

**REACTIONS OF ISOMERIC OXO-2(3)-OXAHOMODIAMANTANES.  
DEHYDRATION OF TETRACYCLIC DIOLS WITH CONCENTRATED  
PHOSPHORIC ACID**

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Reduction of 11-oxo-10-oxapentacyclo[7.4.1.1<sup>4,13</sup>.0<sup>2,7</sup>.0<sup>6,12</sup>]penta-decane (lactone *I*) and 10-oxo-11-oxapentacyclo[7.4.1.1<sup>4,13</sup>.0<sup>2,7</sup>.0<sup>6,12</sup>]penta-decane (lactone *II*) with lithium aluminium hydride afforded 4-hydroxymethyl-12-hydroxytetracyclo[7.3.1.0<sup>2,7</sup>.0<sup>6,11</sup>]tridecane (diol *III*) and 4-hydroxy-12-hydroxymethyltetracyclo[7.3.1.0<sup>2,7</sup>.0<sup>6,11</sup>]tridecane (diol *IV*). Diol *III* reacted with concentrated phosphoric acid to give 3-methyltetracyclo[6.4.1.0<sup>2,6</sup>.0<sup>5,10</sup>]tridecanone-9 (*V*) as practically the sole product. Diol *IV* afforded a complex mixture of products in which were identified 2-methyl-3-oxadiadamantane (*VI*; 57%), 10-oxa-2(3)-homodiamantane (*VII*; 20%), 3-hydroxydiamantane (*VIII*; 3%), diadamantane (*X*; 7%) and diadamantanone (*IX*; 2%).

This paper represents a continuation of our previous communications<sup>1-4</sup> describing the synthesis, separation and some reactions of isomeric cyclic esters with homodiamantane structure.

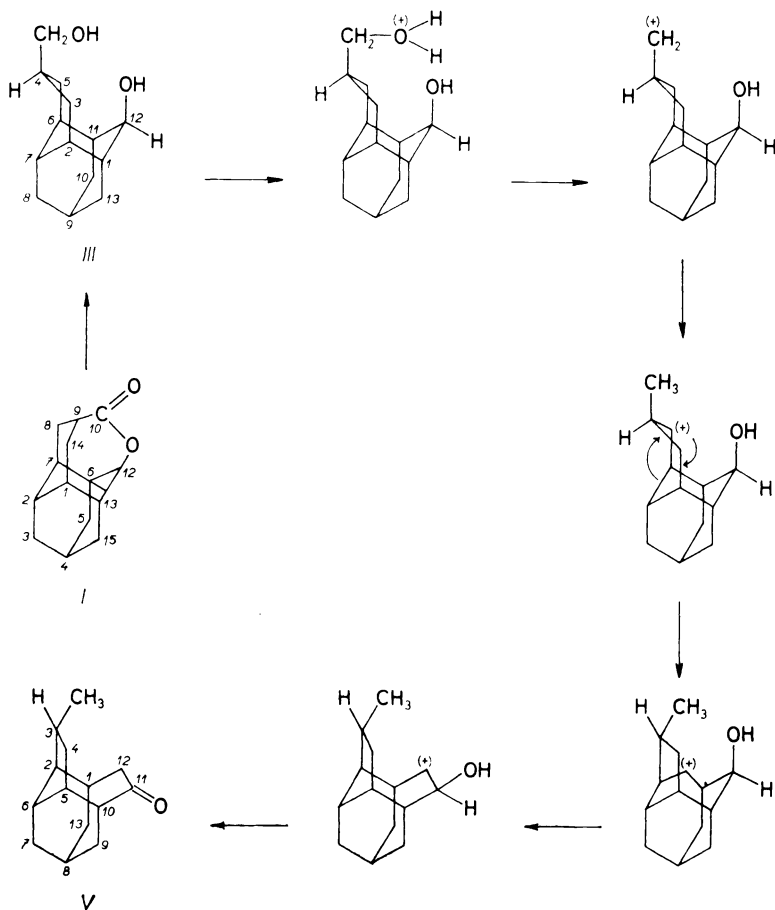
Reduction of lactone *I* and *II* with lithium aluminium hydride afforded 4-hydroxymethyl-12-hydroxytetracyclo[7.3.1.0<sup>2,7</sup>.0<sup>6,11</sup>]tridecane (diol *III*) and 12-hydroxymethyl-4-hydroxytetracyclo[7.3.1.0<sup>2,7</sup>.0<sup>6,11</sup>]tridecane (diol *IV*), respectively, in practically quantitative yield. Their mass spectra are very similar and contain no molecular ion. The ion of the highest mass observed ( $m/z$  204) corresponds to the loss of water from the parent diol. In addition, the diol *III* loses the CH<sub>2</sub>OH group whereas from the diol *IV* a neutral formaldehyde molecule is split off.

