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## TRANSFORMATIONS OF BROMODICHLOROMETHYL-4-CHLOROPHENYL SULFONE INTO NEW COMPOUNDS WITH POTENTIAL PESTICIDAL ACTIVITY

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The synthesis of bromodichloromethyl-4-chlorophenyl sulfone derivatives as new potential pesticides is reported. The title sulfone was obtained in the four-step synthesis, starting from 4-chlorobenzene. It was chlorosulfonated, reduced to the sulfinyl salt, which was transformed into 4-chlorophenyldichloromethyl sulfone, and in the next step it was brominated by bromine chloride to the title compound. Bromodichloromethyl-4-chlorophenyl sulfone was nitrated and then subjected to the  $S_NAr$  reaction with amines and hydrazine to give 2-nitroaniline and 2-nitrophenylhydrazine derivatives. The last ones were transformed into hydrazone and benzotriazole derivatives. Characteristic IR spectroscopic data and microelementary analyses of the new products are reported.

**Key words:** bromine chloride, bromodichloromethylphenyl sulfone derivatives,  $S_NAr$  reaction, 2-nitroaniline and phenylhydrazone derivatives, pesticides

### INTRODUCTION

Many aromatic compounds bearing halogenomethylsulfonyl groups exhibit herbicidal and fungicidal activity [1–6]. It was also proved by our previous investigations, that the chloromethylsulfonyl groups in some nitroaniline and benzimidazole derivatives were favorable to pesticidal activity [7,8]. Some 2-nitroaniline derivatives as herbicides are well known and commonly applied [9].

It was interesting to synthesize some new derivatives bearing bromodichloromethylsulfonyl group in the aromatic ring, in order to test their pesticidal activity, *i.e.* to determine the influence of this group on the range and the intensity of this activity. Many synthesized bromodichloromethyl-4-chlorophenyl sulfone derivatives evaluated in screening tests are very promising fungicides.

### EXPERIMENTAL

All melting points were uncorrected. Elemental microanalyses were obtained by means of a Perkin Elmer 2400 apparatus. IR spectra were recorded in paraffin oil on a Specord M80 Zeiss Jena spectrophotometer.

**Bromodichloromethyl-4-chlorophenylsulfone, 5**

To the solution of potassium hydroxide (2.8 g, 0.05 mol) in methanol (30 mL) chlorophenyl-4 dichloromethyl sulfone (2.6 g, 0.01 mol) was added. The mixture was stirred and cooled below 20°C, then bromine chloride (3 g, 50% solution in carbon tetrachloride) was added dropwise. The mixture was stirred at room temperature for one hour, and the precipitate was filtered off, washed with hexane and dried. Product **5** was obtained in 96.5% yield (3.3 g, m.p. = 153–155°C. IR (cm<sup>-1</sup>) 1590 (CH<sub>ar</sub>), 1330, 1125 (SO<sub>2</sub>), <sup>1</sup>H-NMR, 400MHz, (CDCl<sub>3</sub>): 7.60–7.66 m. (2H) 7.96–8.03 m (2H). Analysis: for C<sub>7</sub>H<sub>4</sub>BrCl<sub>2</sub>O<sub>2</sub>S (338.43) – Calcd.: 24.84%C, 1.18% H, Found: 24.78%C, 1.24% H.

**Bromodichloromethyl-4-chloro-3-nitrophenylsulfone, 6**

Sulfone **5** (0.02 mol) was dissolved in concentrated sulfuric acid (25 mL). The mixture was heated to 60°C and concentrated nitric acid (1.58 g, 0.025 mol) was slowly added, not to increase temperature over 70°C. The mixture was stirred and heated to 80°C for 2 hours, and after cooling it was poured onto ice. The precipitate was filtered, washed with water and dried. Product **6** obtained in 94% yield was crystallized from 2-propanol, m.p. = 164–165°C.

**4-Bromodichloromethylsulfonyl-2-nitrophenylamine derivatives, 7–37**

*Method A:* Nitrosulfone **6** (0.01 mol), appropriate aliphatic amine (0.01 mol) and potassium carbonate (2 g) were added to benzene (30 mL). The mixture was refluxed for 6 hours. After cooling to the room temperature, ether (50 mL) was added. The ethereal solution was washed with: 10% solution of hydrochloric acid, saturated solution of sodium hydrogen carbonate and water. The organic layer was dried over anhydrous magnesium sulfate and the solvents were evaporated. The crude product was crystallized from 2-propanol.

