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Palladium-catalyzed Exchange of Allylic Groups of Ethers and Esters with Active Hydrogen Compounds. II.[1]

Kuniyuki TAKAHASHI, Akihisa MIYAKE, and Go HATA
Basic Research Laboratory, Toray Industries, Inc., Tebiro, Kamakura

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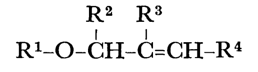
The allylic compounds (I), R^1–O–R (R = allylic groups, R^1 = Ph, Me, $PhCH_2$, MeCO), react with active-hydrogen compounds such as phenols, alcohols, carboxylic acids, primary and secondary amines and active methylene compounds, to give allylic derivatives of the active-hydrogen compounds by an intermolecular exchange of the allylic groups of I with the atom to which the active hydrogens are bonded in the presence of palladium catalysts. Allyl and substituted-allyl ethers are more reactive than the corresponding carboxylates. In the reactions of methyl and benzyl ethers, it is necessary to add phenol to obtain the exchange products in fairly good yields. Bis(triphenylphosphine)palladium chloride plus sodium phenoxide, palladium acetate plus triphenylphosphine, and zerovalent palladium complexes such as tetrakis(triphenylphosphine)palladium and (maleic anhydride)bis(triphenylphosphine)palladium are effective catalysts.

It has been reported that the vinyl group of ethers and esters exchanges with various active-hydrogen compounds such as phenols, alcohols and carboxylic acids in the presence of mercury salts[2,3] or palladium salts.[4] Mercury acetate also catalyzes the exchange of an allyl group of allyl ethers with a hydroxyl group of alcohols.[5] Sabel and his coworkers have reported[4] on the exchange reaction of an allyl group between allyl acetate and propionic acid by $PdCl_2 \cdot NaCl\text{-}CH_3CH_2CO_2Na$ catalyst system.

Recently a new type of palladium catalyzed dimerization of 1,3-dienes completed by the addition of active-hydrogen compounds such as alcohols, phenols, amines, carboxylic acids and active methylene compounds, has been found.[6–9] Smutny found[10] that the palladium complexes, which catalyzed the reaction of phenol with butadiene to the formation of 1-phenoxy-2,7-octadiene, degradated the resulting ether to phenol and 1,3,7-octatriene. The degradation reaction seems to proceed through an allylic intermediate by the insertion of the palladium atom to the C–O bond of the ether. If such an intermediate exists, the intermediate is expected to react with active-hydrogen compounds to afford 2,7-octadienyl derivatives of the corresponding active-hydrogen compounds. In fact, the reaction of 1-phenoxy-2,7-octadiene with methyl acetoacetate gave the expected products. A further research has led to the finding that allylic compounds (I) react with active-hydrogen compounds in the same way to give allylic derivatives of the active hydrogen compounds by the intermolecular exchange of the allylic groups of the allylic compounds to the atom to which the active-hydrogen is bonded. This type of reaction is applied to alcohols, phenols, carboxylic acids, and primary and secondary amines. The same type of exchange reactions of allylic group has been reported independently by Atkins and his coworkers.[11] We reported a part of these reactions in a preliminary communication.[1] The present paper describes the reactions in detail.



$$R^1\text{-O-}\overset{\displaystyle R^2}{\overset{|}{\text{CH}}}\text{-}\overset{\displaystyle R^3}{\overset{|}{\text{C}}}\text{=CH-}R^4$$

I

R^1 = Ph, CH_3, $PhCH_2$, CH_3CO
R^2 = H, $CH_2CH_2CH_2CH{=}CH_2$
R^3 = H, CH_3
R^4 = H, CH_3, $CH_2CH_2CH_2CH{=}CH_2$

An active and easily available catalyst is prepared by mixing dichlorobis(triphenylphosphine)palladium (II) and sodium phenoxide. The combination of palladium acetate and triphenylphosphine, and zerovalent palladium phosphine complexes such as tetrakis(triphenylphosphine)palladium(0) and (maleic anhydride)bis(triphenylphosphine)palladium(0) are also effective catalysts. Platinum catalysts such as the combination of dichlorobis(triphenylphosphine)platinum(II) and sodium phenoxide, and tetrakis(triphenylphosphine)platinum(0) also showed catalytic activity, but the activity of the platinum catalysts was smaller than that of palladium catalysts. It is noted that all of the catalysts are also effective for the dimerization reaction of 1,3-dienes in the presence of active hydrogen compounds.[6–9] The reactions proceeded as shown in the following equation. Only small amounts of the branched products(III) were normally observed.

