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Palladium-catalyzed Reactions of 1,3-Dienes with Active Methylene Compounds. IV.⁽¹⁾ Palladium-diphosphine Complex Catalysts

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Active methylene compounds, such as acetylacetone and ethyl acetoacetate, reacted with 1,3-butadiene in the presence of palladium-diphosphine complex catalysts to yield two 1 : 1 adducts, **1** and **2**. Primary and secondary amines also afforded two 1 : 1 adducts, **10** and **11**. Isoprene, 1,3-pentadiene, and 2,4-hexadiene also reacted with the active methylene compounds and the amines in a manner similar to that of 1,3-butadiene. The most effective and easily available catalyst is the combination of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ and sodium phenoxide.

Recently, the reactions of 1,3-butadiene with active hydrogen compounds by means of palladium catalysts have been reported to afford 2,7-octadienyl derivatives of active hydrogen compounds.[2-5] For example, the addition of 1,3-butadiene to active methylene compounds to which two electronegative groups are attached gives the corresponding 2,7-octadienyl derivatives.[5] In the reactions, tertiaryphosphine complexes of palladium are quite effective catalysts or catalyst components. The reactions seem to proceed through the coordination of the two molecules of 1,3-butadiene to the metal atom. A coordination of a bidentate donor is expected to have an effect on the number of the coordinated 1,3-butadiene molecule. We have investigated the catalytic behavior of bidentate phosphine complexes of palladium in the reactions of 1,3-dienes with active hydrogen compounds such as active methylene compounds, and with primary and secondary amines. In contrast to the reaction catalyzed by the unidentate phosphine complexes of palladium,[4,5] this reaction has been found to give 1 : 1 adducts. In the iron- or cobalt-catalyzed reaction of

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[1] For paper III in this series, see K. Takahashi, A. Miyake, and G. Hata, *Chem. Ind.* (London), **1971**, 488.

[2] S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Lett.*, **1967**, 2451.

[3] E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1968).

[4] S. Takahashi, T. Shibano, and N. Hagihara, This Bulletin **41**, 454 (1968).

[5] G. Hata, K. Takahashi, and A. Miyake, *Chem. Ind.* (London), **1969**, 1836.

1,3-butadiene with ethylene,[6] the coordination of bidentate diphosphine ligands such as $PhPCH_2CH_2PPh_2$ was found to have a drastic effect on the catalytic behavior as a result of the decrease in the number of coordination sites for the 1,3-dienes, thus yielding 1,4-hexadiene quite selectively. The reaction reported in this paper is another example of the change in the catalytic behavior by the coordination of the bidentate diphosphine ligands.

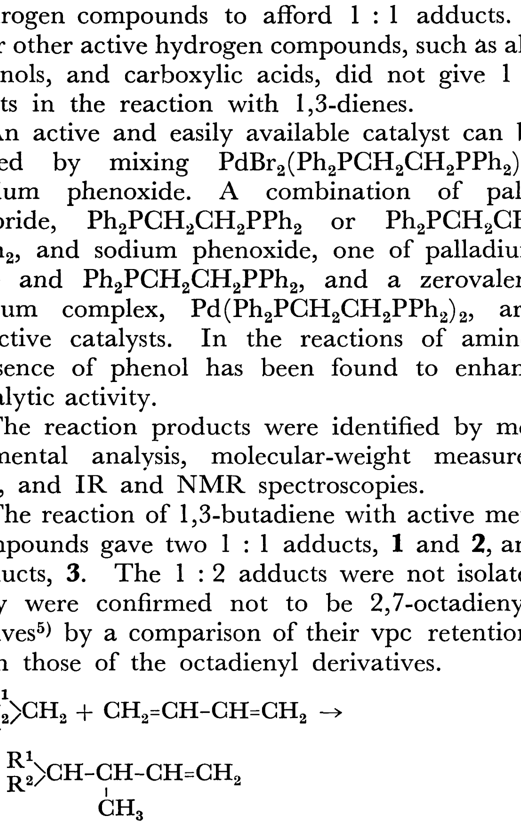
A part of this work has been reported in a preliminary communication.[1] The present paper will describe the reaction in detail.

This type of reaction has been applied to active methylene compounds, such as acetylacetone and ethyl acetoacetate, and to primary and secondary amines. Substituted 1,3-butadienes, such as isoprene, 1,3-pentadiene, and 2,4-hexadiene, reacted with the active hydrogen compounds to afford 1 : 1 adducts. However other active hydrogen compounds, such as alcohols, phenols, and carboxylic acids, did not give 1 : 1 adducts in the reaction with 1,3-dienes.

An active and easily available catalyst can be prepared by mixing $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ and sodium phenoxide. A combination of palladium chloride, $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH_2CH_2CH_2PPh_2$, and sodium phenoxide, one of palladium acetate and $Ph_2PCH_2CH_2PPh_2$, and a zerovalent palladium complex, $Pd(Ph_2PCH_2CH_2PPh_2)_2$, are also effective catalysts. In the reactions of amines, the presence of phenol has been found to enhance the catalytic activity.

The reaction products were identified by means of elemental analysis, molecular-weight measurements, vpc, and IR and NMR spectroscopies.

