1983). Our results indicate that neither 2,4-D, dicamba, nor a combination of the chemicals significantly affected 2,4,5-T metabolism by the dehalogenating consortium. To be useful the consortium must be able to dehalogenate 2,4,5-T in more complex anaerobic environments where a host of biotic and abiotic factors can interact and potentially influence biodegradation. To provide a preliminary indication of this ability, we incubated the consortium in autoclaved and fresh sludge diluted to 10%. Our results indicate that not only can 2,4,5-T still be dehalogenated under these conditions but also the activity was stimulated compared to that of sludge-free controls (Figure 4). Since there was no significant difference in 2,4,5-T degradation between autoclaved and fresh sludge amended cultures, it is likely that the heat-stable component(s) of sludge is (are) responsible for the observed stimulation in dehalogenation. A similar stimulation has been observed with autoclaved and fresh anoxic sediment amended with the consortium (unpublished observations).

The anaerobic bacteria present in the dehalogenating consortium have been cultured in vitro for almost 2 years. The only previous exposure of these cells to 2,4,5-T may have occurred in the sewage sludge from which they were originally enriched. However, even after many generations without exposure to 2,4,5-T, the cells still possess the ability to transform this substrate. Anaerobic microorganisms may possess degradative enzymes for metabolizing xenobiotic molecules that are considered to be recalcitrant under aerobic conditions. The biodegradation potential of anaerobes, and the factors affecting their metabolic transformations, needs to be more extensively investigated.

ACKNOWLEDGMENT

Registry No. 2,4,5-T, 93-76-5; 2,5-D, 582-54-7; 2,4-D, 94-75-7; dicamba, 1918-00-9.

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Herbicidal and Plant Growth Regulant Active 2-Sulfonylpyridine 1-Oxides

William W. Brand,*[1] James M. Gullo, and James Phillips

A series of 2-benzylsulfonylpyridine 1-oxides is described in which the identity of substituents on the pyridine ring, on the benzene ring, and in the α-benzyl position is varied. Preparation via several routes is described including the following: (a) condensation of a 2-halopyridine or a 2-halopyridine 1-oxide with a benzyl mercaptan followed by oxidation; (b) condensation of a 2-mercaptopyridine with a benzyl halide followed by oxidation; (c) a novel three-step one-pot reaction involving metalation, sulfurization, and alkylation of a pyridine 1-oxide unsubstituted in the 2-position. A clear relationship is shown to exist between herbicidal activity and the identity of substituents on each part of the molecule. Good turf growth retardation activity is also described for some compounds in this series.

The novel class of biologically active compounds, the 2-sulfonylpyridine 1-oxides, was recently reported (Plant and Bell, 1976). A wide variety of substituents was reported on the sulfonyl group, but no additional substituents were attached to the pyridine ring. We have explored the area of chemistry described by structure 1, in which
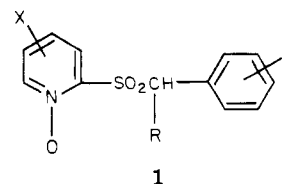
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substituents on both the pyridine ring and the benzene ring were varied. This series was shown to possess good herbicidal activity, primarily against grasses, with good crop selectivity and up to 3 months residual. In addition, a

variety of plant growth regulant (PGR) effects have been observed.

EXPERIMENTAL SECTION

General Comments. NMR spectra were run on a Perkin-Elmer R-24B spectrometer. Infrared spectra were run on a Perkin-Elmer Infracord. Melting points were determined in a Thomas-Hoover melting point apparatus and are uncorrected.

The sodium salt of 2-mercaptopyridine 1-oxide (sodium omadine) was purchased from Olin Chemicals and was 90% pure. All α-unsubstituted benzyl halides, bromodiphenylmethane, and m-chloroperbenzoic acid (MCPBA) were purchased from Aldrich Chemical Co. All purchased compounds were used without purification.

2-[(2,5-Dimethylbenzyl)thio]-4-methylpyridine. A mixture of 17.2 g (0.1 mol) of 2-bromo-4-methylpyridine, 15.2 g (0.1 mol) of (2,5-dimethylbenzyl)mercaptan, 13.8 g (0.1 mol) of potassium carbonate, and 150 mL of DMF was stirred and heated at 90 °C for 24 h. The reaction mixture was then poured into 700 mL of ice water with stirring, and the resulting mixture was extracted 3 times with ether. The combined ether extract was washed with water and then with saturated sodium chloride, dried, and concentrated, leaving 26.02 g of an orange oil that TLC (1:4 ether–hexane) showed to contain three components. Sixteen grams of the material was purified on a silica gel dry column with 10% ether in hexane, to give 7.75 g of a yellow oil (52% yield). Distillation gave 5.23 g (35% yield) of product, bp 172–175 °C/0.85 mm, as a yellow oil: IR 6.30, 6.52, and 6.71 μm; NMR (CDCl$_3$) δ 2.14, 2.24, and 2.35 (3 s, 9 H), 4.41 (s, 2 H), 6.70 (br d, J = 5 Hz, 1 H), 6.93 and 6.95 (2 s, 3 H), 7.16 (br, s, 1 H), and 8.31 (d, J = 5 Hz 1 H). Anal. Calcd for C$_{15}$H$_{17}$NS: C, 74.02; H, 7.04; N, 5.76; S, 13.18. Found: C, 74.0; H, 7.3; N, 5.7; S, 13.3.

