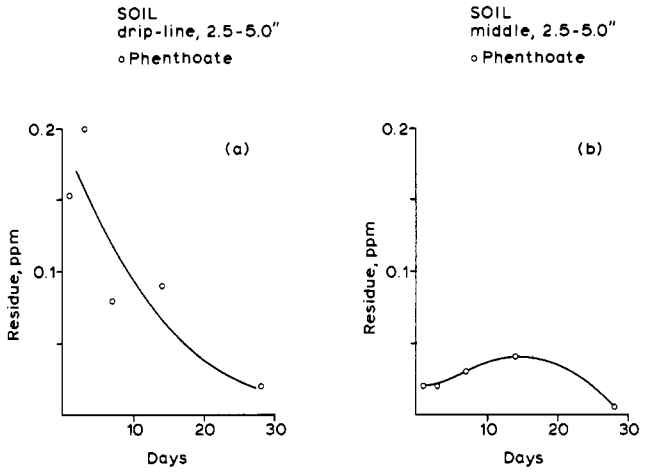

Figure 8. Phenthoate levels sampled at the 2.5–5.0-in. depth: (a) drip line; (b) midline.

the same fractions of oil and lemon, are shown in Figure 6.

Soil. As would be expected, highest levels of phenthoate were found at the tree drip lines and at the shallower sampling depth (0–2.5 in.). In addition, oxon levels were found for these samples only. Figure 7 shows residues for the 0–2.5-in. sampling depth as a function of time after spraying. Immediately after, and the same day, that the chemical was applied the grove received 0.23 in. of rain, accounting for the sharp increase in soil phenthoate levels which decayed slowly. Maximum oxon was measured in the 14-day sample (0.04 ppm). Figure 8 shows the phenthoate residues found at the 2.5–5.0-in. sampling depth. Expectedly, less phenthoate was found and no oxon; maximum phenthoate levels occurred at the drip line 3 days after application (0.2 ppm) and decayed slowly to 28 days. Less phenthoate was found in the soil beneath the tree midline.

Conclusions. Phenthoate disappears by first-order decay from the peel of citrus fruit and never reaches levels above 1 ppm, even immediately after application of the C1X concentration; fruit sprayed at the C2X level gave residues slightly higher. Residues in the interior of the fruit were negligible, with no oxon detectable. Fruit sprayed at the C1X level produced peel oil with 5.5, 7.5, and 3.4 ppm of phenthoate for grapefruit, lemons, and oranges, respectively; for these fruit oxon was found at the 0.48-, 2.0-, and 1.3-ppm levels, respectively. Since the oxon is approximately 70 times more toxic to the rat than is phenthoate it is clearly of more significance in the oil. While dried lemon rind contained 2.6 ppm of phenthoate for fruit sprayed at the C1X rate only 0.01 ppm of oxon was found. Molasses contained insignificant amounts of phenthoate and no oxon. No environmental contamination should be expected from after-water rinse upon disposal. Residues of phenthoate in soil never reached significant levels and decayed away; oxon was generally not measurable.

Registry No. Phenthoate, 2597-03-7; phenthoate oxon, 3690-28-6.

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N-(2,6-Dihalobenzylidene)arenesulfinamide Herbicides and Analogous Compounds. 1. Synthesis and Biological Activity

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A series of benzylidenearenesulfinamides was prepared and evaluated for preemergent herbicidal activity. While *N*-(2,6-dichlorobenzylidene) analogues were shown to decompose in situ to the corresponding benzonitrile (dichlobenil) over extended periods of time, many of these compounds demonstrated both increased activity and crop selectivity with respect to a dichlobenil standard. Structural modification through preparation of analogous thiosulfinates or vinyl sulfoxides resulted in a complete loss of herbicidal properties. Replacement of a benzylidene hydrogen with a methyl group gave increased activity against broadleaf species but resulted in the absence of activity against grasses. This sterically hindered compound type could not be prepared by standard procedures and a new method was developed for its synthesis.

The herbicidal activity of 2,6-dichlorobenzonitrile (dichlobenil) and other nitriles has been known for some time. Dichlobenil, while demonstrating good preemergent activity against a wide variety of grasses and broadleaves, is highly phytotoxic to crops and is therefore not useful for crop application. It was felt that structural modification of nitrile herbicides might result in a more selective and efficacious class of compounds. To this end, a series of *N*-(2,6-dichlorobenzylidene)arenesulfinamides was prepared. Benzylidenearenesulfinamides have been shown to undergo a thermal elimination of an arenesulfenic acid, affording the corresponding nitrile (Davis et al., 1974).

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Table I. *N*-Benzylidenearenesulfenamides

