

THE DIELS-ALDER REACTION OF BUTADIENE WITH HEXACYCLIC OLEFINS IN THE SYNTHESIS OF TRIAMANTANE

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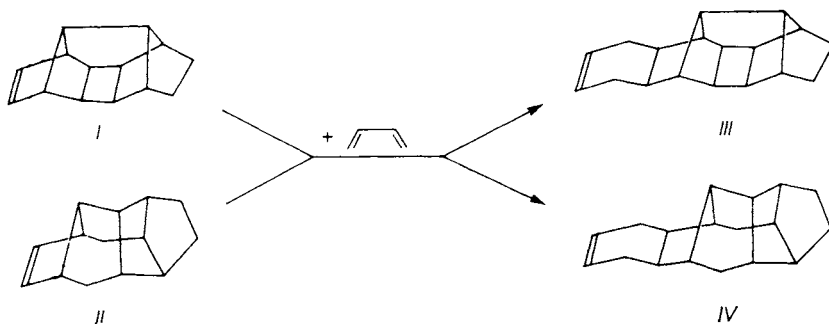
Received May 24th, 1985

The paper describes the composition of products arising from the Diels-Alder reaction of butadiene with 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) under different conditions. The reaction afforded a mixture of heptacyclic olefins (heptacyclo[8,8,0,0^{2,17},0^{3,11},0^{4,9},0^{12,16},0^{13,18}]octadec-6-ene and heptacyclo[8,8,0,0^{2,13},0^{3,11},0^{4,9},0^{12,17},0^{14,18}]octadec-6-ene), which is an important intermediate in the synthesis of triamantane.

The Diels-Alder reaction of butadiene with hexacyclic olefins, *viz.* hexacyclo[8,4,0,0^{2,7},0^{3,14},0^{4,8},0^{9,13}]tetradec-5-ene (*I*) and hexacyclo[6,6,0,0^{2,6},0^{5,14},0^{7,12},0^{9,13}]tetradec-3-ene (*II*), is the third step of the synthesis of triamantane starting from norbornadiene^{1,2}. This cycloaddition reaction of a conjugated diene with unsaturated compounds is an example of the *cis*-addition, towards both the dienophile and the diene. With some dienophiles, especially substituted ones, the reaction occurs even at room temperature and affords high yields. With the less reactive dienophiles the reaction mixture has to be heated to higher temperatures, in some cases the pressure must also be increased. However, conjugated dienes add to one another, giving rise to cyclic hydrocarbons; thus 1,3-butadiene produces 4-vinyl-1-cyclohexene. The reaction may be accompanied by ready polymerization. The addition is usually to positions 1 and 4, and leads to high-molecular-mass substances which are analogues of natural rubber.

In a five-step synthesis of triamantane, isomerization of binor *S* in the presence of phosphorus pentoxide³ gives rise to a mixture of two hexacyclic olefins *I* and *II*, of a common formula C₁₄H₁₆. Since the molecule of the resulting polycyclic hydrocarbon, *viz.* triamantane, contains 18 carbon atoms, the mixture of the isomers *I* and *II* must be treated with butadiene. The addition of butadiene to hexacyclic olefins, which are not activated by the presence of electropositive substituents and, therefore, are little reactive dienophiles, occurs under pressure and at a high temperature. The reaction can be carried out in a sealed glass tube or in a stirred steel autoclave⁴. In the work on a larger scale, however, it is preferable to use a rotary steel autoclave⁵.

The present paper deals with composition of the mixtures produced by the Diels–Alder reaction of butadiene with the hexacyclic olefins *I* and *II* under different conditions. We further concentrated on new ways of working-up the reaction mixture produced by this addition, with a view to obtaining a high yield of a mixture of heptacyclic olefins *III* and *IV*, which can be used directly for the fourth step of the synthesis of triamantane.



