BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 454—460 (1968)

The Dimerization of Butadiene by Palladium Complex Catalysts

Shigetoshi TAKAHASHI, Toshiki SHIBANO and Nobue HAGIHARA

The Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka

(Received September 16, 1967)

It has been found that palladium-phosphine complexes coordinated by dienophile and tetrakis-(triphenylphosphine)palladium catalyzed the linear dimerization of butadiene. The dimerization of butadiene with bis(triphenylphosphine)(maleic anhydride)palladium in aprotic solvents, such as benzene, tetrahydrofuran, and acetone, gave octatriene-1,3,7 selectively in good yields. In such alcohols as methanol, ethanol, and isopropanol, butadiene was converted to 1-alkoxyocta-diene-2, 7 and/or octatriene-1, 3, 7, depending on the nature of the alcohols employed. The dimerization in secondary amines, such as morpholine, piperidine, and diisopropylamine, gave butadiene dimer-amine adducts of the $R_2N(C_8H_{13})$ type, while that in primary amines, such as aniline and *n*-butylamine, gave a mixture of $RNH(C_8H_{13})$ and $RN(C_8H_{13})_2$. Phenoxy- and acetoxyoctadiene were also obtained from the reactions in phenol and acetic acid respectively.

It is well-known that butadiene is converted selectively to cyclic oligomers with various catalysts, for example, Ziegler-type catalysts.[1] Recently, it has been reported that linear dimerizations of butadiene can be carried out with cobalt[2]-, iron[3]- or rhodium[4]-containing catalysts to form methyl-heptatriene and/or *n*-octatriene. The dimerization with a nickel catalyst usually gives cyclic dimers; however, there is a linear dimerization in alcoholic media with low-valent nickel complexes.[5] A large number of reports on the oligomerization of butadiene with nickel catalysts have been presented, but there have been only a few reports[6] on the catalytic behavior of the palladium complex in response to butadiene.

In the course of an examination of the reactions

1) See, for example, G, Wilke, *Angew. Chem.*, **75**, 10 (1963).

2) S. Otsuka, T. Taketomi and T. Kikuchi, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 1094 (1963); T. Saito, T. Ono, Y. Uchida and A. Misono, *ibid.*, **66**, 1099 (1963); S. Otsuka and T. Taketomi, *European Polymer J.*, **2**, 289 (1966); D. Wittenberg, *Angew. Chem.*, **75**, 1124 (1963); S. Tanaka, K. Mabuchi and N. Shimazaki, *J. Org. Chem.*, **29**, 1626 (1964).

3) H. Takahashi, S. Tai and M. Yamaguchi, *J. Org. Chem.*, **30**, 1661 (1965).

4) T. Alderson, E. L. Jenner and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **87**, 5638 (1964).

5) a) T. Yoshida and S. Yuguchi, 19th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965; b) H. Müller, D. Wittenberg, H. Seibt and E. Scharf, *Angew. Chem.*, **77**, 318 (1965); J. Feldman, B. A. Saffer and O. D. Frampton, U. S. Pat. 3284529 (1966) (*Chem. Abstr.*, **66**, 28373 (1967)).

6) a) G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Kiem, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, *Angew. Chem.*, **78**, 157 (1966); b) Neth. Appl. Pat. 6606567 (1966) (*Chem. Abstr.*, **67**, 11427 (1967)).

of dienophile-coordinated palladium-phosphine complexes[7] with butadiene, we have found that bis(triphenylphosphine)(maleic anhydride)palladium catalyzed a dimerization of butadiene, thus forming a linear butadiene dimer in a good yield. The preliminary results have been described in previous papers.[8,9] We have also studied the dimerization of butadiene by palladium complexes in alcohols or amines in considerable detail and have found that the dimerization in these solvents gave butadiene dimer-alcohol or -amine adducts in good yields.

