

Proceeding Paper

# Epoxidation of Hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecanes Under Thermal and Microwave Irradiation <sup>†</sup>

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**Abstract:** In this work, we carried out the epoxidation of hexacyclic dimers of norbornadiene—*exo-exo*-, *exo-endo*-, *endo-exo*-, *endo-endo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradec-12-ene under the influence of Mo-, V-, W-containing catalysts. The following oxidizing agents were tested: 4-methoxy-, 4-ethoxy-, pentafluoro-, 3-chloroperbenzoic acids, and as studies have shown, pentafluoro- and 3-chloroperbenzoic acids are the most effective. The reactions were carried out in chloroform under conditions of thermal (40–120 °C) and microwave irradiation (0.5–1 kW, 40–60 °C). It was found that when conducting experiments at room temperature for 8–48 h, the conversion does not exceed 15%. The maximum yields (64–78%) are observed when carrying out reactions under conditions: 100 °C, 8–12 h, in a sealed ampoule placed in stainless steel autoclave. Interesting results were obtained when conducting experiments under microwave irradiation conditions. The maximum yields (92–96%) of the target products were observed when conducting experiments under the following conditions: 1 kW, 40 °C, 30 min. As a result of the reaction, previously undescribed 12,13-epoxyhexacyclotetradecanes are formed, the structure of which was proven by one- and two-dimensional NMR spectroscopy.

**Keywords:** epoxidation; peracids; metal complex catalysis; microwave irradiation; norbornadiene dimers

## 1. Introduction

Epoxidation of alkenes is an important process in both industry and academia because epoxides are versatile intermediates in organic synthesis [1] and they are widely used as monomers to prepare functional polymers. The presence of strained, volumetric fragments in the structure of the initial monomers makes it possible to obtain polymers with increased strength, heat resistance, and resistance to heating [2,3]. For example, such compounds include norbornadiene (NBD) and its derivatives, which occupy an important place in organic and petrochemical synthesis [4]. Over a short history, NBD derivatives have found application in the perfume industry [5,6], medicine [7,8], agriculture [9,10], microelectronics and photonics [11,12], and as solar energy converters [13–16], in the production of polymer materials with unique properties [17–20] and so on.

Therefore, the synthesis of new compounds containing saturated three-membered oxygen-containing heterocycles is an important and urgent task of modern organic chemistry.

## 2. Experimental Section

### 2.1. General Procedures and Materials

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance-II 400 Ascend instrument (400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C in CDCl<sub>3</sub>). Mass spectra were run on a Shimadzu

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GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30 m × 0.25 mm, helium as the carrier gas, temperature programming from 40 to 300 °C at 8 °C/min, evaporation temperature of 280 °C, ion source temperature of 200 °C, and ionization energy of 70 eV). The elemental composition of the samples was determined on a Carlo Erba 1106 elemental analyzer. The course of the reaction and the purity of the products were monitored by gas liquid chromatography on a Shimadzu GC-9A, GC-2014 instrument [2 m × 3 mm column, SE-30 silicone (5%) on Chromaton N-AW-HMDS as the stationary phase, temperature programming from 50 to 270 °C at 8 °C/min, helium as the carrier gas (47 mL/min)].

Norbornadiene dimers, *exo-exo*- [21], *exo-endo*- [22], *endo-exo*- [23], and *endo-endo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradec-12-enes [24], were prepared as described in Refs.

## 2.2. General Procedure for the Ozonolysis

The O<sub>2</sub>/O<sub>3</sub> mixture (the ozonator productivity was 30 mmol O<sub>3</sub>/h) was passed through a soln. of aldehydes in 5 mL of CCl<sub>4</sub> room temperature with stirring over a period of 3 h.

## 2.3. General Procedure for Epoxidation of Norbornadiene Dimers

0.1 mmol of catalyst, 1 mmol of NBD dimer and 1 mmol of oxidizer were dissolved in 5–10 mL of chloroform. The reaction mixture was stirred at 18–60 °C for 8–48 h. After completion of the reaction, the mixture was filtered through a layer of aluminum oxide, dried over calcined MgSO<sub>4</sub> and concentrated in vacuo. Reactions at 80–100 °C for 8–16 h were carried out in a sealed ampoule (V = 10 mL) placed in a stainless steel microautoclave (V = 17 mL). In the case of experiments with microwave irradiation, the glass reactor was placed in a microwave installation and the necessary reaction parameters were set (0.5–1 kW, 25–60 °C, 15–60 min).

The 12,13-Epoxy-*exo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **5**. White powder, yield 96%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.86 (d, 1H, J = 8 Hz), 1.02–1.09 (m, 2H), 1.32–1.35 (m, 4H), 1.52 (s, 2H), 1.86 (s, 2H), 1.97 (s, 2H), 2.16 (s, 1H), 2.27 (s, 2H), 3.02 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 12.70, 17.29, 22.21, 33.60, 39.94, 40.45, 45.15, 49.00, 52.04. EIMS (70 eV, m/z): 202 (100) [M]<sup>+</sup>. Anal. calcd. for C<sub>14</sub>H<sub>18</sub>O: C 83.12; H 8.97; found: C 82.05; H 9.77.

