LINEAR COPOLYMERIZATION OF PIPERYLENE WITH PROPYLENE

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In continuation of an investigation into the copolymerization of 1,3-dienes with olefins, we have examined the reaction of propylene with cis- and trans-piperylene alone and in mixtures, in the presence of the system $NiCl_2[(C_4H_9)_3P]_2$—$(C_2H_5)_2AlCl$. trans-Piperylene [trans-(I)] reacts with I in a ratio of 1:1 in solution in CH_2Cl_2 to give a mixture of oligomers in 90% overall yield, based on (I) (see Table 1). Approximately 70% of the mixture is composed of 2,3-dimethyl-1,4-hexadiene (II) and 4,5-dimethyl-2,5,8-undecatriene (III), the remainder being hydrocarbons (IV) and (V), formed by isomerization of the diene (II) and triene (III). The total amount of (IV) and (V) varied little from experiment to experiment, but an increase in the reaction temperature from 90 to 110° increased the proportion of the diene (IV), the proportion of the triene (V) falling to 2%.

The IR spectrum of (II) shows bands at 895, 975, 3030, and 3090 cm^{-1}, characteristic of methylene and trans-disubstituted double bonds. The PMR spectrum showed a doublet at 1.58 ppm (J = 4 Hz), of area corresponding to six protons, permitting assignment to the two CH_3 groups at the double bond. The three-proton doublet at 0.95 ppm (J = 7 Hz) corresponds to the CH_3 on C-3. The multiplet at 1.98 ppm, relative intensity 1, corresponds to the proton on C-3. The mass spectrum of (II) displays intense peaks for $[M-15]^+$, $[M-41]^+$, and $[M-69]^+$, arising by loss of CH_3, C_3H_5, and C_5H_9 respectively from the molecular ion.

The PMR spectrum of (III) has a multiplet at 0.87 ppm corresponding to the signals for the two CH_3 groups at C-4 and C-10, and the six-proton doublet (J = 4 Hz) at 1.58 ppm is assigned to the protons of the two CH_3 groups at the double bonds. The five vinyl protons are seen as a group of signals centered at 5.1 ppm. The broad multiplet centered at 1.9 ppm corresponds to the four methylene and one methine protons. The mass spectrum of the triene (III) exhibits intense peaks for the ions $[4-15]^+$, $[M-41]^+$, $[M-69]^+$ and $[M-95]^+$, formed by fission of the fragments CH_3, C_3H_5, C_4H_7, C_5H_9, and C_7H_{11} from the molecular ion (m/e 178). Ozonolysis of the triene afforded 2-acetylpropionic, malonic, and oxalic acids.

The structures of the isomers (IV) and (V) were confirmed by synthesis, by isomerization of hydrocarbons (II) and (III) by means of t-C_4H_9OK in DMSO, and by the spectral data. In particular, the PMR

TABLE 1. Copolymerization of Piperylene with Propylene*

Solvent	Piperylene	Molar ratio of monomers		Overall yield, %	Composition of cooligomers, %				
		piperylene	propylene		(II)	(III)	(IV)	(V)	higher oligomers
CH_2Cl_2	trans	1	1	85	35	30	10	8	17
CH_2Cl_2	trans	1	1,5	90	38	34	8	4	16
CH_2Cl_2	»	1	4	70	30	28	12	8	22
CH_2Cl_2	cis	1	1,5	20	40	25	5	2	28
CH_2Cl_2	cis + trans	1	1,5	95	40	30	10	5	15
C_6H_5Cl	trans	1	1,5	80	30	40	—	4	26
$CHCl_3$	»	1	1,5		Higher oligomers				

*Experimental conditions: 0.5 g of $NiCl_2[(C_4H_9)_3P]_2$, 0.8 g of $(C_2H_5)_2AlCl$, 50 g of piperylene. Quantity of propylene shown in the table, 20 ml of CH_2Cl_2, 90°, 2 h.

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spectrum of the triene (V) contains a six-proton multiplet centered at 0.86 ppm, corresponding to the two CH_3 groups at C-2 and C-10. The singlet at 1.61 ppm corresponds to the six protons of the two CH_3 groups at the double bonds. The methylene protons at C-2, C-7 and C-10 produce the multiplet centered at 2.1 ppm (6H). The group of signals at 4.9-5.3 ppm is assigned to the four vinyl protons. Neither the diene (IV) nor the triene (V) form adducts with maleic anhydride, even on prolonged boiling in xylene solution, due to the highly alkylated double bonds.

