, the mixture was extracted with $CHCl_3$. The extract was dried over K_2CO_3 and evaporated. The residue was recrystallized from acetone–Et_2O to produce the cis amino acetate **8**: 412 mg (93%); mp 184–186 °C; IR ($CHCl_3$) 2800, 2760, 2740, 1725 cm^{-1}; mass spectrum, *m/e* (relative intensity) 411 (M^+, 92), 352 (67), 338 (22), 236 (31), 194 (43), 176 (100).

***trans*-2,3-Methylenedioxy-10,11-dimethoxy-13-(acetoxymethyl)tetrahydroprotoberberine (11).** A mixture of acetic anhydride (1 mL) and the trans amino alcohol **10** (400 mg, 1.08 mmol) was stirred for 1.5 h. Further treatment as above gave the trans amino acetate **11**: 382 mg (86%); mp 162–163 °C; IR ($CHCl_3$) 1723 cm^{-1}; mass spectrum *m/e* (relative intensity) 411 (M^+, 70), 352 (59), 338 (17), 236 (29), 194 (44), 176 (100).

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Conversion of a Primary Amino Group into a Nitroso Group. Synthesis of Nitroso-Substituted Heterocycles[1]

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2-Aminopyridine, 2-amino-4-methylpyridine, 1-aminoisoquinoline, 2-aminopyrimidine, and 2-aminopyrazine have been converted to the corresponding nitroso compounds by reaction with dimethyl sulfide and *N*-chlorosuccinimide, deprotonation of the resulting sulfonium salts with sodium methoxide to the *S,S*-dimethylsulfilimines, and oxidation with *m*-chloroperbenzoic acid. These extremely reactive nitroso compounds condense readily with 1,3-dienes to give 3,6-dihydro-1,2-oxazines and with aromatic amines in the presence of acid to give azo dyes and are smoothly oxidized with ozone or sodium hypochlorite to the corresponding nitro-substituted heterocycles.

Although aromatic nitroso compounds have been known since the early days of organic chemistry,[2] only a few heterocyclic nitroso compounds are known. Direct nitrosation by electrophilic substitution is possible only with electron-rich systems (e.g., many of the five-membered heterocycles and certain six-membered systems which, like 6-aminopyrimidines, react as primary enamines).[3] Some heterocyclic nitroso compounds have been prepared by reduction of the corresponding nitro compounds, but this route is precluded for most electron-poor (π-deficient) heterocycles such as the azines which cannot be nitrated. As a consequence, some of the simplest heterocyclic nitroso compounds were unknown prior to the present study.

It is well-known that cyclic amidines and their vinylogues (e.g., 2- and 4-aminopyridine) react with electrophiles at the ring nitrogen rather than on the exocyclic amino group.[4] It occurred to us that electrophilic attack on the exocyclic amino group should be possible provided that electron density were concentrated at that position; a direct way of assuring this result would be to convert the amino group into a sulfilimine (**1**, Scheme I). Several methods are available for accomplishing this latter transformation.[5] Indeed, the *S,S*-dimethylsulfilimines from various aminopyridines and from 2-aminopyrimidine have been described.[6] These and the other sulfilimines described in this paper are most conveniently prepared from the amino-substituted heterocycle, dimethyl sulfide, and *N*-chlorosuccinimide in methylene chloride followed by deprotonation of the resulting sulfonium salt with sodium methoxide.

These sulfilimines are smoothly converted to the corresponding heterocyclic nitroso compounds (**2**) by oxidation with a slight excess of *m*-chloroperbenzoic acid in dry methylene chloride at 0 °C.[7] The nitroso compounds appear to be monomeric (green) in solution but dimeric (yellow) in the solid state. Some are too unstable to be isolated (see the Experimental Section), but they can be trapped in situ by all of the reactions described below. For example, these heterocyclic nitroso compounds are superb dienophiles and react instantly with dienes such as 2,3-dimethyl-1,3-butadiene or 1,3-diphenylisobenzofuran to

(1) This work was supported in part by a grant from the National Institutes of Health (Grant GM27983). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) Patai, S. "The Chemistry of the Nitro and Nitroso Groups"; Wiley: New York, 1969.

