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Phytotoxic Activity of *N*-Benzylbenzenesulfonamides†

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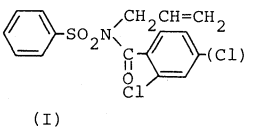
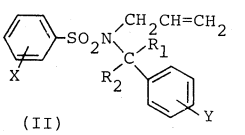
A series of *N*-benzylbenzenesulfonamides were synthesized and their biological activities were tested. Among these compounds, *N*-(2,3-epoxypropyl)-*N*-(α-methylbenzyl)benzenesulfonamide derivatives were found to be the most active against barnyardgrass and to have physiological selectivity between barnyardgrass and rice plants.

Barnyardgrass (*Echinochloa crus-galli* L.) is one of the most harmful weeds in paddy fields. The herbicides which are used most widely in paddy fields to control this weed are 2,4,6-trichlorophenyl 4-nitrophenyl ether (chlornitrofen), *S*-(4-chlorobenzyl) *N,N*-diethylthiocarbamate (benthiocarb) and *N*-butoxymethyl-2-chloro-2′,6′-diethylacetanilide (butachlor). These compounds show rather low physiological selectivity between barnyardgrass and rice plants, and they have to be applied based on the difference of chemical resistance in the different growing stages of barnyardgrass and rice plants.[1] The herbicides of this type are very difficult to apply to the young seedlings of rice plants due to the risk of phytotoxic effects. In the previous paper, we have reported that *N*-phenylsulfonylbenzamides (**I**) have physiologically selective activity between barnyardgrass and rice plants at their germination stage.[2] But it was found that a high dosage above 80 g/are was needed to control barnyardgrass adequately in the paddy field test. In order to obtain more active compounds, other types of benzenesulfonamides were synthesized and their biological activities were tested.

In preliminary tests, *N*-allyl-*N*-(α-methylbenzyl)benzenesulfonamide derivatives (**II**) were found to be as active as compounds **I** and, especially, *N*-(2,3-epoxypropyl)-*N*-(α-methylbenzyl)benzenesulfonamide derivatives (**III**) were found to be ten times as active as compounds **I** and **II**. This has prompted us to the study reported here concerning the structure-activity relationship of compounds **III**.



(I)



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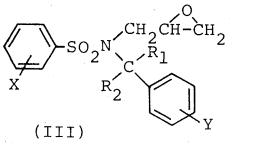
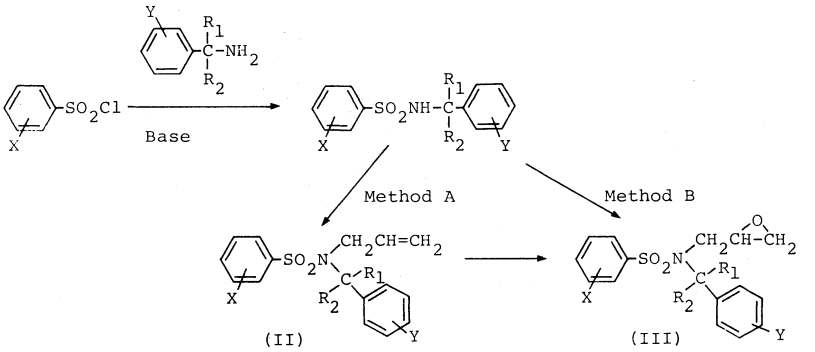


(III)

MATERIALS AND METHODS

Test compounds. The general preparative methods for *N*-(2,3-epoxypropyl)-*N*-(α-methylbenzyl)benzenesulfonamide derivatives are shown in Scheme 1, and their structures were confirmed by IR and PMR spectra. These IR and PMR spectra were obtained with a Shimadzu IR-400 and JEOL JNM PMX-60 spectrometer, respectively. The synthesized compounds are listed in Tables I to IV. Satisfactory analytical data were obtained for all compounds, and the refractive indices and melting points were not corrected.

† Phytotoxic Activity of Benzenesulfonamide Derivatives. Part II. For Part I, see ref. 2.



SCHEME 1. General Preparations of *N*-(2,3-Epoxypropyl)-*N*-(α-methylbenzyl)benzenesulfonamides.