*Method B:* Nitrosulfone **6** (0.01 mol), appropriate aromatic amine (0.01 mol) and triethylamine (0.01 mol) were dissolved in ethanol (25 mL). The mixture was refluxed for 6 hours. After cooling ethanol was evaporated from the reaction mixture and precipitate was dissolved in dichloromethane (40 mL). The solution was washed with: 10% solution of hydrochloric acid, water, saturated solution of sodium hydrogen carbonate and water. The organic layer was dried over anhydrous magnesium sulfate, then dichloromethane was evaporated and product crystallized from 2-propanol.

**4-Bromodichloromethylsulfonyl-2-nitrophenylhydrazine, 8**

Nitrosulfone **6** (0.01 mol) and triethylamine (0.01 mol) was dissolved in tetrahydrofuran (15 mL). The solution was stirred and 40% solution of hydrazine hydrate (1.5 mL) was slowly added, kipping temperature 20°C. The solution was stirred by 1.5 hours in room temperature. The solvent was evaporated and the precipitate was dissolved in dichloromethane (50 mL). The mixture was washed with: 10% solution of hydrochloric acid, water, saturated solution of sodium hydrogen carbonate and water. The organic layer was dried over anhydrous magnesium sulfate, then dichloromethane was evaporated and the crude product (yield 98.5%) was crystallized from ethanol, (m.p. = 199–201°C).

**4-Bromodichloromethylsulfonyl-2-nitrophenylhydrazone derivatives, 38–52**

To the solution of 4-bromodichloromethylsulfonyl-2-nitrophenylhydrazine **8** (0.01 mol) in dioxane (15 mL) concentrated sulfuric acid (0.2 mL) was dropped. The mixture was stirred for a few minutes at room temperature and appropriate ketone or aldehyde (0.01 mol) was added. After stirring for half an hour, the precipitate was filtered, washed with water to the pH = 7, dried and crystallized from 2-propanol.

**6-Bromodichloromethylsulfonyl-1-hydroxybenzotriazole, 53**

Nitrosulfone **6** (0.01 mol) was dissolved in ethanol (27 mL). The solution was heated to 40°C and 80% solution of hydrazine hydrate in water (6.5 mL) was added. The mixture was refluxed for 4 hours. The solvent was evaporated and 20% solution of hydrochloric acid was added slowly into the precipitate. Product was separated, washed with water, dried and purified by crystallization from 2-propanol. (Yield – 76%, m.p. = 199–201°C with decomposition).

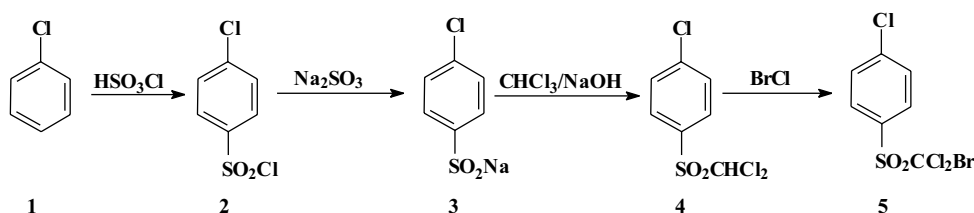
IR ( $\text{cm}^{-1}$ ) 3390 OH, 1615  $\text{C}=\text{C}_{\text{ar}}$ , 1345  $\text{SO}_{2\text{as}}$ , 1155  $\text{SO}_{2\text{sym}}$ .

Analysis: for  $\text{C}_7\text{H}_4\text{BrCl}_2\text{N}_3\text{O}_3\text{S}$  (361.00); Calcd. 23.29% C, 1.10% H, 11.64% N.

Found 23.32% C, 1.22% H, 11.55% N.