compd no.	Ar	ArSN=CHAr' Ar'	% yield	mp, °C (bp, °C)
1	C_6H_5-	2,6-Cl_2-C_6H_3-	25	(94 at 0.2 mmHg, dec)
2	4-F-C_6H_4-	2,6-Cl_2-C_6H_3-	30	44-45
3	4-Cl-C_6H_4-	2,6-Cl_2-C_6H_3-	51	93-94
4	4-Br-C_6H_4-	2,6-Cl_2-C_6H_3-	22	101-102
5	4-CH_3-C_6H_4-	2,6-Cl_2-C_6H_3-	34	*a*
6	3-CH_3,4-Br-C_6H_3-	2,6-Cl_2-C_6H_3-	23	72-74
7	2-CH_3CONH-C_6H_4-	2,6-Cl_2-C_6H_3-	15	118-120
8	4-CH_3CONH-C_6H_4-	2,6-Cl_2-C_6H_3-	35	151-153
9	2-C_5H_4N-	2,6-Cl_2-C_6H_3-	56	73-74
10	4-C_5H_4N-	2,6-Cl_2-C_6H_3-	20	86-87
11	2-pyrimidyl-	2,6-Cl_2-C_6H_3-	50	125-126
12	2-benzothiadiazyl-	2,6-Cl_2-C_6H_3-	23	133-134
13	2-NO_2-C_6H_4-	2,6-Cl_2-C_6H_3-	35	186-187
14	3-NO_2-C_6H_4-	2,6-Cl_2-C_6H_3-	73	130-130.5
15	3-NO_2-C_6H_4-	2-F-C_6H_4-	67	114-115
16	3-NO_2-C_6H_4-	2-Br-C_6H_4-	92	119-120
17	3-NO_2-C_6H_4-	2-Cl-C_6H_4-	80	117-118
18	3-NO_2-C_6H_4-	3-Cl-C_6H_4-	35	121-122
19	3-NO_2-C_6H_4-	4-Cl-C_6H_4-	68	127-128
20	3-NO_2-C_6H_4-	2,4-Cl_2-C_6H_3-	50	146-147
21	3-NO_2-C_6H_4-	3,4-Cl_2-C_6H_3-	60	148-149
22	3-NO_2-C_6H_4-	3,5-Cl_2-C_6H_3-	60	145-147
23	3-NO_2-C_6H_4-	2-Cl,6-F-C_6H_3-	54	121-122
24	3-NO_2-C_6H_4-	2-Cl,6-NO_2-C_6H_3-	83	151-152
25	3-NO_2-C_6H_4-	C_6F_5-	63	123-124
26	3-NO_2-C_6H_4-	2,5-$(CH_3O)_2$-C_6H_3-	58	118-119
27	3-NO_2-C_6H_4-	3,4-$(CH_3O)_2$-C_6H_3-	34	129-130
28	3-NO_2-C_6H_4-	3,4,5-$(CH_3O)_3$-C_6H_2-	60	135-136
29	3-NO_2-C_6H_4-	2-C_2H_5O,3-CH_3O-C_6H_3-	83	121-122
30	3-NO_2-C_6H_4-	3-CH_3O,4-C_2H_5O-C_6H_3-	32	131-132
31	3-NO_2-C_6H_4-	2-C_2H_5O-C_6H_4-	66	136-137
32	3-NO_2-C_6H_4-	1-naphthyl-	58	84-86
33	3-NO_2-C_6H_4-	2-naphthyl-	66	137-139
34	3-NO_2-C_6H_4-	2-HO-1-naphthyl-	64	150-151
35	3-NO_2-C_6H_4-	9-anthryl-	33	151-151.5
36	3-NO_2-C_6H_4-	2-C_4H_3S-	66	89-90
37	3-NO_2-C_6H_4-	4-$(CH_3)_2N$-C_6H_4-	22	155-156
38	3-NO_2-C_6H_4-	3-C_6H_5O-C_6H_4-	40	58-59
39	3-NO_2-C_6H_4-	3-(4-CH_3O-C_6H_4O)-C_6H_4-	51	75-76
40	3-NO_2-C_6H_4-	3-(4-Cl-C_6H_4O)-C_6H_4-	78	103-104
41	3-NO_2-C_6H_4-	3-(3,4-Cl_2-C_6H_3O)-C_6H_4-	45	116-117
42	3-NO_2-C_6H_4-	C_4H_3O-	52	103-104
43	2-pyrimidyl-	C_6H_5-	30	93-94

[a] Liquid (decomposes on attempted distillation).

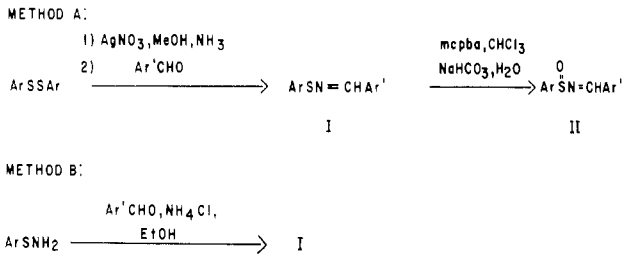
Thus *N*-(2,6-dichlorobenzylidene)arenesulfinamides might be expected to produce dichlobenil upon elimination of a sulfenic acid. The new sulfinamides and some analogous compounds were evaluated for herbicidal activity in the greenhouse against three grass and three broadleaf species and for crop tolerance in corn, cotton, and soybean. The results of this evaluation were contrasted with those obtained for dichlobenil.

EXPERIMENTAL SECTION

Synthetic Methods. *General.* Aromatic disulfides were purchased from commerical sources, or when not commerically available, were prepared by the peroxide (Challenger and Collins, 1924) or iodine oxidation (Danehy and Oester, 1967) of the corresponding commerically obtained thiol.

2-Nitrobenzenesulfinamide was prepared from the sulfenyl chloride by reaction with ammonia, and 3-nitrobenzenesulfenamide was obtained from the corresponding disulfide by the method of Davis et al. (1977). Benzylidenearenesulfenamides, I, were generally prepared by one of two methods [(Davis et al., 1977); compounds **1–13** were synthesized by method A and compounds **14–43** were obtained by method B], and the corresponding sulfinamides II were prepared by peracid oxidation of I (Davis et al., 1974) as shown in Scheme I. A listing of the sulfenamides and sulfinamides synthesized for this study is shown in Tables I and II, respectively.

Scheme I



Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected (degree Celsius). Infrared spectra were recorded on a Perkin-Elmer 137 sodium chloride spectrophotometer, and NMR spectra were recorded on a Hitachi Perkin-Elmer R24B high-resolution nuclear magnetic resonance spectrometer. Unless otherwise indicated, all compounds gave satisfactory elemental analyses.

N-(2,6-Dichlorobenzylidene)-2-pyridinesulfenamide (**9**): *Method A.* A 2-L three-necked flask was equipped with a mechanical stirrer, gas inlet tube, and drying tube. When

