CONCLUSIONS

1. The dipole moments of Cp_2TiCl_2, $CpTiCl_3$, Cp_2TiCl, and $(Cp_2TiCl)_2O$ were determined.
2. The dipole moment of the Cp−Ti bond was calculated.
3. The compound Cp_2TiCl does not form a centrosymmetrical associate in benzene solution.

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SYNTHESIS OF UNSATURATED AMINES FROM BUTADIENE AND ALLYLAMINES IN PRESENCE OF PALLADIUM AND NICKEL COMPLEXES

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UDC 542.91:547.333:541.128

Butadiene reacts with aliphatic or aromatic amines in the presence of Pd [1, 2] or Ni [3-5] complexes to give unsaturated amines that contain either one or two unsaturated radicals. In order to obtain tertiary polyunsaturated amines that have potential interest as monomers and modifiers, we studied the reaction of C_4H_6 with the allyl- and diallylamines in systems that contain Pd and Ni complexes, which are activated by phosphines and phosphites $[(C_4H_9)_3P$, $(C_6H_5)_3P$, $(C_6H_5O)_3P$, $(CH_3-C_6H_4O)_3P]$.

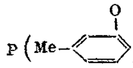
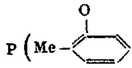
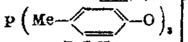
The amination of butadiene with allylamine (4:1) in the system: $Pd(acac)_2-(C_6H_5)_3P-Al(C_2H_5)_3$ (1:3:2, 100°, 6 h), in toluene solution, gives in at least 50% yield, when based on taken C_4H_6, a mixture of oligomers, composed of N-2,7-octadienylbisallylamine (II), N-allylbis(2,7-octadienyl)amine (I), tris(2,7-octadienyl)amine (III) [6], and 4-vinylcyclohexene (VCH) in an 18:50:12:20 ratio.

Both the yield and composition of the butadiene amination products are materially affected by the nature of the activator, the Pd:activator ratio, and the type of solvent. The yield of (I)-(III) is maximum at a Pd:activator ratio = 1:3 and in the presence of alkyl- or arylphosphines, while phosphites direct the reaction toward the predominant formation of VCH (Table 1).

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1412-1414, June, 1978. Original article submitted July 29, 1977.

0568-5230/78/2706-1230$07.50

TABLE 1

Activator	Yield, %	Reaction products*			
		VCH	(I)	(II)	(III)
P(Ph)$_3$	68	26	53	8	13
P(OPh)$_3$	15	20	55	15	10
	10	80	3	15	2
	12	83	4	11	2
	10	79	–	16	5
P(C$_4$H$_9$)$_3$	30	10	34	48	8

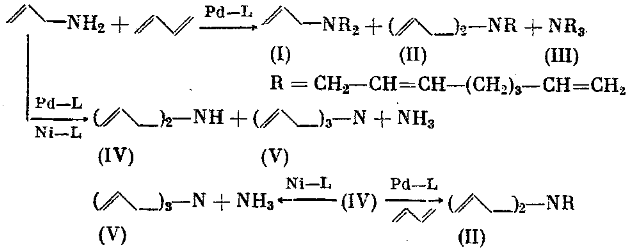
*Experimental conditions: allylamine = 1.2 g; butadiene = 4.8 g; Pd(acac)$_2$ catalyst = 1 mmole; activator = 2.7 mmoles; Al(C$_2$H$_5$)$_3$ = 3 mmoles; benzene = 1 ml; 100°C; 10 h.

The maximum selectivity relative to amines (I)-(III) was obtained in aromatic and ether solvents (toluene, THF, diethyl ether). Aliphatic solvents (heptane, cyclohexane) facilitate an increased amount of (III) and VCH in the catalyzate, which, respectively, are 30 and 31%.

It may be assumed that (II) and (III) are formed by the reaction of C_4H_6 with diallylamine and NH_3. The latter is apparently obtained by the catalytic disproportionation of allylamine to diallylamine and ammonia. Actually, a mixture of diallylamine (IV), NH_3, and small amounts of triallylamine (V) was obtained when allylamine is heated with the system Pd(acac)$_2$–$(C_6H_5)_3P$–Al$(C_2H_5)_3$ in the absence of C_4H_6.

The structures of (I)-(III) were confirmed by spectral methods, and also by counter synthesis. Thus, the amination of C_4H_6 with diallylamine on the mentioned catalysts gave (II) in high yield, while tris(2,7-octadienyl)amine (III) [6] was obtained from C_4H_6 and NH_3.

Butadiene could not be aminated with allylamine in the presence of Ni(acac)$_2$–$(C_6H_5)_3P$–Al$(C_2H_5)_3$. In all of the experiments the allylamine was converted to (IV), (V), and NH_3. Diallylamine under these conditions gives predominantly (V) and NH_3 in a 2 : 3 ratio:



As a result, the amination of butadiene with allylamines in the presence of systems that contain Pd makes it possible to obtain difficultly accessible tertiary polyunsaturated amines in one step.