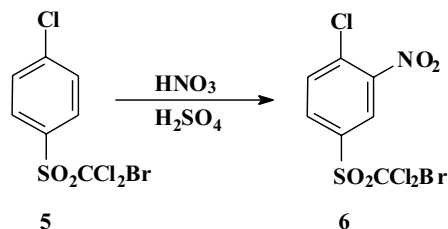
## RESULTS

Bromodichloromethyl-4-chlorophenyl sulfone **5** was obtained by four-step synthesis, according to the following scheme:

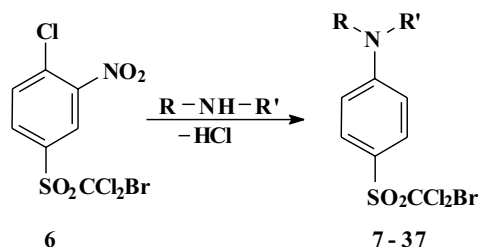


The starting compound – chlorobenzene **1** was chlorosulfonated with chlorosulfonic acid, obtained 4-chlorobenzenesulfochloride **2** was transformed into sodium salt of 4-chlorophenylsulfonic acid **3** by alkaline reduction with sodium sulfite [10]. Sulfinate **3** was converted into dichloromethyl-4-chlorophenyl sulfone **4** by two phase reaction with chloroform in alkaline solution [11]. Obtained sulfone **4** was brominated by bromine chloride freshly prepared from bromine and chlorine as 50% solution in carbon tetrachloride [12]. The bromination process was carried out in methanolic or carbon tetrachloride solution in the presence of potassium hydroxide at room temperature for 1–2 hours. Bromodichloromethyl-4-chlorophenyl sulfone **5** was isolated in over 96% yield. It was very pure and crystallization was not necessary.

Obtained sulfone **5** was converted into 2-nitroderivative applying the mixture of concentrated sulfuric acid and nitric acid [13]. The process was carried out in temperature 80°C for 2 hours. Product **6** was obtained in 94% yield:



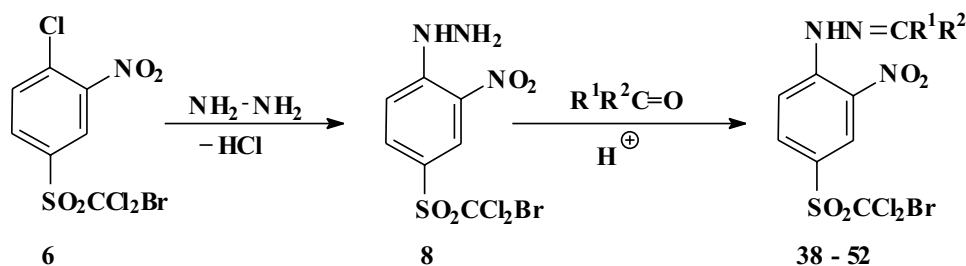
Bromodichloromethyl-4-chloro-3-nitrophenylsulfone was subjected to the aromatic substitution in reactions ( $S_NAr$ ) with amines to give 2-nitroaniline derivatives:



Various amines, *i.e.* primary, secondary, aliphatic, aromatic and heterocyclic were used. Reactions with aliphatic amines were carried out in a benzene solution with potassium carbonate as acceptor of hydrogen chloride (method A). Reactions with aromatic amines were carried out in ethanol and triethylamine as acceptor of hydrogen chloride was added (method B) [14–16]. The mixture of substrates was refluxed for 3–6 hours. Products 7–38 were crystallized from 2-propanol.

Properties and yields of 4-bromodichloromethylsulfonyl-2-nitroaniline derivatives 7–38 are collected in Table 1.

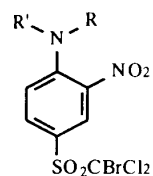
Bromodichloromethyl-4-chloro-3-nitrophenylsulfone 6 was converted with hydrazine hydrate to 4-bromodichloromethylsulfonyl-2-nitrophenylhydrazine 8, which was subjected to the reaction with ketones and aldehydes to give phenylhydrazone derivatives 38–52.



Reaction with 40% solution of hydrazine hydrate was carried out in tetrahydrofuran solution with triethylamine as acceptor of hydrogen chloride. The mixture of substrates was refluxed for one and half an hour to give product with almost quantitative yield. The reactions of phenylhydrazine 8 with ketones and aldehydes were carried out in dioxane at room temperature by stirring substrates for half an hour. Colorless products, yellow or orange were obtained in high yields.

Properties and yields of phenylhydrazone derivatives 38–52 were collected in Table 2.

Table 1. Properties and yields of 4-bromodichloromethylsulfonyl-2-nitroaniline derivatives 7–37.



