TELOMERIZATION OF CYCLIC AND LINEAR GLYCOLS WITH BUTADIENE, CATALYZED BY PHOSPHINE COMPLEXES OF PALLADIUM

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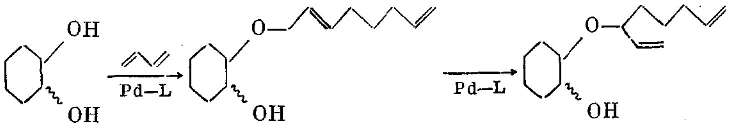
In a continuation of an investigation into the reactions of 1,3-dienes with polyhydric alcohols [1, 2] we have studied the effect of the structure of cyclic cis- and trans-glycols as well as of unsaturated linear 1,4- and 1,8-diols on the direction and selectivity of their telomerization with butadiene (BD) in the presence of the catalytic system $Pd(acac)_2$—PPh_3—$Al(C_2H_5)_3$(Pd—L). As the glycols we chose cis- (I) and trans-1,2-cyclohexanediols (II), trans-1,2-cyclooctanediol (III), trans-1,2-cyclododecanediol (IV), Z-5-cyclooctene-trans-1,2-diol (V), E-5-cyclododecene-trans-1,2-diol (VI), Z-2-butene-1,4-diol (VII), and Z-4-octene-1,8-diol (VIII), which were synthesized by the methods described in [3-5].

On telomerizing (I) with a fivefold excess of BD in absolute tert-butanol at 100°C (10 h) 1,3,7-octatriene (IX) (7%) and the mono-2,7-octadienyl ether (X) are formed in 93% yield. Under analogous conditions (II) reacts with BD, being converted to the monoether (XI) and octatriene (IX) (4:1) in a total yield of ~80%.

Since the nature and structure of the solvent have an appreciable effect on the structural selectivity of the linear and cyclic oligomerization of 1,3-dienes [6-8], we studied the telomerization of (I) and (II) with BD in various solvents (Table 1). The highest yields of the ethers (X) and (XI) are obtained with $t-C_4H_9OH$, DMFA, and THF.

It should be noted that all our attempts to obtain bis-2,7-octadienyl ethers from (I) and (II) and BD were unsuccessful due to an increase in the concentrations of BD and the catalyst, as well a change in the nature and structure of the components in the catalytic system and in the reaction conditions. The bulky 2,7-octadienyl radicals in the ethers (X)—(XIII) evidently hinder the approach and the coordination of the adjacent OH groups with the central atom of the catalyst, thereby exhibiting steric hindrances for the reaction of the OH groups with the bis-π-allyl complexes of Pd under the telomerization conditions



(I), (II) (X), (XI) (XII), (XIII)

The temperature of the telomerization process has a marked effect on the yield and composition of the products from the reaction of (I) and (II) with BD. The experiments were conducted with absolute THF because subsequently not only the initial monomers are readily dissolved but also the telomerization products. In the experiments with (I) an increase in the telomerization temperature from 40 to 120°C promotes a decrease in the content of (X) from 78 to 58% in the reaction mass, but here the fraction of the ether (XII) increases to 15%. In our opinion, the increase in the fraction of (XII) with an increase in the telomerization temperature is associated with the conversion of (X) to (XII) under the action of the Pd complexes. In fact, heating (X) under telomerization conditions over Pd—L gives (XI) with a yield of ~50%. In the case of (II) a change in the telomerization temperature has little effect on the total yield of oligomers and on the content of the unsaturated ethers (XI) and (XIII). An increase in the telomerization period (>10 h), irrespective of the structure of the initial cyclohexanediols, has virtually no effect on

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TABLE 1. Effect of the Nature of the Solvent on the Yield and Composition of the Products from the Telomerization of cis- and trans-1,2-Cyclohexanediols with Butadiene