Table II. N-Benzylidenearenesulfinamides

$$ArS(O)N{=}CHAr'$$

compd no.	Ar	Ar'	% yield	mp, °C (bp, °C)
44	C_6H_5-	2,6-Cl_2-C_6H_3-	47	89-91
45	4-F-C_6H_4-	2,6-Cl_2-C_6H_3-	79	63-64
46	4-Cl-C_6H_4-	2,6-Cl_2-C_6H_3-	63	98-100
47	4-Br-C_6H_4-	2,6-Cl_2-C_6H_3-	45	103-104
48	4-CH_3-C_6H_4-	2,6-Cl_2-C_6H_3-	40	86-87
49	2-CH_3CONH-C_6H_4-	2,6-Cl_2-C_6H_3-	29	109.5-110
50	4-CH_3CONH-C_6H_4-	2,6-Cl_2-C_6H_3-	46	187-190 dec
51	2-C_5H_4N-	2,6-Cl_2-C_6H_3-	50	94-95
52	2-pyrimidyl-	2,6-Cl_2-C_6H_3-	57	121-123
53	2-benzothiadiazyl-	2,6-Cl_2-C_6H_3-	43	94-95 dec
54	2-NO_2-C_6H_4-	2,6-Cl_2-C_6H_3-	37	82-83 dec
55	3-NO_2-C_6H_4-	2,6-Cl_2-C_6H_3-	60	101-102
56	3-NO_2-C_6H_4-	2-Br-C_6H_4-	76	142-143
57	3-NO_2-C_6H_4-	2-Cl-C_6H_4-	81	134-135
58	3-NO_2-C_6H_4-	4-Cl-C_6H_4-	83	127-128
59	3-NO_2-C_6H_4-	2,4-Cl_2-C_6H_3-	77	141-142
60	3-NO_2-C_6H_4-	3,4-Cl_2-C_6H_3-	90	162-163
61	3-NO_2-C_6H_4-	3,5-Cl_2-C_6H_3-	63	159-159.5
62	3-NO_2-C_6H_4-	2-Cl,6-F-C_6H_3-	42	104-106
63	3-NO_2-C_6H_4-	2-Cl,6-NO_2-C_6H_3-	85	123-124
64	3-NO_2-C_6H_4-	2,5-$(CH_3O)_2$-C_6H_3-	60	113-114
65	3-NO_2-C_6H_4-	3,4,5-$(CH_3O)_3$-C_6H_3-	31	152.5-153
66	3-NO_2-C_6H_4-	2-C_2H_5O,3-CH_3O-C_6H_3-	59	111-112
67	3-NO_2-C_6H_4-	2,4,6-$(CH_3)_3$-C_6H_2-	55	109-110
68	3-NO_2-C_6H_4-	1-naphthyl-	62	124-125
69	3-NO_2-C_6H_4-	2-naphthyl-	89	130-131
70	3-NO_2-C_6H_4-	3-HO-1-naphthyl-	20	146-147
71	3-NO_2-C_6H_4-	2-HO-1-naphthyl-	63	135-136
72	3-NO_2-C_6H_4-	2-C_4H_3O-	52	113-114
73	3-NO_2-C_6H_4-	4-$(CH_3)_2N$-C_6H_4-	45	131-132
74	3-NO_2-C_6H_4-	3-(4-CH_3O-C_6H_4O)-C_6H_4-	15	84-85
75	3-NO_2-C_6H_4-	3-(3,4-Cl_2-C_6H_3O)-C_6H_4-	10	110-115
76	2-pyrimidyl-	C_6H_5-	68	93-94
77	3-NO_2-C_6H_4-	2-C_4H_3S-	58	121-122

rapidly stirred, 25.67 g (0.15 mol) of finely powdered silver nitrate was dissolved in 1 L of methanol. After dissolution was complete, 33.05 g (0.15 mol) of 2-pyridyl disulfide was added and stirring was continued for 5 min. The reaction mixture was cooled to 0 °C and dry ammonia gas was bubbled through the solution for 15 min. The flask was then purged with nitrogen to eliminate residual ammonia and 26.36 g (0.15 mol) of 2,6-dichlorobenzaldehyde was added with stirring continued for an additional 18 h. The silver mercaptide byproduct was removed from the reaction mixture by filtration and the filtrate taken to dryness in vacuo. The residue was extracted with two 500-mL aliquots of ether, and the ether solution was washed 3 times with water and dried over anhydrous magnesium sulfate. The drying agent was then removed by filtration, and the ether was removed by distillation under reduced pressure to give an orangish yellow oil which solidified on standing under vacuum. The solid was crystallized from ethanol to give 23.8 g (50%) of product as white crystalline plates, mp 73–74 °C.

N-(2,6-Dichlorobenzylidene)-3-nitrobenzenesulfenamide (14): *Method B.* To a 500-mL round-bottom flask were added 6.81 g (0.04 mol) of 3-nitrobenzenesulfenamide, 7.00 g (0.04 mol) of 2,6-dichlorobenzaldehyde, 2.14 g (0.04 mol) of ammonium chloride, and 250 mL of ethanol. The reaction mixture was then heated to reflux with stirring for 30 min and cooled, and the solvent was removed in vacuo. The residue thus obtained was heated to reflux in 250 mL of chloroform for 5 min and filtered while hot through a sintered glass funnel to remove ammonium chloride. On being cooled, the filtrate deposited 10.48 g of a lemon-yellow solid, mp 125–126 °C. A crystallization from ethanol afforded 9.60 g (73%) of the product as pale yellow acicular crystals, mp 130–130.5 °C.

N-[1-(2,6-Dichlorophenyl)ethylidene]-2-nitrobenzenesulfenamide (78): *Method C.* To a stirred solution of 8.87 g (0.05 mol) of 2,6-dichlorobenzonitrile in 400 mL of ether (dried by distillation over lithium aluminum hydride) was added, at −78 °C under a nitrogen atmosphere, 29.40 mL (0.05 mol) of a 1.7 molar solution of methyllithium in ether. After the addition was complete, the reaction mixture was allowed to warm to −25 °C and maintained at this temperature for 30 min. The brownish orange solution was again cooled to −78 °C and 9.58 g (0.05 mol) of 2-nitrobenzenesulfenyl chloride was added in small portions over a 15-min period. The reaction mixture was slowly warmed to 20 °C and stirring was continued for 18 h. The solid which formed was removed by filtration, affording 5.12 g of 2-nitrophenyl disulfide (66%). The filtrate was evaporated in vacuo to give a viscous oil which solidified on standing and was crystallized twice from ethanol to yield 3.41 g (20%) of yellow-orange plates, mp 134–135 °C.

Sulfinamide Syntheses. *N-(2,6-Dichlorobenzylidene)-3-nitrobenzenesulfinamide* (55). A three-necked 1-L flask was equipped with a dropping funnel and mechanical stirrer. A solution of 2.49 g (0.03 mol) of sodium bicarbonate in 20 mL of water was stirred at 0 °C while 8.18 g (0.025 mol) of *N*-(2,6-dichlorobenzylidene)-3-nitrobenzenesulfenamide (14) in 200 mL of chloroform was added. While vigorous stirring of the two-phase mixture was continued, a solution of 5.08 g (0.025 mol) of *m*-chloroperbenzoic acid was added dropwise during a 30-min period. Stirring was maintained for an additional hour, after which the phases were separated and the chloroform layer was dried over anhydrous potassium carbonate. The drying agent was removed by filtration

followed by solvent removal in vacuo to give a nearly colorless oil which solidified after a few hours of vacuum drying. Crystallization from ether afforded 5.15 g (60%) of product as white crystals, mp 101–102 °C.

N-[Methyl(2,6-dichlorophenyl)methylidene]-2-nitrobenzenesulfinamide (**79**). To a stirred solution of 1.13 g (3.3 mmol) of *N*-[methyl(2,6-dichlorophenyl)-methylidene]-2-nitrobenzenesulfenamide (**78**) in 25 mL of methylene chloride was added dropwise, with stirring, a solution of 0.75 g (3.7 mmol) of *m*-chloroperbenzoic acid in 25 mL of methylene chloride. After the addition was complete (20 min) the reaction mixture was stirred an additional hour, then cooled to −78 °C, and filtered to remove *m*-chlorobenzoic acid. The filtrate was taken to dryness by solvent removal in vacuo, resulting in an orange oil which contained four components (TLC). This material was purified by chromatography on a Florisil column, and the product was eluted from the column with a 1:1 pentane–ether mixture. Analytically pure product was obtained by crystallization from ethanol, as 0.48 g (41%) yellow crystals, mp 128–129 °C dec.