In the <sup>1</sup>H NMR spectra the largest differences are in the hydroxyl proton signals. Whereas for diol *IV* the chemical shifts of both the hydroxyl protons are practically the same ( $\delta = 4.17$ ), they differ considerably for the diol *III* ( $\delta = 4.48$  and 4.12).

Interesting results were obtained in the dehydration of these diols with concentrated phosphoric acid. The diol *III* afforded practically a single product. Mass spectrum of this product exhibited the molecular ion  $m/z$  204 as the most abundant one. Further we observed ions  $m/z$  189 ( $M - CH_3$ , 22%),  $m/z$  176 ( $M - CO$ , 52%) and  $m/z$  161 ( $M - C_3H_7$ , 10%). The IR spectrum confirmed the presence of a car-

bonyl group in the molecule ( $\nu(\text{C}=\text{O}) = 1695 \text{ cm}^{-1}$ ), but did not indicate any hydroxyl group. The  $^1\text{H}$  NMR spectrum exhibited a methyl group signal,  $\delta = 1.05$ , and the  $^{13}\text{C}$  NMR spectrum showed that the molecule has no plane of symmetry. The carbonyl carbon signal had  $\delta = 219.75$  and the adjacent, sole tertiary carbon atom (C-10) appeared as signal at  $\delta = 51.98$ .

If we assume no intramolecular reduction-oxidation reaction in the medium of concentrated phosphoric acid, the molecule must undergo a skeletal rearrangement. The assumed reaction course is depicted in Scheme 1. We assume that in the first



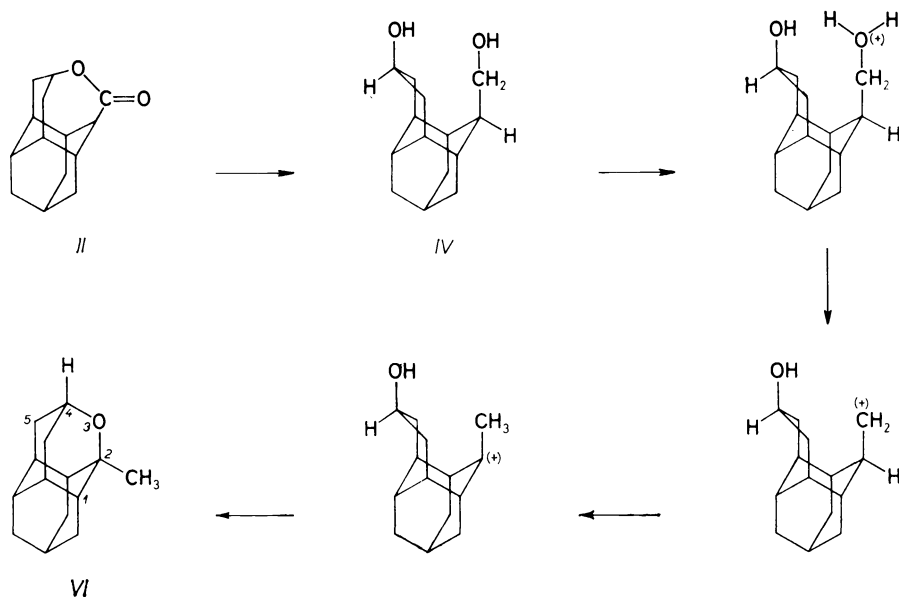
S CHEME 1

step the primary hydroxyl is protonated and split off as water molecule. The arising carbonium ion is further stabilized by a charge shift which is followed by skeletal

rearrangement leading to 3-methyl-11-oxotetracyclo[6.4.1.0<sup>2,6</sup>.0<sup>5,10</sup>]tridecane (*V*) as the final product.

Dehydration of diol *IV* afforded a more complex mixture of products which were separated on a column of silica gel and identified by comparison of their mass, <sup>1</sup>H NMR, <sup>13</sup>C NMR and IR spectra with the data of authentic compounds. The new compound, identified as 2-methyl-3-oxadiadamantane (*VI*), had no carbonyl or hydroxyl bands. Its elemental analysis confirmed the presence of oxygen atom in the molecule. The proton NMR spectrum exhibited a methyl singlet ( $\delta = 1.21$ ) and a multiplet due to a proton adjacent to an oxygen atom ( $\delta = 3.99$ ). The <sup>13</sup>C NMR spectrum confirmed a plane of symmetry and contained a quaternary carbon signal (C-2) at  $\delta = 74.5$  and a tertiary carbon signal (C-4) at  $\delta = 67.2$ . These high chemical shifts confirm that both the carbon atoms are bonded to an oxygen atom. The mass spectrum shows molecular weight 204 and contains an ion arising by loss of methyl.