(3) See, for example: Brown, D. J. "The Chemistry of Heterocyclic Compounds"; Weissberger, A., Taylor, E. C., Eds; Interscience: New York, 1970; Suppl I, Vol. 16.

(4) Taylor, E. C. "Principles of Heterocyclic Chemistry"; American Chemical Society: Washington, DC, 1974.

(5) Gilchrist, T. L.; Moody, C. J. *Chem. Rev.* **1977**, *77*, 409–435.

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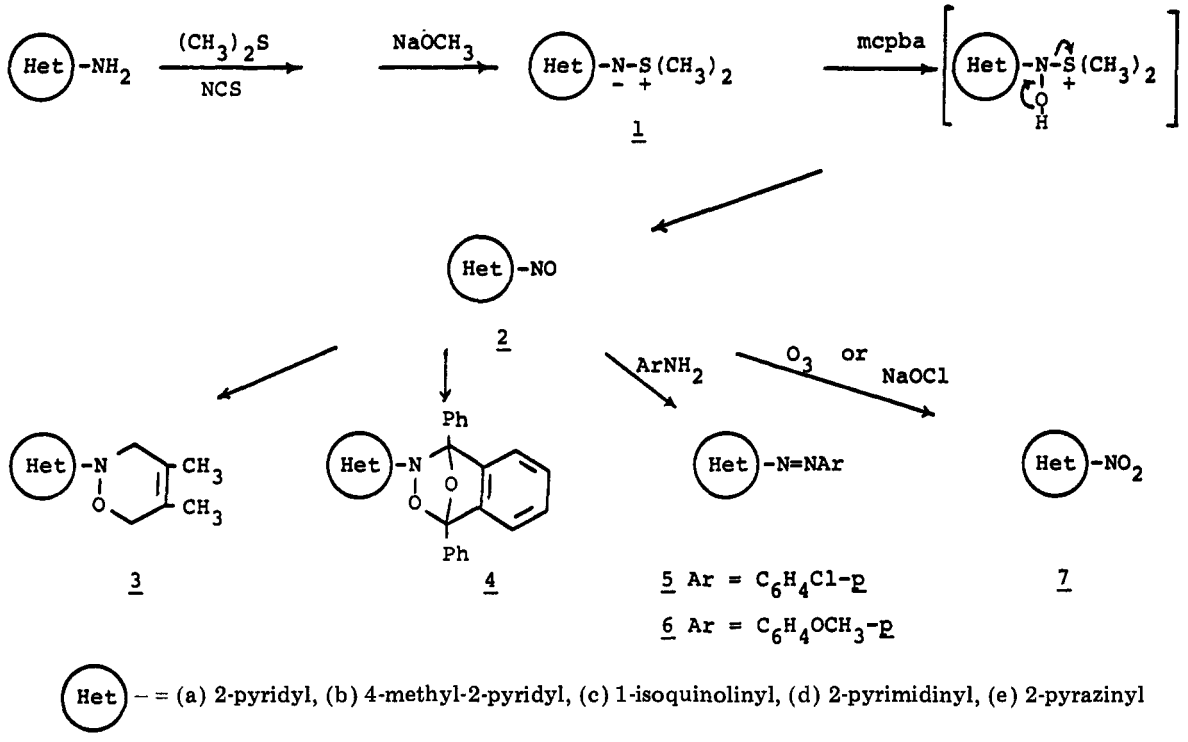
(7) While the work described herein was in progress, a report appeared[8] which described an inadvertent amino-to-nitroso conversion under similar reaction conditions. In an attempt to prepare *S,S*-dimethyl-*N*-(*p*-nitrophenyl)sulfoximine from the corresponding sulfilimine by oxidation with *m*-chloroperbenzoic acid in the presence of potassium carbonate, *p*-nitrosonitrobenzene was unexpectedly formed. The desired sulfoximine could be obtained provided that the *m*-chloroperbenzoic acid was completely converted into its anion prior to addition of the sulfilimine; in the absence of potassium carbonate, the nitroso compound was formed. No attempt was made to pursue the possible generality of this selective oxidation reaction.