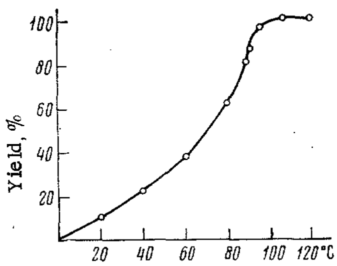
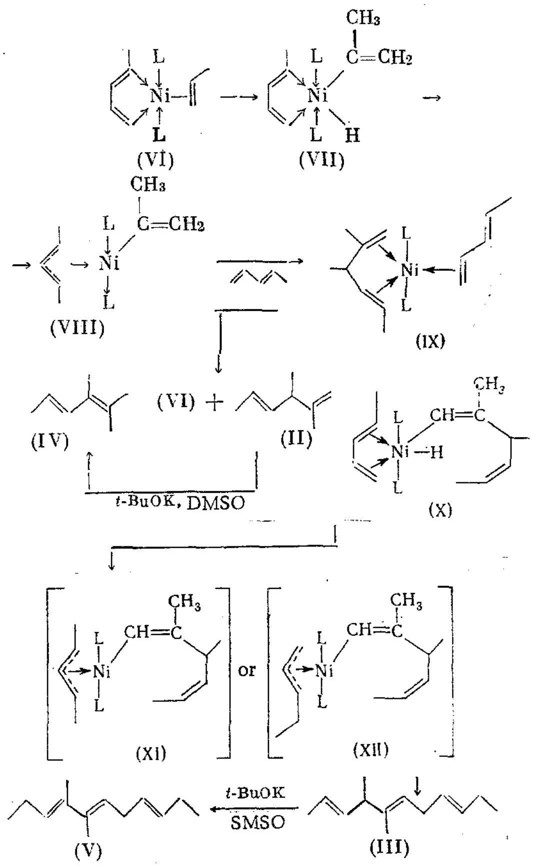


Fig. 1. Temperature dependence of the overall yield of cooligomers of piperylene with propylene. $NiCl_2[P(C_4H_9)_3]_2$ (0.5g), $(C_2H_5)_2AlCl$ (0.8 g), 50 g of a mixture of cis- and trans-piperylene (28 : 72), 46 g of propylene, 20 ml CH_2Cl_2, 2 h.

The nature of the solvent, monomer ratio, and temperature have a considerable effect on the yield and composition of the oligomers. Thus, replacement of CH_2Cl_2 by chlorobenzene results in the formation of (II) and (III) only, isomers (IV) and (V) not being formed, even in traces. Substantial amounts of higher oligomers are formed, however. In chloroform solution, formation of the hydrocarbons (II)—(V) is completely suppressed. The reaction product is composed of undistillable isomers whose identification has proved difficult. An increase in the amount of C_3H_6 employed results in a decrease in the overall yield of (II)–(V), with a simultaneous increase in the proportion of higher oligomers.

Copolymerization of cis-(I) with C_3H_6 under optimum conditions gives a 20% yield of the compounds mentioned above, in the proportions (II) : (III) : (IV) : (V) = 40 : 25 : 5 : 2. A substantial proportion of the reaction product is composed of higher oligomers. Reaction of a mixture of cis-(I) and trans-(I) (28 : 72) with C_3H_6 proceeds quite smoothly with the formation of up to 90% (see Fig. 1) of a mixture of oligomers (II)—(V), in approximately the same proportions as in the case of trans-(I).

On the basis of these results, and those of Ugo [1], the formation of cooligomers (II) and (III) may be represented by the scheme given below. In the first stage, both monomers enter the coordination sphere of the nickel to form the complex (VI). There then follows oxidative addition of propylene accompanied by fission of a C—H bond. The resulting complex (VII) is converted by proton transfer into the π-allyl com-



plex (VIII). Synchronous duplication of the π-allyl ligand with an isopropenyl residue leads to the formation of the 1,4-diene. Subsequently, reaction with an excess of the monomers results in extrusion of 2,3-dimethyl-1,4-hexadiene with the formation of the complex (VI) and (II).

The formation of the triene (III) may be represented as cycloaddition of the diene (II) to (I) via the complex (X), in which the transfer of a proton to the activated molecule (I) results in the formation of the two possible π-complexes (XI) and (XII).

It is suggested that the addition of the hexadiene residue to the monosubstituted π-allyl complex (XII) is preferred to addition to the disubstituted π-allyl moiety in the complex (XI).