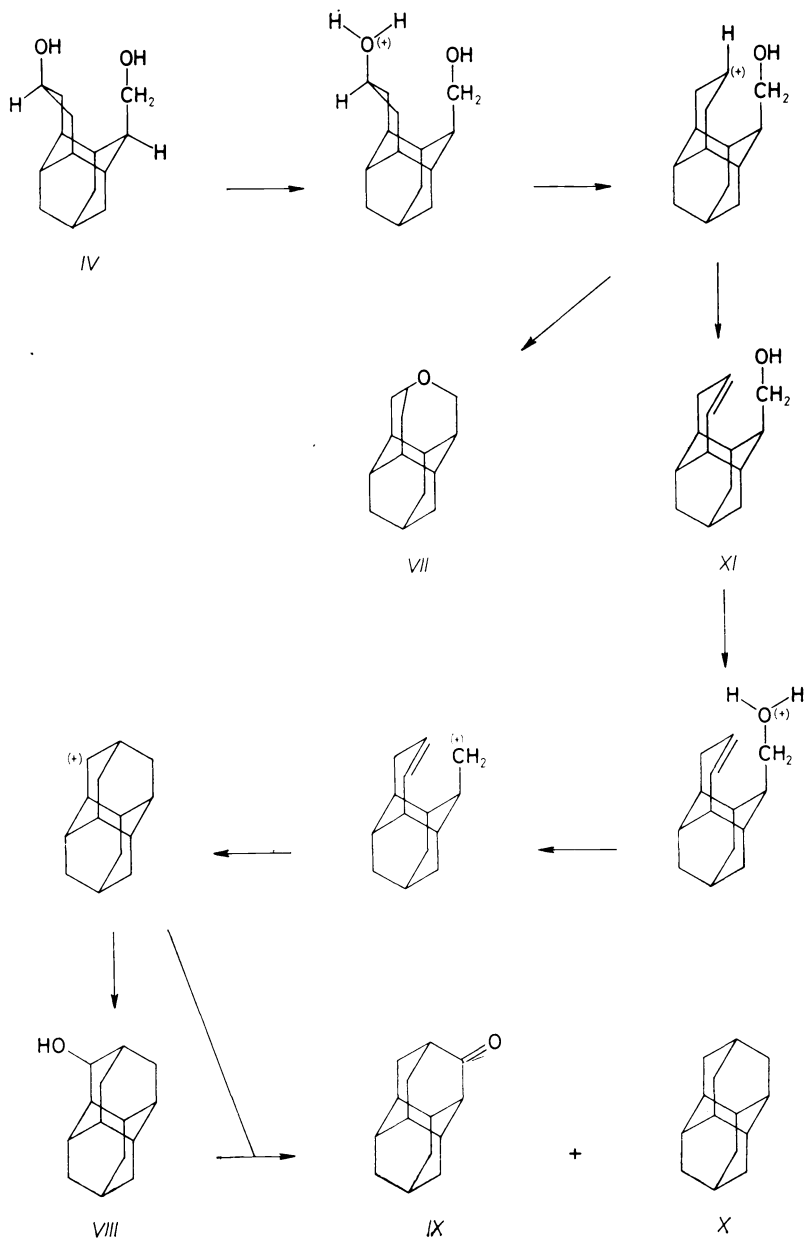
The suggested mechanism is given in Scheme 2 and 3. We assume that in the first case the protonation takes place on the primary hydroxyl with subsequent loss of water molecule. The arising carbonium ion is stabilized by charge transfer to the skeleton and following ring closure to 2-methyl-3-oxadiadamantane *VI* (Scheme 2).



SCHEME 2

In the second case the secondary hydroxyl is protonated, again with subsequent loss of water molecule, the formed carbonium ion being stabilized either by cyclization to 10-oxa-2(3)-homodiamantane (*VII*) or conversion into the neutral unsaturated primary alcohol (*XI*). The latter is further protonated, loses another water molecule

and is stabilized via the diadamantyl cation to give 3-hydroxydiadamantane (*VIII*), diamantanone (*IX*) and diamantane (*X*) (Scheme 3).