The 12,13-Epoxy-*exo-endo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **6**. White powder, yield 94%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.85 (d, 1H, J = 8 Hz), 1.11 (s, 2H), 1.33 (d, 4H, J = 8 Hz), 1.77 (s, 2H), 1.88 (s, 2H), 1.95 (s, 2H), 2.01 (d, 1H), 2.41 (s, 2H), 3.01 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 13.12, 18.18, 21.07, 28.08, 38.49, 45.26, 45.62, 45.80, 53.44. EIMS (70 eV, m/z): 202 (100) [M]<sup>+</sup>. Anal. calcd. for C<sub>14</sub>H<sub>18</sub>O: C 83.12; H 8.97; found: C 83.94; H 7.96.

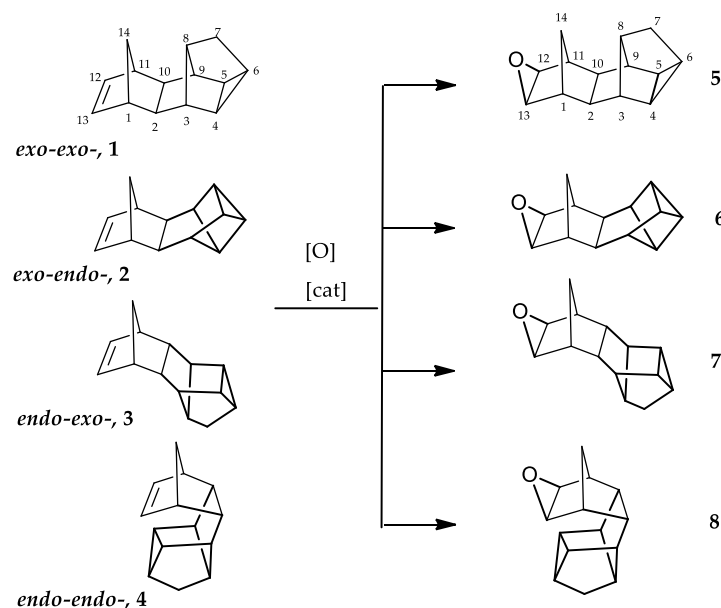
The 12,13-Epoxy-*endo-exo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **7**. White powder, yield 95%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.68 (d, 1H, J = 8 Hz), 0.82 (s, 1H), 1.08 (s, 1H), 1.35 (d, 4H, J = 8 Hz), 1.52 (s, 1H), 1.97 (s, 2H), 2.08 (s, 2H), 2.31 (s, 2H), 2.48 (s, 2H), 3.11 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.22, 18.13, 28.44, 33.71, 40.40, 40.44, 42.70, 48.87, 51.76. EIMS (70 eV, m/z): 202 (100) [M]<sup>+</sup>. Anal. calcd. for C<sub>14</sub>H<sub>18</sub>O: C 83.12; H 8.97; found: C 82.88; H 8.88;

The 12,13-Epoxy-*endo-endo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane **8**. White powder, yield 92%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.82 (d, 1H, J = 8 Hz), 1.14 (s, 2H), 1.38 (d, 4H, J = 8 Hz), 1.81 (s, 2H), 1.91 (s, 2H), 1.99 (s, 2H), 2.09 (d, 1H), 2.48 (s, 2H), 3.11 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 12.15, 19.11, 21.47, 28.27, 38.64, 46.01, 45.71, 45.96, 55.84. EIMS (70 eV, m/z): 202 (100) [M]<sup>+</sup>. Anal. calcd. for C<sub>14</sub>H<sub>18</sub>O: C 83.12; H 8.97; found: C 83.66; H 7.99.

## 3. Results and Discussion

In the present work, epoxy derivatives of hexacyclic dimers of norbornadiene (NBD) are obtained for the first time by the interaction of *exo-exo*-, *exo-endo*-, *endo-exo*-, *endo-endo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecenes-12 (HT) **1–4** with an oxidizing agent under the

action of metalcomplex catalysts. Various salts of molybdenum (VI), vanadium (V) and tungsten (VI) were tested as catalysts, among which, according to experiments, Mo(CO)<sub>6</sub> turned out to be the best, and the following were used as oxidizing agents: methyl-4-formyl-, 4-methoxy-, 4-ethoxy-, pentafluoro- and 3-chloroperbenzoic acids, and, as studies have shown, pentafluoroperbenzoic acid (PFPBA) is the most effective in the epoxidation of 1–4. The reactions were carried out in chloroform medium at the molar ratio of reagents and catalyst: [HT]:[Ox]:[cat.] = [100]:[100]:[10] with the formation of previously undescribed 12,13-epoxyhexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecanes 5–8.



**Figure 1.** Reactions of hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecanes 1–4 with PFPBA under the action of Mo(CO)<sub>6</sub>.

