

**SYNTHESIS OF N-SUBSTITUTED 3-ISOPROPYL-1H-2,1,3-BENZOTHIADIAZIN-(4)-3H-ONE 2,2-DIOXIDE DERIVATIVES**

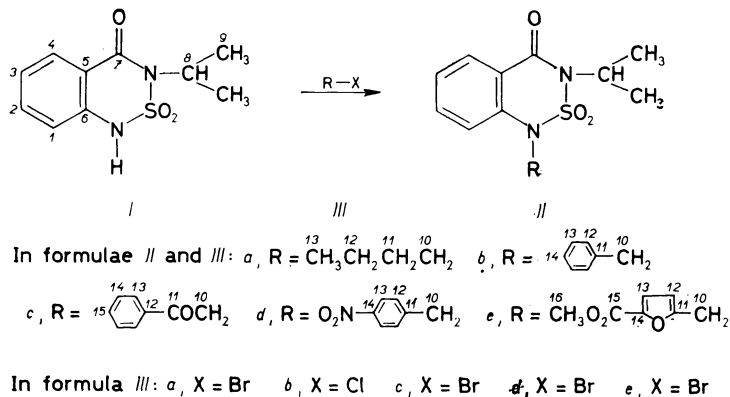
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Bentazone (*I*, 3-isopropyl-1H-2,1,3-benzothiadiazin-(4)-3H-one 2,2-dioxide<sup>1</sup>) is used as a postemergent herbicide (0.1–0.3 mg/m<sup>2</sup>) for protection of agricultural plants against annual broad-leaved weeds. The compound *I* inhibits photosystem *II* in weeds but it also has cytogenetic effects and a negative influence on soil microorganisms, enzymes and pH and is therefore regarded as an environmental contaminant<sup>2</sup>. In the present communication we describe the synthesis of N-substituted bentazone derivatives *Ila–Ile* (Scheme 1, Table I) as new compounds of potential algicidal activity.



SCHEME 1

In preliminary tests compound *IId* exhibited good algicidal activity against the alga *Scenedesmus quadricauda*. The alkylation reactions were performed with benzyl chloride (*IIIb*) and the corresponding alkyl bromides (*IIIa*, *IIIc–IIIe*), using the described<sup>3,4</sup> alkylation method. The derivatives *Ila–Ile* were identified by <sup>1</sup>H and <sup>13</sup>C NMR spectra as well as by elemental analysis. Chemical shifts in the <sup>13</sup>C NMR spectra of derivatives *IId* and *Ile* were assigned on the basis of the pu-

blished data<sup>5-7</sup> for analogous compounds. Compound *I* was characterized also by mass spectrometry.

### EXPERIMENTAL

The melting points were measured on a Kofler block and are uncorrected. <sup>1</sup>H NMR spectra ( $\delta$ , ppm; *J*, Hz) were measured at 28°C with tetramethylsilane as internal standard.

#### 3-Isopropyl-1*H*-2,1,3-benzothiadiazin-(4)-3*H*-one 2,2-Dioxide (*I*)

Pure bentazone, used in the experiments, was obtained from a commercial sample of Basagran (BASF) by acid precipitation and two crystallizations from ethanol; m.p. 135–136°C (reported<sup>8</sup> m.p. 135–136°C). <sup>1</sup>H NMR spectrum (hexadeuterodimethyl sulfoxide): 1.51 d, 6 H ((CH<sub>3</sub>)<sub>2</sub>CH, *J* = 6.84); 4.90 heptet, 1 H (CH=); 8.09–7.13 m, 4 H (arom.); 8.78 s, 1 H (NH). <sup>13</sup>C NMR spectrum (hexadeuterodimethyl sulfoxide): 130.5; 125.3; 120.9 (C-1, C-3, C-4); 135.1 (C-2); 118.7 (C-5); 137.7 (C-6); 162.1 (C-7); 47.9 (C-8); 20.5 (C-9). Mass spectrum, *m/z* (rel. intensity, %): 242 (2, *M* + 2), 241 (4, *M* + 1), 240 (32, *M*<sup>+</sup>), 225 (26), 199 (17), 198 (96), 182 (26), 161 (23), 120 (29), 119 (100), 118 (15), 92 (32), 91 (12), 90 (11), 64 (17).

#### Preparation of Sulfones *Ia–Ie*

A mixture of bentazone (*I*, 2.4 g; 0.01 mol), potassium carbonate (5.8 g; 0.042 mol) and acetonitrile (50 ml) was refluxed in a 100 ml flask for 20 min and then the alkylation reagent (RX;

TABLE I  
N-Substituted bentazone derivatives *Ia–Ie*

Compound Yield, %	Formula (M.w.)	M.p., °C Solvent	Calculated/Found		
			% C	% H	% N
<i>Ia</i> 69	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> SO <sub>3</sub> (296.3)	125–127 a	56.75 56.68	3.40 3.37	9.46 9.41
<i>Ib</i> 52	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> SO <sub>3</sub> (330.4)	88–89 methanol	61.79 61.86	5.49 5.45	8.48 8.53
<i>Ic</i> 75	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> SO <sub>4</sub> (358.5)	139–141 acetone	60.30 60.38	5.06 4.98	7.82 7.90
<i>IId</i> 89	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> SO <sub>5</sub> (375.5)	116–118 acetone	54.37 54.40	4.56 4.53	11.19 11.21
<i>Ile</i> 79	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> SO <sub>6</sub> (378.5)	130–133 acetone	53.94 54.02	4.79 4.81	7.40 7.46

<sup>a</sup> Crude product was purified on a column of Al<sub>2</sub>O<sub>3</sub> (benzene–acetone 9 : 1) and crystallized from acetone.