Synthesis.

N-(2,3-Epoxypropyl)-N-(α-methylbenzyl)benzenesulfonamide (**1**).

Method A: To a solution of 3.0 g (0.01 mol) of *N*-allyl-*N*-(α-methylbenzyl)benzenesulfonamide[3] in 100 ml of chloroform, 4.31 g (0.02 mol) of *m*-chloroperbenzoic acid was added. The mixture was stirred and heated for 3 hr at 50°C. The cooled solution was washed with aqueous sodium bisulfite solution and saturated $NaHCO_3$ aqueous solution. The chloroform solution was dried over anhydrous $MgSO_4$, concentrated and purified by silica gel column chromatography to obtain 2.63 g (83%) of **1**, mp 63~64°C. IR ν_{max}^{Nujol} cm^{-1}: 1330, 1158, 945, 932. PMR δ (CCl_4): 1.34 and 1.44 (total 3H, d, J=7.1 Hz), 1.9~3.3 (5H), 5.15 (1H, q). *Anal.* Found: C, 64.41; H, 6.07; N, 4.43. Calcd. for $C_{17}H_{19}NO_3S$: C, 64.33; H, 6.03; N, 4.41%.

Method B: To a solution of 1.5 g (5.4 mmol) of *N*-(α-methylbenzyl)benzenesulfonamide in 15 ml of chloromethyloxirane, 320 mg (6.4 mmol) of 50% NaH was added at room temperature under nitrogen. The mixture was stirred for 30 min at room temperature and heated under reflux for 3 hr. After completing the reaction, chloromethyloxirane was distilled off *in vacuo*, water was added to the residue and extracted with ethyl acetate. The ethyl acetate solution was dried over anhydrous Na_2SO_4, concentrated and chromatographed over silica gel to give 1.52 g (89%) of **1**.

With a similar method, compounds **2**, **3**, **6~28**, and **34~51** were obtained. The substituted α-alkylbenzylamines were prepared according to known procedures.[4~6]

N-(2,3-Epoxypropyl)-N-(α-methylbenzyl)-4-aminobenzenesulfonamide (**29**). To a mixture of 0.5 g of acetic acid and 3.5 ml of water, 5.2 g of iron was added, followed by agitating at refluxing temperature for 30 min and then cooling to 80°C. Five grams (13.8 mmol) of *N*-(2,3-epoxypropyl)-*N*-(α-methylbenzyl)-4-nitrobenzenesulfonamide (**28**) suspended in 9 ml of isopropyl alcohol was added to the mixture, followed by vigorous agitating at 80°C for 1 hr. The subsequent work-up gave 4.13 g (90%) of **29**, mp 120~121°C. IR ν_{max}^{Nujol} cm^{-1}: 3465, 3365, 1590, 1455, 1150, 1085, 920, 840. PMR δ ($CDCl_3$): 1.38 and 1.44 (total 3H, d, J=7.1 Hz), 1.8~3.5 (5H), 4.1 (2H, broad s), 5.15 (1H, q). *Anal.* Found: C, 61.45; H, 6.08; N, 8.42. Calcd. for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.42%.

N-(2,3-Epoxypropyl)-N-(α-methylbenzyl)-4-hydroxybenzenesulfonamide (**30**). To a solution of 19.3 g (0.12 mol) of *N*-allyl-*N*-(α-methylbenzyl)amine[7] and 8.3 g (0.06 mol) of K_2CO_3 in 100 ml of acetone, 29.7 g (0.1 mol) of 4-benzoyloxybenzenesulfonyl chloride[8] in 100 ml of acetone was added at 0°C. The mixture was stirred for 12 hr at room temperature. The inorganic salts were filtered off and the filtrate was concentrated to dryness. To the residue, 200 ml of 20% KOH aqueous solution was added and heated under reflux for 1 hr. The cooled solution was acidified with conc. HCl and the precipitated *N*-allyl-*N*-(α-methylbenzyl)- 4-hydroxybenzenesulfonamide was filtered off. The crude product was successively washed with saturated $NaHCO_3$ aqueous solution and water, and then recrystallized from hexane-ethyl acetate to give 27.9 g (88%) of pure *N*-allyl-*N*-(α-methylbenzyl)- 4-hydroxybenzenesulfonamide, mp 128°C. Epoxidation and the subsequent work-up gave **30**, mp 92~94°C. IR ν_{max}^{Nujol} cm^{-1}: 3490, 1380, 1150, 1130, 920, 840. PMR δ ($CDCl_3$): 1.40 and 1.45 (total 3H, d, J=7.1 Hz), 1.9~3.5 (5H), 3.03 (1H, s), 5.17 (1H, q). *Anal.* Found: C, 61.25; H, 5.71; N, 4.19. Calcd. for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74; N, 4.20%.

