

# Substituted Sulphones and Sulphonamides and their Cyanoethylation Products as Insecticides

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## Abstract

The insecticidal activity of some substituted sulphones and sulphonamides and their cyanoethylation products is discussed in relation to the already well-known insecticides. Some of the compounds prepared showed excellent activity. In the experimental part, the preparation of the substances thus tested has been described.

In an earlier paper<sup>1)</sup> we have reported over the insecticidal activity of benzylphenylsulphones of the type  $C_6H_5SO_2CH_2C_6H_4R$ , benzylsulphonamides,  $RC_6H_4CH_2SO_2NH_2$  and their cyanoethylation products. p-Chlorobenzylphenylsulphone was found to have the best activity, followed by o-chlorobenzylphenylsulphone. Other compounds were found to possess this activity in more or less degree, but were considered valueless as possible insecticides.

p-Chlorodiphenylsulphone is an important acaricide<sup>2)</sup>. In view of the favourable result obtained from p-chlorobenzyl-phenylsulphone, we prepared a large number of sulphones with a view to finding out a relationship between their structure and insecticidal activity. Where possible these were also cyanoethylated and submitted to biological testing.

In the same way several substituted sulphonamides were prepared by us and then cyanoethylated. Benzenesulphonamide has been reported earlier<sup>3)</sup> to undergo condensation with acrylonitrile to form the dicyanoethylation product,  $C_6H_5SO_2N(CH_2CH_2CN)_2$ . However, no details regarding its method of preparation etc. are available. These cyanoethylated products were also tested for their insecticidal activity.

<sup>1)</sup> G. S. MISRA and R. S. ASTHANA, J. prakt. Chem. 4. Reihe **3**, 4 (1956).

<sup>2)</sup> Chem. Eng. News. **29**, 1983 (1951).

<sup>3)</sup> WEGLER, Report to I.G. Farbenind. A.-G., April 21, 1941.

### Insecticidal Activity

In the following tables 1, 2 and 3 the results on the insecticidal activity of these compounds have been given. In table 4, the values for D.D.T., hexachlorobenzene (HCB) and pyrethrum are given, when

Table 1  
Sulphones

Name of the compound	During the testing time		Knock down in minutes	
	Temp. °C	Relative humidity	50%	100%
1. p-Chlorodiphenyl-sulphone . . . . .	31	67	20% upto 2 hours	
2. p,p'-Dichlorodiphenyl-sulphone. . . . .	30.5	67	1.0	2.5
3. p-Chlorophenylbenzyl-sulphone. . . . .	30.5	67	82.0	124.0
4. p-Chlorophenyl-p'-chloro-benzylsulphone . . . . .	30.5	67	69.0	114.5
5. p-Chlorophenyl- $\beta$ -phenylethylsulphone	30.5	67	58.0	107.5
6. p-Chlorodibenzylsulphone . . . . .	30.5	67	11.5	18.5
7. p,p'-Dichlorodibenzylsulphone . . . . .	30.5	67	1.0	2.0
8. p,p'-Dichlorodibenzylsulphoxide . . . . .	31	67	30% upto 2 hours	

Table 2  
Cyanoethylated sulphones

Name of the compound	During the testing time		Knock down in minutes	
	Temp. °C	Relative humidity	50%	100%
1. $\gamma$ -Phenyl- $\gamma$ -p-chloro-phenylsulphonyl-pimelonitrile . . . . .	31	67	27.0	67.5
2. $\gamma$ -p-Chlorophenyl- $\gamma$ -p'-chlorophenylsulphonylpimelonitrile . . . . .	31	67	1.0	2.0

tested for insecticidal activity under similar conditions. It appears that p,p'-dichlorodiphenylsulphone, p,p'-dichlorodibenzylsulphone,  $\gamma$ -p-chlorophenyl- $\gamma$ -p'-chlorophenylsulphonyl pimelonitrile and N,N-bis-bis-(2-cyanoethyl)- $\beta$ -naphthalene sulphonamide are the most active compounds, closely followed by N,N-bis-(2-cyanoethyl)-p-chlorobenzene-sulphonamide. Other compounds also show the activity in more or less degree. The details of the method of testing these compounds against *Musca Nebulo*, have already been described in an earlier paper<sup>1</sup>).