2-Bromo-3-methylpyridine 1-Oxide. To an ice-cooled solution of 72.03 g (0.42 mol) of 2-bromo-3-methylpyridine in 100 mL of chloroform was added 89.28 g (0.44 mol) of 85% MCPBA (Eastman) in 665 mL of chloroform. The reaction mixture was then stirred overnight at room temperature, at reflux for 6.25 h, and again at room temperature for 3 days. The resultant mixture was cooled in an ice bath and filtered. The filtrate was washed 3 times with aqueous sodium sulfite, followed by three washings with saturated NaHCO$_3$. It was then dried over MgSO$_4$ and sodium sulfite and concentrated, giving 52.69 g (67% yield) of a tan solid. Fifteen grams was recrystallized from 42 g of toluene, giving 7.89 g of a tan solid: mp 94–96.5 °C. This was recrystallized from 25 mL of gylme, giving 2.41 g (11% yield corrected for entire sample) of a tan solid: mp 96.5–98 °C; IR 7.83 μm (NO); NMR (CDCl$_3$) δ 2.46 (s, 3 H), 7.15–7.25 (m, 2 H), and 8.15–8.37 (m, 1 H). Anal. Calcd for C$_6$H$_6$BrNO: C, 38.32; H, 3.22; N, 7.45. Found: C, 38.3; H, 3.3; N, 7.3.

2-[(2,5-Dimethylbenzyl)thio]-3-methylpyridine 1-Oxide. Into a 500-mL flask equipped with a magnetic stirrer and condenser were placed 125 mL of methanol and 2.1 g (0.09 g-atom) of sodium. After the sodium reacted, 13.8 g (0.09 mol) of (2,5-dimethylbenzyl)mercaptan was added and the contents were heated at reflux for 1 h. The contents were cooled and the methanol was removed under vacuum. To the flask containing the sodium salt was added 175 mL of tetrahydrofuran and 17.0 g (0.09 mol) of 2-bromo-3-methylpyridine 1-oxide. The contents were heated at reflux for 15 min and then poured into cold water. The precipitated material was filtered off, water washed, and recrystallized from heptane. Subsequent chromatography on silica gel with CH$_2$Cl$_2$ gave 10.3 g (44% yield) of a white solid: mp 79–97 °C. This material was

oxidized without further purification.

2-Mercapto-4-methylpyridine. Into a 500-mL flask equipped with a magnetic stirrer, heating mantle, and condenser were placed 86 g (0.5 mol) of 2-bromo-4-methylpyridine, 100 mL of 95% ethanol, and 38 g (0.5 mol) of thiourea. The contents were heated at reflux for 1.75 h, then 20 g (0.5 mol) of NaOH dissolved in 80 mL of water was added to the flask, and the contents were heated at reflux for 1 h. Then 75 mL of ethanol was distilled off and the contents were cooled. The precipitated material was filtered off, water washed, hexane washed, and then recrystallized from 1500 mL of ethyl acetate. There was obtained 25.5 g (40.7% yield) of a yellow solid: mp 177–178 °C; IR 3.2–4.9 μm; NMR (CDCl$_3$) δ 2.26 (s, 3 H), 6.66 (d, J = 6 Hz, 1 H), 7.2–7.68 (m, 2 H), and 13.92 (br s, 1 H). Anal. Calcd for C$_6$H$_7$NS: C, 57.56; H, 5.64; N, 11.19. Found: C, 57.1; H, 5.9; N, 11.1.

2-[(α,2,5-Trimethylbenzyl)sulfonyl]-4-methylpyridine 1-Oxide, 13. Into a 500-mL flask equipped with a magnetic stirrer, cooling bath, and condenser were placed 14.1 g (0.0674 mol) of 85% MCPBA and 150 mL of chloroform. To this mixture was added a solution of 9.5 g (0.0347 mol) of 2-[(α,2,5-trimethylbenzyl)thio]-4-methylpyridine 1-oxide in 50 mL of chloroform in small portions. The reaction was stirred at room temperature for 18 h. The precipitated material was filtered off and discarded. The filtrate was washed with aqueous sodium bisulfite and aqueous sodium bicarbonate and then dried over magnesium sulfate. The chloroform was evaporated under vacuum. The resulting material was dissolved in chloroform and passed through a silica gel dry column. The resulting material was crystallized from 400 mL of methanol. There was obtained 8.3 g (78.3% yield) of material: mp 202–203 °C; IR 7.7 and 8.8 (SO$_2$) and 7.85 μm (NO); NMR (CDCl$_3$) δ 1.64 (d, J = 7 Hz, 3 H), 2.52, 2.40, 2.33 (3 s, 9 H), 6.02 (q, J = 7 Hz, 1 H), 7.0–7.5 (m, 4 H), 7.86 (d, J = 2 Hz, 1 H), and 8.13 (d, J = 6 Hz, 1 H). Anal. Calcd for C$_{16}$H$_{19}$NO$_3$S: C, 62.92; H, 6.27; N, 4.59. Found: C, 63.2; H, 6.4; N, 4.5.

