

Dedicated to the memory of  
Professor Mircea D. Banciu (1941–2005)

NOTE

## EPOXIDATION OF POLYCYCLIC HYDROCARBONS.1.

Mircea D. BANCIU,<sup>a\*\*</sup> Luminitza PÂRVULESCU,<sup>a\*</sup> Constantin DRĂGHICI,<sup>b</sup>  
Daniela ISTRATI<sup>a</sup> and George MARTON<sup>a</sup>

<sup>a</sup> Department of Organic Chemistry, “Politehnica” University Bucharest,  
Splaiul Independenței 313; 060042, Bucharest, Roumania

<sup>b</sup> “C.D. Nenitzescu” - Institute of Organic Chemistry, Roumanian Academy,  
Splaiul Independenței 202B; 060023, Bucharest, Roumania

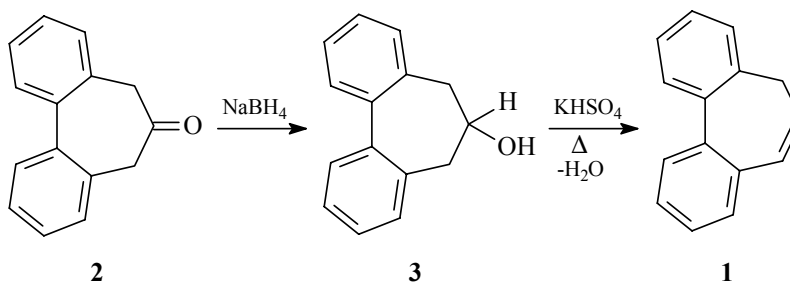
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The synthesis and epoxidation reactions with *m*-chloroperbenzoic acid of 5H-dibenzo[*a,c*]cycloheptene and of 5H-dibenzo[*a,c*]-6H-methyl-6-cycloheptene was described.

The interest for the behavior of the polycyclic systems in the epoxidation reactions, in various conditions, is justified by their utilization in the synthesis of a large variety of compounds.

### RESULTS

5H-Dibenzo[*a,c*]cycloheptene (**1**) was prepared starting from the ketone **2**<sup>1</sup> by reduction with NaBH<sub>4</sub> in methanol;<sup>2</sup> the obtained alcohol **3**<sup>2,3</sup> was dehydrated with better yields by distillation in the presence of KHSO<sub>4</sub> (**Scheme 1**):



Scheme 1

The complete spectral characterization of the alkene **1**<sup>4</sup> is here presented (**Scheme 2**):

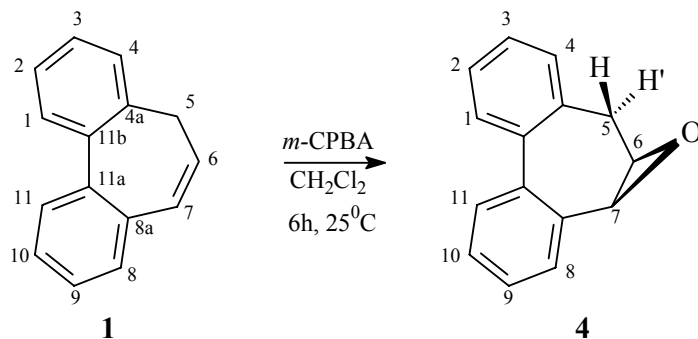
<sup>1</sup>H-NMR spectrum<sup>(\*)</sup> (CDCl<sub>3</sub>; δ, ppm; J, Hz): 3.19 (2H, H<sup>5</sup>); 6.37 (dt, 6.9, 10.1, 1H, H<sup>6</sup>); 6.73 (d, 10.1, 1H, H<sup>7</sup>); 7.38 – 7.54 (m, 6H, H<sup>2,3,4,8,9,10</sup>); 7.69 (m, 1H, H<sup>1</sup>); 7.83 (m, 1H, H<sup>11</sup>).

<sup>13</sup>C-NMR spectrum<sup>(\*)</sup> (CDCl<sub>3</sub>; δ, ppm): 28.16 (C<sup>5</sup>); 121.17 (CH); 121.38 (CH); 121.61 (CH); 121.71 (CH); 122.54 (CH); 124.06 (CH); 124.30 (CH); 124.70 (CH); 124.97 (CH); 126.68 (CH); 131.12 (Cq); 133.38 (Cq); 134.71 (Cq); 137.35 (Cq).