The reaction of 1,3-butadiene with active methylene compounds gave two 1 : 1 adducts, **1** and **2**, and 1 : 2 adducts, **3**. The 1 : 2 adducts were not isolated, but they were confirmed not to be 2,7-octadienyl derivatives[5] by a comparison of their vpc retention times with those of the octadienyl derivatives.



$$R^1R^2{>}CH_2 + CH_2{=}CH{-}CH{=}CH_2 \rightarrow R^1R^2{>}CH{-}CH(CH_3){-}CH{=}CH_2 + R^1R^2{>}CH{-}CH_2CH{=}CHCH_3 + R^1R^2{>}C(C_4H_9)(C_4H_9)$$

1 **2** **3**

	R^1	R^2
a	$COCH_3$	$COCH_3$
b	$COCH_3$	$COOC_2H_5$
c	$COOC_2H_5$	$COOC_2H_5$

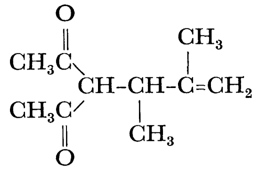
The results of the reactions of 1,3-butadiene with the active methylene compounds catalyzed by $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ and sodium phenoxide are summarized in Table 1. The infrared spectrum of **1** shows absorptions due to the out-of-plane deformation of $-CH{=}CH_2$ near 920 and 998 cm^{-1}, while that of **2** exhibited an absorption due to the out-of-plane deformation of *trans* $-CH{=}CH-$ near 965 cm^{-1} and no absorption due to *cis* $-CH{=}CH-$.

These reactions proceeded fairly rapidly at 150°C. The reaction of acetylacetone with 1,3-butadiene in the presence of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ and sodium phenoxide gave **1a**, **2a**, and **3a**. In the presence of a large excess of 1,3-butadiene, **3a** was the major product. Ethyl acetoacetate and diethyl malonate reacted with the diene to give **1b**, **2b**, and **3b**, and **1c** and **2c**, respectively. The reactivity of diethyl malonate was smaller than that of acetylacetone. No 1 : 2 adduct of diethyl malonate and 1,3-butadiene was observed.

2-Oxocyclododecanecarbaldehyde reacted with 1,3-butadiene to afford 2-oxo-2-(2-butenyl)cyclododecanecarbaldehyde. The reaction was accompanied by the partial elimination of the formyl group of the product.

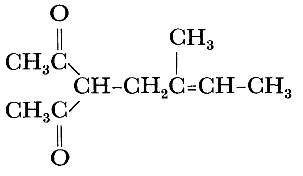
The combination of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ and sodium phenoxide was the most efficient catalyst. The diphosphine complex, $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, showed no catalytic activity. The addition of sodium phenoxide activated the palladium complex. A combination of palladium acetate and $Ph_2PCH_2CH_2PPh_2$, and one of $Pd(NO_2)_2(NH_3)_2$ and $Ph_2PCH_2CH_2PPh_2$, were effective catalysts without any sodium phenoxide. A diphosphine complex of Pd(0), $Pd(Ph_2PCH_2CH_2PPh_2)_2$, also catalyzed the reaction, although the activity was low. The presence of phenol or sodium phenoxide increased the catalytic activity of the complex of Pd(0) remarkably. The chain length of the ditertiaryphosphines, $Ph_2P(CH_2)_nPPh_2$ ($n=1,2,3,4$), was found to have a great effect on the catalytic behavior in the reaction of ethyl aectoacetate with 1,3-butadiene, as is shown in Table 3. It is clear that $Ph_2P(CH_2)_nPPh_2$ ($n=2,3$) is favorable ligand for the formation of the 1 : 1 adducts. The reaction using $Ph_2P(CH_2)_4PPh_2$ as a catalyst component gave mainly a 1 : 2 adduct, ethyl 2-acetyl-4,9-decadienoate, plus a small amount of the 1 : 1 adducts. The former diphosphines would form stable chelate rings with the palladium atom. However, the chelation of the latter diphosphine is much less favored, for the diphosphine behaves like a unidentate ligand.[5] α,α′-Dipyridyl and 2-(diphenylphosphine)ethyl phenyl sulfide, $Ph_2PCH_2CH_2SPh$, showed a ligand effect on the products similar to that of $Ph_2P(CH_2)_nPPh_2$ ($n=2,3$).

Isoprene reacted with acetylacetone to give three kinds of 1 : 1 adducts with unidentified 2 : 1 adducts. The first product to emerge in the vpc (Silicone DC 550 column) was identified as **4** by IR and NMR-spectroscopic measurements.



$$(CH_3CO)_2CH{-}CH(CH_3){-}C(CH_3){=}CH_2$$

4



$$(CH_3CO)_2CH{-}CH_2C(CH_3){=}CH{-}CH_3$$

5

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[6] a) A. Miyake, G. Hata, M. Iwamoto, and S. Yuguchi, "Proceedings of the 7th World Petroleum Congress, Panel Discussion," Vol. 22, (1967), p. 37. b) M. Iwamoto and S. Yuguchi, *J. Org. Chem.*, **31**, 4290 (1966). c) G. Hata and A. Miyake, This Bulletin, **41**, 2762 (1968).