Results and Discussion

The Dimerization Reaction in an Aprotic Solvent. When butadiene was heated at 100—120°C in benzene in the presence of bis(triphenylphosphine)(maleic anhydride)palladium,[7] $Pd(Ph_3P)_2(C_4H_2O_3)$, it was converted to octatriene-1, 3, 7; there were no other butadiene dimers except a small amount of a thermal reaction product, 4-vinylcyclohexene-1.[8]

$$2\ H_2C{=}CH{-}CH{=}CH_2 \rightarrow H_2C{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \quad (1)$$

The dependence of the yield on the reaction temperature was investigated between 80—120°C; the results obtained are summarized in Table 1.

Although the yield of octatriene was good at an elevated temperature, the reaction at 120°C caused the decomposition of the catalyst and the products contained butadiene trimer (ca. 5%) and vinylcyclohexene as by-products. For the preparation of octatriene-1, 3, 7 in benzene, therefore, the reaction might better be carried out at a temperature between 110—115°C.

The reactions in tetrahydrofuran and acetone also gave octatriene-1, 3, 7; the experimental results are shown in Table 1.

Table 1. The dimerization in aprotic solvents

Solvent	Reaction temp., °C	Reaction time, hr	Yield[a] of octatriene-1,3,7, %
Benzene	80	7	trace
Benzene	100	7	23
Benzene	110	7	46
Benzene	120	7	64
T.H.F.	115	7	82
Acetone	115	7	86

a) Gas chromatographic analysis.
Catalyst $Pd(Ph_3P)_2(C_4H_2O_3)$ 219 mg (0.3 mmol); Solvent 20 ml; Butadiene 13 g.

The Dimerization Reaction in Alcohol. The dimerization of butadiene was also carried out in alcohols. In contrast to the reactions in such aprotic solvents as benzene or acetone, the dimerization in alcohols proceeded smoothly even at lower temperatures (40—100°C) to give 1-alkoxyoctadiene-2, 7 and/or octatriene-1, 3, 7, depending on the nature of the alcohols employed. There have been a few reports on the oligomerization of butadiene, which affords a butadiene dimer-alcohol adduct.[5a,6b,10]

In methanol butadiene easily dimerized, at a low temperature and a short reaction time, with the bis(triphenylphosphine)(maleic anhydride)-palladium catalyst to give 1-methoxyoctadiene-2, 7 and its isomer, 3-methoxyoctadiene-1, 7, along with a small amount of octatriene-1, 3, 7 (Eq. (2), $R=CH_3$).

$$2\ H_2C{=}CH{-}CH{=}CH_2 + ROH \rightarrow R{-}O{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2 + H_2C{=}CH{-}CH(OR){-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2 \quad (2)$$

It is obvious that methoxyoctadiene is not derived from the reaction of octatriene with methanol, for octatriene was found not to react with alcohol under the same reaction conditions as these employed in the dimerization reaction of butadiene. The trans-configuration of 1-methoxyoctadiene-2, 7 obtained from the above reactions was suggested by the fact that its infrared spectrum showed a strong band at 970 cm^{-1} which is attributable to the CH out-of-plane deformation of trans -CH=CH-.

Bis(triphenylphosphine)(dimethylfumarate)palladium, bis(triphenylphosphine)(*p*-benzoquinone)-palladium, tetrakis(triphenylphosphine)palladium, and -platinum could also be employed as catalysts, although these complexes were found to be almost ineffective in aprotic solvents. The dependence of the distribution of the products on the catalyst and reaction conditions is shown in Table 2.

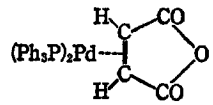
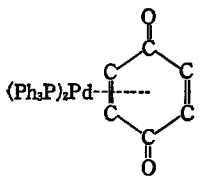
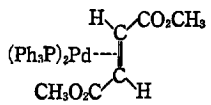
The platinum complex was less effective than palladium complexes.

