

Proceeding Paper

# Synthesis of Hydrazones of Strained Polycyclic Hydrocarbons, Promising Building Blocks in Organic Chemistry <sup>†</sup>

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**Abstract:** For the first time, the synthesis of unsubstituted hydrazones based on various strained polycyclic hydrocarbons, namely *exo-exo-4-exo*-acetoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane, *endo-endo-4-exo*-acetoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane and acetoxihexacyclo[9.2.1.0<sup>2,7</sup>.0<sup>3,5</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>]tetradecane, was carried out in four stages with high yields and selectivity.

**Keywords:** norbornadiene; hydrazones; strained polycyclic hydrocarbons

## 1. Introduction

Hydrazones are a large class of organic compounds, and due to their high reactivity they can act as intermediates in organic synthesis [1] or be used as independent substances in various fields of science and technology [2]. Despite significant research in the field of hydrazone chemistry, we have noted that there is no information in the literature on the synthesis of hydrazones of various strained polycyclic hydrocarbons.

In this work, we have synthesized for the first time unsubstituted hydrazones based on various strained polycyclic hydrocarbons, which are of interest as promising building blocks in organic chemistry and medicine [3]. Polycyclic hydrocarbons are the result of dimerization of norbornadiene with a wide range of unsaturated compounds under Diels-Alder reaction conditions [4–7]. Norbornadiene dimers are numerous, so we have chosen three compounds as model objects of study, as the most frequently formed and with good yields under dimerization reaction conditions, namely *exo-exo-4-exo*-acetoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>] tetradecane, *endo-endo-4-exo*-acetoxypentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>] tetradecane and acetoxihexacyclo[9.2.1.0<sup>2,7</sup>.0<sup>3,5</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>] tetradecane.

## 2. Results and Discussion

The synthesis of hydrazones **1d–3d** includes several successive stages, according to which, at the first stage, acetates **1a–3a** are formed upon boiling in acetic acid of the initial polycyclic hydrocarbons, where the three-carbon cycle of hydrogenated *exo-exo*, *endo-endo*-hexa- and heptacyclic dimers of norbornadiene undergoes acetoxylation [8]. The second stage involves saponification of esters to the corresponding alcohols **1b–3b** under the action of an alcoholic solution of potassium hydroxide [9]. The third and fourth stages involve subsequent oxidation of alcohols to ketones **1c–3c** and the introduction of a new functional group using an excess of hydrazine hydrate. In the first three stages, the yield of the final products was 85–90%. As a result, the corresponding unsubstituted hydrazones **1d–3d** were obtained from strained polycyclic hydrocarbons in quantitative yield (Scheme 1).

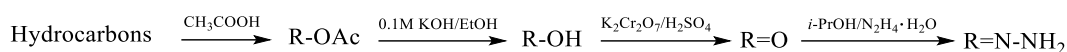
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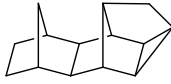
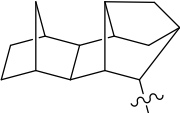

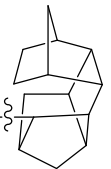

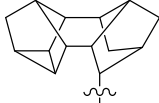
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**Scheme 1.** Synthesis of hydrazones of strained polycyclic hydrocarbons **1d–3d**.

Table 1 shows all the structural formulas of strained polycyclic hydrocarbons, with the yields indicated in parentheses.

**Table 1.** Structural formulas of hydrocarbons.

No	Hydrocarbons	R	R-OAc	R-OH	R=O	R=N-NH <sub>2</sub>
1			<b>1a</b> (90)	<b>1b</b> (90)	<b>1c</b> (90)	<b>1d</b> (~100)
2			<b>2a</b> (90)	<b>2b</b> (90)	<b>2c</b> (85)	<b>2d</b> (~100)
3			<b>3a</b> (90)	<b>3b</b> (90)	<b>3c</b> (89)	<b>3d</b> (~100)

The spectral characteristics and synthesis of compounds **1a**, **1b**, **2a**, **2b**, **3a–3c** are identical to literature data [10,11].

### 3. Materials and Methods

The <sup>1</sup>H and <sup>13</sup>C NMR spectra were procured on a Bruker Avance-500 spectrometer at 500.17 and 125.78 MHz, respectively. A mixture of CDCl<sub>3</sub> was used as a solvent. The chemical shifts are reported as δ values in parts per million relative to the internal standard Me<sub>4</sub>Si. The coupling constants (J) are reported in Hertz.