2-[(α,2,5-Trimethylbenzyl)thio]-4-methylpyridine. Into a 500-mL flask equipped with a magnetic stirrer and condenser were placed 150 mL of methanol and 2.2 g (0.096 g-atom) of sodium. After the sodium had reacted, 12.1 g (0.096 mol) of 2-mercapto-4-methylpyridine was added to the flask and the contents were heated at reflux for 1 h. The methanol was evaporated under vacuum. To the flask containing the sodium salt was added 150 mL of THF and 20.5 g (0.096 mol) of α,2,5-trimethylbenzyl bromide. The contents were heated at reflux for 6 h and then poured into cold water. The mixture was extracted with chloroform 4 times. The chloroform was evaporated under vacuum and the resulting oil was passed through a silica gel dry column with CHCl$_3$. There resulted 22.3 g (90% yield) of the product as a yellow oil: NMR (CDCl$_3$) δ 1.70 (d, J = 7, 3 H), 2.02 (s, 3 H), 2.22 and 2.35 (2 s, 6 H), 5.32 (q, J = 7 Hz, 1 H), 6.55 (br d, J = 4 Hz, 1 H), 6.80 and 6.85 (2 s, 3 H), 7.24 (br s, 1 H), and 8.16 (d, J = 4 Hz, 1 H). Anal. Calcd for C$_{16}$H$_{19}$NS: C, 74.66; H, 7.44; N, 5.44. Found: C, 74.4; H, 7.6; N, 5.3.

2-[(2,5-Dimethylbenzyl)thio]-4-methylpyridine 1-Oxide. A slurry of 1.0 g (0.009 mol) of 4-methylpyridine 1-oxide (Aldrich) in 32 mL of THF was cooled to −70 °C with a dry ice-acetone bath. To this mixture, in a nitrogen atmosphere, was added 5.1 mL (0.009 mol) of a 1.8 M solution of n-butyllithium in hexane (Aldrich) over 5 min. The resulting mixture was stirred for 30 min at −70 °C. Sulfur (0.29 g, 0.009 mol) was then added, and the reaction mixture was stirred for another 30 min at −70 °C. To this

mixture was added dropwise a solution of 1.39 g (0.009 mol) of 2,5-dimethylbenzyl chloride in 2 mL of THF. After addition was complete, the bath was removed, and the reaction mixture was stirred in a nitrogen atmosphere overnight. The resulting mixture was poured into 200 mL of water, and this was stirred for several days. The tan solid was filtered off, taken up in methylene chloride, water washed, dried (MgSO$_4$), and concentrated, leaving 2.06 g of a brown semisolid (88% yield). Infrared spectrum of the product was nearly identical with an IR of an authentic sample. NMR showed 67 mol % purity or 78 wt % purity (assuming the impurity to be 2,5-dimethylbenzyl disulfide, as is suggested by the NMR). This gave a calculated overall yield of 68%.

2-[(2,5-Dimethylbenzyl)sulfonyl)-4-methylpyridine 1-Oxide, 12. A mixture of 2.9 g (0.011 mol) of 2-[(2,5-dimethylbenzyl)thio]-4-methylpyridine 1-oxide, 5.5 mL (.055 mol) of 30% hydrogen peroxide, and 40 mL of acetic acid was stirred and warmed at 90 °C for 2.3 h. The hot reaction mixture was poured into 150 mL of ice water with stirring. The mixture was stirred for 0.5 h and then filtered, and the precipitate was washed with water, giving 2.67 g (83% yield) of an off-white powder: mp 94–134 °C. Recrystallization from 50 mL of ethanol plus 100 mL of water gave 2.38 g of a white solid that was incompletely soluble in chloroform. The solid was slurried with 20 mL of chloroform and filtered, and the filtrate was dried and concentrated, leaving 2.09 g (65% yield) of a yellow solid: mp 133.5–135.5 °C; IR 7.63 and 8.69 (SO$_2$) and 7.81 μm (NO); NMR (CDCl$_3$) δ 2.20 (s, 3 H), 2.37 (s, 3 H), 2.44 (s, 3 H), 5.16 (s, 2 H), 7.05 (s, 3 H), 7.28 (dd, J = 6 Hz, J = 2 Hz, 1 H), 7.71 (d, J = 2 Hz, 1 H), and 8.24 (d, J = 6 Hz, 1 H). Anal. Calcd for C$_{15}$H$_{17}$NO$_3$S: C, 61.83; H, 5.88; N, 4.81; S, 11.01. Found: C, 61.72; H, 5.90; N, 4.78; S, 10.93.