In abs. ethanol the dimerization of butadiene with the bis(triphenylphosphine)(maleic anhydride)-palladium catalyst gave octatriene-1, 3, 7 and 1-ethoxyoctadiene-2, 7, plus a small amount of an isomer of ethoxyoctadiene, whereas in isopropanol octatriene-1, 3, 7 was obtained as the main product. The ratio of ethoxyoctadiene to octatriene was independent of the reaction time, and the use of a large amount of ethanol as the solvent resulted in a higher ratio, as Table 3 shows.

Although bis(triphenylphosphine)(*p*-benzoquinone)palladium was found to exhibit similar catalytic behavior, tetrakis(triphenylphosphine)palla-

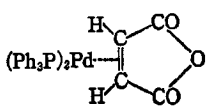
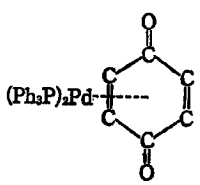
7) S. Takahashi and N. Hagihara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 1306 (1967).
8) S. Takahashi, T. Shibano and N. Hagihara, *Tetrahedron Letters*, **1967**, 2451.
9) S. Takahashi, H. Yamazaki and N. Hagihara, This Bulletin, **41**, 254 (1968).
10) K. C. DeWhirst, *J. Org. Chem.*, **32**, 1297 (1967).

TABLE 2. THE DIMERIZATION IN METHANOL

Catalyst	Reaction temp., °C	Reaction time, hr	Yield, % 1-RO-OD	3-RO-OD*	OT*
	40	2	62	1	0
	70	1	85	5	3
	90	1	73	6	4
	40	2	87	7	1
$(Ph_3P)_4Pd$	70	1	90	8	1
	90	1	86	9	2
	70	1	85	2	1
	70	1	86	4	1
$(Ph_3P)_4Pt$	90	3	26	4	0

* 1-RO-OD: 1-methoxyoctadiene-2,7; 3-RO-OD: 3-methoxyoctadiene-1,7; OT: octatriene-1,3,7
Catalyst 0.1 mmol; Methanol 20 ml; Butadiene 13 g

TABLE 3. THE DIMERIZATION IN ETHANOL OR ISOPROPANOL

Catalyst	Solvent	Reaction temp., °C	Reaction time, hr	Yield, % OT[a]	RO-OD[a]	RO-OD/OT[b]
	C_2H_5OH	110—115	1	50	33	0.66
	C_2H_5OH	110—115	6	49	35	0.71
	C_2H_5OH[c]	100	3	25	68	2.7
	i-C_3H_7OH[d]	100	4	75		
$(Ph_3P)_4Pd$	C_2H_5OH	110—115	6	27	62	
	i-C_3H_7OH[d]	112—116	7.5	11		
	C_2H_5OH	110	1.5	48	39	
	i-C_3H_7OH[d]	110—114	4.5	77		

a) OT: octatriene-1,3,7; RO-OD: 1-ethoxyoctadiene-2,7.
b) Molar ratio of 1-ethoxyoctadiene-2,7 to octatriene-1,3,7.
c) Butadiene 6.5 g; ethanol 50 ml.
d) A small amount of a butadiene dimer-isopropanol adduct was detected by gas chromatography.

dium was less effective in ethanol and was almost entirely inactive in isopropanol. The dependence of the reaction products on the nature of the alcohols employed is of considerable interest in respect to the mechanism of the catalysis.

