

SHORT  
COMMUNICATIONS

## 1,1-Bis(methoxycarbonyl)ethenes Containing Pyridine and Benzimidazole Fragments: Synthesis and Reactions with Nitromethane

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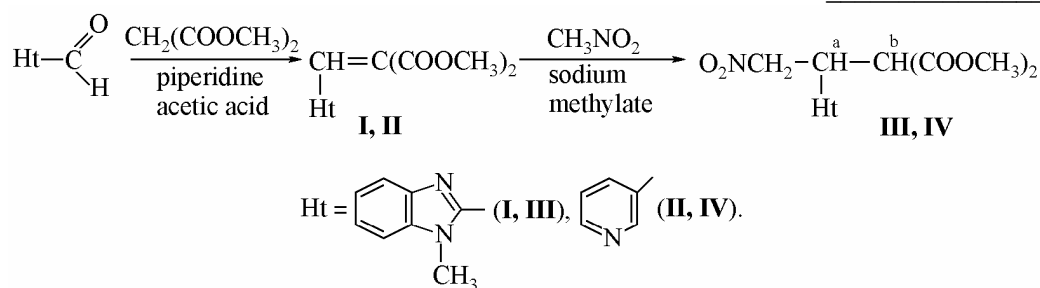
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Both pyridine and benzimidazole as pharmacophoric moieties are contained in the molecules of a number of natural substances and drugs, for instance, of Cordiamin, Dibasol, Bendamustin etc. [1–3]. As convenient synthons for preparation of potential biologically active compounds including the above heterocycles can serve 1,1-bis(alkoxycarbonyl)ethenes containing pyridine and benzimidazole fragments. These compounds possess an activated double bond. However the published procedures for preparation of 2-(3-pyridyl)- and 2-(1-methylbenzimidazol-2-

yl)bis(ethoxycarbonyl)-ethenes [4, 5] are characterized by poor reproducibility and require laborious purification of isolated products; the spectral characteristics of the latter are not reported.

We developed a convenient preparation method for previously unknown 2-methylbenzimidazol-2-yl)- and 2-(3-pyridyl)bis(methoxycarbonyl)ethenes (**I**, **II**) that consisted in the condensation of the corresponding aldehydes with dimethyl malonate in benzene in the presence of catalytic quantities of piperidine and acetic acid at 90°C.



The target bis(methoxycarbonyl)ethenes **I**, **II** were isolated in high yield and were brought into reaction with nitromethane in the presence of sodium alcoholate. As a result we obtained adducts of Michael condensation, nitroesters **III**, **IV**.

The compounds obtained **I–IV** are valuable initial reagents for preparation of organic reagents of various classes containing pyridine and benzimidazole moieties. The IR spectrum of diester **I** contains absorption bands of stretching vibrations of C=C bond

(1640 cm<sup>-1</sup>) and C=O groups (1730 cm<sup>-1</sup>); in the IR spectrum of nitroester **IV** are observed absorption bands of the stretching vibrations of nonconjugated nitro group (1375, 1560 cm<sup>-1</sup>) and ester carbonyls (1735 cm<sup>-1</sup>). In the <sup>1</sup>H NMR spectrum of compound **II** the protons of methoxy groups appear at 3.81 ppm, the protons of the pyridine ring are present as a multiplet at 7.5–8.7 ppm, and to the methine proton belongs a singlet at 7.85 ppm. In the <sup>1</sup>H NMR spectrum (δ, ppm) of compound **III** are present the following signals: 3.51 s,

3.72 s (OCH<sub>3</sub>), 3.87 s (NCH<sub>3</sub>), 4.55 m [CH<sup>a</sup>, <sup>3</sup>J(H<sup>a</sup>H<sup>b</sup>) 8.95 Hz, <sup>3</sup>J(H<sup>a</sup>CH<sub>2</sub>) 5.2 Hz, 9.4 Hz,], 4.1 d [CH<sup>b</sup>, <sup>3</sup>J(H<sup>b</sup>H<sup>a</sup>) 8.95 Hz], 4.98–5.1 m [CH<sub>2</sub>, <sup>2</sup>J(CH<sub>2</sub>) 14 Hz, <sup>3</sup>J(CH<sub>2</sub>H<sup>a</sup>) 9.4 Hz, 5.2 Hz], 7.15–7.65 (benzimidazole ring).

1-Methylbenzimidazole-2-carbaldehyde was prepared by a known procedure [6], the nicotinaldehyde was a commercial product.

**1,1-Bis(methoxycarbonyl)-2-(1-methylbenzimidazol-2-yl)ethene (I).** Into a three-neck flask equipped with a stirrer, thermometer, and a Dean-Stark trap with a reflux condenser was charged benzene (8 ml), *o*-methyl malonate (2 ml, 0.016 mol), benzimidazole-2-carbaldehyde (2.88 g, 0.018 mol), piperidine (0.07 ml, 0.0008 mol), and acetic acid (0.07 ml, 0.001 mol). The mixture was heated at stirring for 2–3 h with distilling off azeotrope benzene-water. Then the reaction mixture was cooled to obtain 4.5 g (90%) of yellow crystalline product, mp 192–194°C (from methanol). Found, %: C 61.29, 61.26; H 5.23, 5.25; N 10.35, 10.34. C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>. Calculated, %: C 61.31; H 5.11; N 10.22.

**1,1-Bis(methoxycarbonyl)-2-(3-pyridyl)ethene (II)** was obtained similarly to compound I. Yield 90%, mp 53–55°C (from benzene). Found, %: C 59.71, 59.69; H 5.70, 5.71; N 5.97, 5.99. C<sub>11</sub>H<sub>11</sub>NO<sub>4</sub>. Calculated, %: C 59.73; H 4.98; N 6.33.

**Methyl 3-(1-methylbenzimidazol-2-yl)-2-methoxycarbonyl-4-nitrobutanoate (III).** Yield 60%, mp 114–116°C (from ethanol). Found, %: C 53.75, 53.77;

H 5.10, 5.11; N 12.57, 12.61. C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>O<sub>6</sub>. Calculated, %: C 53.73; H 5.07; N 12.54.

**Methyl [2-methoxycarbonyl-4-nitro-3-(3-pyridyl)]butanoate (IV).** Yield 30%, mp 67–69°C (from methanol). Found, %: C 51.17, 51.24; H 5.24, 5.19; N 10.01, 10.03. C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub>. Calculated, %: C 51.06; H 4.96; N 9.93.

IR spectra were recorded from solutions in chloroform and mulls in mineral oil on InfraLUM FT-02 instrument. <sup>1</sup>H NMR spectra were registered on spectrometer Bruker-AC-200 (200 MHz), internal reference HMDS.

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