THE MECHANISM OF FORMATION OF 2,7-DIMETHYL-2,6-OCTADIENE IN THE SYNTHESIS OF 3-METHYLENE-7-METHYL-1,6-OCTADIENE

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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 ^{13}C 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-myrcene[1], derived a kinetic model of the reaction[2], and described the effect of structure of the dialkylamine on the reaction of isoprene conversion to β-myrcene[3].

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 previously[1].

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 works[1-3] 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 paper[2]. 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
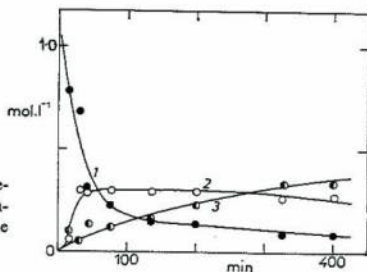

FIG. 1

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:

$$(A)$$

$$(B)$$

$$(C)$$

$$(D)$$
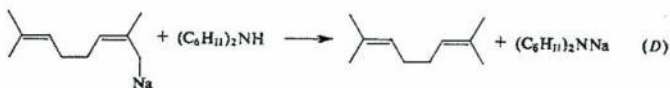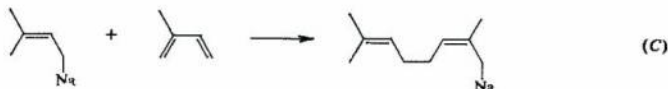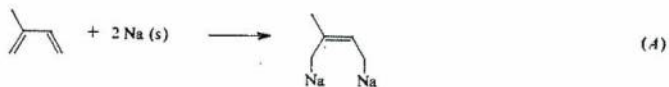
The first step is the addition of isoprene to the surface of the solid sodium giving rise to 1,4-disodium-2-methyl-2-butene (A), which reacts with dicyclohexylamine to give 2-methyl-4-sodium-2-butene (B), the sodium atom bonded at the α-carbon with respect to the methyl group being, probably, more reactive 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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REDUCTION OF GLYCOSYLNITROMETHANES
TO GLYCOSYLMETHYLAMINES WITH FERROUS SALTS

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Reduction of β-D-galactopyranosylnitromethane, β-D-glucopyranosylnitromethane and 1-deoxy-
-1-nitro-D-*glycero*-L-*manno*-heptitol with ferrous hydroxide afforded β-D-galactopyranosylmethyl-
amine (*I*), β-D-glucopyranosylmethylamine (*II*) and 1-amino-1-deoxy-D-*glycero*-L-*manno*-heptitol
(*III*), respectively. Thanks to the high conversion of the nitro derivatives and the simple isolation,
this method is very suitable for preparation of glycosylmethylamines. The structure of products
in their underivatized form was proved by mass spectrometry.

Glycosylmethylamines, *i.e.* 2,6- or 2,5-anhydro-1-amino-1-deoxyalditols, represent
an important group of saccharides which, *e.g.* can be used in the preparation of 1-de-
oxy-2-ketoses[1–4]. β-D-Galactopyranosylmethylamine was employed in the prepara-
tion of β-D-galactopyranosyl-(4-nitrophenyl)triazene, inhibitor of *E. coli* β-galactoxi-
dase[5]. α-D-Mannopyranosylmethylamine exhibits an insulin-like activity[6]. Most
of the synthetic approaches consist in catalytic hydrogenation of glycosylnitro-
methanes, over Raney nickel[7,8] or Adams catalyst[1,7]. β-D-Galactopyranosylmethyl-
amine was prepared by reaction of 2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl bro-
mide with cyanide ions, followed by reduction of the intermediate with lithium
aluminium hydride[2]. Aromatic amines are frequently prepared by reduction of nitro-
aromatic compounds with ferrous hydroxide[9], highly selective for this type of reduc-
tion. In the present communication we utilized this reaction for synthesis of glycosyl-
methylamines from the starting glycosylnitromethanes.

Treatment of an aqueous solution of β-D-galactopyranosylnitromethane with
ferrous sulfate and ammonia at about 100°C (15 min) afforded β-D-galactopyranosyl-
methylamine (*I*) in 96% yield. β-D-Glucopyranosylnitromethane was transformed
in the same way into β-D-gluctopyranosylmethylamine (*II*) in 95% yield. Both gly-
cosylmethylamines were converted also into their crystalline hydrochlorides. The
procedure, applied to 1-deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol, led to 1-amino-
-1-deoxy-D-*glycero*-L-*manno*-heptitol (*III*) with simultaneous formation of D-galac-
tose. The aminoalditol *III* was isolated as its hydrochloride in 26% yield.

In spite of great number of hydroxy groups in the compounds *I–III*, we obtained
their reproducible mass spectra working at electron energy 12 eV. The mass spectra