(8) Huang, S. L.; Swern, D. *J. Org. Chem.* **1979**, *44*, 2510–2513.

0022-3263/82/1947-0552$01.25/0

Scheme I. Synthesis and Reactions of Heterocyclic Nitroso Compounds



Het – = (a) 2-pyridyl, (b) 4-methyl-2-pyridyl, (c) 1-isoquinolinyl, (d) 2-pyrimidinyl, (e) 2-pyrazinyl

give the cycloadducts **3** and **4**, respectively. In view of the ease with which analogous 3,6-dihydro-1,2-oxazines undergo N–O reductive cleavage,[9,10] the sequence of reactions involving conversion of an amino to a nitroso group, Diels–Alder reaction, and final reductive cleavage of the N–O bond provides a potentially powerful method for alkylation of primary heterocyclic amino groups with multifunctional carbon substituents.

These heterocyclic nitroso compounds also react rapidly and in high yield with primary aromatic amines in the presence of acid to give azo dyes (**5** and **6**). Since most heterocyclic amines fail to give diazonium salts upon attempted diazotization and the parent π-deficient heterocycles do not undergo electrophilic substitution with aromatic diazonium salts, these azo compounds represent an unusual class of dyes. The preparation of several of these mixed heterocyclic/aromatic azo dyes from 2-aminopyridine, 2-amino-4-methylpyridine, 1-aminoisoquinoline, 2-aminopyrimidine, and 2-aminopyrazine is given in the Experimental Section.

We have also found that these heterocyclic nitroso compounds may be oxidized in almost quantitative yield either with ozone in methylene chloride solution or with buffered sodium hypochlorite solution[11] to the corresponding nitro compounds **7**. Since nitro substituents α or γ to a ring nitrogen are readily displaced by nucleophiles,[4] this amino-to-nitro conversion allows for the eventual replacement of primary amino groups by a variety of other substituent groups. It also constitutes a potentially useful route to physiologically interesting nitro-substituted heterocycles (which cannot be prepared by direct nitration) from readily accessible amino compounds.

All of the above transformations of primary amino groups via nitroso groups to Diels–Alder adducts, azo dyes, and nitro compounds can be carried out sequentially in one vessel without isolation of either the intermediate sulfilimine or the highly reactive and often unstable nitroso compound.

Experimental Section

***S,S*-Dimethyl-*N*-(2-pyridyl)sulfilimine (1a).** To a solution of 9.40 g (0.10 mol) of 2-aminopyridine and 6.80 g (8.0 mL, 0.11 mol) of dimethyl sulfide in 100 mL of methylene chloride was added dropwise, over a period of 1 h, 13.3 g (0.10 mol) of *N*-chlorosuccinimide in 250 mL of methylene chloride, while the temperature was maintained at −20 °C. After the addition was complete, the reaction mixture was stirred at −20 °C for 1 h and then for an additional hour at room temperature. A solution of sodium methoxide in methanol (from 4.05 g, 0.17 mol, of sodium and 75 mL of methanol) was then added, the mixture stirred for 10 min, 150 mL of water added, and stirring continued for 4 h. The organic layer was separated, and the aqueous layer was extracted with two 50-mL portions of methylene chloride. The combined organic extracts were washed with 50 mL of water, dried, and evaporated to give a thick gum which solidified upon being chilled; yield 11 g (71%). Recrystallization from diethyl ether gave a cream-colored solid, mp 87–88 °C (lit.[6] mp 86–88 °C).

The following sulfilimines were prepared in the same manner.

***S,S*-Dimethyl-*N*-(4-methyl-2-pyridyl)sulfilimine (1b)**: brown oil; crude yield 89%; NMR δ 2.20 (s, 3 H, CH_3), 2.70 (s, 6 H, $S(CH_3)_2$), 6.35 (d, 1 H, H(5), J = 5–6 Hz), 6.55 (s, 1 H, H(3)), 7.90 (d, 1 H, H(6), J = 5–6 Hz); mass spectrum, m/e 168.0723 (M^+), calcd 168.0721.