Saturated Analogues of Benzylidenearenesulfinamide 54 and Precursors. *N-(2,6-Dichlorobenzyl)-phthalimide* (**80**). A solution of 47.99 g (0.2 mol) of α-bromo-2,6-dichlorotoluene and 37.80 g (0.2 mol) of potassium phthalimide in 450 mL of *N,N*-dimethylformamide was stirred at ambient temperature for 8 days. Potassium bromide was removed by filtration and the filtrate poured into 600 mL of cold water. The white precipitate which formed was removed by filtration, dried, and crystallized from ethanol to give 52.37 g (86%) of product, mp 147.5–148 °C, as white acicular crystals.

2,6-Dichlorobenzylamine (**81**). A mixture of 45.77 g (0.15 mol) of *N*-(2,6-dichlorobenzyl)phthalimide and 8.5 mL (0.15 mol) of 85% hydrazine hydrate in 200 mL of methanol was heated with stirring to reflux for 2 h. The solid which formed during the reaction, 21.03 g of dihydrophthalazinedione, was removed by filtration, and 350 mL of water was added to the filtrate which was then taken to dryness in vacuo to remove excess hydrazine. To the residue 250 mL of water was added followed by 15 mL of concentrated hydrochloric acid and a small amount of dihydrophthalazinedione which precipitated was removed by filtration. Removal of the water in vacuo gave the amine hydrochloride which was purified by crystallization from ethanol to give 21.29 g. Conversion to the free base was accomplished by dissolving the salt in 25 mL of water, adding 25 mL of 4.0 molar sodium hydroxide solution, and extracting the amine with ether which was then water washed and dried over anhydrous magnesium sulfate. Removal of the drying agent by filtration and the solvent in vacuo gave 16.7 g (63%) of the product as a nearly colorless oil which was not further purified but used directly in the preparation of **82**.

N-(2,6-Dichlorobenzyl)-2-nitrobenzenesulfenamide (**82**). In a 250-mL flask 5.52 g (0.03 mol) of 2,6-dichlorobenzylamine and 3.04 g of triethylamine in 50 mL of ether were stirred at 0 °C while 6.00 g (0.03 mol) of 2-nitrobenzenesulfenyl chloride in 50 mL of ether was added dropwise over a 10-min period. Stirring was continued for 1 h, after which solvent was removed in vacuo and the residue washed with water, dried, and crystallized from ethanol to give long yellow acicular crystals, 6.70 g (66%), mp 133–134 °C.

N-(2,6-Dichlorobenzyl)-2-nitrobenzenesulfinamide (**83**). A rapidly stirred two-phase mixture of 4.45 g (13.5 mmol) of *N*-(2,6-dichlorobenzyl)-2-nitrobenzenesulfenamide (**82**), 1.83 g (22 mmol) of sodium bicarbonate, 150 mL of chloroform, and 10 mL of water was oxidized at ambient temperature by dropwise addition of 3.03 g (15 mmol) of *m*-chloroperbenzoic acid. After 1 h, the chloroform layer was separated and dried over anhydrous potassium carbonate. Removal of drying agent and solvent afforded 4.44 g of a yellow-white solid which was crystallized from ethanol to give 3.72 g (80%) of acicular white crystals, mp 185–186 °C dec.

Thiosulfinates, Sulfinates, and Precursors. *S-(2,6-Dichlorobenzyl)isothiouronium Bromide* (**84**). A solution of 23.99 g (0.1 mol) of α-bromo-2,6-dichlorotoluene and 7.61 g (0.1 mol) of thiourea in 200 mL of ethanol was heated to reflux for 1 h and cooled to ambient temperature, and the solvent was removed under reduced pressure to give a solid residue which was purified by crystallization from ethanol to afford 28.36 g (90%) of white crystals, mp 208–209 °C.

2,6-Dichlorobenzyl Mercaptan (**85**). A solution of 16.34 g (0.05 mol) of *S*-(2,6-dichlorobenzyl)isothiouronium bromide (**84**) and 2.92 g (0.05 mol) of potassium hydroxide in 20 mL of water and 30 mL of ethanol was heated to reflux with stirring for 3 h and cooled, and stirring was continued an additional 16 h. The solid material which formed was removed by filtration and dried to give 9.13 g (91%) of product, mp 35–36 °C.

2,6-Dichlorobenzyl 2-Nitrophenyl Disulfide (**86**). To 50 mL of ether were added 5.79 g (0.03 mol) of 2,6-dichlorobenzyl mercaptan (**85**) and 3.04 g of (0.03 mol) of triethylamine. While the resulting solution was stirred, a solution of 5.74 g (0.03 mol) of 2-nitrobenzenesulfenyl chloride in 100 mL of ether was added dropwise and stirring was continued for 16 h. The solvent was removed in vacuo and the residue was washed with water, dried, and crystallized from ethanol to give 6.94 g (67%) of glistening yellow flakes, mp 148–149 °C.

2,6-Dichlorobenzyl 2-Nitrobenzenethiosulfinate (**87**). 2-Nitrobenzenesulfinic acid (Zincke and Farr, 1912) was prepared and 2.00 g of this material was reacted with thionyl chloride (20 mL) by heating to reflux for 3 h with stirring. At the end of this period the excess thionyl chloride was removed in vacuo to give 1.66 g (76%) of 2-nitrobenzenesulfinyl chloride (0.008 mol). The sulfinyl chloride was then dissolved in 25 mL of ether and added dropwise to a stirring solution of 1.56 g (0.008 mol) of 2,6-dichlorobenzyl mercaptan (**85**) and 0.81 g (0.008 mol) of triethylamine in 25 mL of ether at 0 °C. Stirring was continued for 1 h after the addition was complete and the precipitated product was removed by filtration, washed with water, dried, and crystallized from ethanol to give 2.05 g (70%) of small yellow plates, mp 92–93 °C.

2-Nitrophenyl (2,6-Dichlorophenyl)methanethiosulfinate (**88**). To a rapidly stirred two-phase mixture of 3.94 g (0.011 mol) of 2,6-dichlorobenzyl 2-nitrophenyl disulfide (**86**) in 125 mL of chloroform and 1.25 g (0.015 mol) of sodium bicarbonate in 10 mL of water maintained at 0 °C was added dropwise a solution of 2.54 g (0.013 mol) of *m*-chloroperbenzoic acid in 125 mL of chloroform. The addition required 30 min, and stirring was continued an additional 30 min, after which the organic phase was separated and dried over anhydrous potassium carbonate. The drying agent was removed by filtration and the chloroform by distillation under reduced pressure to give a yellow solid which was crystallized twice from ethanol, affording yellow acicular crystals (2.51 g, 61%), mp 139–140 °C.

