AMINATION OF CUMULATED DIENE HYDROCARBONS

COMMUNICATION 2. TELOMERIZATION OF PROPADIENE WITH ALLYL AMINES

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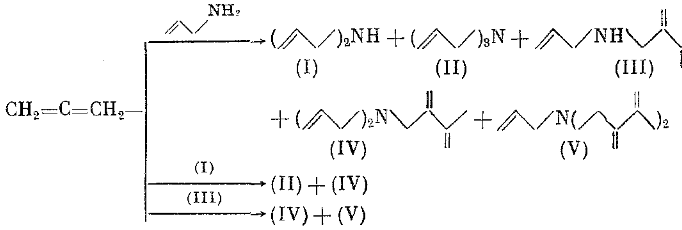
The telomerization of conjugated dienes with various amines yields 2,7-alkadienylamines [1, 2]. The analogous conversions with unsaturated amines yield 2,7-alkadienylamines that contain multiple bonds in all the hydrocarbon substituents [3].

We have carried out the telomerization of propadiene with allyl and diallyl amines, so that we have obtained alkadienylamines that contain conjugated and isolated double bonds.

In the presence of the $PdCl_2-PPh_3-NaBH_4$ system the reaction of allyl amines with propadiene yields secondary and tertiary allylalkadienyl amines (III) and (IV) with up to 85% selectivity. We have also noted the formation of the addition products of propadiene to the starting amines, viz., (I) and (II):



The overall product yield and the III and IV content depends on the reaction conditions (Table 1). Thus, at 60°C after 1 h the conversion of allyl amine was less than 2%. At 130°C after 3 h the product yield was 93%.

In the reaction with the primary amine the increase in conversion leads to a decrease in selectivity with respect to III and simultaneously to an increased product concentration of the tertiary amines IV and V.

The formation of IV is possible both by telomerization of propadiene to form I first, and by addition of a propadiene molecule to III. V is formed by the reaction of propadiene with III. The possibility of similar conversions was confirmed by the direct reaction of propadiene with I and III.

TABLE 1. Product Composition in the Telomerization of Propadiene with Allyl Amines $[C_3H_4]:[RR'NH]:[PdCl_2]:[PPh_3]:[NaBH_4] = 600:300:1:1:1$

Amine	T., °C	τ, h	Conversion, %	Product composition, %					
				(I)	(II)	(III)	(IV)	(V)	other
Allyl amine	60	1	1,7	–	–	–	–	–	–
	100	1	56,1	2,8	Traces	83,8	11,6	4,6	–
	150	1	66,8	11,7	1,3	70,3	8,9	7,8	–
	100	3	71,5	1,3	–	81,0	7,9	9,8	–
	130	3	92,7	1,9	–	67,0	12,5	18,6	–
Diallyl amine	100	1	11,8	–	39,3	–	32,1	–	28,6
	130	6	86,7	–	10,7	–	85,7	–	3,6
N-allyl (2,3-dimethylene)butylamine	130	6	74,3	–	–	–	19,8	46,6	33,6

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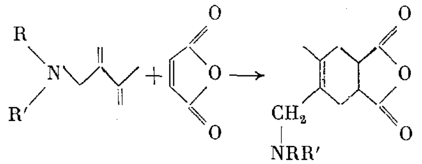
TABLE 2. Physical Constants and Spectral Properties of Synthesized Compounds

Compound	bp, °C (p, mm Hg st.)	n_D^{20}	PMR spectrum (δ, ppm)	IR spectrum (ν, cm^{-1})	UV spectrum (λ_{max}, nm)
(III)	52(4)	1,4830	1,75 s (1H, N–H) 1,88 s (3H, CH_3) 2,97–3,14 m (4H, CH_2) 4,92–5,22 m (6H, CH_2=) 5,80–6,20 m (1H, CH=)	3310 (NH) 1390 (CH_3) 900, 1600, 1640 (C=C–C=C) 910, 1000, 3010, 3090 (CH_2=CH) 1110, 1460 (CH_2)	224 (C=C–C=C)
(IV)	46(3)	1,4820	1,84 s (3H, CH_3) 2,90–3,00 m (4H, CH_2) 3,08 s (2H, CH_2) 4,90–5,10 m (8H, CH_2=) 5,50–6,00 m (2H, CH=)	1380 (CH_3) 1120, 1440 (CH_2) 900, 1600, 1640 (C=C–C=C) 910, 1000 (CH_2=CH)	222 (C=C–C=C)
(V)	94(3)	–	1,85 s (6H, CH_3) 2,90–3,10 m (6H, CH_2) 4,90–5,10 m (10H, CH_2=) 5,50–6,00 m (1H, CH=)	1390 (CH_3) 1120, 1450 (CH_2) 1600, 1640 (C=C–C=C) 900, 1000, 3080 (CH_2=CH)	224 (C=C–C=C)
(VI)	–	–	0,95s (1H, N–H) 1,86s (3H, CH_3) 2,30m (4H, CH_2) 2,90m (4H, CH_2) 3,25m (2H, CH=) 4,90–5,10 m (2H, CH_2=) 5,50–6,10 m (1H, CH=)	3370 (N–H) 1390 (CH_3) 1110, 1460 (CH_2) 910, 1000, 3080 (CH_2=CH) 1780, 1850 $(-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-)$	–
(VII)	–	–	1,80 s (3H, CH_3) 2,30m (4H, CH_2) 2,90m (6H, CH_2) 3,26 m (2H, CH_2) 4,92–5,10 m (4H, CH_2=) 5,40–6,00 m (2H, CH=)	1390 (CH_3) 1110, 1450 (CH_2) 920, 1000, 3090 (CH_2=CH) 1790, 1860 $(-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-)$	–

The conversion rate of the secondary amine, diallyl amine, is 1/5 that of primary allyl amine, Replacement of one allyl group by the branched dimethylenebutyl group (III) reduces the conversion rate further (see Table 1).

