

ISOMERIZATION OF BINOR S

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The isomerization of norbornadiene dimer, heptacyclo[8,4,0,0^{2,12},0^{3,8},0^{4,6},0^{5,9},0^{11,13}]tetradecane (binor S), was studied in the presence of various catalysts. The isomerization resulted in a mixture of hexacyclic olefins (hexacyclo[8,4,0,0^{2,7},0^{3,14},0^{4,8},0^{9,13}]tetradec-5-ene and hexacyclo[6,6,0,0^{2,6},0^{5,14},0^{7,12},0^{9,13}]tetradec-3-ene), which is an important intermediate product in the five-stage synthesis of triamantane.

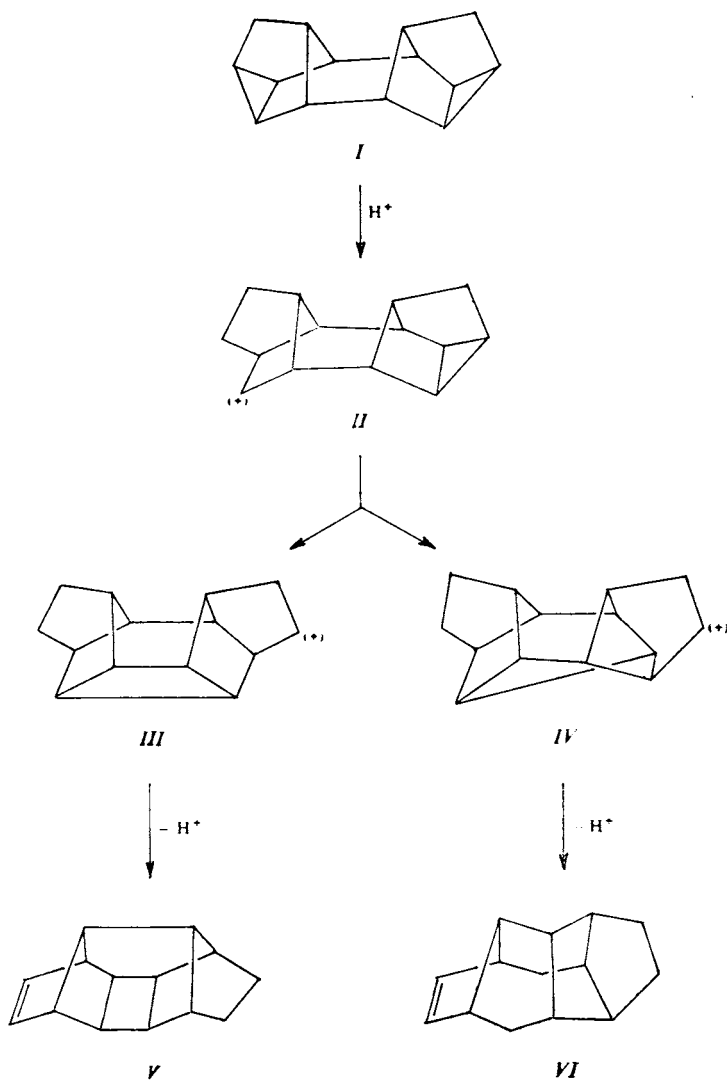
Isomerization of binor S (*I*), the norbornadiene dimer, is the second step in the synthesis of triamantane starting from norbornadiene. This rearrangement, leading to the formation of a mixture of two hexacyclic olefins, starts with the action of a proton on the molecule of *I*. Bond splitting in a cyclopropane ring takes place resulting in the formation of carbocation *II*. The formation of the desired olefins is associated with the intramolecular reaction with the adjacent three-membered ring during which the ring is cleaved and a new C–C bond is formed. Carbocations *III* and *IV* form *via* unstable intermediates, and these transform into two hexacyclic olefins, *viz.* hexacyclo[8,4,0,0^{2,7},0^{3,14},0^{4,8},0^{9,13}]tetradec-5-ene (*V*) and hexacyclo[6,6,0,0^{2,6},0^{5,14},0^{7,12},0^{9,13}]tetradec-3-ene (*VI*), on the elimination of a proton.

The rearrangement of substance *I* resulting in the *V* + *VI* mixture can occur in the presence of various catalysts. In the gas phase, the isomerization can be conducted in a nitrogen stream over a platinum catalyst; in the liquid phase, the rearrangement is carried out in benzene in the presence of silver perchlorate catalyst¹. Phosphorus pentoxide can also serve as a suitable catalyst².

