CONCLUSIONS

1. The condensation of N-(1-hydroxyimino-2-methyl-2-cyclohexyl)hydroxylamine with 1,2-dicarbonyl compounds leads to 2-hydroxy-1',2':2,3-cyclohexa-2,3-dihydropyrazine 1,4-dioxide derivatives.

2. The condensation of N-(1-hydroxyimino-2-cycloalkyl)hydroxylamines with 1,2-dicarbonyl compounds leads to pyrazine 1,4-dioxide derivatives.

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CODIMERIZATION OF ETHYLENE WITH ISOPRENE AND 1,3-CYCLOHEXADIENE IN PRESENCE OF CATALYTIC SYSTEMS BASED ON CYCLOPENTADIENYL COMPLEXES OF TITANIUM

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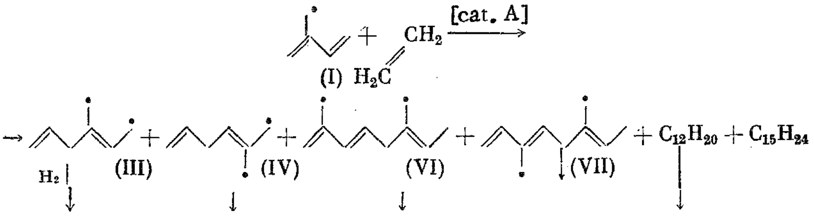
The selective cyclocodimerization of C_2H_4 with 1,3-butadiene or 1,3-pentadiene is catalyzed by the system $CpTi[OSi(CH_3)_3]_3—CH_3MgI$ to give vinylcyclobutanes [1]. Data on the codimerization of C_2H_4 with 1,3-dienes of different structure in the presence of metal complex catalysts based on Ti are practically absent in the literature.*

We studied the codimerization of C_2H_4 with isoprene (I) and 1,3-cyclohexadiene (II) using catalytic systems of the A ($CpTi(X')_2X''—CH_3MgI$, where $X' = X'' = OSi(CH_3)_3$ or $X' = Cl$, $X'' = Br$) and B ($Cp_2TiCl_2—C_2H_5MgBr$) type.

In contrast to butadiene and pentadiene, (I) and (II) do not enter into the [2 + 2]-cycloaddition reaction with C_2H_4 on catalysts of the A type. In the presence of the indicated systems, (I) reacts with C_2H_4 to give 4-methyl-1,4-hexadiene (III), 5-methyl-1,4-hexadiene (IV), and up to 15% of conjugated methylhexadienes (V) with the carbon skeleton of (III) and (IV) [see Scheme (1)]. Independent of the experimental conditions, the (III):(IV) ratio was ∿7:10, while the total yield of (III)-(V) when based on converted (I) did not exceed 30% even with a fourfold excess of C_2H_4. A substantial amount of high-boiling compounds is also present in the reaction products



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*It is mentioned in [2] that 2-methylhexadienes were obtained when isoprene is reacted with C_2H_4 in the presence of $CpTi(CH_2C_6H_5)_3$.

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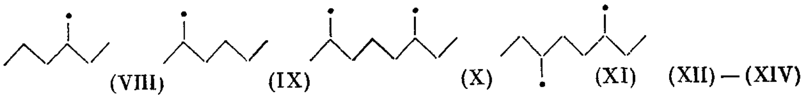
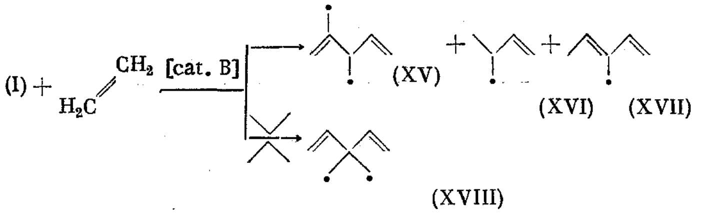


