AMINATION OF DIENE HYDROCARBONS.

1. PREPARATION OF N-(2,3-DIMETHYLENEBUTYL)MORPHOLINE BY TELOMERIZATION OF PROPADIENE

B. P. Krymov, S. S. Zhukovskii,
A. M. Taber, I. M. Zel'dis,
I. V. Kalechits, V. É. Vasserberg,
and S. P. Chernykh

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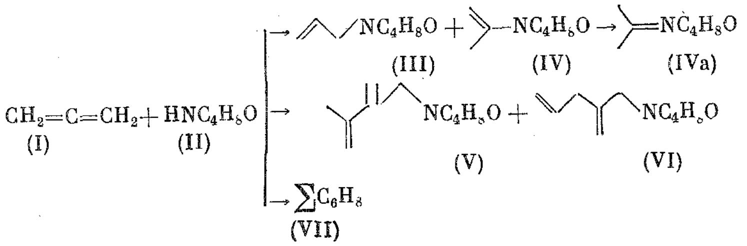
One of the ways of preparing alkenyl- and alkadienylamines is direct amination of conjugated diene hydrocarbons catalyzed by complexes of transition metals [1-3]. Analogous reactions of cumulated dienes make it possible to obtain alkadienylamines with conjugated multiple bonds [4, 5]. In the present paper, we have studied some characteristics of the telomerization of propadiene by morpholine.

With the binary catalytic system $PdCl_2 + (C_6H_5)_3P$ during telomerization of propadiene (I) by morpholine (II) a mixture of products was formed which consisted under optimal conditions primarily of N-(2,3-dimethylenebutyl)morpholine (V), ∿95%, and a small amount of allylmorpholine (III), ∿5% (Table 1). Isopropenylmorpholine (IV) was not detected.

As by-products, we noted the formation of nonaminated propadiene oligomers, whose yield ranged from ∿1 to ∿74% in relation to the reaction conditions (Tables 1 and 2).

The structure of the obtained telomers was established by spectral methods.

Scheme 1



Addition of a reducing agent ($NaBH_4$) to the catalytic system led to some increase in the total catalytic activity with practically constant selectivity of the process (see Table 1). Addition of CF_3COOH, used as an activating additive in the amination of butadiene [6], led in the case of propadiene (see Table 1) to a significant decrease in the yield of the products and to a change in the selectivity of the process toward the formation of heavy products (molecular weight >167).

The use of homogeneous catalytic systems based on $PdCl_2$ was restricted by the insignificant solubility of $PdCl_2$. The use of dimethylformamide as the solvent eliminated this restriction. Carrying out the reaction in the bulk of (II), i.e., presence of the catalyst in the microheterogeneous phase, led to an over tenfold decrease of the yield of the products (see Table 1). The rate of formation of the reaction products and their isomeric composition depended significantly on the ratio of (I) to (II).

The presence of conjugated double bonds in the hydrocarbon substituent of product (V) makes possible its further conversion with the formation of high-molecular-weight products: $(I) + (II) \rightarrow (V) \xrightarrow{+(II)}$ high-molecular-weight products. Therefore, an increase of the initial concentration of (II) with a constant concentration of (I) should lead to an increase of the total rate of the process and simultaneously to an increase of the content of heavy products (see Table 2).

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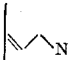
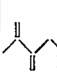
TABLE 1. Effect of the Composition of the Catalytic System on the Yield and Composition of the Products (solvent $HCON\cdot(CH_3)_2$, $[PdCl_2] = 3.4$ $[HNC_4H_8O] = 0.57$ mole/liter; 92°C, 0.5 h)

Composition of the catalytic system	Total yield of products, moles/(g-atom of Pd · h)	Composition of the products, %			
		$\Sigma\ C_6H_8$	 NC_4H_8O	 NC_4H_8O	Σ heavy products
$PdCl_2+(C_6H_5)_3P$ (1 : 1)	25054,8	–	5,4	94,6	Traces
$PdCl_2+(C_6H_5)_3P+NaBH_4$ (1 : 1 :1)	29917,2	<1	8,8	87,7	2,5
$PdCl_2+(C_6H_5)_3P+CF_3COOH$	1957,3	Traces	22,0	67,2	10,8
$PdCl_2+(C_6H_5)_3P$* (1 : 1)	1958,1	–	17,9	73,0	9,1

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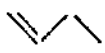
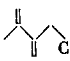
*Without solvent.