Comp. No.	R'-N-R	Mol. formula	(Mol.Wt.) [g/mol]	M.P. [°C]	Yield [%]	Elemental analyses						$\nu_{IR}$ [cm <sup>-1</sup> ]
						Calcd.			Found			
						% C	% H	% N	% C	% H	% N	
7	NH <sub>2</sub>	C <sub>7</sub> H <sub>6</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	363.99	213–15	88	23.10	1.38	7.70	23.08	1.42	7.66	NO <sub>2</sub> 1520, 1370 SO <sub>2</sub> 1355, 1135 NH <sub>2</sub> 3230, 3260
8	NH-NH <sub>2</sub>	C <sub>7</sub> H <sub>7</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	380.02	199–201	98.5	22.12	1.86	11.06	22.10	1.90	11.02	NO <sub>2</sub> 1550, 1365 SO <sub>2</sub> 1325, 1150 NH <sub>2</sub> 3350, 3280
9	N(CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	C <sub>13</sub> H <sub>13</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	444.12	164–6	76	35.16	2.95	6.31	35.24	3.04	6.26	NO <sub>2</sub> 1515, 1355 SO <sub>2</sub> 1340, 1165 C=CH <sub>2</sub> 1660
10	N(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	C <sub>15</sub> H <sub>21</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	476.21	123–5	88	37.83	4.44	5.88	37.87	4.52	5.94	NO <sub>2</sub> 1520, 1350 SO <sub>2</sub> 1345, 1150
11	N(C <sub>4</sub> H <sub>9</sub> -iso) <sub>2</sub>	C <sub>15</sub> H <sub>21</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	476.21	99–101	93	37.83	4.44	5.88	37.89	4.50	5.95	NO <sub>2</sub> 1515, 1370 SO <sub>2</sub> 1340, 1150
12	NH-CH <sub>2</sub> -CH <sub>2</sub> -OH	C <sub>9</sub> H <sub>9</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>5</sub> S	408.05	186–8	67	26.49	2.22	6.87	26.53	2.32	6.85	NO <sub>2</sub> 1535, 1365 SO <sub>2</sub> 1345, 1155 NH 3250 OH 3350
13	NH-CH <sub>2</sub> -C <sub>3</sub> H <sub>5</sub> -cyclo	C <sub>11</sub> H <sub>11</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	418.08	184–6	94	31.60	2.65	6.70	31.65	2.70	6.74	NO <sub>2</sub> 1550, 1360 SO <sub>2</sub> 1345, 1150 NH 3260




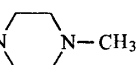
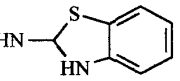
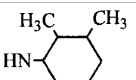
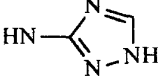
Table 1 (continuation)												
14	NH-C <sub>5</sub> H <sub>9</sub> -cyclo	C <sub>12</sub> H <sub>12</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	431.10	160–2	88	33.43	2.81	6.50	33.45	2.85	6.46	NO <sub>2</sub> 1515, 1365 SO <sub>2</sub> 1340, 1150 NH 3220
15		C <sub>11</sub> H <sub>11</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	434.08	210–12	97	30.44	2.55	6.45	30.46	2.62	6.50	NO <sub>2</sub> 1520, 1370 SO <sub>2</sub> 1335, 1160
16		C <sub>11</sub> H <sub>11</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	418.08	172–4	96	31.60	2.65	6.70	31.62	2.68	6.75	NO <sub>2</sub> 1530, 1365 SO <sub>2</sub> 1335, 1155
17	NH-C <sub>6</sub> H <sub>11</sub> -cyclo	C <sub>13</sub> H <sub>15</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	446.14	192–4	92	35.00	3.39	6.28	35.10	3.42	6.22	NO <sub>2</sub> 1515, 1375 SO <sub>2</sub> 1345, 1160 NH 3345
18		C <sub>10</sub> H <sub>6</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	415.04	145–7	63	28.94	1.46	10.12	28.96	1.49	10.09	NO <sub>2</sub> 1525, 1365 SO <sub>2</sub> 1355, 1170
19		C <sub>12</sub> H <sub>14</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>5</sub> S	447.13	165–7	81	32.23	3.16	9.40	32.15	3.10	9.48	NO <sub>2</sub> 1525, 1360 SO <sub>2</sub> 1350, 1145
20		C <sub>12</sub> H <sub>10</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	499.18	162–4	78	33.69	2.02	8.42	33.72	2.06	8.38	NO <sub>2</sub> 1530, 1370 SO <sub>2</sub> 1340, 1165 NH 3220, 3260
21		C <sub>15</sub> H <sub>19</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	474.19	170–2	81	37.99	4.04	5.91	40.03	4.00	5.86	NO <sub>2</sub> 1530, 1355 SO <sub>2</sub> 1360, 1145 NH 3260
22		C <sub>9</sub> H <sub>6</sub> BrCl <sub>2</sub> N <sub>5</sub> O <sub>4</sub> S	431.04	167–9	73	25.08	1.40	16.25	25.1	1.45	16.31	NO <sub>2</sub> 1530, 1345 SO <sub>2</sub> 1375, 1140 NH 3220, 3250