Glycol	Solvent	Total yield of ethers, %	Telomerization products and their yield, %		
			(X), (XI)	(XII), (XIII)	(IX)
(I)	t-C_4H_9OH	93	93	–	7
	CH_3CN	91	91	–	9
	DMFA	88	86	2	12
	THF	76	69	7	24
	CH_3COCH_3	56	55	1	44
	DMSO	50	47	3	50
(II)	DMFA	83	83		17
	THF	83	81	2	17
	t-C_4H_9OH	81	81		19
	CH_3CN	76	71	5	24
	CH_3COCH_3	65	63	2	35
	DMSO	22	22	–	78

Reaction conditions: 100°C, 4 h, 9 mmole of (I), (II), 36 mmole BD, 0.09 mole $Pd(acac)_2$, 0.27 mmole PPh_3, 0.36 mmole $AlEt_3$.

the composition and total yield of the unsaturated ethers (X)–(XIII), the highest content of which is attained after 8-10 h in the mixture of oligomers.

An increase in the size of the hydrocarbon ring in the cycloalkane-1,2-diols has little effect on the direction and selectivity of their telomerization with BD. In particular, when (III) or (IV) reacts with BD in the presence of Pd–L catalyst (100°C, 10 h) in absolute THF the corresponding mono-2,7-octadienyl ethers (XIV) and (XV) are obtained in fairly high yields. In addition to the ethers (XIV) and (XV), compound (IX) and dodecatetraene (XVI) are formed, the total yield of which is ∼39% in the experiments with (IV).

The structure of the butadiene trimer has been confirmed by IR, UV, PMR, and mass spectrometry. The molecular weight found by mass spectrometry is 162, which corresponds to the combination of three butadiene molecules. The IR spectrum contains the absorption frequencies for vinyl (920, 1000, 3080 cm^{-1}), trans-disubstituted (980, 1645, 3020 cm^{-1}), and conjugated (1600, 1650 cm^{-1}), C=C bonds.

In the UV spectrum there is an absorption maximum at 227 nm (ε 27,000). In the PMR spectrum a signal is observed at 2.7 ppm which is assigned to a CH_2 group located between double bonds. The multiplets having a center at 2.0 and 1.5 ppm correspond to the signals from allyl and methylene protons. The olefinic protons resonate in the range 4.8-6.0 ppm. The results obtained enabled us to propose the structure 1,3,6,11-dodecatetraene (XVI) for the trimer.

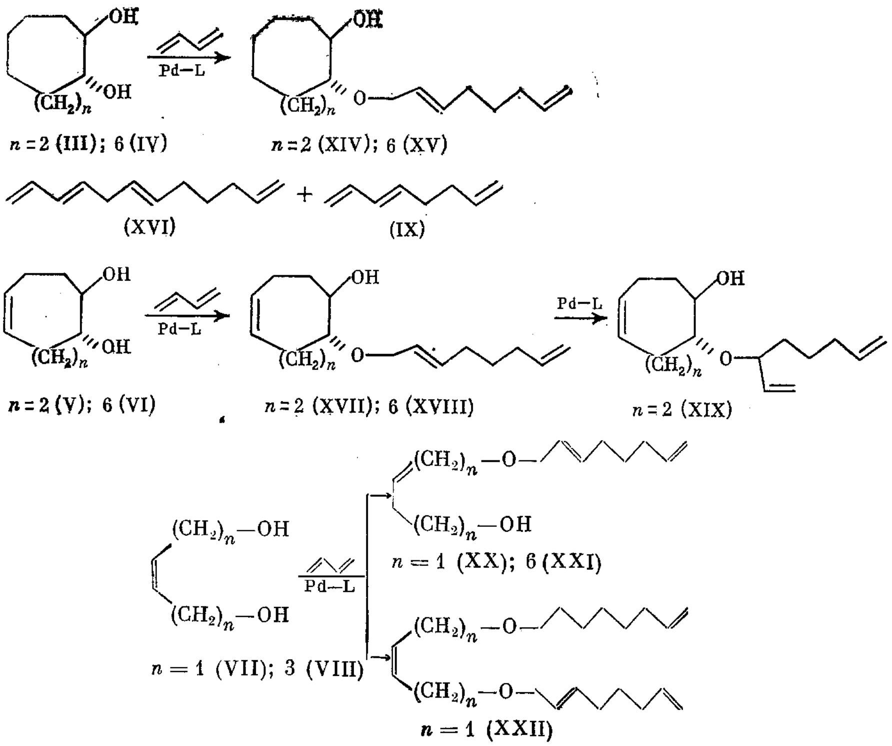
The cycloalkanediols having a double bond promote an increase in the selectivity of telomerization with respect to the mono-2,7-octadienyl ethers. For example, the telomerization of Z-5-cyclooctene-trans-1,2-diol (V) and E-5-cyclododecen-trans-1,2-diol (VI) with BD leads to the monoethers (XVII) and (XVIII). The yields of the latter are increased to 83 and 89%, respectively. The amount of (IX) and (XVI) in these experiments are reduced markedly. This would seem to be due to the double bond in the cycloalkenediol molecules participating in the formation of a ligand environment around the metal, which also leads to an increase in the selectivity of the reaction.