Table 3  
Cyanoethylated sulphonamides

Name of the compound	During the testing time		Knock down in minutes	
	Temp. °C	Relative humidity	50%	100%
1. N,N-bis-(2-cyanoethyl)-benzenesulphonamide . . . . .	31	67	14.5	29.0
2. N,N-bis-(2-cyanoethyl)-p-chlorobenzene-sulphonamide . . . . .	31	67	3.0	7.0
3. N,N-bis-(2-cyanoethyl)-p-bromobenzene-sulphonamide . . . . .	30	80	40% upto 2 hours	
4. N,N-bis-(2-cyanoethyl)-p-toluenesulphonamide . . . . .	30	80	20% upto 2 hours	
5. N,N-bis-(2-cyanoethyl)-p-ethylbenzenesulphonamide . . . . .	30	80	30% upto 2 hours	
6. N-Methyl-N-(2-cyanoethyl)-p-toluenesulphonamide . . . . .	30	80	14.5	27.0
7. N,N-bis-(2-cyanoethyl)- $\alpha$ -naphthalenesulphonamide . . . . .	30	80	10% upto 2 hours	
8. N,N-bis-(2-cyanoethyl)- $\beta$ -naphthalenesulphonamide . . . . .	30	80	1.0	2.0

Table 4  
D. D. T, B. H. C and Pyrethrum

Name of the compound	During the testing time		Knock down in minutes	
	Temp. °C	Relative humidity	50%	100%
1. 1 per cent D.D.T in mineral turpentine	30	83	3.0	5.0
2. 1 per cent B.H.C. in mineral turpentine	30	83	2.0	4.0
3. 0.02 per cent Pyrethrins I and II (2% Pyrethrum extract) in mineral turpentine	30	83	18.5''	38.0''

Certain generalisations regarding the relationship of structure to the insecticidal activity of these compounds can be made. Chlorine atom in the para position of the benzene ring has the effect of enhancing this activity. Whereas p-chlorodiphenyl-sulphone is not at all active, introduction of another chlorine atom in the second benzene ring enhances the activity in p,p'-dichlorodiphenylsulphone to a very marked degree. Strangely enough whereas p-chlorobenzylphenylsulphone exhibits good activity<sup>1)</sup>, in p-chlorobenzyl-p'-chlorophenylsulphone this is

suppressed to a marked degree. On cyanoethylation of the latter, the product obtained,  $\gamma$ -p-chlorophenyl- $\gamma$ -p'-chlorophenylsulphonyl-pimelonitrile is again a valuable insecticide. In the sulphonamide series, the cyanoethylation product from  $\beta$ -naphthalene sulphonamide is very active, whereas the one obtained from  $\alpha$ -naphthalenesulphonamide is comparatively inactive. N,N-bis-(2-cyanoethyl)-p-chlorobenzenesulphonamide, which has a chlorine atom in the para position with respect to the dicyanoethyl sulphonamido group is again found to be active.

## Experimental

### Substituted Sulphones and their Cyanoethylation Products

#### p-Chlorodiphenylsulphone

This compound was prepared in accordance with the method of OLIVIER<sup>4</sup>) and had a m. p. 97°–98° (Literature gives 98°).

#### p,p'-Dichlorodiphenylsulphone

The sulphone was prepared according to the method of ULLMANN and KORSELT<sup>5</sup>) and had a m. p. 146°–147° (Literature gives 148°).

#### p-Chlorophenylbenzylsulphone

It was prepared according to the method of PURGOTTI<sup>6</sup>). The m. p. of the sulphone was found to be 139°, whereas the literature gives a m. p. 257°–258°.