***N*-(1-Isoquinolinyl)-*S,S*-dimethylsulfilimine (1c)**: oil; crude yield 100%; NMR δ 2.74 (s, 6 H, $S(CH_3)_2$), 6.80 (d, 1 H), 7.22–7.68 (m, 3 H), 7.84 (d, 1 H), 8.24–8.55 (m, 1 H).

***S,S*-Dimethyl-*N*-(2-pyrimidinyl)sulfilimine (1d) and *S,S*-dimethyl-*N*-(2-pyrazinyl)sulfilimine (1e)** were prepared as previously described.[6]

2-Nitrosopyridine (2a). To a solution of 20.1 g (0.119 mol, 80–90%) of *m*-chloroperbenzoic acid in 500 mL of dry methylene chloride, cooled to 0 °C, was added, all at once, a solution of 10.9 g (0.07 mol) of **1a** in 100 mL of methylene chloride. The mixture was stirred at 0–5 °C for 90 min, 3–4 mL of dimethyl sulfide added, and stirring continued for an additional 30 min. To the reaction mixture was then added 500 mL of a saturated aqueous solution of sodium carbonate, the layers were separated, and the green organic layer was washed with water and dried (Na_2SO_4). Evaporation of the dried extracts gave a light tan solid which was

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recrystallized from ethanol to give 3.4 g (44%) of **2a** as a light yellow solid, mp 120–122 °C.

Anal. Calcd for $C_5H_4N_2O$: C, 55.56; H, 3.73; N, 25.91. Found: C, 55.32; H, 3.70; N, 25.69.

4-Methyl-2-nitrosopyridine (2b) was prepared as described above to give yellow crystals: mp 137–138 °C (59%); NMR δ 2.57 (s, 3 H, CH_3), 7.20 (d, 1 H, H(5), J = 5 Hz), 7.78 (s, 1 H, H(3), 7.95 (d, 1 H, H(6), J = 5 Hz).

Anal. Calcd for $C_6H_6N_2O$: C, 59.00; H, 4.91; N, 22.95. Found: C, 58.78; H, 4.95; N, 22.75.

1-Nitrosoisoquinoline (2c), 2-nitrosopyrimidine (2d), and 2-nitrosopyrazine (2e) were prepared in analogous fashion; all these compounds proved to be too unstable to be isolated and were characterized by conversion to the derivatives described below.

3,6-Dihydro-4,5-dimethyl-*N*-(2-pyridyl)-1,2-oxazine (3a). Addition of 1.50 g (18 mmol) of 2,3-dimethyl-1,3-butadiene to a solution of 0.15 g (1.40 mmol) of 2-nitrosopyridine in 25 mL of methylene chloride resulted in an instantaneous change of color of the reaction mixture from green to yellow. The solution was stirred at room temperature for 20 min and concentrated under reduced pressure, and the residual oil was chromatographed on a preparative TLC plate (silica gel 60 F-254 with chloroform as the developing solvent) to give 0.12 g (46%) of **3a** as a liquid: NMR δ 1.55 (s, 3 H, CH_3), 1.70 (s, 3 H, CH_3), 4.00 (s, 2 H, NCH_2), 4.25 (s, 2 H, OCH_2), 6.50–6.80 (m, 1 H), 7.00–7.70 (m, 2 H), 8.00–8.20 (m, 1 H, H(6)).

Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.72. Found: C, 69.41; H, 7.16; N, 14.48.

Compound **3a** was obtained in comparable yield directly from 2-aminopyridine by *m*-chloroperbenzoic acid oxidation of the methylene chloride solution of *S,S*-dimethyl-*N*-(2-pyridyl)-sulfilimine prepared as described above, followed by addition of the diene. All of the following derivatives of nitroso compounds could be prepared in an analogous fashion by a one-pot sequence commencing with the amino-substituted heterocycle without the isolation of either the intermediate sulfilimine or the nitroso compound.