TABLE 1. REACTIONS OF ACTIVE METHYLENE COMPOUNDS WITH 1,3-BUTADIENE CATALYZED BY $PdBr_2(DPE)_2$ AND PhONa

Active methylene compound (mol)	BD[a)] mol	Catalyst mmol		Temp. °C	Time hr	Products[c)] (%)[d)]
		$PdBr_2(DPE)_2$[b)]	PhONa			
$CH_3COCH_2COCH_3$ (0.2)	0.3	0.25	2.5	140—151	2	$CH_3COCHXCOCH_3$(17), $CH_3COCHYCOCH_3$(43) $CH_3COC(C_4H_7)_2COCH_3$(5)
$CH_3COCH_2COCH_3$ (0.1)	0.3	0.25	2.5	133—148	1	$CH_3COCHXCOCH_3$(10), $CH_3COCHYCOCH_3$(7) $CH_3COC(C_4H_7)_2COCH_3$(62)
$CH_3COCH_2CO_2C_2H_5$ (0.2)	0.3	0.25	2.5	142—154	2	$CH_3COCHXCO_2C_2H_5$(35), $CH_3COCHYCO_2C_2H_5$(36) $CH_3COC(C_4H_7)_2CO_2C_2H_5$(1)
$CH_3COCH_2CO_2C_2H_5$ (0.1)	0.15	0.25	2.5	90	0.5	——
$CH_3COCH_2CO_2C_2H_5$ (0.1)	0.15	0.25	0.25	150	0.5	——
$CH_3COCH_2CO_2C_2H_5$ (0.1)	0.15	0.25	0.75	150	0.5	$CH_3COCHXCO_2C_2H_5$(8), $CH_3COCHYCO_2C_2H_5$(6)
$CH_2(CO_2C_2H_5)_2$ (0.2)	0.3	0.25	2.5	145—148	2	$CHX(CO_2C_2H_5)_2$(18), $CHY(CO_2C_2H_5)_2$(18)

a) BD=1,3-butadiene, b) DPE=$Ph_2PCH_2CH_2PPh_2$, c) X=$-CH(CH_3)CH=CH_2$, Y=$-CH_2CH=CHCH_3$, C_4H_7=mixture of X and Y
d) Based on the active methylene compounds employed.

TABLE 2. REACTION OF ETHYL ACETOACETATE WITH 1,3-BUTADIENE CATALYZED BY Pd-DPE CATALYSTS

Catalyst[a)] mmol	$CH_3COCH_2CO_2C_2H_5$ mol	BD mol	Temp. °C	Time hr	Products[b)] %[c)]		
					$CH_3COCHXCO_2C_2H_5$	$CH_3COCHYCO_2C_2H_5$	$CH_3COC(C_4H_7)_2CO_2C_2H_5$
$PdBr_2(DPE)_2$ 0.25	0.1	0.15	140—150	16	—	—	—
$PdBr_2(DPE)_2$-PhONa 0.25 2.5	0.2	0.3	142—154	2	35	36	1
$PdCl_2$ DPE 0.5 1.25	0.1	0.15	140—150	16	—	—	—
$PdCl_2$-DPE-PhONa 0.2 0.5 2.5	0.1	0.15	150—152	2	28	33	1
$Pd(NO_2)_2(NH_3)_2$-DPE 0.5 1.25	0.1	0.15	142—150	1	22	25	4
$Pd(OCOCH_3)_2$-DPE 0.2 0.5	0.1	0.15	140—152	16	35	40	18
$Pd(acac)_2$-DPE 0.2 0.5	0.1	0.15	150—152	5	16	22	3
$Pd(DPE)_2$ 0.25	0.1	0.15	140—150	2	12	15	—
$Pd(DPE)_2$-PhOH 0.25 2.5	0.2	0.3	140—150	2	32	40	16
$Pd(DPE)_2$-PhONa 0.25 2.5	0.1	0.15	141—148	2	37	37	16

a) DPE=$Ph_2PCH_2CH_2PPh_2$, acac=acetylacetonate, b) X=$-CH(CH_3)CH=CH_2$, Y=$-CH_2CH=CHCH_3$, C_4H_7=mixture of X and Y
c) Based on ethyl acetoacetate employed.

Table 3. Comparison of effect of bidentate donors in the reaction of ethyl acetoacetate with 1,3-butadiene[a,b]

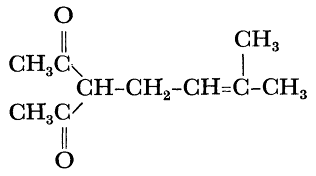
Bidentate donor	Time hr	Products[c) %[d)			
		$CH_3COCHXCO_2C_2H_5$	$CH_3COCHYCO_2C_2H_5$	$CH_3COC(C_4H_7)_2CO_2C_2H_5$	$CH_3COCHZCO_2C_2H_5$
$Ph_2PCH_2PPh_2$	2	trace	trace	—	—
$Ph_2PCH_2CH_2PPh_2$	2	28	33	1	—
$Ph_2P(CH_2)_3PPh_2$	1	29	49	7	7
$Ph_2P(CH_2)_4PPh_2$	1	7	4	—	53
$Ph_2PCH_2CH_2SPh$	20	5	9	—	—
α,α'-Dipyridyl	20	6	25	2	14

a) Catalyst; $PdCl_2$ 0.2 mmol, PhONa 2.5 mmol, bidentate donor 0.5 mmol.
b) Temperature 150°C.
c) $X=-CH(CH_3)CH=CH_2$, $Y=-CH_2CH=CHCH_3$, C_4H_7=mixture of X and Y, $Z=-CH_2CH=CH(CH_2)_3CH=CH_2$.
d) Based on ethyl acetoacetate employed.