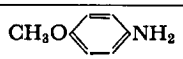
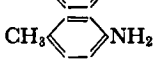
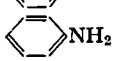
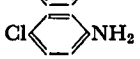
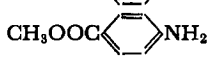
The Dimerization Reaction in Phenol or Acetic Acid. The dimerization of butadiene in more acidic solvents, such as phenol or acetic acid, was attempted; it was found to give a butadiene dimer-phenol or -acetic acid adduct. The reaction of butadiene and phenol in a benzene solution at 80°C with the $Pd(Ph_3P)_2(C_4H_2O_3)$ catalyst proceeded smoothly, giving the phenol adduct in a 57% yield and lower-boiling butadiene dimers

Table 4. The dimerization in amines

Amine, mmol		Solvent[a]	Reaction temp., °C	Reaction time, hr	Yield, % OT[b]	Yield, % $R_2N(C_8H_{13})$	Yield, % $RN(C_8H_{13})_2$
Morpholine	230	None[c]	80	1	0	90	
Piperidine	200	None[c]	110	5	0	60	
Diisopropylamine	140	None[c]	100—110	5	34	51	
Morpholine	160	Acetone	80—90	1	0	97	
Diisopropylamine	160	Acetone	100—104	3	trace	69	
Carbazole	120	Acetone	120—125	5	trace	57	
2-Pyrrolidone	210	None[c]	110—115	6	64	0	
Acetoamide	160	Acetone	114—116	5	64	0	
Aniline	160	Acetone	100—104	0.5	0	60	25
Aniline[d]	160	Acetone	113—115	2	8	44	23
n-Butylamine	200	None[c]	90—98	8	trace	29	42

a) 20 ml. b) OT: octatriene-1,3,7. Gas chromatographic analysis. c) Catalyst 0.3 mmol.
d) $Pd(Ph_3P)_4$ catalyst. Catalyst $Pd(Ph_3P)_2(C_4H_2O_3)$ 0.2 mmol; Butadiene 13 g (240 mmol).

Table 5. The dimerization in aniline derivatives

Amine	pK_a[11]	Reaction temp., °C	Reaction time, hr	Yield, % $RNH(C_8H_{13})$	Yield, % $RN(C_8H_{13})_2$
	5.29	90	0.5	54	33
	5.07	90—95	0.5	48	36
	4.58	90—95	0.5	46	24
	3.81	90—95	0.5	58	0
	2.47	102—104	2.0	48	0

Catalyst $Pd(Ph_3P)_2(C_4H_2O_3)$ 0.2 mmol; Solvent acetone 20 ml;
Butadiene 13 g (240 mmol); Amine 160 mmol.

which were not completely characterized.

The gas chromatograph and the NMR spectrum indicated that the phenol adduct consisted of 78% 1-phenoxyoctadiene-2, 7 and 22% of its isomer, probably 3-phenoxyoctadiene-1, 7 (Eq. (2), R=C_6H_5), which could not been separated by fractional distillation. Recently, it has been reported[6b] that the reaction between butadiene and phenol with palladium chloride gives 1-phenoxyoctadiene-2, 7.

The dimerization of butadiene in acetic acid with $Pd(Ph_3P)_2(C_4H_2O_3)$ or $Pd(Ph_3P)_4$ at 120°C gave a low conversion to a mixture (*ca.* 30% yield) of esters, containing 1-acetoxyoctadiene-2, 7 and its isomer, probably 3-acetoxyoctadiene-1, 7 (Eq. (2), R=CH_3COO), and lower-boiling butadiene dimers.

The reaction at a higher temperature gave a somewhat higher conversion, but the yield of acetic acid adduct was almost unchanged.

The Dimerization Reaction in Amine. Attempts to synthesize butadiene dimer-amine adducts were also carried out. The reactions of butadiene with secondary amines, such as morpholine, piperidine and diisopropylamine, in the presence or absence of the solvent afforded butadiene dimer-amine adducts of the $R_2N(C_8H_{13})$ type, while reactions with primary amines, such as aniline and *n*-butylamine, afforded a mixture of $RNH(C_8H_{13})$ and $RN(C_8H_{13})_2$, as shown in Eqs. (3) and (4). The experimental results are summarized in Table 4.

$$2\ H_2C{=}CH{-}CH{=}CH_2 + R_2NH \rightarrow R_2N{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2 \quad (3)$$