Mass spectrum<sup>(\*\*\*)</sup> (m/e; relative abundance, %): 63 (3); 82 (12); 83 (5); 94 (16); 95 (11); 96 (9); 115 (3); 139 (4); 163 (4); 165 (19); 189 (32); 190 (7); 191 (100; B.P.); 192 (78; M); 193 (10; M+1); 194 (1; M+2).

\* Corresponding author: E-mail: lr\_parvulescu@chim.upb.ro

\*\* Deceased in 2005.



Scheme 2

The epoxidation of the alkene **1** was carried out with *m*-chloroperbenzoic acid (*m*-CPBA), in  $\text{CH}_2\text{Cl}_2$  as solvent, 6 hours at room temperature (**Scheme 2**). Pure epoxide **4** is colorless oil and presents the following spectral data:

*I.R. spectrum*<sup>(\*\*)</sup> (KBr;  $\text{cm}^{-1}$ ): 746 s, 995 w, 1253 m, 1444 m, 1484 m, 2926 w, 2989 w, 3060 w.

*<sup>1</sup>H-NMR spectrum*<sup>(\*)</sup> ( $\text{CDCl}_3$ ;  $\delta$ , ppm; J, Hz): 2.62 (large s, 1H,  $\text{H}^5$ ); 3.03 (dd, 13.4, 3.4, 1H,  $\text{H}^{5'}$ ); 3.51 (dt, 3.8, 3.4; 3.6, 1H,  $\text{H}^6$ ); 3.75 d, 3.8, 1H,  $\text{H}^7$ ); 7.1 – 7.36 (M, 7H,  $\text{H}^{1-4,9-11}$ ); 7.48 (large s, 1H,  $\text{H}^8$ ).

*<sup>13</sup>C-NMR spectrum*<sup>(\*)</sup> ( $\text{CDCl}_3$ ;  $\delta$ , ppm): 35.52 (large s,  $\text{C}^5$ ); 54.49 (large s,  $\text{C}^6$ ); 59.05 (large s,  $\text{C}^7$ ); 127.61 (2 CH); 127.73 (CH); 128.58 (CH); 128.92 (CH); 129.78 (CH); 130.57 (CH); 130.90 (CH); 139.67 (Cq).

Even at  $62^\circ\text{C}$  the complete attribution of the quaternary carbons was impossible.

*Mass spectrum*<sup>(\*\*\*)</sup> (m/e; relative abundance, %): 45 (5); 50 (12); 51 (16); 62 (8); 63 (20); 73 (11); 74 (12); 75 (9); 76 (20); 77 (6); 82 (6); 86 (8); 87 (8); 89 (31); 102 (5); 115 (6); 126 (5); 139 (6); 150 (6); 151 (10); 152 (20); 164 (5); 165 (91); 166 (12); 176 (17); 177 (11); 178 (60); 179 (100; B.P.); 180 (58); 181 (11); 191 (5); 207 (23); 208 (69; M); 209 (18; M+1).

The alkene **6** was synthesized by the route presented in **Scheme 3**.

Addition of the methylmagnesium iodide to the ketone **2** conducted to 6-hydroxy-6-methyl-dibenzo[*a,c*]cycloheptane (**5**), which presents the following spectral data:

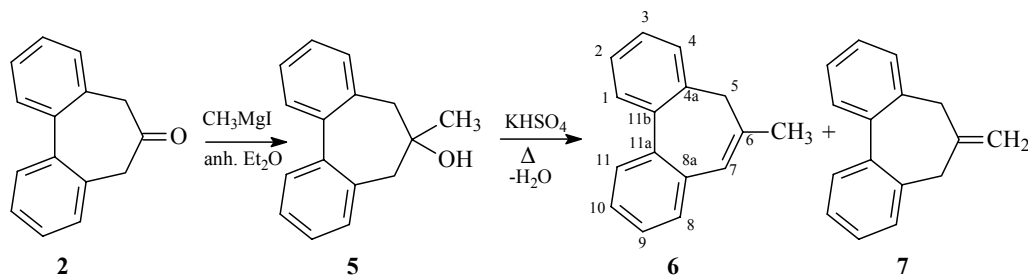
*I.R. spectrum*<sup>(\*\*)</sup> (KBr;  $\text{cm}^{-1}$ ): 750 s, 1066 w, 1224 w, 1444 m, 1693 m, 2924 m, 3435 large ( $\nu_{\text{OH}}$ ).