EXPERIMENTAL METHOD

The purity of the monomers was not less than 99.5%. Analysis of the isomer mixtures was carried out on a "Tsvet-102" chromatograph with a flame ionization detector, column length 2 m, 15% Apiezon L on Celite 545, carrier gas nitrogen. The PMR, IR, and UV spectra were recorded on a "Tesla B-480B" (CCl_4, HMDS), UR-20 (film), and "Specord UV-VIS" (heptane), and mass spectra on an MX-13-06, ionizing electron energy 50 eV, ionization chamber temperature 200°.

Cooligomerization of Piperylene with Propylene. To a solution of 0.5 g of $NiCl_2[(C_4H_9)_3P]_2$ in 20 ml of CH_2Cl_2 or other solvent at 0° was added 0.8 g $(C_2H_5)_2AlCl$, and the mixture was stirred for 30 min. The catalyst was transferred by means of a stream of argon into an autoclave containing 50 g of (I) (trans-, cis, or a mixture of the two, 73 : 27), C_3H_6 was introduced, and the contents heated for 2 h at 90°. The catalyzate was distilled in steam, the distillate separated, and the contents of the flask were extracted with pentane. After working up in the usual way, the oligomers were separated by distillation. The chromatographically pure hydrocarbons had the following constants:

2,3-Dimethyl-1,4-hexadiene (II), bp 105-106°; n_D^{20} 1.4663. Found: C 87.6; H 12.2%; m/e 110. C_8H_{14}. Calculated: C 87.3; H 12.7%.

4,5-Dimethyl-2,6, 9-undecatriene (III), bp 190-191°; n_D^{20} 1.4541. IR spectrum (ν, cm^{-1}): 980, 3030 (trans-CH = CH). Found: C 87.5; H 12.6%; m/e 178. $C_{13}H_{22}$. Calculated: C 87.7; H 12.3%.

2,3-Dimethyl-2,4-hexadiene (IV), bp 111-112°; n_D^{20} 1.4622. UV spectrum, $\lambda_{\max}^{\text{heptane}}$ 231 nm, ε 1200. IR spectrum (ν, cm^{-1}); 975, 3030 (trans-CH = CH). PMR spectrum (δ, ppm): 1.62 (12H), J = 3 Hz; 4.9-5.2 (2H, CH = CH); m/e 110.

4,5-Dimethyl-3,5,8-undecatriene (V), bp 195-196°; n_D^{20} 1.4689. UV spectrum, $\lambda_{\max}^{\text{heptane}}$ 232 nm, ε 13,500. IR spectrum (ν, cm^{-1}): 980, 3030 (trans-CH = CH); m/e 178.

Preparation of the Conjugated Hydrocarbons (IV) and (V). A solution of 10 g of the corresponding hydrocarbon (II) or (III) and 1 g of C_4H_9OK in 29 ml of absolute DMSO was heated at 70° for 2 h, diluted with water, and the product extracted with pentane. After working up in the usual way, the (IV) and (V) obtained were identical with the hydrocarbons isolated from the oligomerization experiments.

Ozonolysis of the Triene (III). Into a solution of 5 g of (III) in 20 ml of CH_3COOH at 10° was passed a stream of O_2 containing 6-7% of O_3, until it escaped from the outlet, whereupon 5 ml of HCOOH and 5 ml of H_2O_2 were added, and the mixture kept for one day at 20°. After evaporation in vacuo, the residue was methylated with diazomethane. From the GLC results, the mixture contained the methyl esters of oxalic, malonic, and 2-acetylproprionic acids. These were isolated by preparative GLC and identified by comparison with authentic samples.

Methyl 2-acetylpropionate, bp 42° (2 mm); n_D^{20} 1.4231. IR spectrum (ν, cm^{-1}); 1708 ($\rangle C = O$), 1740 (CO_2CH_3). PMR spectrum (δ, ppm): 1.11 (3H, CH_3), J = 6 Hz; 2.09 (3H, CH_3C). Found: C 55.5; H 7.6%; m/e 130. $C_6H_{10}O_3$. Calculated: C 55.2; H 7.7%.

CONCLUSIONS

Linear cooligomerization of piperylene with propylene over the catalyst $NiCl_2[P(C_4H_9)_3]_2$—$(C_2H_5)_2AlCl$ results in the formation of 2,3-dimethyl-1,4-hexadiene and 4,5-dimethyl-2,5,8-undecatriene, and to their isomers containing conjugated double bonds.

LITERATURE CITED

1. R. Ugo, Aspects of Homogeneous Catalysis, Reidel (1974).