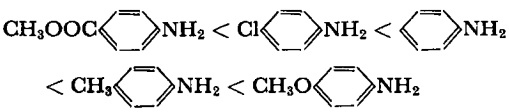
$$2\ H_2C{=}CH{-}CH{=}CH_2 + RNH_2 \rightarrow RNH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2 + CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2$$

$$\text{with } N(R)(CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH{=}CH_2) \quad (4)$$

11) "Constants of Organic Compounds", in Series of Comprehensive Organic Chemistry, ed. by M. Kotake, Asakura, Tokyo (1963), p. 652.

The amine adducts produced from the above reactions were easily isolated by fractional distillation and were found to be somewhat unstable in air. Trans-configurations of octa-2, 7-dienylamine and diocta-2, 7-dienylamine derivatives were suggested by their infrared spectra, which showed a strong band near 970 cm^{-1}, as did 1-alkoxyoctadiene-2, 7. Although the products were thought to include a small amount of an isomer of the amine adduct as well as alcohol adducts, they could not be separated by fractional distillation.

The use of amines, such as morpholine and aniline, gave high conversions to amine adducts under mild reaction conditions, whereas a weak base such as carbazole gave a low rate of conversion to an amine adduct even under more vigorous conditions. When such amines as 2-pyrrolidone and acetoamide were employed, no amine derivatives were formed and octatriene-1, 3, 7 was obtained. The reactivities of aniline derivatives in terms of the dimerization rate of butadiene were investigated (Table 5) and found to increase in the order:



These facts suggest that there is a relationship between the reactivity and the basicity of amine in the dimerization reaction of butadiene.

The tetrakis(triphenylphosphine)palladium catalyst was less effective than the bis(triphenylphosphine)(maleic anhydride)palladium catalyst in amines. Under more vigorous conditions, the reaction in aniline with $Pd(Ph_3P)_4$ gave aniline adducts, as Table 4 shows.

Investigations of the mechanism of catalysis will be reported in a forthcoming publication.

Experimental

Reagents. Butadiene was dried over a molecular sieve. Tetrakis(triphenylphosphine)palladium, $Pd(Ph_3P)_4$, and -platinum, $Pt(Ph_3P)_4$, were prepared by a modification[12] of the method of Malatesta.[13,14] Bis(triphenylphosphine)(maleic anhydride)palladium and other dienophile-coordinated palladium complexes were prepared by the reaction of $Pd(Ph_3P)_4$ and dienophile by a method described in an earlier report.[7]

Analysis. The infrared spectra of the products were taken with a Jasco Model DS-402G grating spectrometer, while the ultraviolet spectra were taken with a Beckman DK-2 spectrophotometer. The NMR spectra were recorded on a Varian Model A-60 instrument, using tetramethylsilane as an internal standard in carbon tetrachloride. The molecular weights were measured in a benzene solution using a Knauer Vapor-pressure Osmometer.

Gas Chromatography. Octatriene-1, 3, 7 and alkoxyoctadiene were analyzed, using a 3 m silicon-grease 550 column, with a Shimadzu Gas Chromatograph, Model GC-2B. The conditions were as follows: octatriene-1, 3, 7: column temperature, 120°C; carrier gas (nitrogen) speed, 38 m*l*/min; internal standard, benzene; methoxyoctadiene: column temperature, 170°C; carrier gas (nitrogen) speed, 28 m*l*/min; internal standard, acetophenone; ethoxyoctadiene: column temperature, 175°C; carrier gas (nitrogen) speed, 27 m*l*/min; internal standard, nitrobenzene.