The reaction products were confirmed by elemental analysis, molecular weight measurement, and IR and NMR spectral measurement or by comparison with authentic samples.[6–10]

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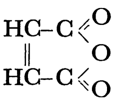
Table 1. Reaction of allyl and substituted-allyl compounds with active-hydrogen compounds[a)]

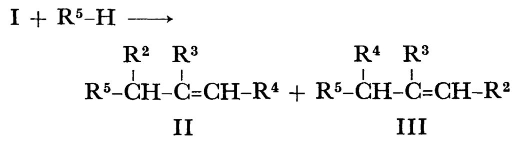
Phenoxy compound mol	Active hydrogen compound mol	Catalyst mol	Time hr	Product[c)] and Yield[d)] %
$PhOCH_2CH=CH(CH_2)_3CH=CH_2$ 0.05	$CH_3COCH_2CO_2CH_3$ 0.1	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	2	X–$CH(COCH_3)CO_2CH_3$ 84 X_2–$C(COCH_3)CO_2CH_3$ 7
$PhOCH_2CH=CH_2$ 0.1	$CH_3COCH_2CO_2CH_3$ 0.05	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	8.5	$CH_2=CHCH_2CH(COCH_3)CO_2CH_3$ 18 $(CH_2=CHCH_2)_2C(COCH_3)CO_2CH_3$ 47
$PhOCH_2CH=CH_2$ 0.08	$CH_3COCH_2CO_2CH_3$ 0.08	$PdCl_2(Ph_3As)_2$–PhONa 0.1 0.5	1	$CH_2=CHCH_2CH(COCH_3)CO_2CH_3$ 6 $(CH_2=CHCH_2)_2C(COCH_3)CO_2CH_3$ 13
$PhOCH_2CH=CH_2$ 0.05	$(C_2H_5)_2NH$ 0.1	$PdCl_2(Ph_3P)_2$–PhONa 0.1 0.5	1	$CH_2=CHCH_2N(C_2H_5)_2$ 100
$PhOCH_2CH=CH_2$ 0.05	$(C_2H_5)_2NH$ 0.1	$Pd(Ph_3P)_2$  0.1	1	$CH_2=CHCH_2N(C_2H_5)_2$ 100
$PhOCH_2C(CH_3)=CH_2$ 0.05	$(C_2H_5)_2NH$ 0.1	$PdCl_2(Ph_3P)_2$–PhONa 0.1 0.5	1	$CH_2=C(CH_3)CH_2N(C_2H_5)_2$ 89
$PhOCH_2CH=CHCH_3$ 0.05	$(C_2H_5)_2NH$ 0.1	$PdCl_2(Ph_3P)_2$–PhONa 0.1 0.5	1	$CH_3CH=CHCH_2N(C_2H_5)_2$ 92
$PhOCH_2CH=CH_2$ 0.05	t-$C_4H_9NH_2$ 0.1	$PdCl_2(Ph_3P)_2$–PhONa 0.2 1.0	1 1	$CH_2=CHCH_2NH$-t-C_4H_9 89 $(CH_2=CHCH_2)_2N$-t-C_4H_9 4
$PhOCH_2CH=CH_2$ 0.1	 0.05	$PdCl_2(Ph_3P)_2$–PhONa 0.1 1.0	1	 33
$PhOCH_2CH=CH(CH_2)_3CH=CH_2$ 0.05	cyclo–$C_6H_{11}NH_2$ 0.1	$PdCl_2(Ph_3P)_2$–PhONa 0.1 1.0	2	X–NH–cyclo–C_6H_{11} 69
$PhOCH_2CH=CH(CH_2)_3CH=CH_2$ 0.05	$PhNH_2$ 0.1	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	1	X–NHPh 84
$PhOCH_2CH=CH_2$ 0.025	p-$CH_3C_6H_4OH$ 0.025	$PdCl_2(Ph_2P)_2$–PhONa 0.05 0.5	3	$CH_2=CHCH_2OC_6H_4$-p-CH_3 41
$PhOCH_2CH=CH_2$ 0.025	p-ClC_6H_4OH 0.025	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	3	$CH_2=CHCH_2OC_6H_4$-p-Cl 26
$PhOC_8H_{13}$[b)] 0.025	$PhCH_2OH$ 0.05	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	2	X–OCH_2Ph 59 Y–OCH_2Ph 2 1,3,7-OT 20
$PhOC_8H_{13}$[b)] 0.05	CH_3COOH 0.1	$Pd(OCOCH_3)_2$–Ph_3P 0.1 0.25	24	X–$OCOCH_3$ 32 Y–$OCOCH_2$ 6 1,3,7-OT 5
$PhOC_8H_{13}$[b)] 0.05	CH_3COOH 0.1	$Pd(OCOCH_3)_2$–Ph_3P 0.1 0.25 in 10 ml DMF	24	X–$OCOCH_3$ 40 Y–$OCOCH_3$ 16 1,3,7-OT trace
$PhOC_8H_{13}$[b)] 0.05	PhCOOH 0.1	$Pd(OCOCH_3)_2$–Ph_3P 0.1 0.25 in 10 ml DMF	24	X–OCOPh 42 Y–OCOPh 18 1,3,7-OT trace

