

## ISOMERIZATION OF HEPTACYCLIC HYDROCARBONS TO TRIAMANTANE

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Received November 3, 1989

Accepted February 1, 1990

Isomerization of heptacyclic hydrocarbons, heptacyclo[8,8,0,0<sup>2,17</sup>,0<sup>3,11</sup>,0<sup>4,9</sup>,0<sup>12,16</sup>,0<sup>13,18</sup>]-octadecane and heptacyclo[8,8,0,0<sup>2,13</sup>,0<sup>3,11</sup>,0<sup>4,9</sup>,0<sup>12,17</sup>,0<sup>14,18</sup>]octadecane under various conditions in the presence of Lewis-type catalysts has been studied. The isomerization gives the heptacyclic diamantoid hydrocarbon triamantane which is the third member of the adamantanologic series.

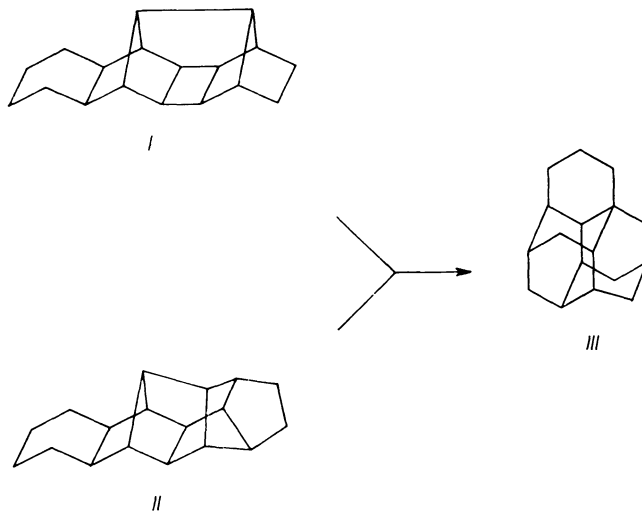
The isomerization of heptacyclic hydrocarbons, heptacyclo[8,8,0,0<sup>2,17</sup>,0<sup>3,11</sup>,0<sup>4,9</sup>,0<sup>12,16</sup>,0<sup>13,18</sup>]octadecane (*I*) and heptacyclo[8,8,0,0<sup>2,13</sup>,0<sup>3,11</sup>,0<sup>4,9</sup>,0<sup>12,17</sup>,0<sup>14,18</sup>]octadecane (*II*) represents the final step in the synthesis of triamantane from norbornadiene<sup>1</sup>. This skeletal isomerization is usually carried out in the presence of Lewis-type catalysts such as aluminium halides. Hollowood and collaborators<sup>2</sup> performed the isomerization with aluminium chloride in boiling cyclohexane. Prolonged heating and stirring gave about 60% of triamantane.

In our present study we investigate the composition of products arising by isomerization of a mixture of hydrocarbons *I* and *II* of the general formula C<sub>18</sub>H<sub>24</sub> in the presence of Lewis-type catalysts at various temperatures, with the aim to prepare in high yield triamantane (heptacyclo[7,7,1,1<sup>3,15</sup>,0<sup>1,12</sup>,0<sup>2,7</sup>,0<sup>4,13</sup>,0<sup>6,11</sup>]octadecane, *III*) which is starting compound for the preparation of some derivatives.

For the isomerization of the mixture of hydrocarbons *I* and *II* we used aluminium chloride or bromide. Since the skeletal isomerization of polycyclic hydrocarbons requires higher temperatures, the reaction was carried out in a sealed glass ampoule. Thus, the hydrogen halide, which forms complexes with aluminium halides and therefore is necessary for the successful reaction course, cannot escape from the reaction mixture and the reaction is completed in a shorter time and in higher yields than reported previously<sup>2</sup>.

We investigated the conversion of the mixture of compounds *I* and *II* to the compound *III* at various reaction temperatures. Practically no isomerization was observed in cyclohexane at 100°C. An increase of temperature to 150°C resulted in partial reaction of the starting compounds and the reaction mixture contained small

amount of compound *III* along with some unidentified fission products. Best results were obtained at 200°C: all the starting material reacted and the reaction mixture contained 65% of compound *III*.



Higher yields were achieved with aluminium bromide which is generally a more active catalyst than aluminium chloride; however, in this case higher reaction temperature was necessary to achieve full conversion. After eight hours the reaction mixture contained up to 70% of compound *III*, besides unidentified products. In dichloromethane as solvent, the temperature could be lowered to 150°C and the reaction time reduced to 5 h.