2,6-Dichlorobenzyl 2-Nitrobenzenesulfenate (**89**). To a solution of 19.15 g (0.1 mol) of 2-nitrobenzenesulfenyl chloride and 7.91 g (0.1 mol) of pyridine in 200 mL of

Table III. Sulfenamide Preemergent Herbicidal Activity

compd no.	rating no.[a] pigweed	velvetleaf	mustard	red millet	foxtail	barnyard grass	corn	cotton	soybean
1	1	1	1	0	0	0	0	0	0
2	1	0	0	0	0	0	0	0	0
3	1	0	0	0	0	0	0	0	0
7	0	0	1	0	0	0	0	0	0
8	0	2	0	0	0	0	0	0	0
10	0	0	1	0	0	0	0	0	0
15	1	0	0	0	0	0	0	0	0
30	1	0	0	0	0	0	0	0	0

[a] See Scheme II for an explanation of the rating numbers.

methylene chloride was added 17.88 g (0.1 mol) 2,6-dichlorobenzyl alcohol, with stirring. After a few minutes, a heavy precipitate formed and stirring was continued for an additional hour. The solid was removed by filtration, water washed, dried, and crystallized from ethanol to give 23.48 g (71%) of yellow acicular crystals, mp 138–139 °C dec.

2,6-Dichlorobenzyl 2-Nitrobenzenesulfinate (**90**). To a rapidly stirred mixture of 15.78 g (0.048 mol) of 2,6-dichlorobenzyl 2-nitrobenzenesulfenate in 375 mL of chloroform and 6.54 g (0.079 mol) of sodium bicarbonate in 50 mL of water was added dropwise a solution of 10.60 g (0.053 mol) of *m*-chloroperbenzoic acid in 375 mL of chloroform. After 18 h the phases were separated and the chloroform layer was dried over anhydrous potassium carbonate and filtered, and the solvent was removed in vacuo to give a residue which was crystallized from ethanol to yield 16.12 g (97%) of yellow crystals, mp 109–110 °C.

Sulfenamide and Sulfinamide Vinylogues and Precursors. *2-Chloro-2-(2,6-dichlorophenyl)ethyl 2-Nitrophenyl Sulfide* (**91**). A solution of 8.83 g (0.05 mol) of 2,6-dichlorostyrene and 7.58 g (0.04 mol) of 2-nitrobenzenesulfenyl chloride in 100 mL of acetic acid was stirred at ambient temperature for 2 days after which the fine yellow crystalline precipitate which formed was removed by filtration and washed several times with cold ethanol to give 8.06 g (56%) of analytically pure product, mp 117–118 °C.

(E)-2-Nitrophenyl 2,6-Dichlorostyryl Sulfide (**92**). To a solution of 3.46 g (0.010 mol) of 2-chloro-2-(2,6-dichlorophenyl)ethyl 2-nitrophenyl sulfide (**91**) in 50 mL of benzene was added dropwise with stirring a solution of 1.68 g (0.011 mol) of 1,5-diazabicyclo[5.4.0]undec-5-ene in 50 mL of benzene. Stirring was continued for 16 h after which the solvent was removed under reduced pressure and the residue was crystallized from ethanol to give 2.50 g (80%) of brilliant orange-yellow acicular crystals, mp 171–172 °C. The NMR spectrum of this compound reveals a trans coupling constant of 10 Hz for the vinylic protons.

(E)-2-Nitrophenyl 2,6-Dichlorostyryl Sulfoxide (**93**). A two-phase mixture of 1.50 g (0.005 mol) of (*E*)-2-nitrophenyl 2,6-dichlorostyryl sulfide (**92**) in 50 mL of chloroform and 0.63 g (0.008 mol) of sodium bicarbonate in 5 mL of water was rapidly stirred while a solution of 1.01 g (0.005 mol) of *m*-chloroperbenzoic acid in 50 mL of chloroform was added dropwise. After 18 h, the chloroform phase was separated and dried over anhydrous potassium carbonate. The drying agents was removed by filtration followed by removal of the solvent under reduced pressure to give a solid which was crystallized from ethanol to yield 1.20 g (70%) of lemon yellow crystals, mp 149–150 °C.

Biological Methods. All new compounds 1–93 were evaluated for preemergent herbicidal activity. Test formulations were prepared by mixing 20 mL of an acetone solution containing 0.0416 g of the test compound with 20 mL of water containing 0.02 mL of Ortho X-77 surfactant. The resultant formulations contained 1040 ppm of test compound, 50% (by volume) of acetone, and 0.05% of surfactant. Lower concentrations were obtained by diluting this formulation with surfactant–acetone solution in order to maintain adjuvant concentrations at their original levels.

Scheme II

RELATIONSHIP BETWEEN TEST RATE AND RATING NUMBER

TEST RATE, kg/ha ≥50% CONTROL AT	BUT	TEST RATE, kg/ha <50% CONTROL AT	RATING NUMBER
8		4	1
4		2	2
2		1	3
1		0.5	4
0.5		0.25	5
0.25		0.125	6

Seeds of three broadleaf species, three grassy weed species, and three crop species were planted in 10 × 8 × 3 in. fiber pans filled with 2.0 in. of pasteurized soil (Kingsville sandy loam). The test broadleaf species were pigweed (*Amaranthus retroflexus* L.), velvetleaf (*Abutilon theophrasti* Medic.), and mustard [*Brassica kaber* (D.C.) Wheeler]; the grasses were red millet (*Panicum milliaceum* L.), green foxtail [*Setaria viridis* (L.) Beauv.], and barnyard grass [*Echinochloa crus-galli* (L.) Beauv.]; the crops were cotton (*Gossypium hirsutum* L. "Stoneville" 213), soybean [*Glycine max* (L.) Merr. "Lancer"], and corn [*Zea mays* (L.) "Pioneer" 3518 F14]. The pans were then sprayed so that the soil surface was uniformly covered with dilutions of the stock formulation, providing dosage rates of the test compounds corresponding to 8, 4, 2, 1, 0.5, etc. kg/h. Two weeks subsequent to treatment the percent control (kill) at each dosage rate was estimated and a rating number assigned. The rating number relates to the applied dose as shown in Scheme II. The rating numbers for each compound are shown in Tables III and IV.