4-Chloro-2-[(2,5-dimethylbenzyl)sulfonyl]pyridine, 9, and 6-Chloro-2-[(2,5-dimethylbenzyl)sulfonyl]pyridine, 8. A mixture of 162.87 g (0.59 mol) of 2-[(2,5-dimethylbenzyl)sulfonyl]pyridine 1-oxide and 343.32 g (5.9 mol) of dry NaCl was stirred in an ice bath. During 15 min, 550 mL (6 mol) of POCl$_3$ was added. After addition was complete, the reaction mixture was warmed on a steam bath for 3 h. POCl$_3$ was then distilled out of the reaction mixture, and the residue was cooled in an ice bath. To the stirred residue was added 300 mL of chloroform and 750 mL of water. KOH (50%) was then added until the aqueous layer remained basic (400 mL). An additional liter of water and 200 mL of chloroform were added, and the layers were separated. The aqueous layer was extracted twice with chloroform. The combined chloroform solution was washed twice with water and then with saturated NaCl. Drying and concentration left 143.7 g of a thick brown oil (82% yield) that partially solidified on standing. NMR showed a 22:78 ratio of 4-chloro to 6-chloro product. The mixture was separated, in three batches, by preparative HPLC using 5% hexane in methylene chloride to give 20.8 g (12% yield) of pure 4-chloro product and 87.18 g (50% yield) of pure 6-chloro product. The 4-chloro product gave the following: mp 105–106 °C; IR 7.56 and 8.72 μm (SO$_2$); NMR (CDCl$_3$) δ 2.22 and 2.35 (2 s, 6 H), 4.61 (s, 2 H), 6.88 (br s, 1 H), 7.03 (br, s, 2 H), 7.50 (dd, J = 2 Hz, J = 7 Hz, 1 H), 7.85 (d, J = 2 Hz, 1 H), and 8.65 (d, J = 7 Hz 1 H). Anal. Calcd for: C$_{14}$H$_{14}$ClNO$_2$S: C, 56.84; H, 4.77; N, 4.74. Found: C, 57.0; H, 4.7; N, 4.6. The 6-chloro product gave the following: mp 91–96 °C; IR 7.53 and 8.55 μm (SO$_2$); NMR (CDCl$_3$) δ 2.21 and 2.33 (2 s, 6 H), 4.63 (s, 2 H), 6.97 and 7.02 (2 br s, 3 H), and 7.4–7.9 (m, 3 H). Anal. Calcd for C$_{14}$H$_{14}$ClNO$_2$S: C, 56.84; H, 4.77; N, 4.74. Found: C, 57.0; H, 4.8; N, 4.9.

4-Chloro-2-[(2,5-dimethylbenzyl)sulfonyl]pyridine 1-Oxide, 10. A mixture of 50 mL of methylene chloride and 2.72 mL (0.1 mol) of 90% hydrogen peroxide (FMC Corp.) was stirred in an ice bath. To this was added 17 mL (0.12 mol) of trifluoroacetic anhydride, followed by dropwise addition of a solution of 15.89 g (0.054 mol) of 4-chloro-2-[(2,5-dimethylbenzyl)sulfonyl]pyridine in 50 mL of methylene chloride. The ice bath was removed, and the reaction mixture was stirred for 1.5 h. It was then poured into 700 mL of ice–water, and the resulting aqueous layer was extracted 5 times with methylene chloride. The combined methylene chloride extract was treated with aqueous ferrous sulfate, dried, and concentrated, leaving 17.73 g of a yellow semisolid. Purification on a silica gel dry column (methylene chloride) gave 6.89 g (41% yield) of product as a white crystalline solid: mp 136–138 °C; IR 7.5 and 8.78 (SO$_2$) and 7.83 μm (NO); NMR δ (CDCl$_3$) 2.18 (s, 3 H), 2.39 (s, 3 H), 4.97 (s, 2 H), 7.02 (s, 3 H), 7.38 (dd, J = 3 Hz, J = 7 Hz 1 H), 7.79 (d, J = 3 Hz, 1 H), and 8.18 (d, J = 7 Hz 1 H). Anal. Calcd for C$_{14}$H$_{14}$ClNO$_3$S: C, 53.93; H, 4.53; N, 4.49. Found: C, 54.0; H, 4.5; N, 4.3. An additional 4.81 g (28% yield) of less pure product was isolated from the column as a yellow solid.

2-[(2,4,6-Trimethylbenzyl)sulfonyl]-4-methylpyridine 1-Oxide, 14. Into a 500-mL flask equipped with a magnetic stirrer and condenser were placed 10.3 g (0.04 mol) of 2-[(2,4,6-trimethylbenzyl)thio]-4-methylpyridine, 200 mL of chloroform, and 32.5 g (0.16 mol) of 85% MCPBA. The contents were left to stir over the weekend at room temperature. The reaction mixture was filtered, and the chloroform solution was washed with aqueous sodium bicarbonate and aqueous ferrous sulfate, dried over magnesium sulfate, and evaporated under vacuum. The resulting solids were dissolved in chloroform and passed through a silica gel dry column with chloroform. The resulting solid was crystallized from 220 mL of methanol. There was obtained 2.0 g (16.4% yield) of solid: mp 219–220 °C; IR 7.6 and 8.8 (SO$_2$) and 7.8 μm (NO); NMR (CDCl$_3$) δ 2.25, 2.38, 2.42 (3 unresolved s, 12 H), 5.16 (s, 2 H), 6.88 (s, 2 H), 7.27 (dd, J = 6 Hz, J = 2 Hz 1 H), 7.84 (d, J = 2 Hz, 1 H), and 8.15 (d, J = 6 Hz, 1 H). Anal. Calcd for C$_{16}$H$_{19}$NO$_3$S: C, 62.92; H, 6.27; N, 4.59. Found: C, 63.1; H, 6.5; N, 4.5.