#### 3.1. General Procedure for the Synthesis of Hydrazones **1d–3d**

A 50% of hydrazine hydrate (2.5 g, 0.05 mol) and triethylamine (20.2 g, 0.2 mol) were added to a solution of ketones **1d–3d** (1 g) in isopropyl alcohol. The mixture was stirred and heated for 5 h. After cooling to room temperature, the mixture was concentrated under vacuum, diethyl ether (3 \* 20 mL) was added to the reaction mass in portions, the organic phase was separated and concentrated under vacuum, obtaining the corresponding hydrazone **1d–3d** in the form of light yellow pastes. Yield is quantitative.

#### 3.2. *exo-exo-4-exo-Ketopentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 1c*

White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 0.93 (d, J = 12 Hz, 1H), 1.04–1.08 (m, 2H), 1.36–1.37 (m, 3H), 1.53 (d, J = 10 Hz, 1H), 1.72–1.75 (m, 3H), 1.88–1.89 (m, 2H), 1.91–1.92 (m, 1H), 1.97–1.99 (m, 2H), 2.07 (s, 1H), 2.10 (s, 1H), 2.22–2.26 (m, 2H), 2.35 (s, 1H), 2.87 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 220.72, 58.56, 57.72, 52.69, 47.61, 46.51, 43.06, 41.98, 41.84, 35.73, 34.90, 34.86, 29.23, 28.69.

#### 3.3. *exo-exo-4-exo-Hydrazone-pentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 1d*

Light yellow pastes. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 0.80 (d, J = 12 Hz, 1H), 0.90–0.96 (m, 2H), 1.29–1.32 (m, 3H), 1.44 (d, J = 10 Hz, 1H), 1.74–1.76 (m, 3H), 1.85–1.86 (m, 2H), 1.98–2.01 (m, 1H), 2.26–2.27 (m, 2H), 2.33 (s, 1H), 2.37–2.38 (m, 2H), 2.57 (s, 1H), 2.79 (s, 1H), 4.69 (s, br, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 166.27, 57.81, 55.67, 53.22, 49.80, 46.91, 43.89, 41.97, 41.33, 38.42, 37.37, 34.97, 29.30, 28.65.

### 3.4. *endo-endo-4-exo-Ketopentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 2c*

White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 1.00 (d, *J* = 10 Hz, 1H), 1.27–1.33 (m, 3H), 1.38–1.43 (m, 4H), 1.73 (d, *J* = 5 Hz, 2H), 1.82–1.85 (m, 1H), 1.89–1.98 (m, 2H), 1.97–1.99 (m, 1H), 2.00–2.04 (m, 1H), 2.06 (s, 1H), 2.21 (s, 1H), 2.29–2.31 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 222.24, 54.88, 54.59, 52.87, 49.71, 49.08, 46.63, 42.08, 41.78, 38.60, 36.43, 35.88, 24.18, 24.01.

### 3.5. *endo-endo-4-exo-Hydrazone-pentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 2d*

Light yellow pastes. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 0.95 (d, *J* = 10 Hz, 1H), 1.49–1.51 (m, 3H), 1.62–1.66 (m, 4H), 1.76 (d, *J* = 5 Hz, 2H), 1.84–1.87 (m, 1H), 1.90–1.97 (m, 2H), 2.03 (s, 1H), 2.25–2.29 (m, 4H), 2.34 (s, 1H), 2.49 (s, 1H), 3.11 (s, 1H), 3.60–3.63 (m, 1H), 4.30 (s, br, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 165.24, 54.20, 53.74, 50.95, 50.36, 43.04, 42.61, 42.60, 41.41, 41.20, 38.82, 37.22, 24.65, 24.64.

### 3.6. *Hexacyclo[9.2.1.0<sup>2,7</sup>.0<sup>3,5</sup>.0<sup>4,8</sup>.0<sup>9,13</sup>]tetradecanyl hydrazone 3d*

Light yellow pastes. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 0.94–0.97 (m, 1H), 1.14–1.29 (m, 8H), 1.31–1.42 (m, 1H), 1.43–1.48 (m, 2H), 1.70 (s, 1H), 1.86–1.90 (m, 1H), 1.96 (s, 2H), 2.00–2.11 (m, 2H), 2.20 (s, 1H), 3.30–3.33 (m, 2H), 4.14–4.19 (m, 2H), 4.79 (s, br, NH<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) = 166.76, 44.96, 43.07, 41.92, 41.42, 40.08, 35.58, 34.47, 33.61, 32.20, 30.21, 14.99, 14.80, 14.08.

## 4. Conclusions

Thus, we have for the first time carried out the synthesis of previously unknown unsubstituted hydrazones of strained polycyclic hydrocarbons **1d–3d**, it has been established that the presence of a double bond at the carbon atoms C12–C13 in the initial polycyclic hydrocarbons **1** and **2** leads to their resinification in successive stages of the introduction of functional groups, therefore their hydrogenated forms were used, and also under the reaction conditions we have chosen, only one three-carbon cycle for polycyclic hydrocarbon **3** undergoes acetoxylation.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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