The ethers (XVII) and (XVIII) formed could probably be coordinated at the central atom of the catalyst, preventing at once the approach and activation of two and more butadiene molecules and, consequently, the formation of homo dimers and trimers of the diene.

To compare the reactivity of the cyclic glycols and linear unsaturated diols, we studied the telomerization of Z-2-butene-1,4-diol and Z-4-octene-1,8-diol with BD, which leads to the mono- and bis-2,7-octadienyl ethers (XX)–(XXII) in fairly high yields. It must be noted that (VII) gives a mixture of mono- and bisethers (XX) and (XXII) in a yield of ∼76%, whereas (VIII) is converted only into the monoether (XXI).

For the series of unsaturated 2,7-octadienyl ethers (X), (XI), (XVII) their isomerization has been studied under the action of complex catalysts of the type $Pd(acac)_2-PPh_3-AlR_3$. These ethers undergo skeletal isomerization fairly easily, which leads to the formation of the corresponding branched 1-vinyl-5-hexenyl ethers (XII), (XIII), and (XIX). It should be noted that thermal isomerization of the 2,7-ethers is not observed.

Thus, this study of the telomerization of cyclic 1,2-glycols and linear unsaturated 1,4- and 1,8-diols enabled us to establish that these alcohols are distinguished by a high reactivity in the telomerization reaction with butadiene in the presence of low-valency palladium complexes. The cycloalkane-1,2-diols react with butadiene, giving mono-octadienyl ethers exclusively, irrespective of the structure of the diol and the size of the hydrocarbon ring, while the linear alcohols are converted into a mixture of mono- and bisethers



n = 2 (III); 6 (IV) n = 2 (XIV); 6 (XV)

(XVI) + (IX)

n = 2 (V); 6 (VI) n = 2 (XVII); 6 (XVIII) n = 2 (XIX)

n = 1 (VII); 3 (VIII) n = 1 (XX); 6 (XXI) n = 1 (XXII)

EXPERIMENTAL

Monomers of ⩾ 99% purity were used. The mixtures of unsaturated ethers were analyzed on a Chrom-41A chromatograph, using a flame-ionization detector and a column 1.2 m long containing SE-30; the carrier gas was nitrogen. The PMR spectra were obtained on a Tesla BS-487B instrument for solutions in CCl_4 (internal standard HMDS). The IR spectra were recorded on a UR-20 spectrophotometer (film), and the mass spectra on an MKh-13-06 instrument having an energy of 70 eV for the ionizing electrons and an ionization chamber temperature of 200°C.

Telomerization of Diols with Butadiene. To a solution of 0.25 g $Pd(acac)_2$, 0.63 g $P(Ph)_3$ in 20 ml abs. THF, cooled to –20 to 15°C, 0.35 g $Al(Et)_3$ was added with stirring under a flow of Ar, and it was maintained over a period of 10-15 min. The solution was transferred to a cooled 300-ml autoclave, where 0.8 mole of the diol and 2.4 moles BD had been placed previously. The autoclave was heated at a given temperature for the period necessary, then the catalyzate was filtered through a mixed bed of Al_2O_3 (100 g) and activated carbon (10 g). After removing the solvent the residue was sublimed under vacuum.