Table 4. Reactions of active methylene compounds with 1,3-dienes catalyzed by $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ and PhONa[a)

Active methylene compound mol	1,3-Diene mol	Temp. °C	Time hr	Products[b) %[c)
$CH_3COCH_2CO_2C_2H_5$ 0.1	isoprene 0.15	141—150	1	$CH_3COCHRCO_2C_2H_5$, $CH_3COCHSCO_2C_2H_5$ 12 46 $CH_3COC(C_5H_9)_2CO_2C_2H_5$ 23
$CH_3COCH_2COCH_3$ 0.1	isoprene 0.15	136—146	2	$CH_3COCHRCOCH_3$, $CH_3COCHR'COCH_3$ 7 60 $CH_3COC(C_5H_9)_2COCH_3$ 6
$CH_3COCH_2CO_2C_2H_5$ 0.1	1,3-pentadiene 0.15	137—148	15	$CH_3COCH[CH(CH_3)CH=CHCH_3]CO_2C_2H_5$ 61 $CH_3COCH(CH_2CH=CHCH_2CH_3)CO_2C_2H_5$ 7
$CH_3COCH_2CO_2C_2H_5$ 0.1	2,4-hexadiene 0.15	140—150	20	$CH_3COCH[CH(CH_3)CH=CHCH_2CH_3]CO_2C_2H_5$ 45

a) Catalyst; $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$ 0.25 mmol, PhONa 2.5 mmol.
b) $R=-CH(CH_3)C(CH_3)=CH_2$, R'=mixture of $-CH_2C(CH_3)=CHCH_3$ and $-CH_2CH=C(CH_3)CH_3$, C_5H_9=mixture of R and R'.
c) Based on the active methylene compounds employed.



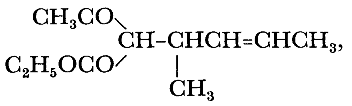
$(CH_3CO)_2CH\text{-}CH_2\text{-}CH{=}C(CH_3)\text{-}CH_3$

6

The compound **4** showed an IR absorption at 884 cm^{-1} due to the out-of-plane deformation of $>C{=}CH_2$, and NMR signals at 9.05 (3H, d, $J=6.0$ Hz), 8.30 (3H, s), 7.75 and 7.99 (6H, two s), 6.7—7.3(1H, m), 6.22(1H, d, $J=11.0$ Hz), and 5.25(2H, s). The spectrum of the second product to emerge showed a pair of triplet signals at 6.43 and 6.23 ($J=7.5$ Hz) due to the active methine hydrogen atom. This indicates that the product consists of two components. The IR spectrum exhibited no absorption characteristic of the $>C{=}CH_2$ or $-CH{=}CH_2$ bond, indicating that the products are not derived from the 1,2-addition of the active methylene to isoprene, but from the 1,4-addition. From the above spectral characteristics, the product can reasonably be estimated to be a mixture of **5** and **6**.

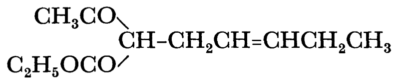
Ethyl acetoacetate also reacted with isoprene to give products similar to those derived from the 1,2- and 1,4-addition of the active methylene to isoprene.

The addition of 1,3-pentadiene to ethyl acetoacetate yielded two 1 : 1 adducts, **7** and **8**, in 61 and 7% yields respectively.



$(CH_3CO)(C_2H_5OCO)CH\text{-}CH(CH_3)CH{=}CHCH_3$,

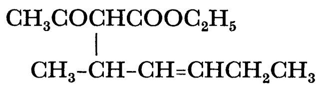
7



$(CH_3CO)(C_2H_5OCO)CH\text{-}CH_2CH{=}CHCH_2CH_3$

8

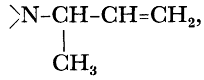
The reaction of 2,4-hexadiene with ethyl acetoacetate afforded a 1 : 1 adduct, **9**, selectively. The reactivity of the diene was much lower than those of 1,3-butadiene and isoprene. The results of the reaction of active methylene compounds with substituted 1,3-butadienes are summarized in Table 4.



$CH_3COCH(COOC_2H_5)\text{-}CH(CH_3)\text{-}CH{=}CHCH_2CH_3$

9

Primary and secondary amines also reacted with 1,3-butadiene in the presence of palladium-diphosphine complex catalysts to afford two 1 : 1 adducts, **10** and **11**. The results are shown in Table 5. The catalytic activity was remarkably enhanced by the addition of a small amount of phenol.



$>N\text{-}CH(CH_3)\text{-}CH{=}CH_2$,

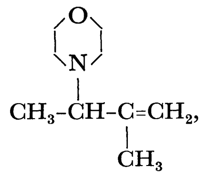
10

$>N\text{-}CH_2CH{=}CHCH_3$

11

A change in the amount of phenol affected the yields of the products and the ratio of **11** to **10**, which was investigated in the reaction of piperidine with 1,3-butadiene. In the presence of a large amount of phenol, *N*-(2-butenyl)piperidine was the predominant product, as is shown in Table 5.

It is interesting to note that the reactivity of amines was associated with their basicity.[7] The more basic amines are more reactive. The reaction of morpholine (pK=9.61) and aniline (pK=9.42) gave the 1 : 1 adducts in 79 and 67% yields respectively. On the other hand, the reaction of less basic amines, such as *n*-butylamine (pK=3.39) and piperidine (pK=2.80), afforded the 1 : 1 adducts in 19 and 29% yields respectively.