SCHEME 3

## EXPERIMENTAL

Gas liquid chromatographic analyses were performed on a Chrom 5 chromatograph (Laboratorní přístroje, Prague) on a  $3 \times 1200$  mm column packed with 3% XF-1150 on Chromaton N-AW-DMCS. Mass spectra were measured on a Jeol 303 instrument (electron impact, 75 eV). NMR spectra were obtained at 24°C with a Bruker AM-400 spectrometer (FT mode, 400.13 MHz for  $^1\text{H}$  and 100.62 for  $^{13}\text{C}$ ) in deuteriochloroform or hexadeuterodimethyl sulfoxide with tetramethylsilane as internal standard. The chemical shifts are given in ppm ( $\delta$ -scale) and coupling constants ( $J$ ) in Hz. The IR spectra were taken on a Perkin-Elmer 325 instrument in chloroform (wavenumbers in  $\text{cm}^{-1}$ ).

4-Hydroxymethyl-12-hydroxytetracyclo[7.3.1.0<sup>2,7</sup>.0<sup>6,11</sup>]tridecane (*III*)

A solution of lactone *I* (2.18 g, 10 mmol) in ether (200 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.74 g, 20 mmol) in ether (100 ml). The reaction mixture was refluxed for 4 h, cooled and decomposed with saturated aqueous solution of sodium sulfate. The ethereal layer was decanted, the precipitate washed with hot tetrahydrofuran ( $2 \times 50$  ml) and the combined ethereal and tetrahydrofuran portions were dried over anhydrous sodium sulfate. Evaporation of the solvents afforded 2.1 g (95%) of diol *III*; an analytical sample was obtained by crystallization from methanol, m.p. 218–220°C. For  $\text{C}_{14}\text{H}_{22}\text{O}_2$  (222.3) calculated: 75.63% C, 9.97% H; found: 75.37% C, 9.92% H. Mass spectrum (direct inlet),  $m/z$  (%): 204 (100), 186 (53), 174 (14), 173 (37), 157 (4), 143 (17), 131 (20), 117 (19), 106 (37), 105 (19), 104 (40), 95 (38), 94 (21), 93 (41), 92 (25), 91 (73), 79 (61).  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{SOCD}_3$ ): 4.48 d, 1 H (CH-OH,  $J = 3.3$ ); 4.12 t, 1 H (CH<sub>2</sub>-OH,  $^3J = 5.2$ ); 3.80 s, 1 H (CHO); 3.16 t, 2 H (CH<sub>2</sub>O,  $^3J = 5.0$ ); 1.55–2.00 m, 17 H.  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{SOCD}_3$ ): 76.31 (C-12), 67.23 (CH<sub>2</sub>-OH), 40.43 (2 C, d), 37.98 (1 C, t), 37.87 (2 C, t), 34.60 (2 C, d), 31.10 (1 C, d), 29.59 (1 C, d), 29.38 (2 C, t), 26.25 (C-9). IR spectrum (nujol): 3 280; (KBr) 3 280.

4-Hydroxy-12-hydroxymethyltetracyclo[7.3.1.0<sup>2,7</sup>.0<sup>6,11</sup>]tridecane (*IV*)

Diol *IV* was prepared from lactone *II* (4.4 g, 20 mmol) by the same procedure as described in the preceding experiment in 96% yield; m.p. 172–174°C (methanol). For  $\text{C}_{14}\text{H}_{22}\text{O}_2$  (222.3) calculated: 75.63% C, 9.97% H; found: 75.80% C, 9.80% H.  $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{SOCD}_3$ ): 4.14–4.18 m, 2 H (OH); 3.92–4.04 m, 1 H (CHO); 3.82 dd, 2 H (CH<sub>2</sub>O,  $J(\text{CH}_2\text{O}, \text{OH}) = 5.1$ ;  $J(\text{CH}_2\text{O}, \text{H}-12) = 8.0$ ); 2.08–2.18 m, 2 H; 1.98–2.02 m, 2 H; 1.87–1.92 m, 4 H; 1.67–1.77 m, 7 H; 1.35–1.42 m, 2 H.  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{SOCD}_3$ ): 63.96 (CH<sub>2</sub>OH), 62.43 (C-4), 49.25 (C-12), 40.76 (2 C, t), 37.75 (C-8), 35.63 (2 C, d), 35.44 (2 C, t), 35.41 (2 C, d), 28.98 (1 C, d), 27.31 (C-9). Mass spectrum (direct inlet),  $m/z$  (%): 204 (100), 186 (49), 174 (83), 173 (21), 161 (4), 145 (11), 131 (29), 117 (27), 105 (31), 95 (62), 94 (61), 93 (45), 92 (39), 91 (72), 79 (66). IR spectrum (nujol): 3 200, 3 270, 3 320; (KBr) 3 280.