Herbicidal Testing. Herbicide tests were run in 8 in. by 10 in. pans. The pans were seeded and then sprayed the same day. They were held in a growth room at 24 °C, 50% relative humidity, and were watered from the bottom. After 2 weeks the pans were evaluated for amount and vigor of plant growth.
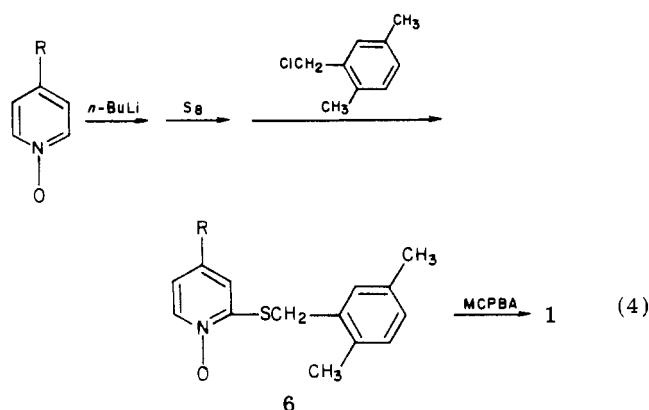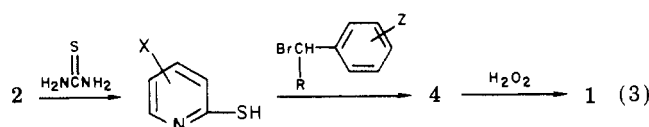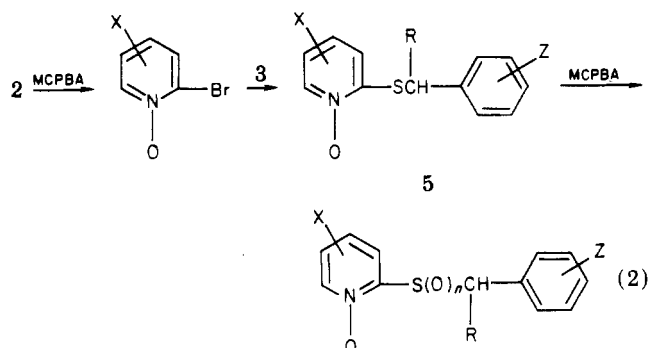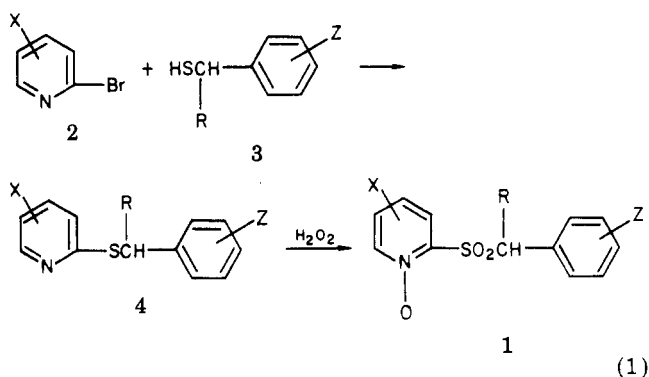
The grassy weeds used to evaluate these compounds were red millet (*Panicum*), green foxtail (*Setaria*), and Johnson grass (*Sorghum*). The pass criterion was 50% control. Primary tests were run at 8 kg/ha, and the rates were subsequently halved until less than 50% control was realized. The rating numbers used herein refer to the number of levels at which the test compound passed the 50% control criterion. Larger numbers indicate more active compounds.

PGR Testing. For primary PGR screening, the compounds were put on a moist filter paper in a Petri dish, and ryegrass, lettuce, and winter wheat seed were allowed to germinate. Germination and root and shoot growth were evaluated after 3 days in the dark and again after 4 days in the light. The growth of ryegrass roots and shoots were used as an indicator of turf retardant activity. Compounds 12–14 showed retardation of shoot growth with no accompanying retardation of growth of roots of ryegrass seedlings.

Follow-up testing was done in 5 in. by 8 in. pans on four grasses: Kentucky blugrass (*Poa pratensis*), red fescue (*Festuca rubra*), perennial ryegrass (*Lolium perenne*), and tall fescue (*Festuca arundinacae*). The grasses were mowed weekly to 3-cm height. Turf at least 6 weeks old was used for the tests. The test compound was sprayed over freshly mowed grass at 8 kg/ha and in follow-up tests at 2-fold dilutions. Two, four, and eight weeks after spraying, the pans were evaluated for grass height, fresh weight of clippings to 3 cm, root dry weight, phytotoxicity, grass color, ratio of root dry weight to clippings fresh weight, and other visual observations. Little or no phytotoxicity or discoloration of the grasses was observed with compounds 12–14.
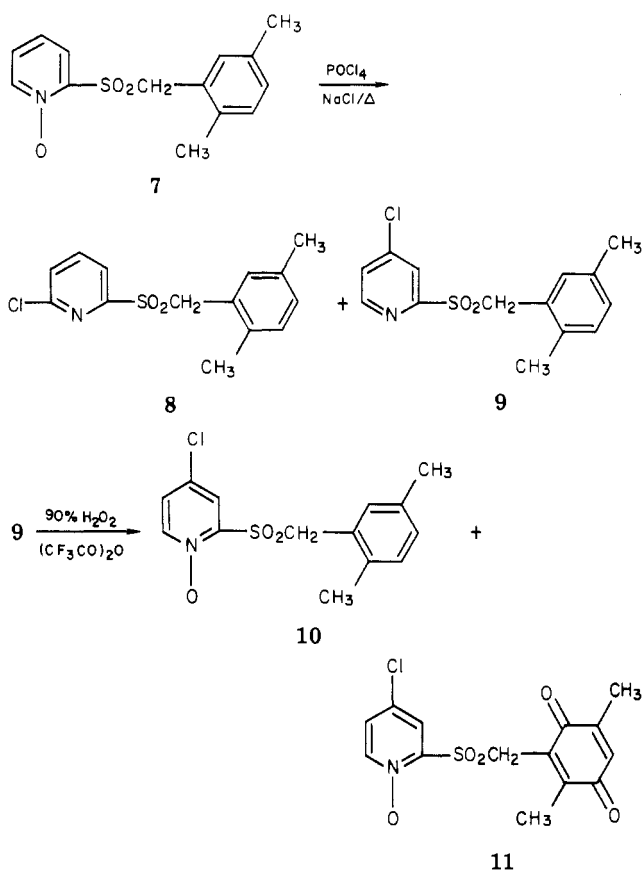
RESULTS AND DISCUSSION