3,6-Dihydro-4,5-dimethyl-*N*-(4-methyl-2-pyridyl)-1,2-oxazine (3b) was prepared as described above from 4-methyl-2-nitrosopyridine and 2,3-dimethyl-1,3-butadiene, except that the crude product was passed over silica gel and eluted with petroleum ether–ether (1:1): yield 41%; mp 88–89 °C; NMR δ 1.64 (s, 3 H, CH_3), 1.76 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 4.00 (s, 2 H, NCH_2), 4.33 (s, 2 H, OCH_2), 6.60 (d, 1 H, H(5), J = 4 Hz), 7.03 (s, 1 H, H(3)), 8.10 (d, 1 H, H(6), J = 4 Hz).

Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.58; H, 7.89; N, 13.72. Found: C, 70.74; H, 7.49; N, 13.82.

3,6-Dihydro-*N*-(1-isoquinolinyl)-4,5-dimethyl-1,2-oxazine (3c). To a solution of 0.26 g (1.3 mmol) of *m*-chloroperbenzoic acid in 10 mL of methylene chloride, cooled to 0 °C, was added all at once a solution of 0.204 g (1 mmol) of *N*-(1-isoquinolinyl)-*S,S*-dimethylsulfilimine in 4 mL of methylene chloride. The reaction mixture was stirred at 0 °C for 30 min, and then 0.41 g (5 mmol) of 2,3-dimethyl-1,3-butadiene was added. The reaction mixture was stirred at room temperature for 40 min and worked up as described above for the preparation of **3a** to give 0.11 g (46%) of **3c**: mp 77–78 °C; NMR δ 1.68 (s, 3 H, CH_3), 1.80 (s, 3 H, CH_3), 4.05 (s, 2 H, NCH_2), 4.44 (s, 2 H, OCH_2), 7.15–7.82 (m, 4 H), 8.02–8.45 (m, 2 H).

Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.79; H, 6.68; N, 11.68.

3,6-Dihydro-4,5-dimethyl-*N*-(2-pyrazinyl)-1,2-oxazine (3e) was prepared from *S,S*-dimethyl-*N*-(2-pyrazinyl)sulfilimine (0.25 g, 1.6 mmol), *m*-chloroperbenzoic acid (1.0 g, 5.0 mmol), and 0.4 g (4.8 mmol) of 2,3-dimethyl-1,3-butadiene as described above for the preparation of **3c**, except that dimethyl sulfide (0.25 g) was added following the *m*-chloroperbenzoic acid oxidation, and the reaction mixture was filtered prior to the addition of the diene: yield 0.122 g (40%) of **3e** as an oil; NMR δ 1.55 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3), 3.94 (s, 2 H, NCH_2), 4.25 (s, 2 H, OCH_2), 7.85–8.25 (m, 2 H), 8.34–8.76 (m 1 H).

Anal. Calcd for $C_{10}H_{13}N_3O$: C, 62.81; H, 6.85; N, 21.91. Found: C, 62.65; H, 6.60; N, 21.74.

Reaction of 2-Nitrosopyridine with 1,3-Diphenylisobenzofuran. A solution of 0.108 g (1.0 mmol) of 2-nitrosopyridine and 0.27 g (1.0 mmol) of 1,3-diphenylisobenzofuran in 10 mL of methylene chloride was stirred for 12 h at room temperature and then evaporated under reduced pressure to give a yellow solid. Recrystallization from ethyl acetate gave 0.25 g (66%) of the adduct **4a**: mp 166–167 °C; NMR δ 7.00 (m, 15 H), 7.80–8.20 (m, 2 H), 8.25–8.50 (m, 1 H).

Anal. Calcd for $C_{25}H_{18}N_2O_2$: C, 79.36; H, 4.76; N, 7.67. Found: C, 79.10; H, 4.99; N, 7.33.