The criterion for passing the preemergent screen at a particular dosage level was 50% control of any of the test species as compared to the untreated check. As shown in Scheme II, a compound giving 50% control of a weed species at 8 kg/ha and less than 50% at 4 kg/ha would receive a rating number of "1". One passing at 4 kg/ha but not at 2 kg/ha would be given a "2" rating number and so on. Thus, each increase of one rating number represents a 2-fold increase in activity in a given test. Tables III and IV have entries only for those compounds which has rating number of at least "1" for at least one weed species. All those compounds not listed are therefore devoid of herbicidal activity at the test rates of application.

RESULTS AND DISCUSSION

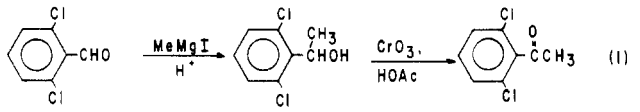
Chemical Studies. A series of sulfenamides, sulfin-

Table IV. Sulfinamide Preemergent Herbicidal Activity

compd no.	rating no.[a] pigweed	velvet-leaf	mustard	red millet	foxtail	barnyard grass	corn	cotton	soybean
44	2	1	4	2	2	2	1	1	1
45	4	1	4	3	3	3	1	0	3
46	3	1	3	3	3	2	2	2	2
47	3	2	3	1	1	3	0	0	1
48	3	3	3	3	3	3	2	2	2
49	6	3	6	3	3	3	3	2	4
50	2	1	1	1	0	0	0	0	0
51	5	4	5	5	4	4	2	3	3
52	3	2	4	2	2	2	2	2	2
53	4	2	3	2	2	2	1	2	2
54	3	2	3	1	2	2	3	3	3
55	5	2	3	1	1	1	0	1	1
60	2	0	0	0	0	0	0	0	0
62	1	0	1	0	0	0	0	0	0
79	6	6	6	0	0	0	0	0	0
dichlobenil	5	4	5	4	4	4	4	5	5

[a] See Scheme II for an explanation of the rating numbers.

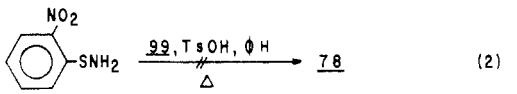
amides, and some related compounds were synthesized for evaluation as potential preemergent herbicides. All *N*-benzylidenearenesulfenamides and sulfinamides were prepared by standard literature procedures, with the exception of compound **78**. Initially it was thought that either method A and B (Scheme I) would be amenable to the preparation of **78**. To this end, 2,6-dichloroacetophenone (**99**) was synthesized (eq 1) by oxidation of the carbinol **98** (Lock and Böck, 1937):



(1)

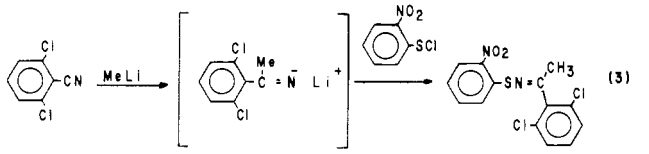
98 **99**

The failure to obtain **78** by either procedure is ostensibly due to steric hindrance from the bulky 2,6-dichloro substituents. A further modification of method B which involved the azeotropic removal of water which would be generated in the formation of **78** also failed (eq 2):



(2)

The hindered sulfenamide **78** was ultimately obtained by method C, which utilized a coupling of the lithium salt of 2,6-dichlorobenzaldimine (**100**) with the corresponding sulfenyl chloride (eq 3). (Interestingly, the substitution of a methyl Grignard for methyl lithium in this reaction did not afford any **78**.)

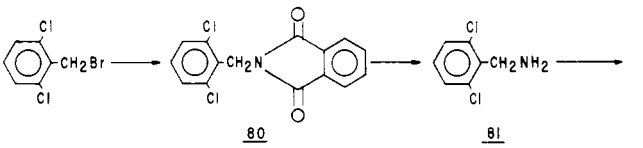


(3)

100 **78**

Peracid oxidation of **78** using the standard procedure (Davis et al., 1974) failed to yield **79**. This procedure was modified so as to be run in the absence of water and with no final aqueous sodium bicarbonate wash. The desired product **79** was obtained by running the reaction in methylene chloride with removal of the *m*-chlorobenzoic acid byproduct through filtration of the chilled (−78 °C) reaction mixture (eq 4).

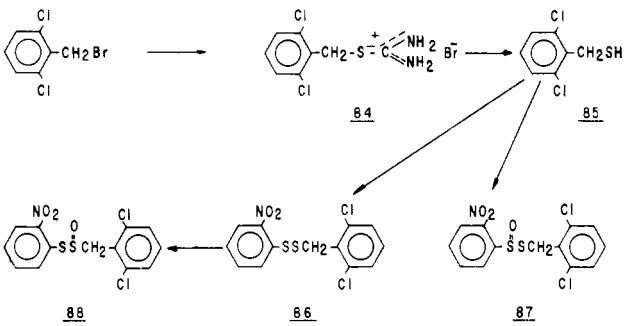
Scheme III



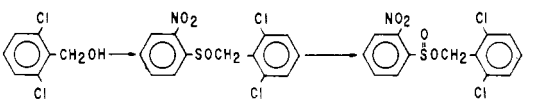
80 **81**

82 **83**

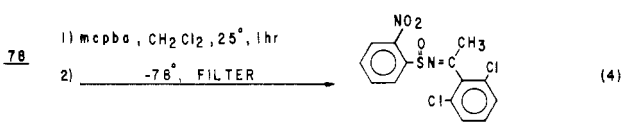
Scheme IV



84 **85** **88** **86** **87**



89 **90**



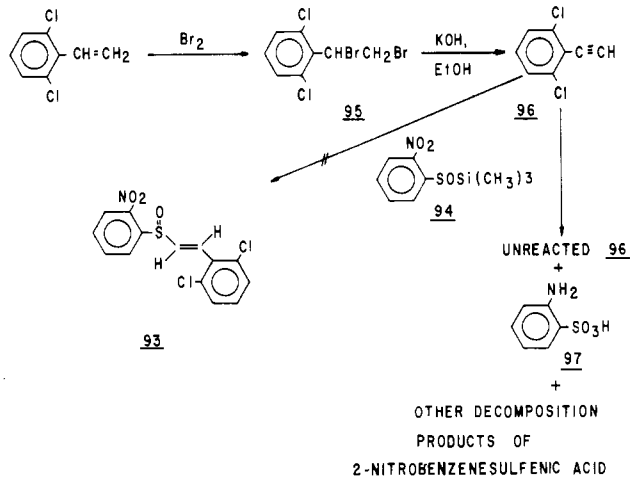
78

(4)

79

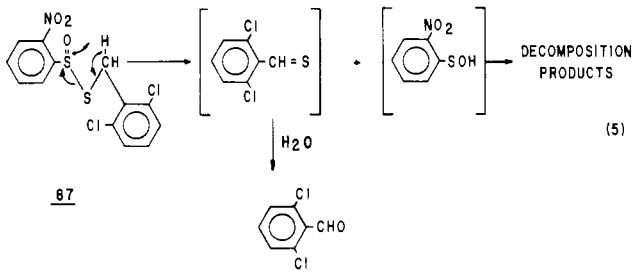
Compound **79** was of special interest in that it was the only sulfinamide prepared which could not undergo the facile elimination of a sulfenic acid at ambient temperatures (Davis and Friedman, 1976), since the hydrogen on the

Scheme V



carbon α to the sulfinamide nitrogen has been replaced by a methyl group. Thus, this compound was anticipated to be much more stable, at least from thermal considerations, than the analogous **54** or other sulfinamides examined in this study.