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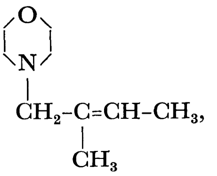

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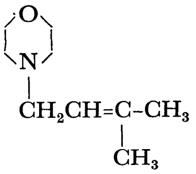

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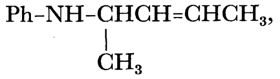
The addition of isoprene to morpholine in the presence of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, sodium phenoxide, and phenol resulted in a formation of 1 : 1 adducts, **12**, **13**, and **14**, in 9, 30, and 16% yields respectively.



$Ph\text{-}NH\text{-}CH(CH_3)CH{=}CHCH_3$,

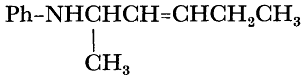
15

$Ph\text{-}NH\text{-}CH_2CH{=}CHCH_2CH_3$

16

The reaction of 1,3-pentadiene with aniline gave two kinds of 1 : 1 adducts, **15** and **16**, in 52 and 5% yields respectively. No 2 : 1 adduct was formed.

The addition of 2,4-hexadiene to aniline also afforded a 1 : 1 adduct, **17**.



$Ph\text{-}NHCH(CH_3)CH{=}CHCH_2CH_3$

17

Experimental

Reagents. $Ph_2P(CH_2)_nPPh_2$,[8] $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$,[9] $Pd(Ph_2PCH_2CH_2PPh_2)_2$,[9] $Pd(OCOCH_3)_2$,[10] $Pd(acac)_2$,[11] and $Pd(NO_2)_2(NH_3)_2$[12] were prepared by the previously-reported methods.

Acetylacetone, ethyl acetoacetate, diethyl malonate, and amines were purified by distillation. 2-Oxocyclododecanecarbaldehyde[13] was prepared according to the procedure

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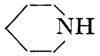
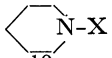
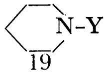
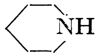
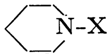
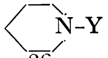
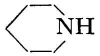
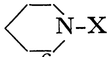
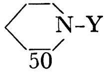
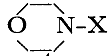
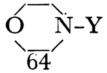
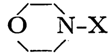
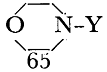
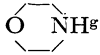
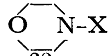
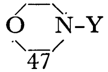
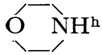
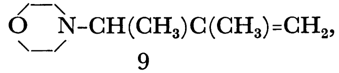
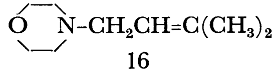
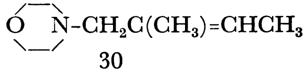
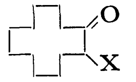
TABLE 5. REACTIONS OF AMINES WITH 1,3-DIENES

Amine[a]	1,3-Diene[b]	Catalyst[c] mmol	Temp. °C	Time hr	Products[d] %[e]		Residue g
$PhNH_2$	BD	$PdBr_2(DPE)_2$, PhONa 0.25 2.5	155—158	20	PhNHX 18	PhNHY 13	1.7
$PhNH_2$	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	155—162	0.5	PhNHX 44	PhNHY 15	3.1
$PhNH_2$	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 5.0	85	3	PhNHX 57	PhNHY 10	1.3
cyclo-$C_6H_{11}NH_2$	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	141—146	20	cyclo-$C_6H_{11}NHX$ 18	cyclo-$C_6H_{11}NHY$ 23	1.3
$(C_2H_5)_2NH$	BD	$Pd(DPE)_2$ PhOH 0.25 2.5	144—148	5	$(C_2H_5)_2NY$ 21		1.0
n-$C_4H_9NH_2$	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	130—139	5	n-C_4H_9NHX 12	n-C_4H_9NHY 7	0.9
$PhCH_2NH_2$	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	145—153	3	$PhCH_2NHX$ 10	$PhCH_2NHY$ 2	5.0
p-$CH_3C_6H_4NH_2$	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	85	3	p-$CH_3C_6H_4NHX$ 32	p-$CH_3C_6H_4NHY$ 6	0.9
	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	138—147	2	 10	 19	2.2
	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 5	150	1	 10	 26	—[f]
	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 10	150	1	 6	 50	—[f]
	BD	$Pd(DPE)_2$ 0.25	136—160	20	 4	 64	1.4
	BD	$Pd(DPE)_2$ PhOH 0.25 2.5	141—152	1	 5	 65	1.3
[g]	BD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	143—152	1	 32	 47	2.4
[h]	IP	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	140—146	2	 9  16	 30	2.4
$PhNH_2$	1,3-PD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	130—140	24	$PhNH-CH(CH_3)CH=CHCH_3$, 52	$PhNHCH_2CH=CHCH_2CH_3$ 5	1.7
$PhNH_2$	2,4-HD	$PdBr_2(DPE)_2$, PhONa, PhOH 0.25 2.5 2.5	136—143	24	$PhNH-CH(CH_3)CH=CHCH_2CH_3$ 9		1.4

a) 0.1 mol, b) 0.15 mol BD=1,3-butadiene, IP=isoprene, 1,3-PD=1,3-pentadiene, 2,4-HD=2,4-hexadiene, c) DPE=$Ph_2PCH_2CH_2PPh_2$, d) X=$-CH(CH_3)CH=CH_2$, Y=$-CH_2CH=CHCH_3$, e) Based on amine employed, f) Not measured, g) N-(2,7-octadienyl)morpholine was formed in an 11% yield, h) N-(dimethyl-2,7-octadienyl)-morpholine was formed in a 7% yield.