The Dimerization Reactions of Butadiene. The boiling points and refractive indices of the products obtained in this work are listed in Tables 6 and 7. The results of the elemental analysis and molecular-weight measurement of the compounds are summarized in Table 8. Typical procedures of the dimerization reactions of butadiene are as follows:

A) In an Aprotic Solvent. A 100 m*l*, stainless-steel autoclave was charged with 30 m*l* of acetone and 219 mg (0.3 mmol) of bis(triphenylphosphine)(maleic anhydride)palladium. Butadiene (20 g) was then condensed into the autoclave. The reaction mixture was heated to 115°C and held there for 8 hr while being stirred. In order to separate the reaction product from the catalyst, the yellow reaction mixture was distilled into a cold trap at ~60°C under reduced pressure. The distillate gave 14 g (70 % yield) of octatriene-1, 3, 7 (bp 124—125°C) by fractional distillation under a nitrogen atmosphere. It also contained a small amount of 4-vinylcyclohexene-1 (*ca.* 5%). The octatriene-1, 3, 7 was characterized[8] by its infrared, ultraviolet, and NMR spectra, and by hydrogenation to *n*-octane. The ultraviolet spectrum (C_2H_5OH solution) showed a band at 225 mμ (ε_{max} 22000). The infrared spectrum showed bands at 1638 (C=C), 1600

TABLE 6. OCTATRIENE AND ITS DERIVATIVES

	Compound	bp, °C/mmHg	n_D^{20}
I	CH_2=CH-CH=CH-CH_2-CH_2-CH=CH_2	124—125	1.4682
IIA$_1$	CH_3-O-CH_2-CH=CH-CH_2-CH_2-CH_2-CH=CH_2	163—164	1.4417
IIA$_2$	CH_2=CH-CH(OCH_3)-CH_2-CH_2-CH_2-CH=CH_2	145—146	1.4321
IIB*	C_2H_5-O-CH_2-CH=CH-CH_2-CH_2-CH_2-CH=CH_2	105—107/70	1.4422
IIC*	C_6H_5-O-CH_2-CH=CH-CH_2-CH_2-CH_2-CH=CH_2	171—174/33	1.5178
III*	CH_3COO-CH_2-CH=CH-CH_2-CH_2-CH_2-CH=CH_2	72—82/6	1.4486

* Contains an isomer.

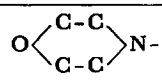
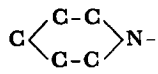
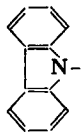
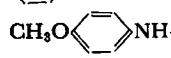
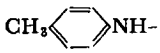
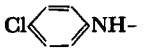
12) S. Takahashi, K. Sonogashira and N. Hagihara, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 610 (1966).

13) L. Malatesta and M. Angoletta, *J. Chem. Soc.*, **1957**, 1186.

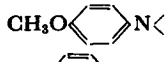
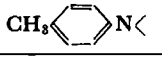
14) L. Malatesta and C. Cariello, *ibid.*, **1958**, 2323.

Table 7. Amine adducts

R_2N-CH_2-CH=CH-CH_2-CH_2-CH_2-CH=CH_2 or RNH-CH_2-CH=CH-CH_2-CH_2-CH_2-CH=CH_2

	R_2N- or RNH-	bp, °C/mmHg	n_D^{20}
IVA		141—142/23	1.4778
IVB		139—140/25	1.4790
IVC	(i-C_3H_7)$_2$N-	132—133/27	1.4568
IVD		217—218/5	1.6193
IVE_1	n-C_4H_9NH-	133—134/35	1.4576
IVF_1		184—186/25	1.5436
IVG_1		148—151/2	1.5444
IVH_1		166—167/8	1.5388
IVI_1		186—188/8	1.5552
IVJ_1		190—192/1	(mp 35—38°C)

RN(-CH_2-CH=CH-CH_2-CH_2-CH_2-CH=CH_2)$_2$

	RN<	bp, °C/mmHg	n_D^{20}
IVE_2	n-C_4H_9N<	167—170/6	1.4774
IVF_2		209—210/5	1.5387
IVG_2		148—151/2	1.5350
IVH_2		215—216/6	1.5338

(conjugated C=C) and 1002, 912, and 898 cm^{-1} (-CH=CH_2). The NMR spectrum showed complex bands at 3.5—4.8 (=CH-), 4.8—5.4 (=CH_2) and centered at 8.0 τ (-CH_2-).