*<sup>1</sup>H-NMR spectrum*<sup>(\*)</sup> ( $\text{CDCl}_3$ ;  $\delta$ , ppm; J, Hz): 1.38 (s, 3H); 2.58 (dl, 2H,  $\text{H}^{5,7}$ ); 2.72 (dl, 2H,  $\text{H}^{7,5}$ ); 7.26 (dl, 7.9, 2H,  $\text{H}^{4,8}$ ); 7.31 (td, 1.6, 7.3, 2H,  $\text{H}^{2,10}$ ); 7.38 (td, 1.8, 7.4, 2H,  $\text{H}^{3,9}$ ); 7.43 (dd, 1.8, 7.4, 2H,  $\text{H}^{1,11}$ ).

*<sup>13</sup>C-NMR spectrum*<sup>(\*)</sup> ( $\text{CDCl}_3$ ;  $\delta$ , ppm): 27.23 ( $\text{CH}_3$ ); 46.94 ( $\text{C}^{5,7}$ ); 81.11 (Cq<sup>6</sup>); 127.19 ( $\text{C}^{10,2(9,3)}$ ); 127.47 ( $\text{C}^{9,3(10,2)}$ ); 128.36 ( $\text{C}^{1,11}$ ); 129.17 ( $\text{C}^{4,8}$ ); 136.86 (Cq<sup>11a,11b</sup>); 140.53 (Cq<sup>4a,8a</sup>).

*Mass spectrum*<sup>(\*\*\*)</sup> (m/e; relative abundance, %): 45 (3); 50 (6); 51 (7); 58 (3); 63 (9); 69 (3); 77 (5); 89 (8); 101 (4); 115 (8); 139 (8); 152 (13); 153 (9); 165 (79); 166 (69); 167 (21); 176 (10); 177 (7); 178 (27); 179 (23); 180 (12); 181 (89); 190 (3); 191 (5); 206 (8); 207 (55); 208 (10); 209 (3); 223 (21); 224 (100; M; B.P.); 225 (15; M+1).

The dehydration on  $\text{KHSO}_4$  of alcohol **5** occurs to a mixture of alkenes **6** and **7** in the molar ratio 7 : 1 (**Scheme 3**):



Scheme 3

(\*) VARIAN GEMINI 300 apparatus working at 300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$  (using TMS as internal standard).

(\*\*) IR-Equinox – FTIR X 55 apparatus.

The pure alkene **6** was separated from this mixture by liquid chromatography on a silica column using pentane as eluent. The spectral data of 5H-dibenzo[*a,c*]-6-methyl-cycloheptene (**6**) are presented as follows:

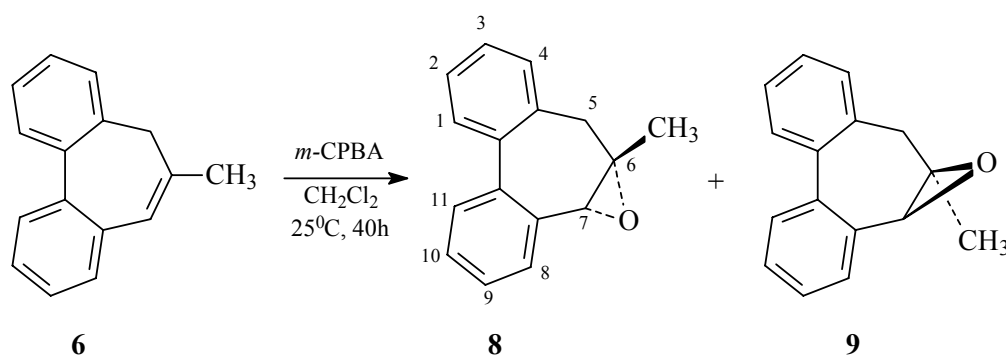
*I.R. spectrum*<sup>(\*\*)</sup> (KBr;  $\text{cm}^{-1}$ ): 750 s, 1430 m, 1480 m, 1695 w, 3018 m, 3058 m.