In this work we concentrated on the composition of the products obtained from the isomerization of *I* in the presence of some catalysts as yet not used for this purpose, with the aim to prepare a mixture of the hexacyclic olefins *V* and *VI*, which can be used without additional separation as the starting material for the third stage of the synthesis of triamantane.

Ethyl metaphosphate was used as the catalyzing agent. Unlike the conventionally used phosphorus pentoxide, this substance is well soluble in chlorinated alkanes, and so the reaction can take place in a homogeneous phase. Chloroform was used as solvent. The yield of substances *V* and *VI* was affected particularly by the *I*-to-cata-

lyst ratio and by the reaction time. With the *I*-to-catalyst ratio 2 : 1, nearly 50% of the starting substance remained unreacted in 1 h; this fraction decreased to 20% in 10 h. When the amount of catalyst was increased so that the ratio was 1 : 2, all the starting substance *I* reacted, the reaction mixture, however, contained, in addition to the hexacyclic olefins *V* and *VI*, also about 20% reaction products of lower molecular weight. This implies that splitting reactions take place besides the isomerization. The reaction time necessary for the complete reaction of *I* was as short as 0.5 h.



A next substance tested as catalyst was aluminium chloride. The reaction involved splittings, and the product contained 10% substances with molecular weight lower than that of substance *I*. Moreover, nearly 80% of the starting substance remained unreacted. This fraction decreased to 20% if tert-butyl chloride was added to aluminium chloride, the fraction of low molecular weight products, however, substantially increased. In both cases the hexacyclic olefins *V* and *VI* were present in fractions as low as 10–20%.

In the presence of titanium tetrachloride, splitting again took place; all binor *S* reacted to give substances with molecular weights both lower and higher than that of *I*; the hexacyclic olefins *V* and *VI*, however, were absent from the product.

EXPERIMENTAL

The gas chromatographic analyses were carried out on a Chrom 5 instrument (Laboratorní přístroje, Prague), the mass spectrometric analyses, on an LKB 9000 instrument.

Heptacyclo[8,4,0,0^{2,12},0^{3,8},0^{4,6},0^{5,9},0^{11,13}]tetradecane (*I*) was prepared by dimerization of norbornadiene in the presence of dibromo-bis-triphenylphosphine cobalt and borotrifluoride etherate³. Ethyl metaphosphate was prepared from phosphorus pentoxide by boiling in ether and chloroform⁴.

Isomerization of Substance *I* in the Presence of Ethyl Metaphosphate

50 g of substance *I* dissolved in 50 ml of chloroform was added dropwise to a constantly stirred solution of 25 g of ethyl metaphosphate in 30 ml of chloroform, and the stirred reaction mixture was heated to boil for 10 h. To the cold mixture was added 50 ml of 30% aqueous potassium carbonate, the whole was agitated, and the aqueous phase was drawn off. The organic layer was extracted with water, the aqueous fractions were reextracted with chloroform, and the combined chloroform extracts were vacuum evaporated. The residue, which became solid on cooling, was extracted repeatedly with boiling ethanol, and the combined ethanolic extracts were evaporated in vacuum. The residue was distilled at 115–118°C/332 Pa. A mixture of substances *V* and *VI*, identified by comparison with authentic samples, was obtained in a yield of 24 g.

Isomerization of Substance *I* in the Presence of Aluminium Chloride

a) 5 g of substance *I* dissolved in 10 ml of cyclohexane was added dropwise to a constantly stirred suspension of 2 g of aluminium chloride in 30 ml of cyclohexane. The stirred mixture was heated to boil for 1 h. To the cooled mixture was added 40 ml of water and the whole was shaken repeatedly in a separatory funnel. The cyclohexane extracts were dried with sodium sulphate, filtered, and evaporated in vacuum. The residue was distilled at 104–110°C/266 Pa. A mixture of substances was obtained in a yield of 4.2 g. By mass spectrometric and gas chromatographic analysis, the system contained 80% unreacted substance *I*, 10% substance of molecular weight 166, and 10% mixture of *V* + *VI*.

b) 5 g of substance *I* in 10 ml of cyclohexane was added dropwise to 5 g of aluminium chloride in 30 ml of cyclohexane to which 2.5 ml of tert-butyl chloride had been added, and the stirred mixture was heated to boil for 1 h. To the cold mixture was added 40 ml of water and the whole was extracted repeatedly in a separatory funnel. The cyclohexane extracts were dried with sodium sulphate, filtered, and evaporated in vacuum. 4.4 g of a product was obtained; according to the

mass spectrometric and gas chromatographic analysis, 60% of a substance of molecular weight 166, 20% of a mixture of substances *V* + *VI*, and 20% of a substance of molecular weight 186 were present.

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