Table 6. Physical and analytical data of the products—1

Product[a)]	Bp °C/mmHg	n_D^{25}	Empirical formula	Calcd C%	Calcd H%	Calcd Mol wt	Found C%	Found H%	Found Mol wt[b)]
X-CH$(COCH_3)_2$	199	1.4479	$C_9H_{14}O_2$	70.10	9.15	154	69.66	9.12	161
Y-CH$(COCH_3)_2$	202	1.4602	$C_9H_{14}O_2$	70.10	9.15	154	70.30	9.23	155
X-CH$(COCH_3)CO_2C_2H_5$	215	1.4372	$C_{10}H_{16}O_3$	65.19	8.70	184	65.18	8.75	183
Y-CH$(COCH_3)CO_2C_2H_5$	220	1.4422	$C_{10}H_{16}O_3$	65.19	8.70	184	64.94	8.48	184
X-CH$(CO_2C_2H_5)_2$	233	1.4330	$C_{11}H_{18}O_4$	61.66	8.47	214	61.76	8.39	207
Y-CH$(CO_2C_2H_5)_2$	235	1.4346	$C_{11}H_{18}O_4$	61.66	8.47	214	61.83	8.37	214
	128/2	1.4880	$C_{16}H_{28}O$	81.29	11.94	236	80.92	12.21	227
R-CH$(COCH_3)_2$	64/5	1.4538	$C_{10}H_{16}O_2$	71.39	9.59	168	71.57	9.65	168
R-CH$(COCH_3)CO_2C_2H_5$	228	1.4443	$C_{11}H_{18}O_3$	66.59	9.15	198	66.79	9.18	199
$CH_3CH=CHCH(CH_3)CH-(COCH_3)CO_2C_2H_5$	62/1	1.4414	$C_{11}H_{18}O_3$	66.59	9.15	198	66.50	9.08	201
$CH_3CH_2CH=CHCH_2CH-(COCH_3)CO_2C_2H_5$	—	1.4448	$C_{11}H_{18}O_3$	66.59	9.15	198	67.35	9.08	191
$CH_3CH_2CH=CHCH(CH_3)CH-(COCH_3)CO_2C_2H_5$	96—8/5	1.4460	$C_{12}H_{20}O_3$	67.89	9.50	212	67.81	9.52	206

a) X=-CH$(CH_3)CH=CH_2$, Y=-$CH_2CH=CHCH_3$, R=-CH$(CH_3)C(CH_3)=CH_2$.
b) Measured by vapor pressure osmometry.

described before.

The purification of 1,3-butadiene was accomplished by the vaporization of the liquid diene containing triethylaluminum. Isoprene, 1,3-pentadiene, and 2,4-hexadiene were distilled under an argon atmosphere.

General Procedure for the Reaction of Active Methylene Compounds and Amines with 1,3-Butadiene. A 100 m*l* stainless steel autoclave was charged with an active methylene compound or amine and catalyst components. The liquid 1,3-butadiene was vaporized in order to condense it in an autoclave chilled with dry ice and methanol which had been evacuated beforehand. The reaction was carried out by stirring at 140—150°C. The reaction mixture was distilled and analyzed by vpc. The products were separated by fractional distillation and by the use of preparative gas chromatography. The analytical and physical data of the products are listed in Tables 6 and 7.

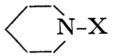
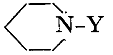
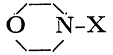
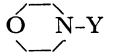
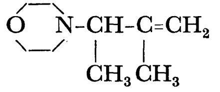
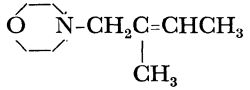
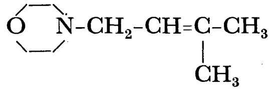
Reaction of Acetylacetone with 1,3-Butadiene. A mixture of 0.2 mol of acetylacetone, 0.3 mol of 1,3-butadiene, 0.25 mmol of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, and 2.5 mmol of sodium phenoxide was stirred at 140—151°C for 2 hr. The products consisted of **1a** (5.3 g, 17%), **2a** (13.2 g, 43%), **3a** (2.1 g, 5%), and a residue (1.6 g). The spectroscopic data of the products are as follows: **1a** ν_{max} 1722 and 1700 cm^{-1} (β-diketone), 1644, 998 and 922 cm^{-1} (–$CH=CH_2$); τ 9.03 (d, J=6.5 Hz, CH_3-C-C=), 7.95 and 7.87 (CH_3CO–), 6.7—7.3 (m, CO-C-CH–), 6.45 (d, J=10.0 Hz, CO-CH-CO) and 4.0—5.2 (m, olefinic protons), **2a** ν_{max} 1725, 1701 and 1605 cm^{-1} (β=diketone), 968 cm^{-1} (*trans* –CH=CH–); 8.36 (d, J=6.0 Hz, CH_3-C=), 7.95 and 7.92 (CH_3CO–), 7.70—7.35 (br. t, CO-C-CH_2-C=, keto form), 7.09 (br, s, CO-C-CH_2-C=, enol form), 6.40 (t, J=7.0 Hz, CO-CH-CO, keto form), and 4.8—4.4 (m, olefinic protons).