Reaction of 4-Methyl-2-nitrosopyridine with 1,3-Diphenylisobenzofuran. The adduct **4b** was prepared from 0.122 g (1.0 mmol) of 4-methyl-2-nitrosopyridine and 0.27 g (1.0 mmol) of 1,3-diphenylisobenzofuran as described above for the preparation of **4a**: yield 0.31 g (79%); mp 142–143 °C; NMR δ 2.20 (s, 3 H, CH_3), 6.80–7.70 (m, 14 H), 7.80–8.32 (m, 3 H).

Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.59; H, 5.10; N, 7.14. Found: C, 79.50; H, 5.18; N, 7.12.

2-[(*p*-Chlorophenyl)azo]pyridine (5a). A solution of 0.216 g (2.0 mmol) of 2-nitrosopyridine and 0.5 g (4.0 mmol) of *p*-chloroaniline in 35 mL of methylene chloride containing 2 drops of glacial acetic acid was stirred at room temperature for 12 h and then evaporated to dryness under reduced pressure. The residue was dissolved in 50 mL of hexane–chloroform (2.5:1) and filtered, and the filtrate was concentrated and passed over a short column of silica gel (elution with chloroform) to give 0.218 g (50%) of **5a** as an orange solid, mp 114–117 °C (lit.[12] mp 115–118 °C).

2-[(*p*-Chlorophenyl)azo]-4-methylpyridine (5b) was prepared as described above from 0.244 g (2.0 mmol) of 4-methyl-2-nitrosopyridine and 0.279 g (2.0 mmol) of *p*-chloroaniline: yield 0.36 g (78%) of light yellow crystals; mp 93–94 °C (from petroleum ether); NMR δ 2.50 (s, 3 H, CH_3), 7.10–7.35 (m, 1 H, H(3)), 7.35–7.75 (m, 3 H), 8.03 (d, 2 H, J = 9 Hz), 8.62 (d, 1 H, H(6), J = 4 Hz)).

Anal. Calcd for $C_{12}H_{10}ClN_3$: C, 62.33; H, 4.33; Cl, 15.15; N, 18.18. Found: C, 61.95; H, 4.33; Cl, 15.26; N, 18.08.

2-[(*p*-Chlorophenyl)azo]pyrazine (5e). To a solution of 1.0 g (5.0 mmol) of *m*-chloroperbenzoic acid in 25 mL of methylene chloride was added dropwise, over a period of 30 min, a solution of 2.5 g (1.6 mmol) of *S,S*-dimethyl-*N*-(2-pyrazinyl)sulfilimine in 10 mL of methylene chloride. Stirring was continued for 15 min, and the mixture was filtered. To the filtrate was added 0.279 g (2.0 mmol) of *p*-chloroaniline, and the reaction mixture was worked up as described above for **5a** except that the crude product was first filtered through basic alumina prior to silica gel: yield 0.225 g (63%) of **5e** as a red solid; mp 133–134 °C; NMR δ 7.53 (d, 2 H), 8.03 (d, 2 H), 8.70 (br, 2 H), 9.09 (br, 1 H).

Anal. Calcd for $C_{10}H_7ClN_4$: C, 54.93; H, 3.23; Cl, 16.22; N, 25.62. Found: C, 54.68; H, 3.26; Cl, 16.43; N, 25.41.

2-[(*p*-Methoxyphenyl)azo]pyridine (6a) was prepared in 70% yield as yellow-orange crystals [mp 51–52 °C (lit.[12] mp 50–52 °C)] from 2-nitrosopyridine and *p*-anisidine by the procedure described above for the preparation of **5a**.

2-[(*p*-Methoxyphenyl)azo]-4-methylpyridine (6b) was prepared in 83% yield as orange crystals [mp 84–85 °C (from petroleum ether)] from 4-methyl-2-nitrosopyridine and *p*-anisidine by the procedure described above for the preparation of **5a**: NMR δ 2.48 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 6.90–7.27 (m, 3 H), 7.60 (s, 1 H, H(3)), 8.08 (d, 2 H, J = 8 Hz), 8.60 (d, 1 H, J = 5 Hz).