0.01–0.02 mol) was added. After 5 h the crude product was filtered and purified by crystallization (charcoal) or on a column of alumina (Brockman II).

*Ila*:  $^1\text{H}$  NMR spectrum (hexadeuterodimethyl sulfoxide): 0.91 t, 3 H ( $\text{CH}_3\text{CH}_2$ ); 1.24 d, 4 H ( $\text{CH}_2\text{CH}_2$ ); 1.56 d, 6 H ( $(\text{CH}_3)_2\text{CH}$ ); 3.94 t, 2 H ( $\text{CH}_2$ ); 5.01 septet, 1 H ( $\text{CH}=\text{}$ ); 8.17–7.39 m, 4 H (arom.).  $^{13}\text{C}$  NMR spectrum (hexadeuterodimethyl sulfoxide): 141.4, 135.7, 130.7, 126.7, 122.8, 121.2 (C-1–C-6); 163.0 (C-7); 49.7 (C-8); 20.8 (C-9); 52.7 (C-10); 26.0 (C-11, C-12); 13.8 (C-13).

*Ilb*:  $^1\text{H}$  NMR spectrum (hexadeuterodimethyl sulfoxide): 1.24 d, 6 H ( $(\text{CH}_3)_2\text{CH}$ ); 4.88 septet, 1 H ( $\text{CH}=\text{}$ ); 5.11 s, 2 H ( $\text{CH}_2$ ); 7.27 s, 5 H (benzyl); 8.12–7.35 m, 4 H (arom.).  $^{13}\text{C}$  NMR spectrum (deuteriochloroform): 121.8, 123.3, 126.1, 128.2, 128.4, 128.8, 130.3, 134.4, 140.1 (C-1–C-6, C-11–C-14); 162.3 (C-7); 49.3 (C-8); 20.5 (C-9); 55.9 (C-10).

*Ilc*:  $^1\text{H}$  NMR spectrum (hexadeuteroacetone): 1.03 d, 6 H ( $(\text{CH}_3)_2\text{CH}$ ); 4.49 septet, 1 H ( $\text{CH}=\text{}$ ); 5.37 s, 2 H ( $\text{CH}_2$ ); 7.18 s, 5 H (benzoyl); 7.81–6.90 m, 4 H (arom.).  $^{13}\text{C}$  NMR spectrum (hexadeuteroacetone): 120.8, 122.2, 125.5, 129.4, 134.8, 133.7 (C-1–C-6); 161.7 (C-7); 48.7 (C-8); 20.2 (C-9); 56.8 (C-10); 193.3 (C-11); 128.1, 128.9, 134.2, 140.1 (C-12–C-15).

*Ild*:  $^1\text{H}$  NMR spectrum (hexadeuteroacetone): 1.42 d, 6 H ( $(\text{CH}_3)_2\text{CH}$ ); 4.85 septet, 1 H ( $\text{CH}=\text{}$ ); 5.27 s, 2 H ( $\text{CH}_2$ ); 7.50 d, 2 H (nitrobenzyl,  $J = 8.0$ ); 8.22 d, 2 H (nitrobenzyl); 8.08 to 7.35 m, 4 H (arom.).  $^{13}\text{C}$  NMR spectrum (hexadeuteroacetone): 122.24 (C-1); 135.51, 130.35, 126.73 (C-2–C-4); 123.03 (C-5); 140.39 (C-6); 162.22 (C-7); 49.54 (C-8); 20.38 (C-9); 54.66 (C-10); 143.28 (C-11); 129.58 (C-12); 124.15 (C-13); 148.18 (C-14).

*Ile*:  $^1\text{H}$  NMR spectrum (hexadeuteroacetone): 0.99 d, 6 H ( $\text{CH}_3)_2\text{CH}$ ); 4.41 septet, 1 H ( $\text{CH}=\text{}$ ); 4.78 s, 2 H ( $\text{CH}_2$ ); 3.31 s, 3 H ( $\text{CO}_2\text{CH}_3$ ); 5.96 d, 1 H (H-3 furan,  $J(3, 4) = 3.5$ ); 6.72 d, 1 H (H-4 furan); 7.62–6.96 m, 4 H (arom.).  $^{13}\text{C}$  NMR spectrum (hexadeuteroacetone): 122.7, 23.0, 126.8, 129.4, 135.0, 138.8 (C-1–C-6); 161.4 (C-7); 48.7 (C-8); 20.2 (C-9); 48.0 (C-10), 143.8 (C-11); 118.8 (C-12); 112.6 (C-13); 152.3 (C-14); 157.8 (C-15); 51.7 (C-16).

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