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CYCLODIMERIZATION OF BUTADIENE IN PRESENCE OF SECONDARY AMINES AND CATALYZED BY CHIRAL NICKEL COMPLEXES

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According to [1], the reaction of morpholine with butadiene in the presence of the catalytic system  $Ni(acac)_2-PhP(o-menthyl)_2-Al(C_2H_5)_3$  gives the optically active 3-morpholyl-1-butene (I) and 1-morpholyl-2,7-octadiene (II).

For a more detailed study of the effect of the nature of chiral ligands, the structure of secondary amines, and the process conditions on the indicated reaction we studied the telomerization of butadiene with various amines in the presence of Ni complexes, activated by chiral phosphites. As the chiral activators or ligands we selected the following:



The experiments were run using an excess of the diene (amine : diene = 1 : 3) in a sealed glass ampul at -8 to  $60^{\circ}$ C and a reaction time of 140-840 h. The catalytically active complex was prepared at -10° by reducing Ni(acac)<sub>2</sub> with Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> in the presence of a chiral phosphite. Then the catalyst solution was transferred in an argon stream to the ampul, into which had previously been loaded the necessary amount of butadiene and appropriate secondary amine, and the mixture was kept at the given temperature.

Of the phosphites tested by us, only bis(menthyl) phenylphosphite (VI) facilitates the formation of a mixture of the previously described unsaturated amines [1]. When using phosphites (III) and (V) the sole reaction product is the optically active 4-ethyl-1-cyclohexene (X).



Phosphites (VII)-(IX) with low-valence nickel compounds form in the given reaction catalytically inactive complexes and completely block the polymerization of butadiene. The structure of (X) was confirmed by spec-

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TABLE 1. Effect of Nature and Structure of Chiral Phosphite and Structure of Amine on  $[\alpha]_D^{20}$  (+) of 4-Ethyl-1-cyclohexene (X) (reaction conditions: 0.002 mole of Ni(acac)<sub>2</sub>, 0.006 mole of phosphite, 0.008 mole of AlEt<sub>3</sub>, 0.6 mole of butadiene, and 0.3 mole of amine in 20 ml of benzene; 840 h; -8°C)

| Amine  | Chiral  | Total yield                                | {a} <sup>20</sup> (X),                             |
|--|---|--|--|
|  | phosphite   | of (X), %                                  | deg  |
| Piperidine<br>"a<br>Diethylamine<br>Hexamethylenimine<br>"b<br>Piperazine<br>Morpholine<br>Piperidine <sup>C</sup><br>"d<br>"e<br>"a | (III)<br>(V)<br>(VI)<br>(III)<br>(III)<br>(III)<br>(III)<br>(III)<br>(III)<br>(III)<br>(IV) | 14,77,210,428,416,24,69,030,716,813,412,1- | +115 +0.23 +104 +126 +90 +93 +54 +20.2 +37.2 +34.7 |

<sup>a</sup>A mixture of 12-18% of 1-piperidyl-2,7-octadiene and 3-piperidyl-1,7-octadiene is formed. <sup>b</sup>Reaction time 140 h.

c, d, eThe reactions were run at 20° and 1.8 and 130 atm, respectively.

tral methods, and also by counter synthesis. Thus, the reduction of 4-vinylcyclohexene (XI) [2] with a stoichiometric amount of  $H_2$  on 5% Pd/C in methanol leads to obtaining the optically inactive 4-ethyl-1-cyclohexene, which in its physicochemical properties is identical with (X).

It may be assumed that the cyclodimerization of butadiene in the presence of secondary amines initially gives the optically active (XI), which is then hydrogenated to (X). This is in agreement with the data given in [3, 4], where it was shown that unsaturated compounds can be reduced via the transfer of hydrogen from an amine or alconol to the olefin using transition metal complexes.

Actually, the heating of (XI) with an equimolar amount of a secondary amine, for example, with piperidine, in the presence of the catalytic system  $Ni(acac)_2 - (VI) - Al(C_2H_5)_3$  (1:3:3) leads to (X) in high yield. Unfortunately, the dehydrogenation products of piperidine could not be identified precisely. Consequently, in subsequent experiments we used 2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine (XII) as the hydrogen source, which is not only easily dehydrogenated in the presence of Pd complexes [3], but is also easily separated from the reaction products.