The catalytic disproportionation of the allyl- and diallylamines on Ni-containing catalysts can serve as a convenient method for the preparation of triallylamine.

EXPERIMENTAL

The employed monomers were at least 99% pure. The mixture of oligomers was analyzed on a Tswett-102 chromatograph, which was equipped with a flame-ionization detector, at 160°, and using a 1 m × 3 mm column packed with 15% Apiezon L deposited on Chromaton and N_2 as the carrier gas. The IR spectra were recorded on a UR-20 spectrophotometer (as a film). The PMR spectra were recorded on a Tesla 480B instrument (80 MHz), using CCl_4 as the solvent and HMDS as the internal standard. The mass spectra were taken on an MKh-13-06 instrument and here the energy of the ionizing electrons was 70 eV and the temperature of the ionization chamber was 200°.

Reaction of Butadiene with Allylamine. To a solution of 1 g of Pd(acac)$_2$, 3.0 g of PPh_3, and 10 ml of butadiene in 30 ml of toluene at 0° was added, in an argon stream, 4.0 ml of $AlEt_3$ and the mixture was held for

10 min. The catalyst solution was transferred to a 300-ml steel autoclave, which had been previously charged with 23 g of allylamine and 180 ml of butadiene, and the mixture was heated for 10 h at 100°. The catalyzate was cooled, separated from the precipitate, and then analyzed by GLC. A total of 35 g of mixed oligomers was obtained. The compounds were isolated by fractional distillation through a column.

N-Allylbis(2,7-octadienyl)amine (I), bp 90-93° (1 mm), n_D^{20} 1.4860. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3080 ($C-CH_2$); 975, 3030 (trans-$CH=CH$). PMR spectrum (δ, ppm): 1.5 d (4H, CH_2), 1.95 d (8H, $CH_2CH=$), 2.9 d (6H, NCH_2), 4.9 m (6H, $C=CH_2$), 5.4 m (7H, $CH=C$); m/e 273. Found: C 83.3; H 11.2; N 5.2%. $C_{19}H_{31}N$. Calculated: C 83.6; H 11.3; N 5.1%. Five moles of H_2 is absorbed when (I) is hydrogenated to give the known N-propyldioctylamine with bp 106-107° (1 mm), n_D^{20} 1.4420; m/e 283.

N-2,7-Octadienylbisallylamine (II), bp 102-106° (3 mm), n_D^{20} 1.4780. Infrared spectrum (ν, cm^{-1}): 920, 1000, 3080 ($C=CH_2$), 980, 3030 (trans-$CH=CH$). PMR spectrum (δ, ppm): 1.5 d (2H, CH_2); 1.95 d (4H, $CH_2CH=$); 2.9 d (6H, NCH_2); 4.9 m (6H, $C=CH_2$), 5.4 m (5H, $CH=C$); m/e 205. Found: C 81.9; H 11.0; N 6.6%. $C_{14}H_{23}N$. Calculated: C 82.1; H 11.2; N 6.7%. Four moles of H_2 is absorbed when (II) is hydrogenated to give the previously unknown dipropyloctylamine, bp 112-114° (8 mm), n_D^{20} 1.440; m/e 213.

Reaction of Diallylamine with Butadiene. a) To a solution of 0.5 mmole of $Pd(acac)_2$, 1.5 mmoles of $P(Bu\text{-}n)_3$, and 1 mmole of 1,5-cyclooctadiene in 2 ml of benzene at −5 to 0° was added in an argon atmosphere 1.5 mmoles of $AlEt_3$ and the mixture was stirred for 0.5 h. Then the catalyst solution was transferred to a 17-ml steel autoclave, which had been previously charged with 50 mmoles of diallylamine and 100 mmoles of butadiene. The mixture was heated for 5 h at 100° and then cooled. After the usual workup we obtained 9.6 g of amines, which, based on the GLC analysis, contained diallylamine and N-2,7-octadienylbisallylamine in a 1:9 ratio.

b) We obtained 4.5 g of amines when 4.85 g of diallylamine was heated with a mixture of 0.5 mmole of $Ni(acac)_2$, 1.5 mmoles of $(n\text{-}Bu)_3P$, 1 mmole of 1,5-cyclooctadiene, 1.5 mmoles of $AlEt_3$, and 5 mmoles of AcOH, which was prepared as described in a). Based on the GLC data, the mixture contains 69% of triallylamine and 31% of diallylamine.

Triallylamine (V), bp 56° (25 mm), n_D^{20} 1.4486; m/e 123. Infrared spectrum (ν, cm^{-1}) 922, 1003, 3083 ($CH=CH_2$). PMR spectra (δ, ppm): 2.91 d (6H, $-NCH_2$, J = Hz); 5.0 m ($C=CH_2$); 5.65 m (3H, $CH=C$).

CONCLUSIONS

1. It was shown that polyunsaturated amines can be obtained by the reaction of allylamines with butadiene in the presence of Ni- and Pd-containing complex catalysts.

2. A convenient and simple method was developed for the preparation of triallylamine from diallylamine.

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