C<sub>13</sub>H<sub>11</sub>O<sub>2</sub>ClS required: S, 12.02%, found: S, 11.49%.

#### $\gamma$ -Phenyl- $\gamma$ -p-chlorophenylsulphonylpimelonitrile

To a well stirred mixture of p-chlorophenylbenzylsulphone (3 g.), dioxane (20 ml.) and 40% benzyltrimethylammonium hydroxide (0.5 g.) was added acrylonitrile (1.5 g.) dropwise. The reaction mixture was stirred for forty hours at room temperature, neutralised with dilute hydrochloric acid and then poured on ice. A white solid separated, which was recrystallised from dilute dioxane in white plates, m. p. 179°–180°. Yield, 3.5 g. (78% of theory).

C<sub>19</sub>H<sub>17</sub>O<sub>2</sub>N<sub>2</sub>ClS required: N, 7.51%, found: N, 7.08%.

#### p-chlorophenyl-p'-chlorobenzylsulphone

A mixture of p-chlorobenzene sodium sulphinate and p-chlorobenzyl bromide (3 g.) was refluxed with ethanol (20 ml.) for twenty hours. At the end of the reaction, the mixture was poured on ice, and the white solid separating was recrystallised from ethanol in white plates, m. p. 148° (Literature gives m. p. 148°). Yield, 4 g. (88% of theory).

<sup>4</sup>) S. C. T. OLIVIER, *Rec. Trav. chim. Pays-Bas* **33**, 247 (1914).

<sup>5</sup>) F. ULLMANN and J. KORSELT, *Ber. dtsh. chem. Ges.* **40**, 642 (1907).

<sup>6</sup>) A. PURGOTTI, *Ann. r. Scuola d'agr. in Portici* (2), **13**, 8 (1915–16).

$\gamma$ -p-Chlorophenyl- $\gamma$ -p'-chlorophenylsulphonylpimelonitrile

Freshly distilled acrylonitrile (0.8 g.) was slowly added to a well stirred solution of p-chlorophenyl-p-chlorobenzylsulphone (2 g.) and benzyltrimethylammonium hydroxide (0.5 g.) in dioxane (15 ml.). The reaction mixture was stirred at room temperature for forty-eight hours, neutralised with dilute hydrochloric acid and poured on ice. The white solid which separated was recrystallised from dilute dioxane in white plates m. p. 184°—185°. Yield, 2 g. (80% of theory).

$C_9H_{16}O_2N_2Cl_2S$  required: N, 6.87%, found: N, 6.39%.

p-chlorophenyl- $\beta$ -phenylethylsulphone

A mixture of sodium-p-chlorobenzene sulphinate (2 g.),  $\beta$ -phenyl ethyl bromide (2 g.) and ethanol (10 ml.) was refluxed for twenty hours on a water bath. The reaction mixture was poured on ice and the oil that separated was kept in a vacuum desiccator for some time when it slowly crystallised out. It was recrystallised from ethanol, m. p. 74°—75°. Yield, 1.8 g. (64% of theory).

$C_{11}H_{13}O_2ClS$  required: S, 11.42%, found: S, 10.94%.

## p-chlorodibenzylsulphone

Sodium benzyl sulphinate (3 g.), p-chlorobenzyl bromide (3.5 g.) and ethanol (20 ml.) were refluxed together on a water-bath for a period of twenty hours and then poured on ice. The white solid obtained was recrystallised from ethanol, m. p. 167°—168°. Yield, 2.5 g. (55% of theory).

$C_{14}H_{13}O_2ClS$  required: S, 11.42%, found: S, 10.89%.

## p,p'-dichlorodibenzylsulphone

This was prepared according to the method of OVERBERGER et al<sup>7</sup>) and had a m. p. 246° (Literature gives 246°—247°).