Other experiments on the dimerization of butadiene in aprotic solvents are summarized in Table 1.

B) In Methanol. The autoclave described above was charged with 30 m*l* of methanol, 73 mg (0.1 mmol) of bis(triphenylphosphine)(maleic anhydride)palladium, and 20 g of butadiene. The reaction mixture was heated to 70°C and held there for 2 hr while being stirred. The yellow reaction mixture was distilled into a cold trap at ~70°C under reduced pressure. The distillate gave 20 g (77% yield) of 1-methoxyoctadiene-2, 7 (bp 103—105°C/83 mmHg) by fractional distillation, which contains a small amount (*ca.* 3%) of 3-methoxyoctadiene-1, 7 (bp 145—146°C). The methoxyoctadiene was characterized[8,9] by its infrared and NMR spectra. The infrared spectrum of 1-methoxyoctadiene-2,7 showed bands at 1670 (internal C=C), 1638 (terminal C=C), 1115 (CH_3-O-), 970 (trans -CH=CH-) and 991, and 910 cm^{-1} (-CH=CH_2). Its NMR spectrum showed bands at 4.0—4.7 (multiplet, =CH-), 4.7—5.2 (multiplet, =CH_2), 6.22 (doublet, J=4 cps, O-CH_2-C=), 6.78 (singlet, O-CH_3), 7.7—8.2 (multiplet, =C-CH_2-C-CH_2-C=), and 8.2—8.7 τ (multiplet, -C-CH_2-C-).

Gas chromatography was employed to isolate 3-methoxyoctadiene-1, 7. Its infrared spectrum showed bands at 1643 (C-C), 1101 (CH_3-O-) and 994, 923, and 910 cm^{-1} (-CH=CH_2). The NMR spectrum showed bands at 3.9—4.7 (multiplet, =CH-), 4.7—5.3 (multiplet, =CH_2), 6.3—6.8 (multiplet, -C-$\underset{\underset{O}{|}}{CH}$-C), 6.88 (singlet, O-$CH_3$), 7.7—8.3 (multiplet, =C-CH_2-C-CH_2-C=), and 8.3—8.8 τ (multiplet, -C-CH_2-C-).

1-Methoxyoctadiene-2, 7 was hydrogenated over a platinum catalyst in n-hexane to give 1-methoxyoctane (bp 161—162°C, n_D^{20} 1.4137), and with a $Ru(Ph_3P)_3Cl_2$ catalyst[15] in ethanol-benzene to give 1-methoxyoctene-2[9] (bp 82—83°C/33 mHg, n_D^{20} 1.4307).

The results of other experiments on dimerization in methanol and other alcohols are summarized in Tables 2 and 3.

C) In Aniline. The autoclave described above was charged with 20 m*l* of acetone, 15 g (160 mmol) of

15) P. S. Hallman, D. Evans, J. A. Osborn and G. Wilkinson, *Chem. Commn.*, **1967**, 305.