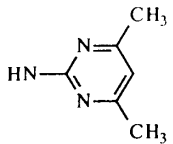
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23		$C_{13}H_{11}BrCl_2N_4O_4S$	470.12	135-6	87	33.213	2.36	11.92	33.18	2.32	11.89	NO <sub>2</sub> 1540, 1375 SO <sub>2</sub> 1350, 1155 NH 3300
24	HN-CH <sub>2</sub> -CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	$C_{15}H_{13}BrCl_2N_2O_4S$	468.14	186-7	83	38.48	2.80	5.98	38.4	2.75	6.02	NO <sub>2</sub> 1515, 1370 SO <sub>2</sub> 1360, 1140 NH 3265
25	HN-CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub>	$C_{14}H_{11}BrCl_2N_2O_4S$	454.12	163-5	87	37.03	2.44	6.17	37.01	2.49	6.12	NO <sub>2</sub> 1520, 1370 SO <sub>2</sub> 1340, 1150 NH 3285
26	N(CH <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	$C_{21}H_{17}BrCl_2N_2O_4S$	544.24	135-6	77	46.34	3.15	5.15	46.36	3.19	5.12	NO <sub>2</sub> 1525, 1365 SO <sub>2</sub> 1345, 1165
27	C <sub>2</sub> H <sub>5</sub> -N-C <sub>6</sub> H <sub>5</sub>	$C_{15}H_{13}BrCl_2N_2O_4S$	468.14	152-4	82	38.48	2.80	5.98	38.44	2.76	6.02	NO <sub>2</sub> 1515, 1370 SO <sub>2</sub> 1355, 1175
28	C <sub>6</sub> H <sub>5</sub> -N-CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	$C_{20}H_{15}BrCl_2N_2O_4S$	530.22	179-80	93	45.31	2.85	5.28	45.35	2.91	5.26	NO <sub>2</sub> 1525, 1375 SO <sub>2</sub> 1355, 1175
29	CH <sub>3</sub> -N-C <sub>6</sub> H <sub>5</sub>	$C_{14}H_{11}BrCl_2N_2O_4S$	454.12	143-5	88	37.03	2.44	6.17	37.01	2.47	6.14	NO <sub>2</sub> 1530, 1370 SO <sub>2</sub> 1345, 1165
30	NH-C <sub>6</sub> H <sub>4</sub> -3-CH <sub>3</sub>	$C_{14}H_{11}BrCl_2N_2O_4S$	454.12	190-2	92	37.03	2.44	6.17	37.05	2.44	6.19	NO <sub>2</sub> 1530, 1370 SO <sub>2</sub> 1355, 1165 NH 3280
31	NH-C <sub>6</sub> H <sub>4</sub> -3-Br	$C_{13}H_8Br_2Cl_2N_2O_4S$	518.99	163-4	94	30.09	1.55	5.40	30.11	1.60	5.38	NO <sub>2</sub> 1535, 1375 SO <sub>2</sub> 1360, 1165 NH 3310
32	NH-C <sub>6</sub> H <sub>3</sub> -3-NO <sub>2</sub> -4-F	$C_{13}H_7BrCl_2FN_2O_6S$	503.08	159-60	96	31.04	1.40	8.35	31.06	1.46	8.37	NO <sub>2</sub> 1520, 1355 SO <sub>2</sub> 1340, 1150 NH 2270
33	NH-C <sub>6</sub> H <sub>4</sub> -2-Br	$C_{13}H_8Br_2Cl_2N_2O_4S$	518.99	166-7	77	30.09	1.55	5.40	30.11	1.60	5.36	NO <sub>2</sub> 1535, 1370 SO <sub>2</sub> 1345, 1165 NH 3260