N-(2,3-Epoxypropyl)-N-(α-methylbenzyl)-2-methoxycarbonylbenzenesulfonamide (**31**). A solution of 20.5 g (0.01 mol) of *o*-sulfobenzimide sodium salt and 14.1 g (0.01 mol) of 1-phenethyl chloride in 200 ml of DMF was stirred and heated under reflux for 4 hr. The subsequent work-up gave 20.7 g of *N*-(α-methylbenzyl)-*o*-sulfobenzimide, mp 83°C (recrystallized from EtOH). This was added to 200 ml of 20% KOH aqueous solution and heated under reflux for 3 hr. The subsequent work-up gave 19.1 g (88%) of 2-[*N*-(α-methylbenzylamino)sulfonyl]benzoic acid, mp 154~156°C. This was converted to its methyl ester with diazomethane and reacted with allyl bromide. Epoxidation and the subsequent work-up gave crude **31**. This was purified by silica gel column chromatography to

give pure **31**, $n_D^{26.5}$ 1.5449. IR ν_{max}^{film} cm^{-1}: 1725, 1430, 1330, 1290, 1255, 1150, 1110, 1060, 920, 880. PMR δ (CCl_4): 1.39 and 1.55 (total 3H, d, $J=7.1$ Hz), 1.9~3.5 (5H), 3.83 (3H, s), 5.11 (1H, q). *Anal.* Found: C, 61.43; H, 5.69; N, 3.75. Calcd. for $C_{19}H_{21}NO_5S$: C, 60.78; H, 5.63; N, 3.73%.

N-(2,3-Epoxypropyl)-N-(α-methylbenzyl)-4-methoxycarbonylbenzenesulfonamide (**32**). To a solution of 18.6 g (0.092 mol) of 4-methoxycarbonylbenzenesulfonamide (prepared from *p*-toluenesulfonamide[9]) in 50 ml of DMF, 5.5 g (0.11 mol) of 50% NaH was added at room temperature under nitrogen. The mixture was stirred for 30 min at 60°C and cooled. To the mixture, 19.7 g (0.14 mol) of 1-phenethyl chloride was added at 0°C and heated under reflux for 1 hr. The subsequent work-up gave 19.7 g (67%) of *N*-(α-methylbenzyl)-4-methoxycarbonylbenzenesulfonamide, mp 83~84°C. Then, 16 g (0.05 mol) of this was reacted with allyl bromide to give 13.5 g (75%) of *N*-allyl-*N*-(α-methylbenzyl)-4-methoxycarbonylbenzenesulfonamide, mp 56~57°C. Epoxidation and the subsequent work-up gave crude **32**. This was recrystallized from EtOH to give prisms, mp 90~93°C. The yield was 12.5 g (89% from the *N*-allyl intermediate). IR ν_{max}^{Nujol} cm^{-1}: 1725, 1455, 1345, 1280, 1165, 1140, 1105, 1095, 860. PMR δ (CCl_4): 1.38 and 1.49 (total 3H, d, $J=7.1$ Hz), 1.9~3.5 (5H), 3.88 (3H, s), 5.13 (1H, q). *Anal.* Found: C, 61.07; H, 5.75; N, 4.00. Calcd. for $C_{19}H_{21}NO_5S$: C, 60.78; H, 5.63; N, 3.73%.