Reaction of 2-Oxocyclododecanecarbaldehyde with 1,3-Butadiene. A mixture of 0.036 mol of 2-oxocyclododecanecarbaldehyde, 0.1 mol of 1,3-butadiene, 0.18 mmol of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, and 1.8 mmol of phenoxide was stirred at 138—142°C for 15 hr. The distillation of the resultant solution gave 4.9 g of a fraction boiling at 168—170°C/3 mmHg. The IR spectrum of the fraction showed an absorption due to the out-of-plane deformation of *trans* –CH=CH– near 960 cm^{-1}, and no absorptions due to the out-of-plane deformation of –$CH=CH_2$. The intensity of the NMR signal due to –CHO corresponded to only about 0.2 H (τ 1.39, s). This fact indicates that the decarbonylation from the aldehyde group of the first formed product, 1-(2-butenyl)-2-oxocyclododecanecarbaldehyde, takes place. The treatment of the fraction with sodium ethoxide in ethanol gave 2-(2-butenyl)cyclododecanone. It exhibited the following spectral characteristics: ν_{max} 1708 cm^{-1} (>C=O) and 965 cm^{-1} (*trans* –CH=CH–); τ 4.8—4.3 (m, olefinic protons).

Reaction of Acetylacetone with Isoprene. A mixture of 0.1 mol of acetylacetone, 0.15 mol of isoprene, 0.25 mmol of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, and 2.5 mmol of sodium phenoxide was stirred at 136—146°C for 2 hr to afford **4** (1.1 g, 7%) and a mixture of **5** and **6** (10.1 g, 60%). The product **4** showed the following spectral characteristics: ν_{max} 1710 and 1700 cm^{-1} (β-diketone), 1644 and 898 cm^{-1} (>$C=CH_2$); τ 9.05 (d, J=6.0 Hz, CH_3-C-C=), 8.30 (s, CH_3C=), 7.99 and 7.75 (CH_3CO–), 7.3—6.7 (m, -CH-C-CO–), 6.22 (d, J=11.0 Hz, -CH-CO–), and 5.25 (s, CH_2=C–).

Reaction of Ethyl Acetoacetate with 1,3-Pentadiene. A mixture of 0.1 mol of ethyl acetoacetate, 0.15 mol of 1,3-pentadiene, 0.25 mmol of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, and 2.5 mmol of sodium phenoxide was stirred at 137—148°C for 15 hr to yield **7** (12.0 g, 61%) and **8** (1.4 g, 7%). The product **7** showed the following spectral characteristics: ν_{max} 1745 and 1715 cm^{-1} (keto ester), 970 cm^{-1} (*trans* –CH=CH–); 9.05 and 9.01 (two d, J=6.5 Hz, CH_3-C-C=), 8.80 and 8.76 (two t, J=7.0 Hz, CH_3C-O–), 8.41 (d, J=5.0 Hz, CH_3-C=), 7.95 and 7.91 (two s, CH_3CO–), 6.81 (d, J=10.0 Hz, -CO-CH-CO–), 5.92 and 5.87 (two q, J=7.0 Hz, -O-CH_2-C), and 4.9—4.3 (m, olefinic protons). Two kinds of signals due to acetyl, ethyl, and one of the methyl groups on the side chain indicate that the compound is a mixture of the *erythro* and *threo* isomers. The product **8**

Table 7. Physical and analytical data of the products—2

Product[a)]	Bp °C/mmHg	n_D^{25}	Empirical formula	Calcd % C	Calcd % H	Calcd % N	Found % C	Found % H	Found % N
PhNH-X	98/12	1.5451	$C_{10}H_{13}N$	81.45	8.90	9.51	81.43	8.93	9.62
PhNH-Y	113/12	1.5537	$C_{10}H_{13}N$	81.45	8.90	9.51	81.38	8.83	9.75
cyclo-C_6H_{11}NH-X	187	1.4598	$C_{10}H_{19}N$	78.36	12.49	9.14	78.07	12.38	9.09
cyclo-C_6H_{11}NH-Y	209	1.4701	$C_{10}H_{19}N$	78.36	12.49	9.14	78.27	12.25	8.62
$(C_2H_5)_2$N-Y	57—58/42	1.4313	$C_8H_{17}N$	75.52	13.47	11.09	75.44	13.27	10.72
n-C_4H_9NH-X	143	1.4220	$C_8H_{17}N$	75.52	13.47	11.09	75.46	13.46	11.01
n-C_4H_9NH-Y	164	1.4332	$C_8H_{17}N$	75.52	13.47	11.09	75.22	13.58	11.01
$PhCH_2$NH-X	218	1.5102	$C_{11}H_{15}N$	81.94	9.38	8.68	81.82	9.38	8.87
$PhCH_2$NH-Y	240	1.5192	$C_{11}H_{15}N$	81.94	9.38	8.68	82.03	9.48	8.71
p-CH_3-C_6H_4-NH-X	237	1.5380	$C_{11}H_{15}N$	81.94	9.38	8.68	81.97	9.53	8.87
p-CH_3-C_6H_4-NH-Y	260	1.5455	$C_{11}H_{15}N$	81.94	9.38	8.68	82.03	9.48	8.71
 N-X	169	1.4607	$C_9H_{17}N$	77.64	12.37	9.99	77.46	12.35	10.04
 N-Y	180	1.4634	$C_9H_{17}N$	77.64	12.37	9.99	77.47	12.37	10.08
 O N-X	171	1.4601	$C_8H_{15}NO$	68.04	10.71	9.92	67.99	10.80	9.92
 O N-Y	187	1.4633	$C_8H_{15}NO$	68.04	10.71	9.92	67.98	10.69	9.86
 O N-CH-C=CH_2 CH_3 CH_3	193	1.4620	$C_9H_{17}NO$	69.63	11.04	9.02	69.93	11.12	8.89
 O N-CH_2C=$CHCH_3$ CH_3	197	1.4635	$C_9H_{17}NO$	69.63	11.04	9.02	69.56	11.03	9.03
 O N-CH_2-CH=C-CH_3 CH_3	240	1.4681	$C_9H_{17}NO$	69.63	11.04	9.02	69.55	11.12	8.88
PhNH-$CH(CH_3)C$=$CHCH_3$	74—76/2	1.5418	$C_{11}H_{15}N$	81.94	9.38	8.68	82.05	9.35	8.46
PhNH-CH_2CH=$CHCH_2CH_3$	92—93/2	1.5412	$C_{11}H_{15}N$	81.94	9.38	8.68	82.00	9.35	8.68
PhNH-$CH(CH_3)CH$=$CHCH_2CH_3$	94—95/2.5	1.5353	$C_{12}H_{17}N$	82.23	9.78	7.99	81.96	9.68	8.12