TABLE 2. Effect of the Initial Concentration of HNC_4H_8O on the Reaction Rate and Isomeric Composition of the Resulting Products ($[PdCl_2] = 0.12$ mole/liter; $PdCl_2:(C_6H_5)_3P:CF_3COOH = 1:1:1$; $V_0 = 11.6$ ml, solvent $HCON(CH_3)_2$; $P_{C_3H_4} = 543$ mm)

$[HNC_4H_8O]$, moles/liter	W, moles of $C_3H_4\cdot 10^3$/(g of Pd · min)	Composition of the products, wt. %			
		$\Sigma\ C_6H_8$	 C_4H_8O	 C_4H_8O	Σ heavy products
6,5	14,4	3,7	6,9	5,8	83,5
1,1	3,3	Traces	22,0	67,2	10,8
0,65	0,3	74,0	5,5	14,5	6,0
		Traces			

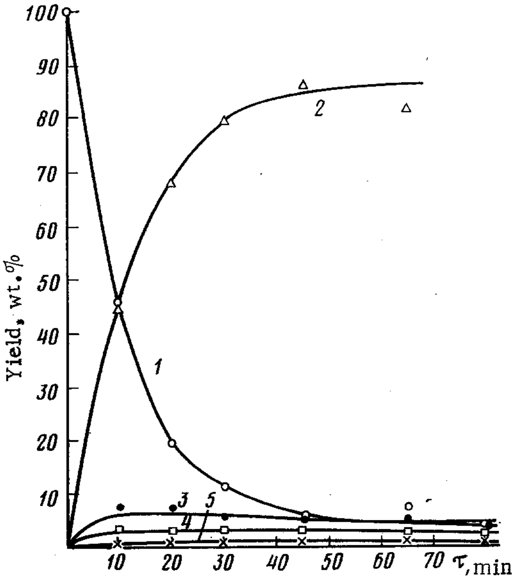


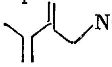
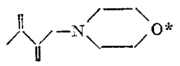
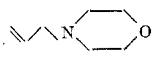
Fig. 1. Change of the composition of the reaction products with time: 1) HNC_4H_8O; 2)  NC_4H_8O; 3)  NC_4H_8O; 4) Σ heavy products; 5) $\Sigma\ C_6H_8$. $[HNC_4H_8O] = 0.57$, $[PdCl_2] = 3.4$ mmoles/liter, $V_0 = 22$ ml, 92°, $P_{C_3H_4} = 552$ mm.

TABLE 3. Spectral Characteristics of the Obtained Products

Product	PMR spectrum (δ, ppm)	IR spectrum (ν, cm^{-1})
	2,32 m (4H, α-N) 3,56 m (4H, α-O) 4,64–5,56 m (4H, $CH_2{=}C{-}C{=}CH_2$) 3,03 s (2H, CH_2) 1,88 s (3H, CH_3)	870, 900 1038, 1073 1120 1378 1600, 1650 2850, 3092
	2,31 m (4H, α-N) 2,92 m (2H, CH_2) 3,51 m (4H, α-O) 4,99–5,16 m (3H, $CH_2{=}CH$)	865 900, 1005 1030, 1072, 1130 2860 3015, 3090

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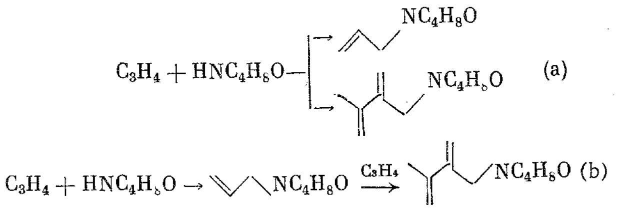
*UV spectrum: λ 228 nm.

A decrease of the initial concentration of (II) led to a decrease of the overall reaction rate and to an increase of the yield of nonaminated propadiene oligomers (see Table 2). Complete removal of (II) deactivated the catalytic system (see Table 2), possibly indicating that (VII) was also formed via morpholine-containing palladium adducts.

We can suggest two routes for the formation of (III) and (V): as a result of parallel reactions or a consecutive reaction of the initially formed (III) (reactions *a* and b in Scheme 2).

Scheme 2



The absence of an induction period (Fig. 1) in the formation of (V) indicates parallel formation of (III) and (V). This scheme was confirmed by a direct experiment: during contact of product (III), isolated from the reaction mixture, with propadiene on the $PdCl_2 + (C_6H_5)_3P + NaBH_4$ catalytic system no further reactions of (III) were observed.

EXPERIMENTAL

Allene with a purity of 93% and morpholine with a purity of 99% were used. The reaction products were analyzed with an LKhM-8MD chromatograph with a flame-ionization detector with temperature programming from 120 to 215°C (4 deg/min), a column length of 2 m, and a stationary phase of SE-30 + PEG-1500 on Dynochrome P. The IR spectra were recorded on a UR-20 spectrometer; the PMR spectra of solutions in CCl_4 were recorded on a Tesla BS-467 instrument, and the internal standard was HMDS; the UV spectra were recorded on a Specord UV-VIS instrument, and the solutions were in n-heptane.