Preparations of 2-Sulfonylpyridine 1-Oxides. These compounds were prepared by four general routes, outlined in eq 1–4. In the first route, a halopyridine, 2, was con-

Scheme I

7

$\xrightarrow[\text{NaCl}/\Delta]{\text{POCl}_4}$

8 + 9

9 $\xrightarrow[\text{(CF}_3\text{CO)}_2\text{O}]{90\% \text{ H}_2\text{O}_2}$ 10 +

11

chloroperbenzoic acid (MCPBA) was used in the oxidation step, only the sulfur was oxidized. Presumably the sulfonyl group deactivates the pyridine ring toward further oxidation, and a stronger oxidant is required to form the *N*-oxide.
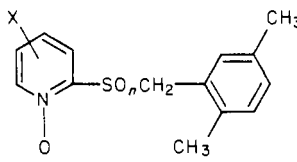
An alternative route (eq 2) involved prior oxidation of the 2-halopyridine to the analogous 2-halopyridine 1-oxide before condensation with 3. The intermediate, 5, could then be oxidized to either the sulfoxide (*n* = 1) or the sulfone (*n* = 2) by varying the amount of oxidant used.

A third procedure (eq 3) involved generation of the 2-mercaptopyridine from as 2-halopyridine and subsequent condensation with a benzyl halide to give the intermediate, 4. In general, eq 2 and 3 gave higher yields in the condensation steps than did eq 1 in which an unactivated halide is displaced from a pyridine ring.

The fourth approach to these compounds was suggested by a literature report on metalation followed by thiation of 4-substituted pyridine 1-oxides (Abramovitch and Knaus, 1975). We took this procedure one step further. After successive metalation and sulfurization, the appropriate benzyl chloride was added to the reaction mixture before warming and hydrolysis. The yield of the product, 6, in the case where R is methyl, was considerably higher than the reported yield of the analogous mercaptan isolated from the first two steps of this sequence. This represents a simple, one-pot synthesis of the intermediate, 6, from a 4-substituted pyridine 1-oxide. The reaction failed when 4-chloropyridine 1-oxide was used in this procedure.

The 4-chloro-2-sulfonylpyridine 1-oxide, 10, was prepared by the procedure of Scheme I. The 2-sulfonylpyridine 1-oxide, 7, was heated with POCl₃ and NaCl to give a mixture of 8 and 9, which were separated chromatographically. 9 was then oxidized to the desired product by using 90% hydrogen peroxide and trifluoroacetic anhydride. This reaction was accompanied by a small
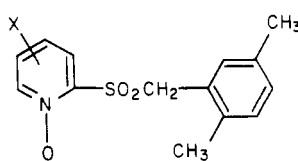
$$2 + 3 \longrightarrow 4 \xrightarrow{\text{H}_2\text{O}_2} 1 \quad (1)$$

$$2 \xrightarrow{\text{MCPBA}} \quad 3 \xrightarrow{} 5 \xrightarrow{\text{MCPBA}} \quad (2)$$

$$2 \xrightarrow{\text{H}_2\text{NCNH}_2} \quad \xrightarrow{\text{BrCH}} 4 \xrightarrow{\text{H}_2\text{O}_2} 1 \quad (3)$$

$$\xrightarrow{n\text{-BuLi}} \xrightarrow{\text{S}_8} \xrightarrow{\text{ClCH}_2} 6 \xrightarrow{\text{MCPBA}} 1 \quad (4)$$

densed with a benzylmercaptan, 3, to give the intermediate sulfide, 4, which was oxidized to the sulfonylpyridine 1-oxide, 1, with hydrogen peroxide. In most cases, if *m*-

2-Sulfonylpyridine 1-Oxides

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Table I. Herbicidal Activity of Sulfoxides vs. Sulfones

X	n	rating[a]		
		RM	GF	JG
H	1	6	5	6
	2	4	5	5
4-CH$_3$	1	4	6	6
	2	5	6	6
3-CH$_3$	1	3	5	5
	2	4	4	5

[a] RM = red millet; GF = green foxtail; JG = johnson grass. See the text for the meaning of rating numbers.

