

SHORT  
COMMUNICATIONS

## Dimethyldioxirane as a New Reagent for the Synthesis of Benzoxazines

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Received July 11, 2001

*o*-(1-Alkenyl)anilides readily react with HCl [1] or Br<sub>2</sub> [2] (20–25°C) to give the corresponding 3,1-benzoxazines. Up to now, dimethyldioxirane (**I**), which is known as highly efficient epoxidating agent toward primary and secondary *N*-alkenylamines [3], has not been used for the preparation of 3,1-benzoxazines from such anilides.

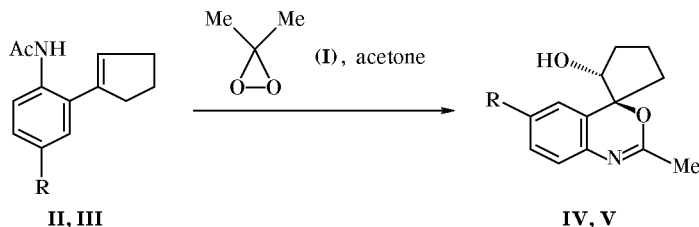
We have found that treatment of anilides **II** [4] and **III** in methylene chloride with a solution of dioxirane **I** in acetone at 20°C leads to formation of 2'-hydroxy-2-methyl-4*H*-3,1-benzoxazine-4-spirocyclopentanes **IV** [4] and **V** in quantitative yield. Analogous 4*H*-benzoxazines are formed by reaction of alkenylanilides with hydrogen peroxide in 60–80% yield [4]. The structure of heterocyclic compounds **IV** and **V** was confirmed by the data of elemental analysis and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

In the <sup>1</sup>H NMR spectrum of **IV** the 2'-H signal appears as a doublet at δ 4.0 ppm, and signal from the hydroxy proton is a doublet at δ 2.8 ppm. The <sup>13</sup>C NMR spectra of compounds **IV** and **V** contain a doublet signal from C<sup>2'</sup> at δ<sub>C</sub> 76 ppm and a singlet from C<sup>4</sup> at δ<sub>C</sub> 90 ppm. In the aliphatic region three triplets corresponding to C<sup>3'</sup>, C<sup>4'</sup>, and C<sup>5'</sup> of the cyclopentane ring were observed. Compound **V**

showed in the mass spectrum the molecular ion peak with *m/z* 231.

*N*-Acetyl-4-methyl-2-(1-cyclopentenyl)aniline (**III**) was synthesized from 4-methyl-2-(1-cyclopentenyl)aniline by the procedure described in [1]. Yield 96%, mp 89°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 1.2 t (3H, CH<sub>3</sub>, *J* = 6.1 Hz), 1.9–2.0 m (2H, CH<sub>2</sub>), 2.1 s (3H, CH<sub>3</sub>), 2.4–2.6 m (4H, 2CH<sub>2</sub>), 5.9 s (1H, =CH), 6.9–7.1 m (2H, H<sub>arom</sub>), 7.7 br.s (1H, NH), 7.9 d (1H, H<sub>arom</sub>, *J* = 8.5 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 20.7, 24.2 (2CH<sub>3</sub>); 23.2, 33.6, 36.3 (3CH<sub>2</sub>); 122.3 (C<sup>6</sup>); 127.9 (C<sup>2'</sup>); 128.2 (C<sup>3</sup>); 129.2 (C<sup>4</sup>); 129.9 (C<sup>5</sup>); 131.8 (C<sup>1'</sup>); 133.6 (C<sup>2</sup>); 140.7 (C<sup>1</sup>); 168.2 (C=O). Found, %: C 77.83; H 7.81; N 6.60. C<sub>15</sub>H<sub>19</sub>NO<sub>2</sub>. Calculated, %: C 78.10; H 7.96; N 6.51.

2'-Hydroxy-2-methyl-4*H*-3,1-benzoxazine-4-spirocyclopentanes **IV** and **V**. To a solution of 100 mg (0.5 mmol) of anilide **II** or **III** in 1 ml of CH<sub>2</sub>Cl<sub>2</sub> we added a solution of dioxirane **I** in acetone (*c* = 0.8 M) to attain a **III**-to-**I** molar ratio of 1:1.2. After 14 h, the presence of peroxide **I** in the reaction mixture was checked by iodine–starch test. The solvent was distilled off on a rotary evaporator, and pure benzoxazines **IV** and **V** were obtained in quantitative yield.



**II**, **IV**, R = H; **III**, **V**, R = Me.

**2'-Hydroxy-2,6-dimethyl-4*H*-3,1-benzoxazine-4-spirocyclopentane (V).** Yield 95%, mp 136°C. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>), δ, ppm: 1.7–2.0 m (2H, CH<sub>2</sub>), 2.0 s (3H, CH<sub>3</sub>), 2.2 s (3H, CH<sub>3</sub>), 2.1–2.2 m (2H, CH<sub>2</sub>), 2.4–2.50 m (2H, CH<sub>2</sub>), 2.8 br.s (1H, OH), 4.0 d (1H, CH, *J* = 5.6 Hz), 7.0–7.3 m (3H, H<sub>arom</sub>). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>), δ<sub>C</sub>, ppm: 21.0, 21.5 (CH<sub>3</sub>); 20.7, 31.6, 34.7 (CH<sub>2</sub>); 76.1 (CHOH); 90.5 (C<sup>4</sup>); 123.5 (C<sup>4a</sup>); 124.1 (C<sup>8</sup>); 125.8 (C<sup>5</sup>); 129.4 (C<sup>7</sup>); 135.9 (C<sup>6</sup>); 136.5 (C<sup>8a</sup>); 160.4 (C=N). *M*<sup>+</sup> 231. Found, %: C 72.31; H 7.62; N 6.56. C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub>. Calculated, %: C 72.70; H 7.41; N 6.06. *M* 231.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-300 instrument at 300.13 MHz for <sup>1</sup>H and 75.47 MHz for <sup>13</sup>C. The mass spectra were run on an MKh-1320 spectrometer (70 eV).

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