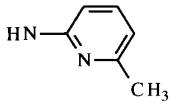
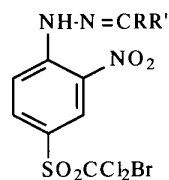
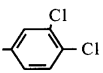
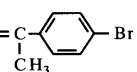
Table 1 (continuation)												
34	NH-C <sub>6</sub> H <sub>3</sub> -2,4-(CH <sub>3</sub> ) <sub>2</sub>	C <sub>15</sub> H <sub>11</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	468.14	179–81	79	38.48	2.80	5.98	38.45	2.82	6.00	NO <sub>2</sub> 1515, 1375 SO <sub>2</sub> 1355, 1170 NH 3245
35	NH-C <sub>6</sub> H <sub>5</sub> -3,5-(CF <sub>3</sub> ) <sub>2</sub>	C <sub>15</sub> H <sub>7</sub> BrCl <sub>2</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> S	576.09	143–4	89	31.27	1.22	4.86	31.31	1.26	4.91	NO <sub>2</sub> 1525, 1365 SO <sub>2</sub> 1350, 1175 NH 3260
36		C <sub>13</sub> H <sub>10</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	455.11	164–5	84	34.31	2.21	9.23	34.33	2.18	9.19	NO <sub>2</sub> 1525, 1365 SO <sub>2</sub> 1355, 1155 NH 3265
37	HN-2-naphthyl	C <sub>17</sub> H <sub>11</sub> BrCl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> S	490.15	194–5	94	41.66	2.26	5.72	41.69	2.23	5.68	NO <sub>2</sub> 1525, 1360 SO <sub>2</sub> 1355, 1165 NH 3210



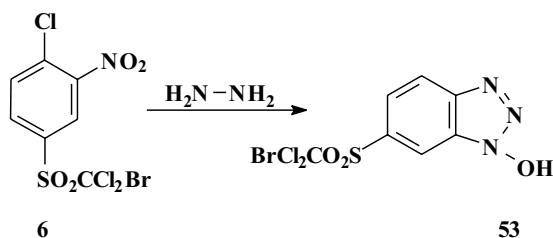
Table 2. Properties and yields of 4-bromodichloromethylsulfonyl-2-nitrophenylhydrazone derivatives 38–52.



Comp. No.	HN-N=CRR'	Mol. formula	(Mol.Wt.) [g/mol]	M.P. [°C]	Yield [%]	Elemental analyses						$\nu_{IR}$ [cm <sup>-1</sup> ]
						Calcd.			Found			
						% C	% H	% N	% C	% H	% N	
38	NH-N-CH <sub>2</sub>	C <sub>18</sub> H <sub>6</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	391.02	184–5	96	24.57	1.55	10.75	24.63	1.62	10.70	NO <sub>2</sub> 1520, 1350 SO <sub>2</sub> 1365, 1140 NH 3280
39	NH-N=C(CH <sub>3</sub> ) <sub>2</sub>	C <sub>10</sub> H <sub>10</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	419.07	193–5	98.5	28.66	2.41	10.03	28.71	2.40	10.05	NO <sub>2</sub> 1560, 1365 SO <sub>2</sub> 1315, 1155 NH 3285
40	HN-N=CH-CH-CH-CH <sub>3</sub>	C <sub>11</sub> H <sub>10</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	431.08	205–6	78	30.65	2.34	9.75	30.72	2.29	9.78	NO <sub>2</sub> 1525, 1355 SO <sub>2</sub> 1340, 1160 NH 3310
41	HN-N=CH-CH-CH-C <sub>6</sub> H <sub>5</sub>	C <sub>16</sub> H <sub>12</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	493.15	239–40	89	38.97	2.45	8.52	38.95	2.37	8.48	NO <sub>2</sub> 1510, 1350 SO <sub>2</sub> 1355, 1160 NH 3295
42	HN-N=CH- 	C <sub>15</sub> H <sub>11</sub> Br <sub>2</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	536.01	276–7	82	31.37	1.50	7.84	31.42	1.45	7.92	NO <sub>2</sub> 1525, 1360 SO <sub>2</sub> 1340, 1165 NH 3280
43	HN-N=C(  CH <sub>3</sub> )	C <sub>15</sub> H <sub>8</sub> BrCl <sub>4</sub> N <sub>3</sub> O <sub>5</sub> S	560.04	245–6	94	32.17	1.98	7.50	32.22	2.02	7.61	NO <sub>2</sub> 1530, 1360 SO <sub>2</sub> 1345, 1160 NH 3270