Telomerization of propadiene with morpholine was carried out in a solution of DMFA at a constant pressure of (I) of 720 MPa. Constancy of pressure was achieved by feeding (I) into the reaction part from a standard volume; the rate of absorption of (I) was assessed from the pressure change in this volume.

The amination products were isolated by rectification at reduced pressure. The IR and PMR spectra are given in Table 3.

CONCLUSIONS

1. The telomerization of propadiene by morpholine in the presence of palladium chloride and triphenylphosphine leads mainly to the formation of conjugated alkadienylmorpholine $CH_3C(CH_2)C(CH_2)CH_2NC_4H_8O$. Allylmorpholine, nonaminated propadiene oligomers, and high-molecular-weight products are formed together with (2,3-dimethylenebutyl)morpholine, with the composition of the products depending on the ratio of propadiene to morpholine.

2. Allylmorpholine is not an intermediate reaction product, and the formation of it and (2,3-dimethylenebutyl)morpholine occurs as a result of parallel reactions.

LITERATURE CITED

1. R. Beker, A. Onions, R. J. Popplestone, and T. N. Smith, J. Chem. Soc. Perkin Trans., No. 2, 1133 (1975).
2. W. E. Walker, R. M. Manyik, K. Atkins, and M. Farmer, Tetrahedron Lett., 3817 (1970).
3. U. M. Dzhemelev, A. Z. Yakupova, S. K. Minsker, and G. A. Tolstikov, Zh. Org. Khim., 15, 1164 (1979).
4. R. Beker and A. H. Cook, J. Chem. Soc., Perkin Trans., No. 2, 443 (1976).
5. D. R. Coulson, J. Org. Chem., 38, 1483 (1973).
6. R. N. Fakhretdinov, G. A. Tolstikov, and U. M. Dzhemilev, Neftekhimiya, 19, 468 (1979).

SOME REACTIONS OF 4-METHYL-5,6-DIHYDROPYRAN AND ITS ISOMERS

U. G. Ibatullin, D. Ya. Mukhametova,
S. A. Vasil'eva, R. F. Talipov,
L. V. Syurina, M. G. Safarov,
and S. R. Rafikov

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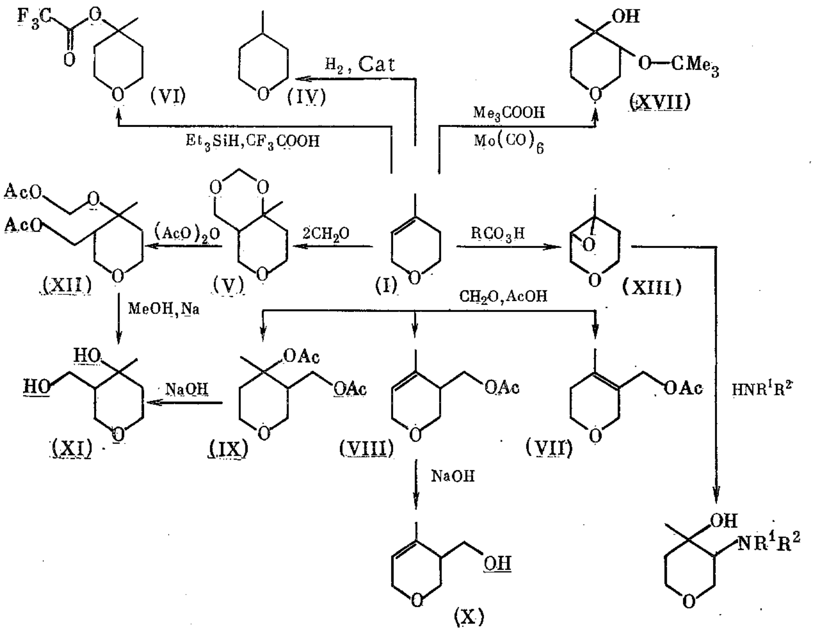
In the present work we studied some reactions of 4-methyl-5,6-dihydropyran (I) and 4-methylenetetrahydropyran (II), which are side products in the industrial synthesis of isoprene from isobutylene and formaldehyde [1], and of 2-methyl-5,6-dihydropyran (III), and also the transformations of pyrans formed in these reactions. For pyran (I), the reactions studied are indicated in the following scheme:



The behavior of (I) in an H_2 atmosphere in the presence of Pd, Pt, and Ni—Cr catalysts was studied at temperatures varying from 120-305°C, and at feedstock space velocities of 0.6-1.5 h^{-1}. The main product of hydrogenation over palladium (GIPKh-108) and nickel—chromium (Ni/Cr_2O_3) catalysts is 4-methyltetrahydropyran (IV). A quantitative yield of the product is attained, depending on the feeding rate of (I) in the range of 120-180°C. At 200°C and above, the amount of normal and isoalkanes (n-hexane, 2- and 3-methylpentanes), identified by GLC, increased. Platinum catalysts (AP-64 and AP-15) cause cleavage of the pyran

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