Compound **83** was prepared in order to test the effect of saturation of the C=N bond on herbicidal activity (Scheme III). The thiosulfinate analogue of **83**, compound **87**, was of particular interest since compounds of this type can also undergo the thermolytic formation of a sulfenic acid (Block, 1972) in analogy to the arenesulfinamides. Thus, **87** would be expected to lose 2,6-dichlorothiobenzaldehyde and form 2-nitrobenzenesulfenic acid (eq 5):



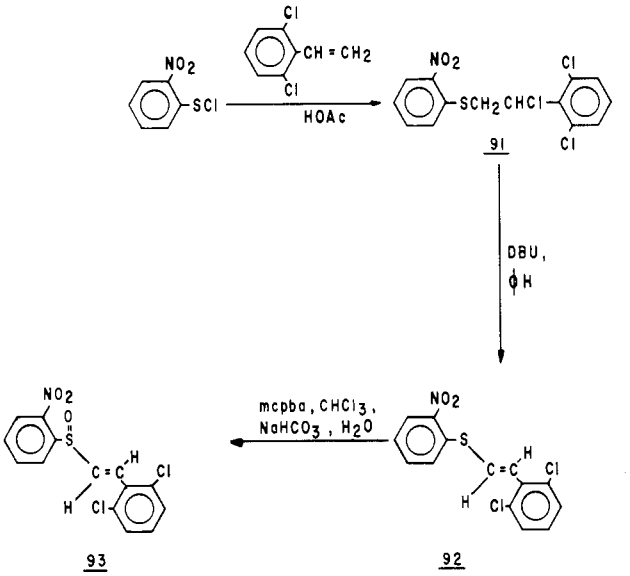
(5)

If the presence of a sulfenic acid intermediate contributes to the herbicidal activity of benzylidenearenesulfinamides, compound **87** might be similarly active by virtue of sulfenic acid elimination. Compound **87**, its precursor disulfide **86**, the isomeric thiosulfinate **88**, and the sulfenate and sulfinate analogues **89** and **90** were all prepared according to the reactions shown in Scheme IV.

In a final attempt to modify the basic sulfinamide structure while maintaining herbicidal activity, compound **93**, the vinylogue of **54**, was synthesized. Initially it was thought that this compound could be obtained by 2-nitrobenzenesulfenic acid addition [generated in situ from the corresponding trimethylsilyl ester **94** (Davis and Friedman, 1976)] to (2,6-dichlorophenyl)acetylene (**96**). The latter compound was prepared by bromination of 2,6-dichlorostyrene to give **95** followed by dehydrobromination with alcoholic potassium hydroxide. The attempted reaction of the sulfenic acid with **96** was, however, unsuccessful and only the unreacted phenylacetylene and decomposition products of 2-nitrobenzenesulfenic acid, principally orthanilic acid, **97**, could be isolated (Scheme V). Compound **93** was finally obtained via the route shown in Scheme VI.

Biological Evaluation. As can be seen in Table III, the sulfenamides screened in this study demonstrated little or no activity. The corresponding sulfinamides were also

Scheme VI



generally inactive, with the exception of the *N*-(2,6-dichlorobenzylidene)arenesulfinamides **44–55**, all of which displayed moderate to excellent herbicidal activity and crop selectivity. Due to the facile elimination of arenesulfenic acids from *N*-benzylidenearenesulfinamides, it was initially felt that compounds **44–55** might simply be undergoing thermal decomposition to dichlobenil.

While such decomposition undoubtedly does occur to some extent over a long period of time (as shown by the appearance of a nitrile band in the IR spectra of sulfinamides which had been stored at ambient temperature for several months), an examination of the herbicidal data in Table IV suggests that this is not the basis for herbicidal activity. There is essentially no rate of application of dichlobenil at which the herbicidal activity and crop phytotoxicity rating numbers are not the same; that is, no selectivity is observed. In the case of the sulfinamides there are several compounds in which a 2–5 rating number difference between a particular weed and crop exists. This degree of crop tolerance, as well as the wide variation in rating numbers among the sulfinamides tested, indicates that simple decomposition to dichlobenil cannot be responsible for the observed activity. The fact that only those sulfinamides bearing substituents at the 2- and 6-benzylidene positions have any appreciable herbicidal activity is believed to be due to steric phenomena which are discussed in detail in the following paper (Friedman and Hopfinger, 1983).

Replacement of the benzylidene methine hydrogen at **54** with a methyl group to give **79** results in an unusual modification of herbicidal activity. While **79** was inactive on grasses, it was quite active on broadleaf species. This activity is not due to the presence of hydrolysis products since both 2-nitrobenzenesulfinamide and 2,6-dichloroacetophenone are herbicidally inactive. The differences in the type of activity shown by **79** vs. **54**, or other *N*-(2,6-dichlorobenzylidene)arenesulfinamides, strongly suggest that **79** exerts its herbicidal effects through a different biological mechanism than do compounds **44–60**.

Attempted modification of the basic *N*-benzylidenearenesulfinamide structure by reduction of the N=C bond of **54** to give **83**, or by the preparation of **87** and **90** (the chalcogen analogues of **83**), resulted in the complete loss of herbicidal activity. Finally, compound **93**, the vinylogue of **54**, was found to be devoid of herbicidal activity. As in the previous examples, the loss of activity appears to

be due to conformational effects which are described in detail in part 2 of this series.

In summary, good to excellent herbicidal activity with crop selectivity was found among representatives of a new class of *N*-benzylidenearenesulfinamide herbicides. Compound **51** was more active and considerably more selective than the standard, dichlobenil, while compound **79** had excellent broadleaf activity but was inactive on grasses. All other attempts at structural modification to improve stability or increase efficacy resulted in a complete loss of activity. The conformational study presented in the following paper [part 2, Friedman and Hopfinger (1983)] has suggested a potential explanation for the biological effects described here.