The reactions of III and IV with maleic anhydride forms the adducts VI and VII:



(VI), (VII)

R = CH_2=CH—CH_2; R′ = H (VI), CH_2 = CH—CH_2 (VII).

EXPERIMENTAL

Propadiene was 93% pure, allyl and diallyl amines were 99% pure, maleic anhydride was "analytically pure" grade. Products were analyzed on a LKhM-8MD chromatograph with a flame ionization detector, 2-m column, stationary phase SE-30 + PEG-1500 on Dinochrome-P, He carrier gas. PMR spectra were obtained on a Tesla 480-B apparatus for CCl_4 solutions, with HMDS internal standard. IR spectra were recorded on a UR-20 spectrophotometer (film). UV spectra were recorded on a Specord UV VIS for n-heptane solutions.

Telomerization was carried out in a rocking steel autoclave of 50 cm^3 volume in the 60-150°C range. The products (Table 2) were separated by fractional distillation at reduced pressure.

Diene synthesis was carried out by mixing stoichiometric amounts of IV or III with maleic anhydride in absolute benzene at 18°C for 4 h. After distillation of the solvent, an oily liquid was obtained (~100%).

CONCLUSIONS

1. In the telomerization of propadiene with allyl and diallyl amines in the presence of $PdCl_2-PPh_3-NaBH_4$ the corresponding conjugated alkadienylamines are formed. Tertiary alkadienylamines form by subsequent conversions of the secondary amines that form first.

2. N-allyl (2,3-dimethylenebutyl)amine, N-diallyl (2,3-dimethylenebutyl)amine, N-allyl bis-(2,3-dimethylenebutyl)amine and their maleic anhydride adducts were synthesized and characterized for the first time.

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SPECIFIC CHAIN TRANSFER CONSTANTS AND STEREOSPECIFICITY OF PROPYLENE TELOMERIZATION IN CCl_4 INITIATED BY $Mn_2(CO)_{10}$ ALONE AND IN COMBINATION WITH DIMETHYLFORMAMIDE

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In the course of our investigation of the relative kinetics of olefin telomerization with carbon tetrachloride we have studied the telomerization of propylene in CCl_4 initiated by $Mn_2(CO)_{10}$ alone and in combination with DMFA over a wide range of proportions of all components. Propylene telomerization with CCl_4, initiated by such compounds was studied for the first time in [1]. The reaction is described by the scheme:

$$CCl_4 + nCH_2{=}CHCH_3 \xrightarrow{\text{Initiator}} CCl_3[CH_2CH(CH_3)]_n\,Cl\ (T_n)$$

The purpose of the present investigation was to determine the specific chain transfer constants, C_n, and the relative yields of the racemic diastereomeric forms of the telomer T_3. It was of interest to compare our data with those already known for the same telomerization initiated by the mononuclear carbonyls $Fe(CO)_5$ and $Cr(CO)_5$ in the presence and absence of DMFA.

EXPERIMENTAL

GLC analysis was carried out on a LKhM-8MD apparatus in a current of He (2.8 liter/h) with a katharometer, and a steel column 3000 × 3 mm with 5% SE-30 on Chromatone N-AW at 175°C. GLC analysis of reaction

TABLE 1. Propylene Telomerization with CCl_4, Initiated by Benzoyl Peroxide (BP), $Mn_2(CO)_{10}$, and $Mn_2(CO)_{10}$ + DMFA* (120°C, 30 min)

Test no.	Initiator, mmole · 10^2	Conversion, %		Content of $CCl_3[CH_2CH(CH_3)]_nCl(T_n)$ telomers with n = 1, 2, or 3; mole %			Racemic diastereomeric forms of T_3, %		
		C_3H_6	CCl_4	T_1	T_2	T_3	h-T_3	s-T_3	i-T_3
1	BP, 3,7	16,5	34,7	39,2	50,3	10,5	37,4	48,0	14,6
2	$Mn_2(CO)_{10}$, 0,3	1,9	4,1	36,6	53,7	9,7	38,1	47,0	14,9
3	$Mn_2(CO)_{10}$, 2,0	5,7	11,7	36,7	54,3	9,0	38,3	46,7	15,0
4	$Mn_2(CO)_{10}$, 12,0	17,5	37,3	38,6	50,7	10,7	38,2	48,4	13,4
5	$Mn_2(CO)_{10}$, 20,5	24,6	50,3	36,0	53,5	10,5	39,0	47,1	13,9
6	$Mn_2(CO)_{10}$+DMFA 2,0+2,3	5,2	10,7	35,8	54,8	9,8	38,0	46,9	15,1
7	$Mn_2(CO)_{10}$+DMFA, 2,0+6,3	6,4	12,7	35,7	54,6	9,7	37,7	46,7	15,6
8	$Mn_2(CO)_{10}$+DMFA 2,0+35,4	7,5	15,5	32,4	57,2	10,4	38,2	47,3	14,5
9	$Mn_2(CO)_{10}$+DMFA 2,0+121,0	5,2	10,7	32,9	57,2	9,9	37,7	46,8	15,5
10	$Mn_2(CO)_{10}$+DMFA, 20,6+208,0	22,5	47,3	33,6	56,9	9,5	37,6	47,5	14,9

*21.1 ± 1.1 mmole C_3H_6, 5.9 ± 0.1 mmole CCl_4, $C_3H_6/CCl_4 = 3.6 \pm 0.1$.

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