a) All reactions were carried out at 85°C.

b) A mixture of 1-phenoxy-2,7-octadiene (92%) and 3-phenoxy-1,7-octadiene (8%)

c) X=$CH_2=CH(CH_2)_3CH=CHCH_2$-, Y=$CH_2=CH(CH_2)_3CH(CH=CH_2)$-, 1,3,7-OT=$CH_2=CHCH=CHCH_2CH_2CH=CH_2$

d) Based on the phenoxyl compound employed.



$$\mathrm{I} + \mathrm{R^5{-}H} \longrightarrow \underset{\mathrm{II}}{\mathrm{R^5{-}\overset{R^2}{\overset{|}{C}}H{-}\overset{R^3}{\overset{|}{C}}{=}CH{-}R^4}} + \underset{\mathrm{III}}{\mathrm{R^5{-}\overset{R^4}{\overset{|}{C}}H{-}\overset{R^3}{\overset{|}{C}}{=}CH{-}R^2}}$$

		R^2	R^3	R^4	R^5
IIa	—	H	H	$-(CH_2)_3CH=CH_2$	$CH_3COCHCO_2CH_3$
IIb	—	H	H	$-(CH_2)_3CH=CH_2$	$CH_3COC(C_8H_{13})CO_2CH_3$
IIc	—	H	H	H	$CH_3COCHCO_2CH_3$
IId	—	H	H	H	$CH_3COC(C_3H_5)CO_2CH_3$
IIe	—	H	H	$-(CH_2)_3CH=CH_2$	cyclo-C_6H_{11}-NH-
IIf	—	H	H	$-(CH_2)_3CH=CH_2$	PhNH-
IIg	—	H	CH_3	H	$(C_2H_5)_2N-$
IIh	—	H	H	H	*p*-Cl-C_6H_4O-
IIi	—	H	H	H	*p*-CH_3-C_6H_4O-
IIj	IIIj	H	H	$-(CH_2)_3CH=CH_2$	CH_3O-
IIk	IIIk	H	H	$-(CH_2)_3CH=CH_2$	$PhCH_2O-$
IIl	—	H	H	H	$PhCH_2O-$
IIm	IIIm	H	H	$-(CH_2)_3CH=CH_2$	CH_3COO
IIn	IIIn	H	H	$-(CH_2)_3CH=CH_2$	PhCOO

