
**THE MECHANISM OF FORMATION OF 2,7-DIMETHYL-2,6-OCTADIENE
IN THE SYNTHESIS OF 3-METHYLENE-7-METHYL-1,6-OCTADIENE**Jan BARTOŇ^a and Ivan KMÍNEK^b^a *Department of Organic Technology,
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2,7-Dimethyl-2,6-octadiene is formed in the catalytic solution for the dimerization of 2-methyl-1,3-butadiene to β -myrcene (3-methylene-7-methyl-1,6-octadiene), as revealed by mass spectrometry and ¹³C NMR spectroscopy. Visual observations together with the results of gas chromatographic analysis of the catalytic solution suggest that the formation of 2,7-dimethyl-2,6-octadiene is associated with the transition of the alkali metal (sodium) from the solid phase into the solution. A reaction pathway is suggested accounting for the formation of 2,7-dimethyl-2,6-octadiene in the system.

Dealing with the dimerization of isoprene (2-methyl-1,3-butadiene) to β -myrcene (3-methylene-7-methyl-1,6-octadiene), we discussed the mechanism of formation of β -myrcene¹, derived a kinetic model of the reaction², and described the effect of structure of the dialkylamine on the reaction of isoprene conversion to β -myrcene³.

In the present work we are concerned in more detail with the composition of the catalytic solution, formed by dissolving solid sodium in a mixture of tetrahydrofuran, isoprene, and dicyclohexylamine. Based on the structure of the product formed during the transfer of sodium from the solid phase into the solution, we suggest a possible mechanism of the reaction occurring during this transfer.

EXPERIMENTAL**Chemicals**

Isoprene, tetrahydrofuran, dicyclohexylamine, sodium, and nitrogen were purified as reported previously¹.

Preparation of 2,7-Dimethyl-2,6-octadiene

Equimolar quantities of sodium powder, isoprene (7.5 g), and dicyclohexylamine were mixed in a thirteenfold excess of tetrahydrofuran in a 200 ml glass reactor and cooled to 5°C. After 80 min of the reaction, during which the sodium was transferred into the solution and the mixture acquired a brown-red colour, water (10 ml) was added and the mixture was shaken with

dilute hydrochloric acid and filtered. The organic layer (3.9 g) was distilled to give 1 g of a distillate, b.p. 167–170°C at 100 kPa. Mass spectrometry, ^{13}C NMR spectroscopy, and gas chromatography measurements revealed that the substance was 2,7-dimethyl-2,6-octadiene.

Preparation of the Catalytic Solution

The catalytic solution was prepared as in the previous works¹⁻³ at room temperature. 5 μl samples were taken from the reactor for gas chromatographic analysis.

Gas Chromatographic Analysis

The composition of the catalytic solution was determined on a Chrom 4 apparatus (Laboratorní přístroje, Prague) with flame ionization detection. The column used and the conditions applied were as reported in paper². The concentrations of isoprene and 2,7-dimethyl-2,6-octadiene were determined from calibration curves. The concentration of higher isoprene oligomers was calculated as the balance to isoprene and 2,7-dimethyl-2,6-octadiene, and expressed as the concentration of isoprene dimer.

RESULTS AND DISCUSSION

The time dependences of the concentrations of isoprene, 2,7-dimethyl-2,6-octadiene, and higher isoprene oligomers (expressed as isoprene dimer) in the preparation of the catalytic solution are shown in Fig. 1. The concentration of 2,7-dimethyl-2,6-octadiene attained its maximum 30 min after the start of the reaction, and thereafter remained constant. The concentration of higher isoprene oligomers increased slightly with time, so that 300 min after the start the selectivity of the reaction, defined as the concentration ratio of 2,7-dimethyl-2,6-octadiene to the higher oligomers, was unity.

The time moment when the concentration of 2,7-dimethyl-2,6-octadiene reached its maximum was identical with the moment that solid sodium ceased to be seen. It can be deduced that the presence of solid sodium, or the process of its transfer

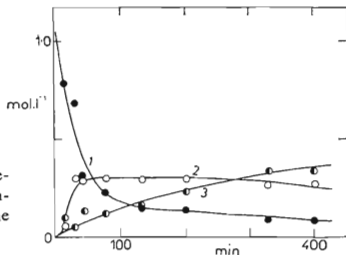
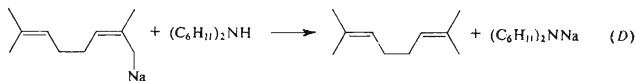
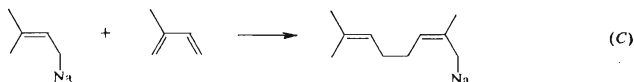
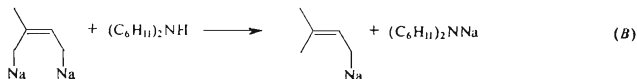
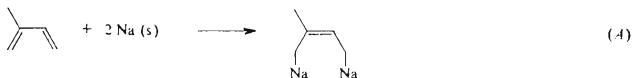


FIG. 1

Dependences of concentrations of 1 isoprene, 2 2,7-dimethyl-2,6-octadiene and 3 higher isoprene oligomers (expressed as isoprene dimer) on time

into the solution, is a prerequisite for the formation of 2,7-dimethyl-2,6-octadiene.

We suggest that the process of the transfer of sodium from the solid phase into the solution can be represented by the following pathway:



The first step is the addition of isoprene to the surface of the solid sodium giving rise to 1,4-disodium-2-methyl-2-butene (*A*), which reacts with dicyclohexylamine to give 2-methyl-4-sodium-2-butene (*B*), the sodium atom bonded at the α -carbon with respect to the methyl group being, probably, more reactive than that bonded at the β -carbon atom. The reaction of 2-methyl-4-sodium-2-butene with isoprene affords 1-sodium-2,7-dimethyl-2,6-octadiene (*C*), which reacts further with dicyclohexylamine to yield 2,7-dimethyl-2,6-octadiene (*D*). β -Myrcene was not traced in the formation of the catalytic solution.

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