## p,p'-dichlorodibenzylsulphoxide

This was also prepared according to the method of OVERBERGER et al<sup>7</sup>) and had a m. p. 164°—165° (Literature gives m. p. 164.8°—165.1°).

## Cyanoethylation of Substituted Sulphonamides

## N,N-bis-(2-cyanoethyl)-benzenesulphonamide

To a well stirred solution of benzene sulphonamide (2 g.) and 40% benzyltrimethylammonium hydroxide (0.5 g.) in dioxane (10 ml.) was added acrylonitrile (1.2 g.) dropwise at room temperature. The mixture was stirred for forty-eight hours and neutralised

<sup>7</sup>) C. G. OVERBERGER, S. P. LIGTHELM and E. A. SWIRE, J. Amer. chem. Soc. **72**, 2858 (1950).

with dilute hydrochloric acid. The white precipitate which separated was recrystallised from ethanol in white needles, m. p. 91°–92°. Yield, 2.4 g. (72% of theory).

$C_{12}H_{13}O_2N_3S$  required: N, 15.96%, found: N, 15.58%.

*N,N*-bis-(2-cyanoethyl)-*p*-chlorobenzenesulphonamide

Acrylonitrile (1.2 g.) was slowly added to a stirred solution of *p*-chlorobenzenesulphonamide (2 g.) and benzyltrimethylammonium hydroxide (0.5 g.) in dioxane (10 ml.). The reaction mixture was stirred at room temperature for forty-eight hours and neutralised with dilute hydrochloric acid. The white solid thus obtained was recrystallised from ethanol in white needles, m. p. 132°. Yield, 2.8 g. (87% of theory).

$C_{12}H_{13}O_2N_3ClS$  required: N, 14.11%, found: N, 13.78%.

$\beta$ -(*p*-chlorobenzenesulphonamido)-propionic acid

The above nitrile (1 g.) was refluxed with a solution of sodium hydroxide (2 g.) in water (15 ml.) for twenty hours on a sand-bath. The reaction mixture was acidified and extracted with ether. The ether was evaporated off, and the solid left was recrystallised from hot water in crystals, m. p. 155°–156°. Yield, 0.5 g. (62% of theory).

Neutralisation equivalent: required, 263.56, found, 261.54.

*N,N*-bis-(2-cyanoethyl)-*p*-bromobenzenesulphonamide

Acrylonitrile (1 g.) was added to a well stirred mixture of *p*-bromobenzenesulphonamide (2 g.), dioxane (10 ml.) and benzyltrimethylammonium hydroxide (0.5 g.). A white solid was obtained by following the above procedure. It was recrystallised from ethanol in crystals, m. p. 133°. Yield, 2 g. (66% of theory).

$C_{12}H_{12}O_2N_3BrS$  required: N, 12.27%, found: N, 12.68%.

$\beta$ -(*p*-bromobenzenesulphonamido)-propionic acid

0.5 g. of the above nitrile was refluxed on a sand-bath with a solution of sodium hydroxide (1 g.) in water (10 ml.) for fifteen hours. The solution was cooled and acidified. A brownish solid precipitated and had a m. p. 149°–151°. It was recrystallised from water m. p. 154°–155°. Yield, 0.3 g. (38% of theory).

Neutralisation equivalent: required, 308.06, found, 306.88.

*N,N*-bis-(2-cyanoethyl)-*p*-toluenesulphonamide

To a stirred solution of *p*-toluene sulphonamide (3 g.), dioxane (10 ml.) and benzyltrimethylammonium hydroxide (0.5 g.) was added dropwise acrylonitrile (2 g.). The mixture was stirred for fortyeight hours and the product isolated as above. The white solid was recrystallised from ethanol in white needles, m. p. 105°–106°. Yield, 4.2 g. (88% of theory).

$C_{13}H_{15}O_2N_3S$  required: N, 15.15%, found: N, 14.72%.