From 10 g of (I) and 28 g of BD (80°, 4 h) we obtained the mixture 17 g (68%) of the ether (X), 2 g (8%) of the ether (XII), and 6 g (24%) of (IX). By subliming this mixture (X) and (XII) were isolated separately.

Mono-2,7-octadienyl Ether of cis-1,2-Cyclohexanediol (X). bp 92°C (1 mm), n_D^{20} 1.4818. IR spectrum (ν, cm^{-1}): 920, 1000, 3085 ($CH=CH_2$), 980, 1645, 3010 (trans-CH=CH), 1110 (COC), 3450 (OH). PMR spectrum (δ, ppm): 1.48 m (10 H, CH_2), 2.0 m (4 H, $CH_2C=C$), 2.42 m and

3.69 m (2H, CHO), 3.25 (1H, OH), 3.88 d (2H, $OCH_2C=C$, 4.9 m (2H, $C=CH_2$), 5.5 m (3H, CH=CH, CH=C), M$^+$ 224.

Mono-1-vinyl-5-hexenyl Ether of cis-1,2-Cyclohexanediol (XII). bp 78°C (1 mm), n_D^{18} 1.4748. IR spectrum (ν, cm^{-1}): 920, 1000, 3085 ($CH=CH_2$), 1110 (COC), 3480 (OH). PMR spectrum (δ, ppm): 1.42 m (12H, CH_2), 2.0 m (3H, $CH_2C=C$, OH), 3.23 m (1H, CHO), 3.66 m (2H, CHO), 4.92 m (4H, $C=CH_2$), 5.5 m (2H, CH=C), M$^+$ 224.

From 10 g (II) and 28 g BD (60°C, 10 h) 18 g (90%) of the ether (XI) and 2 g (10%) of (IX) are obtained.

Mono-2,7-octadienyl Ether of trans-1,2-Cyclohexanediol (XI). bp 103.5°C (1 mm); n_D^{18} 1.4824. IR spectrum (ν, cm^{-1}): 920, 1000, 3080 (CH=CH), 975, 1640, 3005, (trans-CH=CH), 1110 (COC), 3450 (OH). PMR spectrum (δ, ppm): 1.2 m (2H, CH_2), 1.5 m (8H, CH_2), 2.0 m (4H, $CH_2C=C$), 2.84 m (2H, CHO), 3.32 m (1H, OH), 3.94 d (2H, $OCH_2C=C$), 4.87 m (2H, $C=CH_2$), 5.52 m (3H, CH=CH, CH=C), M$^+$ 224.

From 10 g (III) and 22 g BD (100°C, 10 h) 11 g (53%) of the ether (XIV), 5 g (24%) of (III), 3 g (14%) of (XVI), and 2 g (9%) of (IX) are obtained.

Mono-2,7-octadienyl Ether of trans-1,2-Cyclooctanediol (XIV). bp 117°C (1 mm), n_D^{25} 1.4920. IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH=CH_2$), 980, 1650, 3005 (trans-CH=CH), 1110 (COC), 3450 (OH). PMR spectrum (δ, ppm): 1.2-1.53 m (14H, CH_2), 2.0 m (2H, $CH_2C=C$), 3.48 m (3H, OH, CHO), 3.82 m (2H, OCH—C=C), 4.86 m (2H, $CH=CH_2$), 5.53 m (3H, CH=C, CH=CH), M$^+$ 252.

From 10 g of (IV) and 16 g of BD (100°C, 8 h) 15 g (60%) of the ether (XV), 6 g (24%) of (XVI), and 4 g (16%) of (IX) are obtained.