The cyclodimerization of butadiene using the complex Ni catalyst Ni(acac)<sub>2</sub>-(III)-Al( $C_2H_5$ )<sub>3</sub> at 11° in the presence of (XII) leads to a mixture of the optically active (X) and (XI), and also to 2,6-dimethyl-3,5-dicarb-ethoxypyridine:



The exclusive formation of (XI) is observed when the reaction temperature is lowered to  $-8^{\circ}$ , while the amount of (X) in the catalyst does not exceed 0.5%. The hydrogenation of (XI) on Pd/C gives (X) with  $[\alpha]_D^{20} + 14.4^{\circ}$ .

In order to obtain data on the mechanism of hydrogen transfer from the amine to the olefin during the conversion of butadiene to 4-ethylcyclohexene we studied the cyclodimerization of butadiene in the presence of 1,2,2,5,5-pentadeuteropiperidine using the catalytic system Ni(acac)<sub>2</sub>-(III)-Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (1:3:3,60°). As a result we obtained 4-ethylcyclohexene, M<sup>+</sup> 112, in 28% yield. The presence in the PMR spectrum of a one-proton multiplet signal at 0.83 ppm indicates that the ethyl group is represented mainly by the CH<sub>2</sub>CD<sub>2</sub>H fragment.



Fig. 1. Specific rotation of (X) as a function of the reaction temperature. Conditions: 0.002 mole of Ni(acac)<sub>2</sub>, 0.006 mole of phosphite, 0.008 mole of AlEt<sub>3</sub>, 0.6 mole of butadiene, and 0.3 mole of amine in 20 ml of benzene, 840 h.

On the basis of the obtained results it may be concluded that the reduction of (XI) to (X) is accomplished via hydrogen transfer from the amine to the olefin, in which connection evidently via the step of the oxidative cleavage of the N-H bond [5] with the intermediate formation of hydride complexes of type  $R_2N-Ni-H$ . For a rigid proof of the expressed assumption it is necessary to make a more detailed study of the mechanism of the indicated reaction, with an identification of the structure of the intermediate labile active complexes.

The structure of the secondary amine has a noticeable effect on the value of the specific rotation of (X). As can be seen from Table 1, the value of the optical activity of (X) falls from  $+126^{\circ}$  to  $+20.2^{\circ}$  in the series: diethylamine, piperidine, hexamethylenimine, piperazine, morpholine. In the given reaction, morpholine and piperazine apparently play the role of a bidentate ligand and in this way facilitate equalizing the formation rates of both 4-ethylcyclohexene enantiomers from butadiene.

The reaction temperature exerts a strong effect on the value of the specific angle of rotation of (X). For example, the value of the specific rotation angle of (X) increases from  $\pm 22.7$  to  $\pm 115^{\circ}$  with decrease in the cyclodimerization temperature from 60 to  $\pm 8^{\circ}$  (Fig. 1). The time of butadiene cyclodimerization has practically no effect on the  $[\alpha]_{D}^{20}$  of (X), but here its total yield increases somewhat (see Table 1).

According to [8], in the reaction of butadiene with fumaric acid the degree of asymmetric synthesis of tetrahydro-o-phthalic acid increases noticeably with increase in the pressure up to 5000 atm. In this connection we studied the effect of pressure on the cyclodimerization of butadiene and found that the specific rotation angle of (X) varies in the range  $30-90^{\circ}$  with increase in the pressure from 1 to 130 atm (see Table 1), which is in agreement with the data given in [6].

As a result, a study of the cyclooligomerization of butadiene in the presence of secondary amines on complex Ni catalysts, activated by chiral phosphites, made it possible to develop for the first time a convenient method for the one-step preparation of the optically active 4-ethylcyclohexene and 4-vinylcyclohexene.