TABLE 8. ELEMENTAL ANALYSIS

Compound		Found				Calcd			
		C%	H%	N%	Mol wt	C%	H%	N%	Mol wt
I	C_8H_{12}	88.75	11.66		111*	88.82	11.18		108.2
IIA_1	$C_9H_{16}O$	76.63	11.46		140*	77.09	11.50		140.2
IIA_2	$C_9H_{16}O$	77.17	11.51			77.09	11.50		
IIB	$C_{10}H_{18}O$	77.74	11.66		153*	77.87	11.76		154.2
IIC	$C_{14}H_{18}O$	83.12	8.97		205	82.95	8.91		202.3
III	$C_{10}H_{16}O_2$	71.16	9.52		171	71.39	9.59		168.2
IVA	$C_{12}H_{21}NO$	73.50	10.78	7.05	193	73.80	10.84	7.17	195.3
IVB	$C_{13}H_{23}N$	80.95	12.03	7.01	197	80.77	11.99	7.24	193.3
IVC	$C_{14}H_{27}N$	80.21	12.88	6.27	214	80.31	13.00	6.69	209.4
IVD	$C_{20}H_{21}N$	87.57	7.61	5.07	275	87.23	7.69	5.09	281.2
IVE_1	$C_{12}H_{23}N$	79.76	12.76	7.47	190	79.49	12.79	7.73	181.3
IVE_2	$C_{20}H_{35}N$	82.80	11.94	4.67	274	82.97	12.19	4.84	289.5
IVF_1	$C_{14}H_{19}N$	83.27	9.59	6.57	205	83.53	9.51	6.96	201.3
IVF_2	$C_{22}H_{31}N$	85.05	10.16	4.74	313	85.38	10.10	4.53	309.5
IVG_1	$C_{15}H_{21}NO$	77.96	9.03	6.10	232	77.88	9.15	6.05	231.3
IVG_2	$C_{23}H_{33}NO$	71.48	9.86	4.33	337	81.36	9.80	4.13	339.5
IVH_1	$C_{15}H_{21}N$	83.60	9.85	6.46	222	83.66	9.83	6.51	215.3
IVH_2	$C_{23}H_{33}N$	85.28	10.44	4.09	336	85.39	10.28	4.33	323.5
IVI	$C_{14}H_{18}NCl$	71.59	7.85	5.99	246	71.32	7.69	5.94	235.1
IVJ	$C_{16}H_{21}NO_2$	74.38	8.26	5.45	263	74.10	8.16	5.40	259.3

* Cryoscopic method in benzene.

aniline, 146 mg (0.2 mmol) of bis(triphenylphosphine)-(maleic anhydride)palladium, and 13 g (240 mmol) of butadiene. The reaction mixture was then heated to 100°C and held there for 0.5 hr while being stirred. The yellow reaction mixture was distilled to give 14.4 g (60% yield) of phenylocta-2, 7-dienylamine (bp 184—186°C/25 mmHg) and 4.8 g (25% yield) of phenyldiocta-2, 7-dienylamine (bp 209—210°C/5 mmHg).

The infrared spectrum of Phenylocta-2,7-dienylamine showed bands at 3420 (N-H), 1640 (C=C), 1605 (conjugated C=C), 971 (trans -CH=CH-), 993, 913 (-CH=CH_2) and 750, and 695 cm^{-1} (-C_6H_5). The NMR spectrum showed bands at 2.6—3.7 (multiplet, C_6H_5-), 4.2—4.7 (multiplet, =CH-), 4.7—5.3 (multiplet, CH_2), 6.36 (doublet, J=4 cps, N-CH_2-C=), 6.54 (singlet, N-H), 7.7—8.2 (multiplet, =C-CH_2-C-CH_2-C) and 8.2—8.8τ (multiplet, -C-CH_2-C-).

The infrared spectrum of phenyldiocta-2, 7-dienylamine showed bands at 1642 (C=C), 1602 (conjugated C=C), 971 (trans -CH=CH-), 993, 913 (-CH=CH_2) and 750, and 695 cm^{-1} (-C_6H_5). The NMR spectrum showed bands at 2.6—3.7 (multiplet, C_6H_5-), 4.0—4.7 (multiplet, =CH-), 4.7—5.4 (multiplet, =CH_2), 6.20 doublet, J=4 cps, N-CH_2-C=), 7.5—8.2 (multiplet, =C-CH_2-C-CH_2-C=), and 8.2—8.9 τ (multiplet, -C-CH_2-C-). Other experiments on dimerization in amines are summarized in Tables 4 and 5.