44	NH-N-C <sub>6</sub> H <sub>10</sub> -cyclo	C <sub>13</sub> H <sub>11</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	459.14	189–90	88	34.01	3.07	9.15	34.08	3.02	9.08	NO <sub>2</sub> 1525, 1365 SO <sub>2</sub> 1345, 1150 NH 3280
45	NH-N=CH-CH <sub>3</sub>	C <sub>9</sub> H <sub>8</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	405.05	195–197	78	26.29	1.99	10.37	26.32	1.92	10.33	NO <sub>2</sub> 1520, 1370 SO <sub>2</sub> 1335, 1160 NH 3210
46	HN-N=C(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	C <sub>11</sub> H <sub>12</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	433.10	165–6	98	30.51	2.79	9.70	31.00	2.83	9.76	NO <sub>2</sub> 1525, 1365 SO <sub>2</sub> 1335, 1155 NH 3325
47	HN-C(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	C <sub>12</sub> H <sub>14</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	447.13	126–7	88	32.23	3.16	9.40	32.25	3.18	9.52	NO <sub>2</sub> 1515, 1375 SO <sub>2</sub> 1345, 1160 NH 3325
48	$\text{HN} - \text{N} = \text{C} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH} = \text{CH}_2 \end{array}$	C <sub>11</sub> H <sub>10</sub> Br <sub>2</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	431.08	196–8	93	30.65	2.34	9.75	30.95	2.40	9.82	NO <sub>2</sub> 1525, 1365 SO <sub>2</sub> 1355, 1170 NH 3320
49	$\text{HN} \cdot \text{N} = \text{C} \begin{array}{l} \text{CH}_3 \\   \\ \text{C} - \text{CH}_3 \\ / \quad \backslash \\ \text{CH}_3 \end{array}$	C <sub>13</sub> H <sub>16</sub> BrCl <sub>4</sub> N <sub>3</sub> O <sub>4</sub> S	461.15	137–8	94	33.86	3.50	9.11	33.92	3.57	9.18	NO <sub>2</sub> 1525, 1360 SO <sub>2</sub> 1350, 1145 NH 3310
50	HN-C(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	C <sub>16</sub> H <sub>22</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	503.23	93–4	87	38.19	4.41	8.35	38.27	4.48	8.38	NO <sub>2</sub> 1530, 1370 SO <sub>2</sub> 1340, 1165 NH 3330
51	$\text{NH} \cdot \text{N} = \text{CH} - \text{C}_6\text{H}_4\text{Cl}$	C <sub>14</sub> H <sub>9</sub> BrCl <sub>3</sub> N <sub>3</sub> O <sub>4</sub> S	501.56	274–5	93	33.53	1.81	8.38	33.70	1.92	8.43	NO <sub>2</sub> 1530, 1350 SO <sub>2</sub> 1375, 1140 NH 3260
52	$\text{HN} \cdot \text{N} = \text{C} \begin{array}{l} \text{CH}_3 \\   \\ \text{C} - \text{CH}_2 - \text{C}_6\text{H}_5 \end{array}$	C <sub>16</sub> H <sub>14</sub> BrCl <sub>2</sub> N <sub>3</sub> O <sub>4</sub> S	495.17	177–8	87	38.81	2.85	8.49	38.87	2.90	8.44	NO <sub>2</sub> 1535, 1375 SO <sub>2</sub> 1350, 1155 NH 3300

Bromodichloromethyl-4-chloro-3-nitrophenylsulfone was transformed also into 6-bromodichloromethylsulfonyl-1-hydroxybenzotriazole **53** according to the following scheme:



Synthesis conditions of benzotriazole **53** were quite different from synthesis of phenylhydrazine **8**. Much more concentrated and bigger excess of hydrazine hydrate was applied. The first stage of one pot synthesis of benzotriazole **53** was nucleophilic substitution of chlorine atom by hydrazine and other one – cyclization combined with reduction of nitro group.

Reaction was carried out in ethanol at boiling temperature for 4 hours, according to the method [17]. Obtained 1-hydroxybenzotriazole derivative was purified by crystallization from 2-propanol.

All compounds **7–53** were tested for their fungicidal and herbicidal activity. The results of these investigations will be published elsewhere.

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