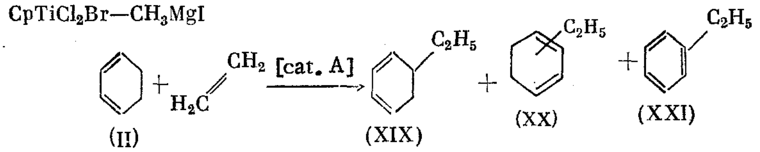
The selectivity of the codimerization is determined by the (I) conversion and the catalyst concentration. When the amount of the latter is decreased from 0.025 to 0.005 mole/liter the dimerization of (I) to 2,6-dimethyloctatriene-1,trans-3,6 (VI) and 3,6-dimethyloctatriene-1,3,6 (VII) in a ratio of ∿3:1 predominates, and due to this the overall selectivity of the codimerization drops to 10%. The structure of the C_{10}-trienes (VI) and (VII) was established on the basis of the IR, PMR, UV, and mass spectral data, and also on the basis of the hydrogenation and ozonolysis results. When the conversion of the starting diene exceeds 60% the dimers (VI) and (VII), which accumulate in the catalyzate, react with C_2H_4 to give predominantly i-C_{12}-trienes with the skeleton of the 3,6-(XII) and 3,7-dimethyldecanes (XIII) and 2,6-dimethyl-4-ethyloctane (XIV).

The codimerization of (I) with C_2H_4 on the catalytic system B is more selective. The same as in the reaction with butadiene, the ethylene moiety adds almost exclusively to the inner [C^3] atom of the diene to give dimethylpentadienes (XV)-(XVII) [3].

 (1)

The amount of the isomerization products of (XV), namely conjugated dienes (XVI) and (XVII), varied in the range from 15 to 50%, depending on the conversion of the starting diene. Codimer (XVIII), another product that is possible due to the unsymmetrical nature of the (I) molecule, was not detected in the catalyzate.

When (II) is reacted with C_2H_4 in the presence $CpTiCl_2Br—CH_3MgI$ system,

 (2)

the expected cyclocodimerization (bicyclo[4.2.0]octene) and linear codimerization (3-vinyl-1-cyclohexene) products were not detected [4]. Reaction between the comonomers leads to ethylcyclohexadienes (XIX), (XX) and ethylbenzene (XXI). The formation of (XIX) and (XX) can formally be depicted as being "dienylation," with the transfer of hydrogen from the cyclodiene to C_2H_4 [5]. Also not excluded is the fact that they are formed by migration of the multiple bond of the vinyl group into the ring of the initially formed vinylcyclohexene. The yield of the ethylcyclohexadienes when based on converted (II) reaches 90%, while the conversion of (II) does not exceed 20%. In THF solution the selectivity of forming (XIX) (73%) is nearly twice that in toluene as the medium.

EXPERIMENTAL

The employed monomers were at least 99% pure. The procedure for the codimerization of dienes with C_2H_4 is reported in [1, 6].

The PMR spectra were measured on a Tesla BS-467 spectrometer (60 MHz) in CCl_4 solution relative to TMS. The IR spectra were taken on a UR-20 instrument (CCl_4, film). The mass spectra were obtained on an LKB-2091 instrument, while the UV spectra were obtained on a Specord VIS instrument (hexane or heptane). The GLC analysis was run on an LKhM-8MD chromatograph, using a 500 × 0.3 cm column packed with 5% SE-30 and a 50-m capillary column packed with squalane, and N_2 as the carrier gas. The preparative separation was run on a Pye—Unicam-105 chromatograph, using a 200 × 0.8 cm column packed with 10% PEGA deposited on Chromosorb P, a 450 × 0.8 cm column packed with 15% Apieson deposited on Chezasorb-AW, a temperature of 80-150°C, and N_2 as the carrier gas.

<u>Codimerization of C_2H_4 with Isoprene.</u> a) To 0.23 g (0.6 mmole) of $CpTi[OSi(CH_3)_3]_3$, 6.8 g (100 mmoles) of (I), and 12.5 g (445 mmoles) of C_2H_4 in 6.0 ml of benzene at −10° was