Mono-2,7-octadienyl Ether of trans-1,2-Cyclododecanediol (XV). bp 130°C (1 mm), $n_D^{19.5}$ 1.4898. IR spectrum (ν, cm^{-1}): 920, 1005, 3085 ($CH=CH_2$), 980, 1645 (trans-CH=CH), 1130 (COC), 3480 (OH). PMR spectrum (δ, ppm): 1.65 m (26H, CH_2, $CH_2C=C$, CHO), 3.32 m (1H, OH), 3.83 m (2H, $OCH_2C=C$), 4.86 m (2H, $C=CH_2$), 5.5 m (3H, CH=C, CH=C), M$^+$ 308.

1,3,6,11-Dodecatetraene (XVI). bp 61.5°C (5 mm), n_D^{25} 1.4696. IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH=CH_2$), 980, 1645, 3020 (trans-CH=CH). PMR spectrum (δ, ppm): 1.44 m (2H, H^9), 2.0 m (4H, H^8, H^{10}), 2.7 m (2H, H^5), 4.87 m (4H, H^1, H^{12}), 5.5 m (6H, H^2, H^3, H^4, H^6, H^7, H^{11}), M$^+$ 162.

From 10 g of (V) and 22 g of BD (10 h, 100°C) 16 g (84%) of the ether (XVII) and 3 g (16%) of (IX) are obtained.

Mono-2,7-octadienyl Ether of Z-5-Cyclooctene-trans-1,2-diol. bp 121°C (1 mm), n_D^{25} 1.4927. IR spectrum (ν, cm^{-1}): 920, 1000, 3090 ($CH=CH_2$), 980, 1645, 3010 (trans-CH=CH), 730, 3030 (cis-CH=CH), 1105 (COC), 3520 (OH). PMR spectrum (δ, ppm): 1.48 m (6H, CH_2), 2.0 m (8H, $CH_2C=C$), 2.8 s (1H, OH), 3.4 m (2H, OCH), 3.82 m (2H, $OCH_2C=C$), 487 m (2H, $C=CH_2$), 5.49 m (5H, CH=CH, CH=C), M$^+$ 250.

From 10 g (VI) and 16 g BD (100°C, 10 h) 15 g (91.5%) of the ether (XVIII), 0.4 g (2.4%) of (XVI), and 1 g (6.1%) of (IX) are obtained.

Mono-2,7-octadienyl Ether of E-5-Cyclododecene-trans-1,2-diol (XVIII). bp 142.5°C (1 mm), n_D^{19} 1.5059. IR spectrum (ν, cm^{-1}): 915, 1000, 3080 ($CH=CH_2$), 980, 1640, 3010 (trans-CH=CH), 1110 (COC), 3460 (OH). PMR spectrum (δ, ppm): 1.42 m (14H, CH_2), 1.92 m (8H, CHC=C), 2.46 m (1H, OH), 3.28 (2H, CHO), 3.82 d (2H, $OCH_2C=C$), 4.84 m (2H, $C=CH_2$), 5.36 m (5H, CH=CH, CH=C), M$^+$ 306.

From 10 g (VII) and 37 g BD (100°C, 10 h) 15 g (39%) of the ether (XX), 14 g (37%) of the ether (XXII), and 9 g (24%) of the ether (IX) are obtained.

Mono-2,7-octadienyl Ether of Z-2-Butenediol-1,4 (XX). bp 105°C (1 mm), n_D^{20} 1.4819. IR spectrum (ν, cm^{-1}): 915, 1000, 3080 ($CH=CH_2$), 980, 1645 (trans-CH=CH), 730, 3030 (cis-CH=CH), 1110 (COC), 3400 (OH). PMR spectrum (δ, ppm): 1.47 m (2H, CH_2), 2.0 m (4H, $CH_2C=C$), 3.55 s (1H, OH), 3.92 m (6H, CH_2O, $OCH_2C=C$), 4.92 m (2H, $C=CH_2$), 5.56 m (5H, $CH=CH_2$, CH=C), M$^+$ 196.