N-(2,3-Epoxypropyl)-*N*-(α-methylbenzyl)-4-dimethylaminocarbonylbenzenesulfonamide (**33**) was prepared from *N*-allyl-*N*-(α-methylbenzyl)-4-methoxycarbonylbenzenesulfonamide in three steps, *i.e.*, hydrolysis to the corresponding free acid, reaction with *N,N*-dimethylamine,[10] and epoxidation.

N-(2,3-Epithiopropyl)-*N*-(α-methylbenzyl)-4-propylbenzenesulfonamide (**4**) was prepared by the reaction of *N*-(2,3-epoxypropyl)-*N*-(α-methylbenzyl)-4-propylbenzenesulfonamide (**17**) and thiourea according to known procedures.[11,12] *N*-(2,2-Dichlorocyclopropylmethyl)-*N*-(α-methylbenzyl)benzenesulfonamide (**5**) was prepared from *N*-allyl-*N*-(α-methylbenzyl)benzenesulfonamide according to known procedure.[13]

Biological tests. Biological tests were done as described in the previous paper.[2] We mainly used the pot test to evaluate activity, because highly active compounds in the petri dish test were not always active in the pot test.

In Tables I and II, the results in the pot test expressed as ED_{90} refer to the lowest application rate of the compounds (g/are) in which the weight of the above-ground part of the treated plants was less than 10% that of untreated plants.[14]

In Tables III and IV, the herbicidal activities against barnyardgrass at a dosage of 1.5 g/are and the rice phytotoxicities at a dosage of 6 g/are are expressed by a zero to 10 rating system (zero = no effect, 10 = complete killing).

RESULTS AND DISCUSSION

The results in Tables I and II suggest certain structural requirements for *N*-benzylbenzenesulfonamide derivatives to show high activity.

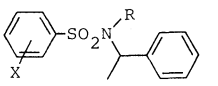
Firstly, in the chemical structures, the 2,3-epoxypropyl group played the most important role in herbicidal activity as shown in Table I. Substitutions of the 2,3-epoxypropyl group at C_2 or C_3 dramatically decreased the activity, and 2,3-epithiopropyl (**4**) and 2,2-dichlorocyclopropylmethyl (**5**) derivatives exhibited no activity. Accordingly, it was concluded that *N*-(2,3-epoxypropyl) substitution is essential for high activity. Furthermore, 2-hydroxypropyl and 2,3-dihydroxypropyl derivatives were not active even at a dosage of 200 g/are, it may be necessary that the epoxide structure is not changed before they reach the specific receptor sites.

Secondly, the activity of *N*-benzyl derivative (**6**) was higher than those of *N*-phenyl (**11**) and *N*-(2-phenethyl) (**12**) derivatives as shown in Table II. This may indicate that one carbon atom between the phenyl ring and the nitrogen atom of sulfonamide is necessary to exhibit higher activity. Alkyl substitutions at the α-position of the *N*-benzyl moiety also affected the activity. α-Methylbenzyl derivative (**1**) showed the highest activity, which was decreased with increases in the number of carbon atoms. In the case of *N*-allyl-*N*-benzylbenzenesulfonamide type, α,α-dimethylbenzyl derivatives were active as α-methylbenzyl derivatives. But in the case of *N*-(2,3-epoxypropyl)-*N*-benzylbenzenesulfonamide type, the activity of α-methylbenzyl derivatives always exceeded those of α,α-dimethylbenzyl derivatives.

Thus, *N*-(2,3-epoxypropyl)-*N*-(α-methylbenzyl)benzenesulfonamide derivatives were found to be the most active compounds, and we tried to clarify the effect of aromatic substitutions on their herbicidal activities.

As shown in Table III, sufficient herbicidal activity associated with a wide range of substituents on the phenyl ring of the phenylsul-

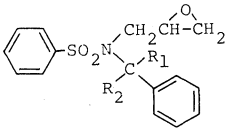
TABLE I. EFFECT OF THE 2,3-EPOXYPROPYL GROUP ON HERBICIDAL ACTIVITY



Compound no.	X	R	mp (°C) or n_D	Herbicidal activity barnyardgrass (ED_{90}: g/are)[a]
1	H	2,3-Epoxypropyl	63～64	1.0
2	H	2-Methyl-2,3-epoxypropyl	Amorphous	12.5
3	H	2,3-Epoxybutyl	63～65	100
4	4-Propyl	2,3-Epithiopropyl	n_D^{23} 1.5765	100
5	H	2,2-Dichlorocyclopropylmethyl	$n_D^{26.5}$ 1.5630	100

[a] See METHOD.