added 2.4 mmoles of CH_3MgI in ether and the stirred mixture was heated for 1.5 h at 145°. The catalyzate was distilled and here we collected 1.14 g of a fraction with bp 82-113°, which, based on the GLC analysis data, contains 40.5% of (III), 49.7% of (IV), 7.6% of (V), and the remainder is C_6H_6. A mixture of (III) and (IV) (75:25) and the pure (IV) were isolated by preparative GLC. The IR and PMR spectra of (IV) are identical with those given in [7]. The exhaustive hydrogenation of the codimers fraction on Pt/C gave a mixture of (VIII), (IX), and methylcyclohexane (55:40:2), which were identified by GLC. The residue was extracted with benzene, the solvent was removed under reduced pressure, and the residue was vacuum-distilled, collecting the C_{10}- and C_{12}-trienes fractions. The 29-66° (0.5 mm) fraction was separated by preparative GLC to give: 1.23 g (72%) of (VI), bp 170-171°. Mass spectrum, m/e (%): 136(31), 121(47), 107(100), 94(38), 93(77), 91(69), 81(17), 79(67), 67(24), and 55(25). Ultraviolet spectrum: λ_{max} (hexane) 229 nm (ε 26000); 0.34 g (21%) of (VII), bp ∿176°. The IR and PMR spectra of (VI) and (VII) corresponded to those given in [8, 9]. The hydrogenation of the dimers fraction gave (X) (bp 159-160°, n_D^{20} 1.4108) and (XI), which was identified by comparing with an authentic sample, in a 70:23 ratio.

Ozonolysis of Isoprene Dimers (VI) and (VII). A stream of O_2, containing ∿5% of O_3, was passed through a solution of 0.9 g of a (VI)-(VII) mixture in 8.0 ml of AcOH at 5° until O_3 appeared at exit from the reactor. The mixture was treated with 10 ml of H_2O_2 solution and kept for 40 h at 20°. The solvent was evaporated, and the residue was methylated with an ether solution of diazomethane. After removal of the ether and vacuum-distillation the mixture contained the methyl esters of pyruvic and acetylacetic acids, which were identified by GLC.

Based on the chromato-mass spectrometry data, the fraction of dodecatrienes (yield 0.42 g), with bp 59-94° ($5\cdot10^{-3}$ mm), contained a mixture of (VI), (VII) (7%), seven hydrocarbons with m/e 164 (82%), and a small amount of isoprene trimers with m/e 204. After hydrogenation the mixture was found to be predominantly isododecanes, whose mass spectra proved to be close. To identify (XII)-(XIV) (respectively 37, 21, and 10%) we used an authentic mixture (2:1) of isoprene cotrimers with C_2H_4, which was hydrogenated in the presence $Ni(acac)_2-(C_6H_5O)_3P-(C_2H_5)_2AlOC_2H_5$ [10]. The conversion of (I) was 60%, and the yields of (III)-(V), (VI) + (VII), and $C_{12}H_{20}$ when based on converted (I) were respectively 18, 37, and 7%.

b) In a similar manner, the codimerization of 6.8 g of isoprene and 12 g of C_2H_4, in the presence of 0.249 g (1.0 mmole) of Cp_2TiCl_2 and 1.9 ml (2.6 mmoles) of an ether solution of EtMgBr, in 10 ml of toluene at 155-160° for 1 h gave 2.15 g of (XV), which was identical (bp, n_D^{25}, IR and PMR spectra) with that described previously [7], and 0.88 g of a mixture of (XVI) and (XVII). According to the PMR spectrum [(δ, ppm): 6.78 double d, 5.38-5.92 m, 4.72-5.20 m, 1.85 s, 1.78 s, and 1.67 d ($J = 6.5$ Hz), with relative integral intensities of 0.3:1.0:2.3:3.1:4.1:3.2], the (XVI)/(XVII) ratio is equal to ∿3.5:1. Ultraviolet spectrum of the mixture: λ_{max} (heptane) 232 nm (ε 25000). Hydrogenation of the codimers fraction gave 93% of 2,3-dimethylpentane, 2.8% of 2-methylhexane, and 4.1% of unidentified hydrocarbons. The conversion of (I) was 60%, and the yield of (XV)-(XVII) was 55%.