a) X=-$CH(CH_3)CH$=CH_2, Y=-CH_2CH=$CHCH_3$.

showed the following spectral characteristics: $\nu_{\max}$ 1745 and 1715 cm^{-1} (keto ester), 1648 and 967 cm^{-1} (*trans* -CH=CH-); τ 9.05 (t, J=7.5 Hz, CH_3C-C=), 8.75 (t, J=7.0 Hz, CH_3C-O-), 8.20—7.75 (m, C-CH_2-C=), 7.90 (s, CH_3CO-), 7.56 (t, J=7.0 Hz, -CO-C-CH_2-C), 6.68 (t, J=7.0 Hz, -CO-CH-CO-), 5.87 (q, J=7.0 Hz, -O-CH_2-C), and 4.9—4.3 (m, olefinic protons).

Reaction of Ethyl Acetoacetate with 2,4-Hexadiene. The reaction was carried out for 24 hr under the same conditions as those used in the reaction of ethyl acetoacetate with 1,3-pentadiene. The product (9.6 g, 45%) was identified as **9**: $\nu_{\max}$ 1745 and 1715 cm^{-1} (keto ester), 1650 and 968 cm^{-1} (*trans* -CH=CH-); τ 9.1—8.8 (m, CH_3-C-C= and CH_3-C-C-CO), 8.68 and 8.66 (two t, J=7.0 Hz, -O-C-CH_3). 8.1—7.7 (m, C-CH_2-C=), 7.81 and 7.76 (two s, CH_3CO-), 7.4—6.8 (m, C-CH-C=), 6.60 (d, J=10.0 Hz, -CO-CH-CO-), 5.80 and 5.75 (two q, J=7.0 Hz, -O-CH_2-C), and 4.8—4.2 (m, olefinic protons).

Reaction of Aniline with 1,3-Butadiene. A mixture of 0.1 mol of aniline, 0.15 mol of 1,3-butadiene, 0.25 mmol of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, 2.5 mmol of sodium phenoxide, and 2.5 mmol of phenol was stirred at 85° for 3 hr to afford *N*-(1-methyl-2-propenyl)aniline (8.4 g, 57%) and *N*-(2-butenyl) aniline (1.4 g, 10%). The former product showed the following spectral characteristics: $\nu_{\max}$ 3430 cm^{-1} (N-H), 1644, 992, and 915 cm^{-1} (-CH=CH_2); τ 8.77 (d, J=7.0 Hz, CH_3-C-C=), 6.60 (s, -NH-), 6.3—5.8 (m, -N-CH-), 5.15—4.27 (m, -CH=CH_2), and 3.65—2.75 (m, phenyl protons). *N*-(2-Butenyl)aniline exhibited the following spectral characteristics: $\nu_{\max}$ 3410 cm^{-1} (N-H), 963 cm^{-1} (*trans* -CH=CH-); 8.35 (d, J=5.0 Hz, CH_3-C=), 6.55 s, N-H), 6.5—6.25 (m, -N-CH_2-C=), 4.8—4.1 (m, olefinic protons), and 3.65—2.75 (m, phenyl protons).

Reaction of Morpholine with Isoprene. A mixture of 0.1 mol of morpholine, 0.15 mol of isoprene, 0.25 mmol of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, 2.5 mmol of sodium phenoxide, and 2.5 mmol of phenol was stirred at 140—146°C for 2 hr to yield **12** (1.4 g, 9%), **13** (4.7 g, 30%), **14** (2.4 g, 16%), and a small amount of *N*-(dimethyl-2,7-octadienyl)morpholine. The products showed the following spectroscopic data: **12**: $\nu_{\max}$ 1653 and 896 cm^{-1} ($>$C=CH_2); τ 8.93 (d, J=6.5 Hz, CH_3-C-C=), 8.36 (s, CH_3-C=), 7.7 and 6.45 (protons of morpholine), 7.34 (q, J=6.5 Hz, C-CH-C=), 5.29 and 5.22 (olefinic protons); **13**: $\nu_{\max}$ 1674 ($>$C=C$<$); τ 8.44 (d, J=3.0 Hz, CH_3-C-N-), 8.42 (s, CH_3-C=), 7.55 and 6.45 (morpholine protons), 7.28 (s, -N-CH_2-C=), and 4.85—4.5 (m, -C=CH-); **14**: $\nu_{\max}$ 1676 cm^{-1} ($>$C=C$<$); τ 8.40 and 8.31 (two s, =C$(CH_3)_2$), 7.70 and 6.50 (morpholine protons), 7.18 (d, J=7.0 Hz, -N-CH_2-C=), and 4.85 (t, J=7.0 Hz, -N-C-CH=).