<sup>1</sup>*H-NMR spectrum*<sup>(\*)</sup> ( $\text{CDCl}_3$ ;  $\delta$ , ppm; J, Hz): 2.08 (d, 1.6, 3H,  $\text{CH}_3$ ); 2.99 (s, 2H,  $\text{H}^5$ ); 6.33 (q, 1.6, 1H,  $\text{H}^7$ ); 7.69 (dd, 2.2, 7.0, 1H,  $\text{H}^{1(1)}$ ); 7.51 (m, 1H,  $\text{H}^{1(1)}$ ); 7.20 – 7.40 (m, 6H,  $\text{H}^{2,3,4,8,9,10}$ ).

<sup>13</sup>*C-NMR spectrum*<sup>(\*)</sup> ( $\text{CDCl}_3$ ;  $\delta$ , ppm): 24.36 ( $\text{CH}_3$ ); 38.92 ( $\text{C}^5$ ); 123.57 (CH); 125.70 (CH); 126.27 (CH); 126.39 (CH); 126.70 (CH); 127.50 (CH); 128.69 (CH); 128.82 (CH); 129.39 (CH); 136.85 (Cq); 138.31 (Cq); 139.01 (Cq); 141.41 (Cq); 141.82 (Cq).

*Mass spectrum*<sup>(\*\*\*)</sup> (m/e; relative abundance, %): 51 (3); 63 (5); 89 (3); 115 (3); 139 (3); 152 (3); 164 (5); 165 (23); 166 (5); 176 (5); 178 (6); 179 (4); 189 (22); 190 (19); 191 (100; B.P.); 192 (17); 202 (12); 203 (7); 205 (26); 206 (97; M); 207 (16; M+1).

The epoxidation of alkene **6** takes place with *m*-CPBA in  $\text{CH}_2\text{Cl}_2$  solvent, at 25°C for 40 hours and affords the epoxides **8** and **9** (Scheme 4):



Scheme 4

The spectral data of 5H-dibenzo[*a,c*]-6-methyl-cycloheptan-6,7-epoxide (**8**) are presented as follows:

<sup>1</sup>*H-NMR spectrum*<sup>(\*)</sup> ( $\text{CDCl}_3$ ;  $\delta$ , ppm; J, Hz): 1.40 (s, 3H,  $\text{CH}_3$ ); 2.64 (d, 14.0, 1H,  $\text{H}^5(5)$ ); 2.92 (d, 14.0,  $\text{H}^5(5)$ ); 3.65 (s, 1H,  $\text{H}^7$ ); 7.10 – 7.94 (m, 8H,  $\text{H}^{\text{arom}}$ ).

<sup>13</sup>*C-NMR spectrum*<sup>(\*)</sup> ( $\text{CDCl}_3$ ;  $\delta$ , ppm): 20.50 ( $\text{CH}_3$ ); 45.51 ( $\text{C}^5$ ); 60.04 (Cq,  $\text{C}^6$ ); 64.11 (Cq,  $\text{C}^7$ ); 127.50 (CH); 127.75 (CH); 128.60 (CH); 128.92 (CH); 129.90 (CH); 130.12 (Cq); 130.69 (Cq); 133.52 (CH); 134.54 (Cq); 134.85 (Cq); 139.38 (Cq); 139.58 (Cq).

*Mass spectrum*<sup>(\*\*\*)</sup> (m/e; relative abundance, %): 50 (5); 63 (5); 151 (5); 152 (13); 165 (B.P.; 100); 166 (14); 176 (10); 177 (7); 178 (50); 179 (39); 180 (7); 193 (7); 222 (M; 8).

## CONCLUSIONS

In this paper there were synthesized the prochiral alkene **6** and two models of epoxides: **4** and (**8**, **9**). Next studies of asymmetric epoxidation, on specific catalysts, which may permit to control this reaction, will be done.

## REFERENCES

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4. M. Banciu, Phan Le Tui, M. Elian, C. Drăghici and E. Ciorănescu, *Rev. Roum. Chim.*, **1981**, *26*, 1115-1125.

(\*\*\*) VARIAN 3400 gas-chromatograph with split/splitless injector coupled with a VARIAN SATURN II mass-spectrometer provided with ion trap. Column: capillary DB-5 (30 m length, 0.25 mm internal diameter); Analysis conditions: injector temperature: 250°C; temperature program: 100 - 250°C with 5°C/min; carrier gas: helium (flow-rate 2 mL/min); temperature of transfer line, 250°C; temperature of the manifold, 170°C; ionization energy, 70eV.