We also studied the conversion of pure compound *I* (obtained by crystallization of the mixture of *I* and *II* from heptane) into compound *III*. In this case, the reaction product contained almost 80% of *III* and no starting compound *I*. On the other hand, isomerization of a mixture containing only 20% of the isomer *I* led to 15% of compound *III*. As follows from these experiments, the isomer *I* reacted preferentially whereas compound *II* remained almost unchanged.

Study of various reaction times has shown that the isomerization of compounds *I* and *II* requires about 8 h and that longer reaction time has no substantial effect on the yield of the desired compound *III*.

#### EXPERIMENTAL

Gas-liquid chromatographic analyses were performed on a Chrom 5 apparatus combined with a CI-100 integrator (both from Laboratorní přístroje, Prague). The isomers were separated on 50 m capillary columns (stationary phase SE-30 or Apiezon L). Mass spectrometric analyses were obtained with an LKB 9000 instrument.

Heptacyclo[8,8,0,0<sup>2,17</sup>,0<sup>3,11</sup>,0<sup>4,9</sup>,0<sup>12,16</sup>,0<sup>13,18</sup>]octadecane (*I*) and heptacyclo[8,8,0,0<sup>2,13</sup>,0<sup>3,11</sup>,0<sup>4,9</sup>,0<sup>12,17</sup>,0<sup>14,16</sup>]octadecane (*II*) were prepared by Diels–Alder reaction of hexacyclo[8,4,0,0<sup>2,7</sup>,0<sup>3,14</sup>,0<sup>4,8</sup>,0<sup>9,13</sup>]tetradec-5-ene and hexacyclo[6,6,0,0<sup>2,6</sup>,0<sup>5,14</sup>,0<sup>7,12</sup>,0<sup>9,13</sup>]tetradec-3-ene with butadiene<sup>3</sup> followed by hydrogenation of the obtained adducts.

#### Isomerization of Mixture of *I* and *II* with Aluminium Chloride

A mixture of *I* and *II* (1 g), aluminium chloride (0.5 g) and cyclohexane (10 ml) was heated in a sealed ampoule (electrically heated air bath) to 200°C for 8 h. The reaction mixture was mixed with water (10 ml). The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. The solution was filtered, concentrated in vacuo and the residue was mixed with acetone. On cooling, the acetone solution deposited compound *III* (65%;  $M^+$  240) which was identified (as in all other cases) by comparison with an authentic specimen.

#### Isomerization of Mixture of *I* and *II* with Aluminium Bromide

*A*) A mixture of compounds *I* and *II* (1.0 g), aluminium bromide (0.5 g) and cyclohexane (10 ml) was heated in a sealed ampoule to 200°C for 8 h. The reaction product was filtered, the solid on the filter was dissolved in water and the aqueous solution extracted with cyclohexane. Both organic layers were combined, washed with water and dried over anhydrous sodium sulfate. The solution was filtered and concentrated in vacuo. The residue was mixed with acetone, cooled and the product *III* (0.7 g) was collected.

*B*) A mixture of compounds *I* and *II* (1.0 g), aluminium bromide (0.5 g) and dichloromethane (10 ml) was heated in a sealed ampoule to 150°C for 5 h. The reaction mixture was worked up as described in the experiment *A*) and afforded 70% of *III*.

#### Isolation of Compound *I* and Isomerization with Aluminium Chloride

A mixture of compounds *I* and *II* (5.0 g) was three times crystallized from boiling heptane to give 2.0 g of chromatographically homogeneous product *I*, m.p. 115–116°C ( $M^+$  240; reported<sup>2</sup> m.p. 117–119°C).

A mixture of compound *I* (1.0 g), aluminium chloride (0.5 g) and cyclohexane (10 ml) was heated in a sealed ampoule to 200°C for 8 h. The reaction product was processed as described in the preceding experiments. Yield 78% of compound *III*.

#### REFERENCES

1. Hamilton R., McKervey M. A., Rooney J. J., Malone J. F.: *J. Chem. Soc., Chem. Commun.* 1976, 1027.
2. Hollowood F. S., McKervey M. A., Hamilton R., Rooney J. J.: *J. Org. Chem.* 45, 4954 (1980).
3. Kafka Z., Vodička L.: *Collect. Czech. Chem. Commun.* 51, 1083 (1986).

Translated by M. Tichý.