Anal. Calcd for $C_{13}H_{13}N_3O$: C, 67.84; H, 5.72; N, 18.54. Found: C, 68.27; H, 5.79; N, 18.40.

1-[(*p*-Methoxyphenyl)azo]isoquinoline (6c) was obtained as described above for the preparation of **3c** except that *p*-anisidine rather than 2,3-dimethyl-1,3-butadiene was added, the reaction mixture was stirred at room temperature for 12 h, and the crude product was first passed over basic alumina prior to silica gel: mp 54–55 °C (54%); NMR δ 3.72 (s, 3 H, OCH_3), 6.82 (d, 2 H), 7.25–7.67 (m, 4 H), 7.92 (d, 2 H), 8.30 (d, 1 H), 8.38–8.70 (m, 1 H).

Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.73; H, 4.92; N, 15.93.

2-[(*p*-Methoxyphenyl)azo]pyrimidine (6d). To a solution of 0.31 g (2.0 mmol) of *S,S*-dimethyl-*N*-(2-pyrimidinyl)sulfilimine in 30 mL of methylene chloride under nitrogen at −7 °C was added all at once a solution of 0.5 g (2.5 mmol) of *m*-chloroperbenzoic

(12) Faessinger, G. W.; Brown, E. V. *J. Am. Chem. Soc.* **1951**, *73*, 4606–4608.

acid in 20 mL of methylene chloride. To the reaction mixture, which was allowed to warm to 20 °C over a period of 40 min, was then added 0.5 g of dimethyl sulfide followed (after 5 min) by a solution of 0.3 g (2.4 mmol) of *p*-anisidine in 10 mL of methylene chloride. The mixture was stirred at room temperature for 12 h, filtered, and the filtrate was concentrated and passed over basic alumina (elution with chloroform) to give 0.136 g (32%) of **6d** as a brown solid: mp 108–109 °C; NMR δ 3.94 (s, 3 H, OCH_3), 7.05 (d, 2 H), 7.35 (t, 1 H), 8.18 (d, 2 H), 8.96 (d, 2 H).

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.15. Found: C, 61.46; H, 4.78; N, 26.00.

2-[(*p*-Methoxyphenyl)azo]pyrazine (6e) was prepared in 64% yield as an orange solid from *S,S*-dimethyl-*N*-(2-pyrazinyl)sulfilimine as described above for **6d**: mp 116–117 °C; NMR δ 3.83 (s, 3 H, OCH_3), 6.90 (d, 2 H), 7.91 (d, 2 H), 8.47 (s, 2 H), 8.88 (s, 1 H).

Anal. Calcd for $C_{11}H_{10}N_4O$: C, 61.67; H, 4.71; N, 26.15. Found: C, 61.87; H, 4.38; N, 26.44.

2-Nitropyridine (7a). Method A. Ozone carried by oxygen was bubbled through a solution of 1.0 g of 2-nitrosopyridine in 200 mL of methylene chloride maintained at 0 °C until the green color disappeared (~2 h). The solution was then purged with nitrogen and evaporated to dryness under reduced pressure to give 1.14 g (100%) of crude 2-nitropyridine, mp 68–69 °C. Recrystallization from ethanol raised the melting point to 71 °C (lit.[13] mp 71 °C).

Method B. To a solution of 540 mg (5 mmol) of 2-nitrosopyridine in 50 mL of benzene was added a freshly prepared solution of 580 mg (1.7 mmol) of tetra-*n*-butylammonium hydrogen sulfate in 20 mL (10 mmol) of commercial bleach (5.25% NaOCl) adjusted to pH 10 with dilute sulfuric acid. The two-phase system was stirred vigorously for 12 min, by which time it had become colorless. The layers were separated, the aqueous phase was extracted several times with benzene, and the combined benzene extracts were washed with water, dried (Na_2SO_4), and evaporated to give 560 mg (90%) of pale yellow crystals of 2-nitropyridine, mp 70–71 °C, identical with the material prepared above by method A.