Dehydration of Diol *III* with 85% Phosphoric Acid

A mixture of diol *III* (1.0 g, 4.5 mmol) and 85% phosphoric acid (25 ml, 370 mmol) was heated under reflux condenser to 170–190°C for 2 h. After cooling, the product was poured into water and extracted with chloroform, the extract was washed with sodium hydrogen carbonate solution and water, dried over anhydrous sodium sulfate and the solvent was evaporated to give 0.88 g (92%) of a viscous material, containing (as shown by gas-liquid chromatography) principally one compound of shorter elution time than that of the starting diol, along with small amount of impurities. The product was dissolved in a 5 : 95 ether-hexane mixture and filtered through

a small column of activated silica gel 25 g): yield 0.65 g (71%) of 3-methyl-11-oxotetracyclo-[6.4.1.0<sup>2,6</sup>.0<sup>5,10</sup>]tridecane (*V*), m.p. 58--59°C. For C<sub>14</sub>H<sub>20</sub>O (204.3) calculated: 82.26% C, 9.87% H; found: 82.26% C, 10.07% H. Mass spectrum, *m/z* (%): 204 (M<sup>+</sup>, 100), 189 (M - CH<sub>3</sub>, 22), 176 (M - CO, 52), 161 (10), 147 (9), 133 (37), 119 (16), 105 (16), 91 (40), 79 (49). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>): 1.30–2.65 m, 17 H; 1.01–1.09 m, 3 H (CH<sub>3</sub>). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>): 219.75 (C=O), 51.98 (C-10), 26.78 (C-8), 13.87 (CH<sub>3</sub>), 39.79 (d), 37.80 (t), 37.46 (t), 35.98 (d), 35.82 (t), 34.75 (d), 33.99 (t), 32.80 (d), 30.71 (d), 29.58 (t), IR spectrum (CHCl<sub>3</sub>): 1 695, 1 455, 1 370, 1 100.

#### Dehydration of Diol *IV* with 85% Phosphoric Acid

A mixture of diol *IV* (1.5 g, 7.3 mmol) and 85% phosphoric acid (50 ml, 740 mmol) was heated to 180°C under reflux condenser for 2 h. The product which had sublimed into the condenser was washed with ether and the reaction mixture was partitioned between ether and water (100 ml). The combined extract layers were washed with water to neutral reaction, dried over anhydrous sodium sulfate and the ether was distilled off to give 1.2 g of a mixture of products (gas-liquid chromatography). This was separated by chromatography on a column of silica gel (80 g) in light petroleum with a gradient of ether (0–50%). Five fractions were collected. Light petroleum eluted fraction 1 (90 mg, 7%) containing diamantane (*X*) as the principal constituent whose m.p., mass and <sup>13</sup>C NMR spectra agreed with those of an authentic sample. Fraction 2 (470 mg, 57%) consisted of pure 2-methyl-3-oxadiazolane (*VI*). Mass spectrum, *m/z* (%): 204 (100, M<sup>+</sup>), 189 (38), 171 (6), 161 (22), 146 (5), 91 (25), 79 (22). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>): 3.97–4.01 m, 1 H (H-4); 1.21 s, 3 H (CH<sub>3</sub>); 1.55–2.00 m, 16 H. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>): 41.22 (C-1), 74.54 (C-2), 67.23 (C-4), 37.01 (C-5), 36.90 (C-6), 41.22 (C-7), 35.02 (C-8), 25.58 (C-9, or CH<sub>3</sub>), 37.95 (C-10), 35.89 (C-11), 36.90 (C-12), 35.02 (C-13), 37.01 (C-14), 25.42 (CH<sub>3</sub>, or C-9). IR spectrum (CHCl<sub>3</sub>): 3 000, 2 920, 2 890, 2 860, 1 470, 1 450, 1 435, 1 383, 1 375, 1 328, 1 160, 1 120, 1 092, 1 058, 1 000, 990, 890, 862. Fraction 3 (80 mg, 20%) contained 10-oxa-2(3)-homodiamantane (*VII*); its m.p., elution time, <sup>13</sup>C NMR spectrum and mass spectrum were identical with those of a standard<sup>3</sup>. Fraction 4 (30 mg, 2%) contained diamantanone<sup>5</sup> (*IX*). Fraction 5 (40 mg, 3%) was 3-hydroxydiamantane (*VIII*) whose elution time, m.p., <sup>13</sup>C NMR spectrum and mass spectrum were identical with those of an authentic sample<sup>5,6</sup>.

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