TABLE II. EFFECT OF BENZYLIC SUBSTITUTIONS ON HERBICIDAL ACTIVITY



Compound no.	R_1	R_2	mp (°C) or n_D	Herbicidal activity barnyardgrass (ED_{90}: g/are)[a]
6	H	H	n_D^{26} 1.5724	25
1	H	Methyl		1.0
7	Methyl	Methyl	$n_D^{25.5}$ 1.5691	4.0
8	H	Ethyl	$n_D^{26.5}$ 1.5582	6.0
9	H	Propyl	$n_D^{26.5}$ 1.5563	12.5
10	H	Isopropyl	$n_D^{26.5}$ 1.5494	25
11	*N*-Phenyl		93～94	50
12	*N*-(2-Phenethyl)		$n_D^{26.5}$ 1.5605	100

[a] See METHOD.

fonyl moiety (X). Although compound **1** (X=H) showed low selectivity between barnyardgrass and rice plants, the introduction of alkyl substituents on the phenyl ring of the phenylsulfonyl moiety improved the selectivity without any marked decrease in herbicidal activity. In particular, 2,4-dimethyl derivative (**20**) exhibited a highly selective activity between barnyardgrass and rice plants at their germination stage.

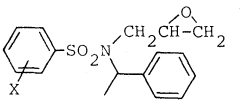
High activities in 2-methyl (**13**), 2,4-dimethyl (**20**), 2,5-dimethyl (**21**) and 2,4,6-trimethyl (**22**) derivatives suggested that *ortho*-methyl substitution increased the activity. Decreased activity in the higher *ortho*-alkyl homologues, *i.e.*, **23** and **24**, may be attributed to the steric effects of bulkier *ortho* substituents on the epoxide moiety.

On the other hand, in the case of *para* substituents, higher alkyl homologues exhibited moderate activities. This may indicate that the steric effect of substituents is not as pronounced at the *para* position in comparison with that of the *ortho* position.

Other compounds in Table III such as 3-chloro (**26**) and 4-dimethylaminocarbonyl (**33**) derivatives exhibited high activities, but they showed lower selectivity between barnyardgrass and rice plants.

Substitutions on the phenyl ring of the

TABLE III. EFFECT ON HERBICIDAL ACTIVITY OF SUBSTITUENTS ON THE PHENYL RING OF THE PHENYLSULFONYL MOIETY (X)



Compound no.	X	mp (°C) or n_D	Herbicidal activity[a]	
			Barnyardgrass[b]	Rice[c]
1	H		10	10
13	2-Methyl	n_D^{25} 1.5680	10	6
14	3-Methyl	n_D^{24} 1.5660	8	10
15	2-Ethyl	$n_D^{26.5}$ 1.5648	9	0
16	4-Ethyl	67～69	9	8
17	4-Propyl	n_D^{25} 1.5445	9	4
18	4-Isopropyl	$n_D^{24.5}$ 1.5438	10	4
19	4-*t*-Butyl	83～84	8	4
20	2,4-Dimethyl	$n_D^{25.5}$ 1.5688	10	0
21	2,5-Dimethyl	n_D^{25} 1.5701	10	3
22	2,4,6-Trimethyl	90～92	10	4
23	2,5-Diethyl	$n_D^{24.5}$ 1.5582	8	0
24	2,5-Diisopropyl	$n_D^{25.5}$ 1.5780	0	0
25	2-Cl	$n_D^{25.5}$ 1.5790	6	0
26	3-Cl	$n_D^{26.5}$ 1.5747	10	6
27	4-Cl	79～81	6	10
28	4-NO_2	108～110	0	6
29	4-NH_2	120～121	10	10
30	4-OH	92～94	4	2
31	2-COOMe	$n_D^{26.5}$ 1.5449	6	2
32	4-COOMe	90～93	8	2
33	4-$CON(Me)_2$	98～100	10	6

[a] 0=no effect; 10=complete killing.
[b] Dosage of 1.5 g/are.
[c] Dosage of 6 g/are.

benzyl moiety (Y) generally reduced the activity as shown in Table IV.