Table II. Effect of a Pyridyl Substituent on Herbicidal Activity

X	rating[a]		
	RM	GF	JG
H	4	5	5
4-CH$_3$	5	6	6
4-C(CH$_3$)$_3$	6	6	7
4-C$_6$H$_5$	2	3	4
4-Cl	8	9	8
5-Br	6	6	7
4-CN	0	1	1
5-NO$_2$	0	0	0

[a] See footnote a of Table I.

Table III. Effect of the Position of a Methyl Group on Herbicidal Activity

CH$_3$ position	rating[a]		
	RM	GF	JG
3	4	4	5
4	5	6	6
5	1	1	3
6	0	0	0
3,4-(CH$_3$)$_2$	5	5	5
4,5-(CH$_3$)$_2$	0	4	4

[a] See footnote a of Table I.

Table IV. Effect of α-Benzyl Substituents on Herbicidal Activity

R	rating[a]		
	RM	GF	JG
H	5	6	6
CH$_3$	8	8	8
CH(CH$_3$)$_2$	0	0	0
n-C$_6$H$_{13}$	0	0	0
C$_6$H$_5$[b]	0	1	1

[a] See footnote a of Table I.   [b] (Diphenylmethyl)-sulfonyl in place of α-R-benzylsulfonyl.

Table V. Effect of Phenyl Substituents on Herbicidal Activity

Z	rating[a]		
	RM	GF	JG
2,6-Cl$_2$	8	9	9
2,4,6-(CH$_3$)$_3$	7	8	7
2,5-(CH$_3$)$_2$	5	6	6
2-CH$_3$	5	6	6
H	4	4	5
4-C(CH$_3$)$_3$	2	3	3
4-Cl	3	5	5
4-F	4	4	4
4-C$_6$H$_5$	0	3	4
4-NO$_2$	2	3	3
3-CN	3	4	4
3-CF$_3$	3	4	4

[a] See footnote a of Table I.

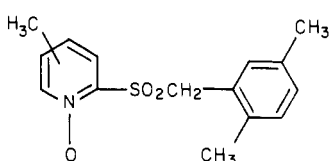amount of the overoxidation product, 11. With an excess of oxidizing reagents, 11 became the major reaction product.

Herbicidal Activity. The sulfide intermediates, **4**, showed very little or no herbicidal activity. However, for any substituent, X, there was very little differnece in activity between the sulfoxide (*n* = 1) and the sulfone (*n* = 2), Table I. Because preparation of the sulfone was simpler than preparation of the sulfoxide, most subsequent work was done using the sulfones.

The nature of substituents on the prydine ring was varied to test for electronic effects. In general, alkyl and halo groups in the 4- and 5-positions maintained or improved activity over that of the unsubstituted analogue, X = H (Table II). Electron withdrawing groups other than halo such as phenyl, cyano, or nitro lowered activity considerably.

The significance of the position of a substituent on the pyridyl ring was probed by using a methyl group, Table III. The 4-position appeared to be marginally better than the 3-position. These were both better than the 5-position, and a methyl in the 6-position completely eliminated herbicidal activity. When the benzylsulfonyl group was moved to the 3- or 4-position of the pyridine 1-oxide ring, all activity was lost.
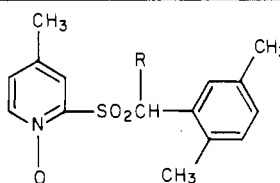
A methyl group in the α-benzyl position also significantly improved the herbicidal activity in this series. However, larger groups in this position had an adverse effect on activity (Table IV).

Finally, a pattern was also evident in the effect exerted by the substituent on the benzene ring (Table V). The compounds divided nicely into three groupings based on the number of ortho substituents present. 2,6-Disubstituted compounds were uniformly more active than 2-substituted compounds, which were more active than

compounds with substituents only in the 3-, 4-, or 5-position. Within each of these three groupings, the activity was surprisingly similar regardless of the electronic and hydrophobic character of the substituents. This, along with the data on the α-benzyl substituents, strongly suggests the desirability of some steric congestion in the region between the two rings. It also suggests a certain insensitivity toward overall hydrophobic effects on the molecule.

PGR Activity. The compounds 12–14 showed turf

12   13

14
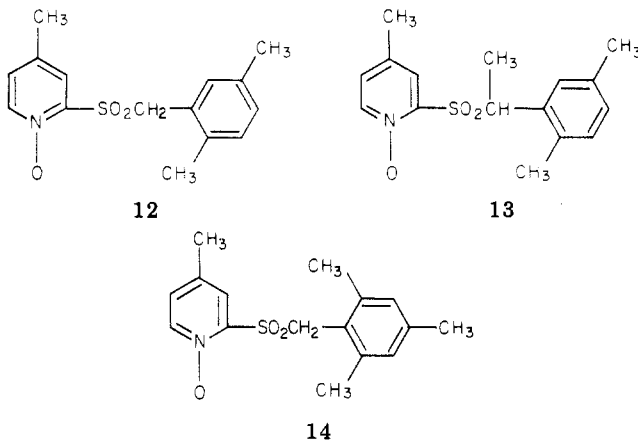
retardation activity that was superior to that of both the standard, Embark, and the analogous compounds without a 4-methyl substituent on the pyridine ring, from the standpoint of both grass regrowth and phytotoxicity to the grasses.