## N,N-bis-(2-cyanoethyl)-p-ethylbenzenesulphonamide

Acrylonitrile (2.8 g.) was added dropwise to a stirred mixture of p-ethylbenzenesulphonamide (3 g.), dioxane (10 ml.) and benzyltrimethylammoniumhydroxide (0.5 g.). The mixture was stirred at room temperature for forty-eight hours and isolated as above. The white solid was recrystallised from ethanol in white needles, m. p. 75°–76°. Yield, 4.5 g. (80% of theory).

$C_{14}H_{17}O_2N_3S$  required: N, 14.43%, found: N, 14.22%.

## N-methyl-N-(2-cyanoethyl)-p-toluene sulphonamide

To a stirred solution of p-toluene-N-methylsulphonamide (2.5 g.) dioxane (10 ml.) and benzyltrimethylammoniumhydroxide (0.5 g.) was added dropwise freshly distilled acrylonitrile (1.3 g.). The reaction mixture was stirred for forty-eight hours at room temperature. The white solid was isolated as above. It was recrystallised from ethanol in white needles, m. p. 105°–106°. Yield, 2.4 g. (87% of theory).

$C_{11}H_{14}O_2N_2S$  required: N, 11.76%, found: N, 11.27%.

 $\beta$ -(p-toluene-N-methylsulphonamido)-propionic acid

The above nitrile (1 g.) was refluxed with a solution of sodium hydroxide (2 g.) in water (15 ml.) for twenty hours on a sand-bath. It was cooled, acidified and extracted with ether. The ether layer was washed with water, dried and the ether distilled off. The residual oil solidified when rubbed with alcohol. It was recrystallised from ethanol. M. p. 73°–74°. Yield, 0.6 g. (60% of theory).

Neutralisation equivalent: required, 257.06, found, 254.84.

N,N-bis-(2-cyanoethyl)- $\alpha$ -naphthalenesulphonamide

$\alpha$ -Naphthalene sulphonamide (3 g.), dioxane (15 ml.) and 40% benzyltrimethylammonium hydroxide (0.5 g.) were stirred together at room temperature till a clear solution was obtained, and acrylonitrile (1.5 g.) added dropwise. The reaction mixture was stirred at room temperature for forty-eight hours, acidified with hydrochloric acid, poured on ice and extracted with ethylene dichloride. The ethylene dichloride layer was separated, washed with water and dried over calcium chloride. The solvent was evaporated off, a drop of ethanol added to the residue and it was allowed to stand in a vacuum desiccator for a few days. The crystals thus obtained were recrystallised from ethanol, m. p. 120°–121°. Yield, 3 g. (66% of theory).

$C_{16}H_{15}O_2N_3S$  required: N, 13.04%, found: N, 12.64%.

N,N-bis-(2-cyanoethyl)- $\beta$ -naphthalenesulphonamide

To a stirred solution of  $\beta$ -naphthalene sulphonamide (3 g.), dioxane (20 ml.) and benzyltrimethylammoniumhydroxide (0.5 g.) was added slowly and dropwise acrylonitrile (1.5 g.). The mixture was stirred at room temperature for forty-eight hours and neutralised with dilute hydrochloric acid. The solid obtained was recrystallised from ethanol in white needles, m. p. 109°–110°. Yield, 3.5 g. (78% of theory).

$C_{15}H_{15}O_2N_3S$  required: N, 13.04%, found: N, 13.38%.

$\beta$ -( $\beta$ -naphthalenesulphonamido)-propionic acid

The above dinitrile (1 g.) and sodium hydroxide (2 g.) in water (20 ml.) were refluxed together on a sand-bath for twenty hours. The solution was cooled, neutralised with dilute hydrochloric acid and extracted with nitromethane. The solid obtained on evaporating the nitromethane was recrystallised from dilute ethanol in white crystals, m. p. 134°–135°. Yield, 0.5 g. (56% of theory).

Neutralisation equivalent: required, 279.06, found, 276.68.

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