Bis-2,7-octadienyl Ether of Z-2-Butenediol-1,4 (XXII). bp 147°C (1 mm), n_D^{20} 1.4930. IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH=CH_2$), 980, 1645, 3010 (trans-CH=CH), 730, 3030 (cis-CH=CH), 1110 (COC). PMR spectrum (δ, ppm): 1.45 m (4H, CH_2), 2.00 m (8H, $CH_2C=C$), 3.84 (8H, CH_2O, $OCH_2C=C$), 4.92 m (4H, $C=CH_2$), 5.50 m (8H, CH=CH, CH=C), M$^+$ 304.

From 10 g (VIII) and 22 g BD (100°C, 10 h) 17.0 g (59%) of the ether (XXI), 7 g (24%) of (XVI), and 5 g (17%) of (IX) are obtained.

Mono-2,7-octadienyl Ether of Z-4-Octenediol-1,8 (XXI). bp 134°C (1 mm), $n_D^{19.5}$ 1.4788. IR spectrum (ν, cm^{-1}): 925, 1005, 3090 ($CH=CH_2$), 980, 1645, 3025 (trans-CH=CH), 730, 3030 (cis-CH=CH), 1115 (COC), 3400 (OH). PMR spectrum (δ, ppm): 1.48 m (6H, CH_2), 1.98 m (8H, $CH_2C=C$), 3.45 m (7H, CHO, $OCH_2C=C$), 4.84 m (2H, C=CH), 5.4 m (5H, CH=CH, CH=C), M^+ 252.

Isomerization of the Ethers. 0.075 g $AlEt_3$ was added with stirring to a solution of 0.05 g $Pd(acac)_2$ and 0.126 g PPh_3 in 2 ml abs. THF under a current of Ar and kept for 10-15 min. The solution was transferred to a cooled 17-ml autoclave, in which 16 mmole of the 2,7-octadienyl ether had previously been placed. The autoclave was heated for 7 h at 100°C, then the catalyzate was filtered through a mixed bed of Al_2O_3 (50 g) and activated carbon (5 g). After removing the solvent the residue was sublimed under vacuum.

Mono-1-vinyl-5-hexenyl Ether of cis-1,2-Cyclohexanediol (XII). Yield 50%, bp 78°C (1 mm), n_D^{20} 1.4748.

Mono-1-vinyl-5-hexenyl Ether of trans-1,2-Cyclohexanediol (XIII). Yield 35%, bp 92°C (1 mm), n_D^{20}1.4754. IR spectrum (ν, cm^{-1}): 910, 1000, 3080 ($CH=CH_2$), 1100 (COC), 3460 (OH). PMR spectrum (δ, ppm): 1.4 m (12H, CH_2), 2.0 m (2H, $CH_2C=$), 3.23 m (2H, CHO, OH), 3.7 m (2H, CHO), 4.8 m (4H, $=CH_2$), 5.4 m (2H, CH=C), M^+ 224.

Mono-1-vinyl-5-hexenyl Ether of Z-5-Cyclooctene-trans-1,2-diol (XIX). Yield 90%, bp 105°C (1 mm), n_D^{20} 1.4860. IR spectrum (ν, cm^{-1}): 920, 1010, 3080 ($CH=CH_2$), 730, 3030 (cis-CH=CH), 1105 (COC), 3500 (OH). PMR spectrum (δ, ppm): 1.4 (8H, CH_2), 2.0 m (6H, $CH_2C=$), 2.8 (1H, OH), 3.3 m (2H, OCH), 3.7 m (1H, OCHC=), 4.9 m (4H, $=CH_2$), 5.5 m (4H, CH=CH, CH=C), M^+ 250.

CONCLUSIONS

1. The telomerization of butadiene with cyclic 1,2-glycols and unsaturated linear 1,4- and 1,8-diols catalyzed by low-valency palladium complexes leads to the corresponding 2,7-octadienyl and 1-vinyl 5-hexenyl ethers in high yield.

2. Under the influence of low-valency palladium complexes cyclic 2,7-octadienyl ethers are isomerized to 1-vinyl 5-hexenyl ethers.

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