Registry No. 1 (X = 3-Me, R = H, Z = 2,5-Me₂), 81167-56-8; 1 (X = 4-t-Bu, R = H, Z = 2,5-Me₂), 81167-62-6; 1 (X = 4-Ph,

R = H, Z = 2,5-Me₂), 81167-59-1; 1 (X = 4-Cl, R = H, Z = 2,5-Me₂), 81167-77-3; 1 (X = 5-Br, R = H, Z = 2,5-Me₂), 81167-73-9; 1 (X = 4-CN, R = H, Z = 2,5-Me₂), 81167-64-8; 1 (X = 5-NO₂, R = H, Z = 2,5-Me₂), 88496-43-9; 1 (X = 5-Me, R = H, Z = 2,5-Me₂), 81167-72-8; 1 (X = 6-Me, R = H, Z = 2,5-Me₂), 81167-66-0; 1 (X = 3,4-Me₂, R = H, Z = 2,5-Me₂), 81167-76-2; 1 (X = 4,5-Me₂, R = H, Z = 2,5-Me₂), 81167-75-1; 1 (X = 4-Me, R = i-Pr, Z = 2,5-Me₂), 88496-44-0; 1 (X = 4-Me, R = n-hexyl, Z = 2,5-Me₂), 88496-45-1; 1 (X = 4-Me, R = Ph, Z = 2,5-Me₂), 88496-46-2; 1 (X = 4-Me, R = H, Z = 2,6-Cl₂, 81167-84-2; 1 (X = 4-Me, R = H, Z = 2-Me), 81167-78-4; 1 (X = 4-Me, R = H, Z = 4-t-Bu), 81167-80-8; 1 (X = 4-Me, R = H, Z = 4-F), 88496-47-3; 1 (X = 4-Me, R = H, Z = 4-Ph), 81167-81-9; 1 (X = 4-Me, R = H, Z = 4-NO₂), 81167-87-5; 1 (X = 4-Me, R = H, Z = 3-CN), 81167-85-3; 1 (X = 4-Me, R = H, Z = 3-CF₃), 81167-82-0; 2 (X = 4-Me), 4926-28-7; 2 (X = 3-Me), 3430-17-9; 3 (R = H, Z = 2,5-Me₂), 22182-98-5; 4 (X = 4-Me, R = H, Z = 2,5-Me₂), 81167-55-7; 4 (X = 4-Me, R = Me, Z = 2,5-Me₂), 88496-48-4; 4 (X = 4-Me, R = H, Z = 2,4,6-Me₃), 88496-51-9; 5 (X = 3-Me, R = H, Z = 2,5-Me₂), 81167-57-9; 6 (R = Me), 81167-67-1; 7, 60263-80-1; 8, 88496-50-8; 9, 88496-49-5; 10, 81167-79-5; 12, 81167-93-3; 13, 81167-91-1; 14, 81167-88-6; MCPBA, 937-14-4; 2-[(2,5-dimethylbenzyl)-sulfinyl]pyridine 1-oxide, 60264-17-7; 2-[(2,5-dimethylbenzyl)-sulfinyl]-4-methylpyridine 1-oxide, 81167-68-2; 2-[(2,5-dimethylbenzyl)sulfinyl]-3-methylpyridine 1-oxide, 81167-92-2; 2-mercapto-4-methylpyridine, 18368-65-5; 4-methylpyridine 1-oxide, 1003-67-4; 2-bromo-3-methylpyridine 1-oxide, 19230-57-0.

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Photodecomposition of Propachlor

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The photolysis of solutions of propachlor (I) was investigated. Photolysis carried out under UV light (5 h) led to about 80% decomposition of I. The three photodegradation products isolated were *N*-isopropyloxindole (II), *N*-isopropyl-3-hydroxyoxindole (III), and a spiro compound (IV). Photolysis performed under visible light (12 h) of the solution of I containing riboflavin led to the almost complete photodegradation of the title compound. From the irradiated solutions, only minute amounts of one photodegradation product were isolated and identified: *m*-hydroxypropachlor (V). The chemical structures of the photodegradation products were determined by spectroscopic methods. The structures of II and V were also confirmed by comparison with those of the authentic samples prepared by chemical methods. The photodegradation products in the reaction mixture from visible light experiments were checked for phytotoxicity and found to be nontoxic to the test plants.

Propachlor (2-chloro-*N*-isopropylacetanilide, I) is a preemergence herbicide effective against annual grasses and certain broad-leaved weeds (Martin, 1972). It was selected as a representative of the anilide herbicide group for photodecomposition studies aimed at finding a photochemical method of detoxification of water from organic

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pollutants. Such studies have already been carried out with uracil (Acher and Dunkelblum, 1979; Acher and Saltzman, 1980; Acher et al. 1981; Saltzman et al., 1982) and with *s*-triazine herbicides (Rejtö et al., 1983).

Herbicides from the anilide group are known as general growth inhibitors of young seedlings or inhibitors of root growth. Studies of the specific mode of action of I showed that it causes a reduction in cell elongation and cell division rate, by inhibiting protein synthesis in root tips (Ashton and Crafts, 1973). The degradation of I in corn and soybeans has been reported (Jaworski, 1969), but the structure