Codimerization of C_2H_4 with 1,3-Cyclohexadiene. A mixture of 0.315 g (1.2 mmoles) of $CpTiCl_2Br$, 4.5 mmoles of MeMgI in ether, 8.8 g (110 mmoles) of (II), and 12 g of C_2H_4 in 10 ml of THF was stirred for 30 min at 160°. The mixture was treated with 5% HCl solution and 0.5 ml of ethanol, extracted with ether, and distilled in a N_2 stream, where we collected 1.64 g of a fraction with bp 121-138°, which analyzed 74% of (XIX), 23% of (II), and 3% of (XXI), which were isolated by preparative GLC. Compound (XIX): n_D^{20} 1.4722; mass spectrum, m/e (%): 108(24), 93(6), 79(100); PMR spectrum (δ, ppm): 5.77 br. s (4H, CH=CH), 2.12 m (3H, $CH<$ and CH_2), 1.37 m (2H, CH_2-CH_3), and 0.92 t (3H, CH_3); IR spectrum (ν, cm^{-1}): 2980, 2965, 1460, 1380 (CH_3), 2930, 2862, 1430 (CH_2), 3040, 1635, 1585, and 675 (CH=CH); (XX) (mixture of 1- and 2-ethylcyclohexadienes), mass spectrum: 108(32), 93(36), 91(47), and 79 (100); PMR spectrum: 6.20 q (0.3H, CH-), 5.25-5.87 m (2.7H, $>C{=}CH$ and CH=CH), 2.05 m (4H, CH_2), 1.33 m (2H, CH_2-CH_3) and 1.04 t (3H, CH_3). Compound (XXI), mass spectrum: 106(34), 91(100); PMR spectrum: 7.17 s (5H), 2.62 (2H, CH_2), and 1.24 t (3H, CH_3).

The total yield of (XIX) and (XX) was 87%, and the conversion of (II) was 17%.

CONCLUSIONS

Isoprene and 1,3-cyclohexadiene react with ethylene under the influence of catalytic systems based on the mono- and dicyclopentadienyl complexes of titanium to give linear codimerization and oligomerization products. The reaction of isoprene with ethylene in the presence of $Cp_2TiCl_2—C_2H_5MgBr$ proceeds selectively on the type of 3,4-addition to give 2,3-dimethylpentadienes.

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HOMODIMERIZATION OF BICYCLO[2.2.1]-2-HEPTENE IN PRESENCE OF COMPLEX NICKEL CATALYSTS

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According to [1-3], bicyclo[2.2.1]-2-heptene (norbornene, NB) reacts with 1,3-dienes in the presence of homogeneous metal complex catalysts to give both linear and cyclic cooligomers. The homodimerization of NB to a mixture of isomeric bi-2,2-norbornylidenes proceeds on WCl_6, activated with small amounts of added water [4].

We were the first to establish that when NB is heated in the presence of a catalytic system, composed of $Ni(acac)_2$, $P(OEt)_3$ and $Al(C_2H_5)_3$, the cyclic hydrocarbon (I) is formed in high yield (∿70%), whose molecular weight, based on the mass spectral data, is equal to 188. The IR spectrum has bands at 690, 890, 3030, and 3075 cm^{-1}, which are characteristic for a cis double bond and a terminal methylene group. The PMR spectrum contains, together with the signals of the CH and CH_2 protons, two-proton signals with centers at 4.62 and 5.55 ppm, which belong to olefinic protons. The signals in the ^{13}C NMR spectrum at 48.24, 37.04, 39.95, 37.94, 30.08, 29.59, and 25.89 ppm indicate the presence of a norbornane skeleton with a 2-exo substituent in the obtained dimer (I) [5]. The UV spectrum has an absorption band with a maximum at 240 nm ($\varepsilon \sim 800$), which is apparently caused by the presence, along with (I), of a conjugated isomer (II) of the phellandrene type [6], the amount of which in the mixture, judging by the extinction value, does not exceed 5%.

The dehydrogenation of (I) with chloranil in refluxing tert-butanol for 8 h [7] leads to exo-2-(o-tolyl)norbornane (III), whose structure was confirmed by spectral methods, and also by counter synthesis. Thus, the hydrogenation of exo-5-(o-tolyl)-2-norbornene, obtained as described in [8], on Pd/C in methanol proceeds with the absorption of the stoichiometric amount of H_2 to give exo-2-tolylnorbornane, which is completely identical with (I).

On the basis of the obtained data, the structure of exo-2-(4'-methylenecyclohex-1'-en-3'-yl)norbornane (I) was proposed for the NB dimer.

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