1-Nitroisoquinoline (7c). Ozone was bubbled through a solution of 1-nitrosoisoquinoline, prepared in situ from *N*-(1-isoquinolinyl)-*S,S*-dimethylsulfilimine as described above for the preparation of **3c**, and the reaction mixture was worked up in the same manner as described for **7a** to give 1-nitroisoquinoline: 36% yield; mp 65–66 °C (lit.[14] mp 65–66 °C).

2-Nitropyrimidine (7d). Ozone was bubbled through a solution of 2-nitrosopyrimidine, prepared in situ from *S,S*-dimethyl-*N*-(2-pyrimidinyl)sulfilimine as described above for the preparation of **6d**, and the reaction mixture was worked up in the same manner as described for **7a** to give 2-nitropyrimidine (33%; mp 57–58 °C) after purification by preparative TLC (silica gel 60 F-254, with chloroform as the developing solvent): NMR δ 7.83 (t, 1 H), 9.08 (d, 2 H).

Anal. Calcd for $C_4H_3N_3O_2$: C, 38.41; H, 2.42; N, 33.59. Found: C, 38.37; H, 2.51; N, 33.75.

2-Nitropyrazine (7e). This compound was prepared in 70% yield by ozone oxidation of 2-nitrosopyrazine, prepared in situ from *S,S*-dimethyl-*N*-(2-pyrazinyl)sulfilimine as described above under **3e**: mp 58–59 °C; NMR δ 8.81 (dd, 1 H), 9.16 (dd, 1 H), 9.67 (d, 1 H).

Anal. Calcd for $C_4H_3N_3O_2$: C, 38.41; H, 2.42; N, 33.59. Found: C, 38.48; H, 2.42; N, 33.59.

Registry No. a, 42860-85-5; **1b**, 79917-35-4; **1c**, 79917-36-5; **1d**, 54214-58-3; **1e**, 62135-46-0; **2a**, 79917-37-6; **2b**, 79917-38-7; **2c**, 79933-06-5; **2d**, 79917-39-8; **2e**, 79917-40-1; **3a**, 79917-41-2; **3b**, 79917-42-3; **3c**, 79917-43-4; **3e**, 79917-44-5; **4a**, 79917-45-6; **4b**, 79917-46-7; **5a**, 14458-12-9; **5b**, 79917-47-8; **5e**, 79917-48-9; **6a**, 79917-49-0; **6b**, 79917-50-3; **6c**, 79917-51-4; **6d**, 79917-52-5; **6e**, 79917-53-6; **7a**, 15009-91-3; **7c**, 19658-76-5; **7d**, 79917-54-7; **7e**, 79917-55-8; 2,3-dimethyl-1,3-butadiene, 513-81-5; 1,3-diphenylisobenzofuran, 5471-63-6; *p*-chloroaniline, 106-47-8; *p*-anisidine, 104-94-9.

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Synthesis of α-Chlorothiosulfenyl Chlorides. A New Class of Reactive Organosulfur Compounds

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The reaction of various aromatic and suitably substituted aliphatic thiones with sulfur dichloride in dry carbon disulfide affords the corresponding α-chlorothiosulfenyl chlorides ($R_2C(Cl)SSCl$), the first simple compounds of this type. Reaction of the α-chlorothiosulfenyl chlorides with triphenylphosphine regenerates the thiones, accompanied by the corresponding ketones. Possible mechanisms for these transformations are presented.

Several reports have appeared on the reactions of sulfur dichloride with thiocarbonyl compounds such as dithio acids,[1] thio amides,[2] thiocarbamate esters,[3] and 1,2-dithiole-3-thiones,[4] but the reaction of simple thiones with this reagent has not been previously reported. Our current interest in thiosulfines[5-7] led us to investigate this reaction as a possible source of these novel compounds from thiones such as **1** (Scheme I).

Results and Discussion

Addition of sulfur dichloride to thiobenzophenone **1a** in diethyl ether at −78 °C yielded a white precipitate. When this solid was filtered off and allowed to warm to room temperature, it quickly reverted to the starting thione **1a**. By analogy with the reaction of 4-methoxy-*N,N*-di-

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