The main patterns of the reaction were studied using the example of the interaction of the *exo-exo*-dimer of NBD with PFPBA, under the conditions of 18–120 °C, 8–48 h. As a result of a series of experiments, it was established that when conducting experiments at room temperature for 8–48 h, the conversion of hydrocarbon 1 does not exceed 15%, an increase in temperature (40–60 °C) contributes to an increase in the conversion of the initial compounds, while the yield of epoxy derivative 5 does not exceed 44% (Table 1, entry 9).

**Table 1.** Epoxidation of *exo-exo*-dimer NBD 1 with *m*-CPBA under the action of Mo(CO)<sub>6</sub><sup>1</sup>.

Entry	Temp., °C	Time, h	Yield of 5 (%)	Entry	Temp., °C	Time, h	Yield of 5 (%)
1	18–23	8	≤1	8	60	16	38
2	18–23	16	6	9	60	24	44
3	18–23	24	10	10 <sup>a</sup>	80	8	67
4	18–23	48	15	11 <sup>a</sup>	80	12	79
5	40	16	29	12 <sup>a</sup>	100	8	64
6	40	24	33	13 <sup>a</sup>	100	12	78
7	40	48	36	14 <sup>a</sup>	100	16	65

<sup>1</sup> Reaction in a sealed ampoule.

The maximum yields (64–78%) of compound 5 are observed when reactions are carried out under the following conditions: 100 °C, 8–12 h in a sealed ampoule placed in a stainless-steel autoclave (Table 1, entries 12, 13). In addition, it was found that increasing the reaction duration to 16 h contributes to a decrease in the yield of epoxy derivative 5, which is possibly associated with resin formation (Table 1, entry 14).

Interesting results were obtained when conducting experiments under microwave irradiation (MW). Epoxidation of HT 1 with PFPBA was carried out under the following conditions: 0.5–1 kW, 25–60 °C, 15–60 min under the action of Mo(CO)<sub>6</sub> in a chloroform medium. The experiments showed that at a power of 0.5–0.8 kW, a temperature of 25–60 °C and a reaction time of 15 to 60 min, the maximum yields of compound 5 do not exceed 68% (0.8 kW, 40 °C, 60 min), and a further increase in temperature and/or reaction time does not affect the yield of compounds 5. In order to increase the yields of the target products, it was decided to conduct the experiments at the maximum power (1 kW) MW. According to the experimental results presented in Table 2, it was found that carrying out reactions at temperatures from 25 to 40 °C for 15–60 min, a gradual increase in the conversion of HT 1 is observed. In addition, it was experimentally determined that during epoxidation under MW conditions: 40 °C, 30 min, the maximum yield of 96% of *exo-exo*-12,13-epoxyhexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane 5 is observed (Table 2, entry 6), and an increase in the duration of the experiment to 60 min leads to a decrease in the yield of 5, possibly due to the formation of by-products of the reaction. Probably, the same reason is for the experiments at a temperature of 60 °C, according to the data in Table 2, only with a reaction duration of 15 min the yield of compound 5 is higher than when carrying out the reaction at 40 °C.

**Table 2.** Synthesis of *exo-exo*-12,13-epoxyhexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecane 5 under the influence of MW (1 kW) <sup>2</sup>.

Entry	Temp., °C	Time, min	Yield of 5 (%)	Entry	Temp., °C	Time, h	Yield of 5 (%)
1	25	15	19	7	40	45	91
2	25	30	37	8	40	60	88
3	25	45	54	9	60	15	77
4	25	60	72	10	60	30	86
5	40	15	66	11	60	45	80
6	40	30	96	12	60	60	71

<sup>2</sup> Reagents: PFPBA, Mo(CO)<sub>6</sub>, CHCl<sub>3</sub>.

Then, under the developed conditions (1 kW, 40 °C, 30 min), epoxidation reactions of *exo-endo*-, *endo-exo*-, *endo-endo*-hexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecenes-12 2–4 with PFPBA were carried out under the action of Mo(CO)<sub>6</sub> in a chloroform medium to form *exo-endo*-, *endo-exo*-, *endo-endo*-12,13-epoxyhexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecanes 6–8 in high yields.

#### 4. Conclusions

Thus, by the reaction of epoxidation of four norbornadiene dimers of different configurations with pentafluoroperbenzoic acid under the action of Mo(CO)<sub>6</sub>, the syntheses of *exo-exo*-, *exo-endo*-, *endo-exo*-, *endo-endo*-12,13-epoxyhexacyclo[9.2.1.0<sup>2,10</sup>.0<sup>3,8</sup>.0<sup>4,6</sup>.0<sup>5,9</sup>]tetradecanes 5–8 were accomplished for the first time in 92–96% yields and the conditions for their preparation were developed. It was established that the maximum yields of compounds 5–8 were observed when conducting experiments in a sealed ampoule under the following conditions: 100 °C, 8 h and under microwave irradiation (1 kW) at 40 °C for 30 min.

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