## EXPERIMENTAL

The employed butadiene, piperidine, hexamethylenimine, 2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine, diethylamine, piperazine, and morpholine were at least 99.8% pure. The chiral phosphites:  $P(OC_{10}H_{19})_{3}$ ,  $[\alpha]_{D}^{20} + 24.2^{\circ}$ ;  $PhP(OC_{10}H_{19})_{2}$ ,  $[\alpha]_{D}^{20} + 60^{\circ}$ ;  $P(OC_{27}H_{48})_{3}$ ,  $[\alpha]_{D}^{20} + 13.8^{\circ}$ ;  $P(OC_{12}H_{19}O_{6})_{3}$ ,  $[\alpha]_{D}^{20} + 18.8^{\circ}$ ;  $PhP(C_{12}-H_{19}O_{6})_{2}$ ,  $[\alpha]_{D}^{20} + 31.5^{\circ}$ ;  $P(C_{9}H_{19}O_{3}, [\alpha]_{D}^{20} - 3.0^{\circ}$ ;  $P(C_{10}H_{17}O_{3}, [\alpha]_{D}^{20} + 0.2^{\circ}$  were obtained as described in [7]. The PMR spectra were recorded on a Tesla BS480-B instrument (CCl<sub>4</sub>, internal standard = HMDS), and the IR spectra were taken on a UR-20 spectrophotometer as a thin layer. The GLC analysis of the catalytic mixture was run on a Chrom-41 chromatograph equipped with a flame-ionization detector and a 2.4 m×3 mm column packed with 15% PM 1322/300 deposited on Chromosorb GAW-DMCS (60-80 min), and using helium as the carrier gas at a flow rate of 40 ml/min. The specific angles of rotation were determined using a Perkin-Elmer 141 polarimeter. The mass spectra were taken on an MX-13-06 instrument using an electron ionizing energy of 70 eV and an ionization chamber temperature of 200°C.

<u>4-Ethyl-1-cyclohexene (X) and 4-Vinylcyclohexene (XI)</u>. To a solution of 0.002 mole of Ni(acac)<sub>2</sub>, 0.006 mole of phosphite, and 10 ml of butadiene in 20 ml of benzene, in an argon stream, at  $-5^{\circ}$ , was added 0.008 mole of AlEt<sub>3</sub> and the mixture was stirred for 20 min. The catalyst solution was transferred in an argon stream to a 100-ml glass ampul, into which had previously been loaded 0.6 mole of butadiene and 0.2 mole of amine. The sealed ampul was thermostatted at the given temperature for a preset time. At the end of reaction the catalyzate was fractionally distilled through a column. The amine impurities were removed by chromatographing on a  $300 \times 28$  mm column packed with  $Al_2O_3$  (II activity), and using a 1:10 methanol-benzene mixture as the eluant. The results of the experiments are given in Table 1 and Fig. 1.

Compound (X), bp 134°,  $n_D^{20}$  1.3655,  $[\alpha]_D^{20}$  + 126°. Infrared spectrum ( $\nu$ , cm<sup>-1</sup>): 730, 3030 (cis-CH = CH), 1380, 1460 (CH<sub>3</sub>). PMR spectrum ( $\sigma$ , ppm): 0.89 m (3H, CH<sub>3</sub>), 1.25 m (4H, CH<sub>2</sub>), 1.58 m (1H, CH), 1.93 m (4H, CH<sub>2</sub>C = C), 5.5 (2H, CH = CH); M<sup>+</sup> 110. Found: C 88.1; H 12.3%. C<sub>8</sub>H<sub>14</sub>. Calculated: C 87.3; H 12.7%.

Compound (XI),  $[\alpha]_{D}^{20} + 18.2^{\circ}$  (from [2], bp 129°,  $n_{D}^{20}$  1.4650).

Partially deuterated 4-ethyl-1-cyclohexene, bp  $134^{\circ}$ , nD<sup>20</sup> 1.3595. PMR spectrum (o, ppm): 0.83 m (1H, CD<sub>2</sub>H), 1.5 m (5H, CH<sub>2</sub>, CH); 1.92 m (4H, CH<sub>2</sub>C=C), 5.5 m (2H, CH=CH).

## CONCLUSIONS

In the presence of secondary amines, nickel complexes with chiral phosphorus-containing ligands catalyze the asymmetric cyclodimerization of butadiene to 4-ethyl-1-cyclohexene and 4-vinyl-1-cyclohexene.

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