Since the activities of 4-alkyl derivatives (**36**～**39**) reduced with increases in the number of carbon atoms, there may be a limit in the bulkiness of the *para* substituents.

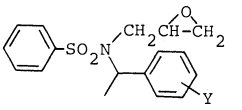
The compound with both substituents in *ortho* positions, *i.e.*, 2,4,6-trimethyl derivative (**43**), showed a marked reduction in activity. This may be attributed to an unsuitable spatial relationship between the *ortho* substituents and the epoxide moiety on account of their steric hindrance.

Among the compounds listed in Table IV, only 3,4-dimethoxy derivative (**47**) showed both high activity and selectivity. Accordingly, compounds in which the phenyl ring of the benzyl moiety was unsubstituted, *i.e.*, Y=H, were found to have higher activities and selectivities.

From the results shown in Tables I to IV, it was found that *N*-(2,3-epoxypropyl)-*N*-(α-methylbenzyl)benzenesulfonamide derivatives exhibited significant herbicidal activities against barnyardgrass and also have the selectivity between barnyardgrass and rice plants. Furthermore, the spatial relationships between the epoxide moiety and the other parts of the molecule seems to be most important for high activity.

As in the case of dieldrin, activation with the epoxidation of an unsaturated compound, al-

TABLE IV. EFFECT ON HERBICIDAL ACTIVITY OF SUBSTITUENTS ON THE PHENYL RING OF THE BENZYL MOIETY (Y)



Compound no.	Y	mp (°C) or n_D	Herbicidal activity[a]	
			Barnyardgrass[b]	Rice[c]
1	H		10	10
34	2-Methyl	$n_D^{24.5}$ 1.5579	8	2
35	3-Methyl	$n_D^{24.5}$ 1.5592	8	8
36	4-Methyl	69～70	6	10
37	4-Ethyl	$n_D^{24.5}$ 1.5560	6	0
38	4-Isopropyl	$n_D^{24.5}$ 1.5481	6	2
39	4-*t*-Butyl	$n_D^{24.5}$ 1.5433	0	0
40	2,4-Dimethyl	127～130	8	2
41	2,5-Dimethyl	n_D^{25} 1.5698	6	4
42	3,4-Dimethyl	$n_D^{25.5}$ 1.5448	10	10
43	2,4,6-Trimethyl	90～92	0	0
44	3-Methoxy	87～88	8	8
45	4-Methoxy	$n_D^{24.5}$ 1.5555	6	6
46	2,5-Dimethoxy	98～100	6	4
47	3,4-Dimethoxy	$n_D^{24.5}$ 1.5550	10	4
48	3-Cl	74～77	10	10
49	4-Cl	$n_D^{25.5}$ 1.5692	2	10
50	3,4-Cl_2	$n_D^{25.5}$ 1.5685	8	0
51	4-Br	n_D^{25} 1.5609	6	10

[a] 0=no effect; 10=complete killing.
[b] Dosage of 1.5 g/are.
[c] Dosage of 6 g/are.

drin, is a well-known process.[15] Thus, whether the *N*-(2,3-epoxypropyl) derivatives were the active forms of *N*-allyl derivatives is an interesting question. If the activation process occurred on *N*-allyl derivatives, many of them should exhibit at least moderate activity. Of over 100 *N*-allyl derivatives tested, however, only a few compounds were one-tenth as active as compound **1**. Consequently, activation with the epoxidation of *N*-allyl derivatives hardly seems to occur under natural conditions.

N-(2,3-Epoxypropyl)-*N*-(α-methylbenzyl)-benzenesulfonamide derivatives consist of four stereoisomers due to two asymmetric carbons (C_2 in the epoxypropyl group and the benzylic carbon), but their separation was not attempted in this report. Studies on the stereochemisty of four isomers and their biological activities are now in progress.

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