ACKNOWLEDGMENT

I express sincere gratitude to Phillip Orwick and Henry McElravy for their technical support in this study.

Registry No. **1**, 83364-37-8; **2**, 83364-38-9; **3**, 83364-39-0; **4**, 83364-40-3; **5**, 83364-41-4; **6**, 83364-42-5; **7**, 83364-43-6; **8**, 83364-44-7; **9**, 83364-45-8; **10**, 83364-46-9; **11**, 83364-47-0; **13**, 83364-48-1; **14**, 83364-49-2; **15**, 83364-50-5; **16**, 83364-51-6; **17**, 83364-52-7; **18**, 83364-53-8; **19**, 66883-77-0; **20**, 83364-54-9; **21**, 83364-55-0; **22**, 83364-56-1; **23**, 83364-57-2; **24**, 83364-58-3; **25**, 83364-59-4; **26**, 83364-60-7; **27**, 83364-61-8; **28**, 83364-62-9; **29**, 83364-63-0; **30**, 83364-64-1; **31**, 83364-65-2; **32**, 83364-66-3; **33**, 83364-67-4; **34**, 83364-68-5; **35**, 83364-69-6; **36**, 83364-70-9; **37**, 83364-71-0; **38**, 83364-72-1; **39**, 83364-73-2; **40**, 83364-74-3; **41**, 83364-75-4; **42**, 40576-76-9; **43**, 83364-76-5; **44**, 83364-77-6; **45**, 83364-78-7; **46**, 83364-79-8; **47**, 83364-80-1; **48**, 83364-81-2; **49**, 83364-82-3; **50**, 83364-83-4; **51**, 83364-84-5; **52**, 83364-85-6; **54**, 83364-86-7; **55**, 83364-87-8; **56**, 83364-88-9; **57**, 83364-89-0; **58**, 83364-90-3; **59**, 83364-91-4; **60**, 83364-92-5; **61**, 83364-93-6; **62**, 83364-94-7; **63**, 83364-95-8; **64**, 83364-96-9; **65**, 83364-97-0; **66**, 83364-98-1; **67**, 83364-99-2; **68**, 83365-00-8; **69**, 83365-01-9; **70**, 83365-02-0; **71**, 83365-03-1; **72**, 83365-04-2; **73**, 83365-05-3; **74**, 83365-06-4; **75**, 83365-07-5; **76**, 83365-08-6; **77**, 83365-09-7; **78**, 83365-10-0; **79**, 83365-11-1; **80**, 64204-46-2; **81**, 6575-27-5; **82**, 83365-12-2; **83**, 83365-13-3; **84**, 83365-14-4; **85**, 66279-47-8; **86**, 83365-15-5; **87**, 83365-16-6; **88**, 83365-17-7; **89**, 83365-18-8; **90**, 83365-19-9; **91**, 83365-20-2; **92**, 83365-21-3; **93**, 83365-22-4; (2-C_5)H_4N)SS(2-C_5H_4N), 2127-03-9; 2,6-$Cl_2C_6H_3$CHO, 83-38-5; 2-$O_2NC_6H_4SCl$, 7669-54-7; 2,6-$Cl_2C_6H_3CN$, 1194-65-6; 2,6-$Cl_2C_6H_3CH_2Br$, 20443-98-5; 2,6-$Cl_2C_6H_3CH{=}CH_2$, 28469-92-3; (2-$CH_3CONHC_6H_4$)SS(2-$CH_3CONHC_6H_4$), 4490-97-5; (4-$CH_3CONHC_6H_4$)SS(4-$CH_3CONHC_6H_4$), 16766-09-9; (2-$O_2NC_6H_4$)SS(2-$O_2NC_6H_4$), 1155-00-6; 4-FC_6H_4CHO, 446-52-6; 4-BrC_6H_4CHO, 6630-33-7; 2-ClC_6H_4CHO, 89-98-5; 3-ClC_6H_4CHO, 587-04-2; 4-ClC_6H_4CHO, 104-88-1; 2,4-$Cl_2C_6H_3CHO$, 874-42-0; 3,4-$Cl_2C_6H_3CHO$, 6287-38-3; 3,5-$Cl_2C_6H_3CHO$, 10203-08-4; 2-Cl,6-FC_6H_3CHO, 387-45-1; 2-Cl,6-$O_2NC_6H_3CHO$, 6361-22-4; C_6F_5CHO, 653-37-2; 2,5-$(CH_3O)_2C_6H_3CHO$, 93-02-7; 3,4-$(CH_3O)_2C_6H_3CHO$, 120-14-9; 3,4,5-$(CH_3O)_3C_6H_2CHO$, 86-81-7; 2-C_2H_5O,3-$CH_3OC_6H_3CHO$, 66799-97-1; 4-C_2H_5O,3-$CH_3OC_6H_3CHO$, 120-25-2; 2-$C_2H_5OC_6H_4CHO$, 613-69-4; (2-C_4H_3S)CHO, 98-03-3; 4-$(CH_3)_2NC_6H_4CHO$, 100-10-7; 3-$C_6H_5OC_6H_4CHO$, 39515-51-0; 3-(4-$CH_3OC_6H_4O$)C_6H_4CHO, 62373-80-2; 3-(4-ClC_6H_4O)C_6H_4CHO, 69770-20-3; 3-(3,4-Cl_2-C_6H_3O)C_6H_4CHO, 79124-76-8; (C_4H_3O)CHO, 98-01-1; C_6H_5CHO, 100-52-7; 2-$C_2NC_6H_4SCl$, 7669-54-7; C_6H_5S-SC_6H_5, 882-33-7; (4-FC_6H_4)SS(4-FC_6H_4), 405-31-2; (4-ClC_6H_4)S-S(4-ClC_6H_4), 1142-19-4; (4-BrC_6H_4)SS(4-BrC_6H_4), 5335-84-2; (4-$CH_3C_6H_4$)SS(4-$CH_3C_6H_4$), 103-19-5; (3-CH_3,4-BrC_6H_3)SS(3-CH_3,4-BrC_6H_3), 83365-24-6; (4-C_5H_4N)SS(4-C_5H_4N), 2127-03-9; potassium phthalimide, 1074-82-4; dihydrophthalazinedione, 20116-64-7; bis(2-pyrimidyl) disulfide, 15718-46-4; 1-naphthylformaldehyde, 66-77-3; 2-naphthylformaldehyde, 66-99-9; 2-hydroxy-1-naphthylformaldehyde, 708-06-5; 9-anthrylformaldehyde, 642-31-9.

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