The composition of the reaction mixtures arising from the addition of butadiene was considerably dependent on the ratio of the reacting components. A higher excess of butadiene caused its dimerization and trimerization in the course of the reaction; prior to working up the reaction mixture the dimers and trimers had to be distilled off. By distillation *in vacuo* the unreacted starting compounds *I* and *II* were removed from the reaction product, containing the compounds *III* and *IV*. Elevation of temperature to 200°C led to formation of polymeric substances, which made it difficult to isolate the individual products from the reaction mixture. In such cases the most advantageous method was repeated extraction of the polymeric substances with boiling ethanol or some higher alcohol (isobutanol, pentanol). Dioxan also proved a good solvent. The combined extracts were then distilled to separate the compounds *III* and *IV*. If a reaction mixture did not contain a great amount of by-products it could also be worked up by crystallization. Alcoholic extracts, concentrated *in vacuo* to half volumes, were allowed to crystallize and the mother liquors, composed mainly of the unreacted starting substances *I* and *II*, were used directly for the diene synthesis. The advantage of this method was high purity of the isolated compounds *III* and *IV*.

The over-all yield of the heptacyclic olefins *III* and *IV* (50–60%) was affected by the mentioned side reactions (dimerization, polymerization), accompanying the diene synthesis under certain reaction conditions. The composition of a reaction mixture depended on which of the reactions were the prevailing ones. The yields of the heptacyclic olefins *III* and *IV* also varied with the way in which the reaction mixture was worked up, especially if the reaction products contained great amounts

of polymeric substances and repeated extraction with a suitable solvent had to be carried out.

Further we investigated the effect of reaction time on composition of the reaction products and on yields of the compounds *III* and *IV*. Experiments in a rotary autoclave, allowed to proceed for different times, have shown that the reaction of butadiene with the compounds *I* and *II* takes, on an average, 15 h to obtain a yield of 50–60%. With further extension of the reaction time no significant increase in the yields of *III* and *IV* was observed.

EXPERIMENTAL

Gas chromatography was performed in an apparatus Chrom 5 (Laboratorní přístroje, Praha), mass spectrometry in an apparatus LKB 9000.

Hexacyclo[8,4,0,0^{2,7},0^{3,14},0^{4,8},0^{9,13}]tetradec-5-ene (*I*) and hexacyclo[6,6,0,0^{2,6},0^{5,14},0^{7,12},0^{9,13}]tetradec-3-ene (*II*) were prepared by isomerization of binor S with phosphorus pentoxide in boiling tetrachloromethane.

Diels-Alder Reaction of *I* and *II* with Butadiene

a) A mixture of *I* and *II* (100 g) and butadiene (180 ml) was heated in a steel rotary autoclave to 180°C for 18 h and the product was distilled. The head fraction, collected at 50–55°C/2.6 kPa, was composed mainly of the dimer ($M^+ = 108$) and trimer ($M^+ = 162$) of butadiene. The residue was distilled at 138–142°C/133 Pa; yield 77 g (59%) of a mixture of *III* ($M^+ = 238$) and *IV* ($M^+ = 238$), identified by comparison with authentic samples (as in examples *b* and *c*).

b) A mixture of *I* and *II* (100 g) and butadiene (150 ml) was heated in a rotary steel autoclave to 200°C for 12 h. The head fraction was distilled off and the residue was extracted with boiling tert-butanol (2 × 100 ml) and pentanol (2 × 100 ml). The combined alcoholic extracts were concentrated *in vacuo*; yield 68 g (53%) of a mixture of isomers *III* and *IV*.

c) A mixture of *I* and *II* (100 g) and butadiene (130 ml) was heated in a rotary steel autoclave to 180°C for 15 h. The product was concentrated and the residue extracted with boiling ethanol (3 × 100 ml). The combined ethanolic extracts were concentrated to half a volume and allowed to crystallize; yield 66 g (51%) of a crystalline mixture of isomers *III* and *IV*.

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Translated by J. Salák.