$C_8H_{13} = -CH_2CH=CH(CH_2)_3CH=CH_2$, $C_3H_5 = -CH_2CH=CH_2$

Reaction of Allyl and Substituted-allyl Phenoxide. The reaction of methyl acetoacetate with 1-phenoxy-2,7-octadiene in the presence of dichlorobis(triphenylphosphine)palladium(II) and sodium phenoxide at 85°C gave methyl 2-acetyl-4,9-decadienoate(IIa) and methyl 2-acetyl-2-(2,7-octadienyl)-4,9-decadienoate (IIb), in 84 and 7% yields, respectively, besides phenol. These products are also formed by the reaction of methyl acetoacetate with 1,3-butadiene in the presence of the palladium catalyst.[9]

1-phenoxy-2-propene similarly reacted with methyl acetoacetate in the presence of $PdCl_2(Ph_3P)_2$ and sodium phenoxide to give methyl 4-acetyl-4-pentenoate (IIc) and methyl 2-acetyl-2-allyl-4-pentenoate(IId) in 18 and 47% yields, respectively. The catalytic activity of the combination of $PdCl_2(Ph_3As)_2$ and sodium phenoxide is slightly smaller than that of $PdCl_2(Ph_3P)_2$ and sodium phenoxide.

Allyl and substituted-allyl phenoxide also reacted with substituted phenols, alcohols, amines and carboxylic acids in the presence of the palladium or platinum catalyst to give corresponding allylic derivatives. Results of the reactions of allyl and substituted allyl phenoxide with active hydrogen compounds are summarized in Table 1.

In the reactions of 1-phenoxy-2,7-octadiene with amines, neither branched products, 1-vinyl-5-hexenylamines, nor 1,3,7-octatriene were detected. The formation of diallylpiperadine could be confirmed in the reaction of 1-phenoxy-2-propene with piperadine. In the reaction of 1-phenoxy-2,7-octadiene with cyclohexylamine and aniline, *N*-(2,7-octadienyl)-cyclohexylamine and -aniline, (IIe) and (IIf), were formed.

The reaction of 1-phenoxy-2-propene with *p*-chlorophenol and with *p*-cresol afforded the corresponding exchange products (IIh) and (IIi) in 26 and 41% yields, respectively. The reaction mixture of 1-phenoxy-2-propene and *p*-cresol was confirmed to consist of 1-phenoxy-2-propene, *p*-cresol, 1-(*p*-methylphenoxyl)-2-propene (IIi) and phenol as expected, while in the reaction mixture of 1-phenoxy-2-propene and *p*-chlorophenol an unidentified product was observed besides four expected components.

Results of the reactions of alcohols with phenoxyoctadienes consisting of 1-phenoxy-2,7-octadiene(92%) and 3-phenoxy-1,7-octadiene(8%) in the presence of dichlorobis(triphenylphosphine)palladium(II) and sodium phenoxide are summarized in Table 2. The reaction of methanol with the phenoxyoctadienes gave a mixture of IIj(93%) and IIIj(7%) in an 89% yield. Formation of a small amount of 1,3,7-octatriene was observed. The reactivity of methanol was much

TABLE 2. REACTIONS OF PHENOXYOCTADIENE[a] WITH ALCOHOLS

Alcohol[b]	Catalyst mmol	Temp. °C	Time hr	Conv.[c] %	Products, %[d]		
					$-O-CH_2CH=CH(CH_2)_3-CH=CH_2$	$-O-CH(CH=CH_2)(CH_2)_3-CH=CH_2$	1,3,7-Octatriene
CH_3OH	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	60	3	100	83	6	6
C_2H_5OH	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	60	3	70	35	—	17
iso-C_3H_7OH	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	60	3	20	—	—	13
$PhCH_2OH$	$PdCl_2(Ph_3P)_2$–PhONa 0.05 0.5	85	1.5	90	57	2	28
$PhCH_2OH$	$Pd(Ph_3P)_4$ 0.05	85	2.5	100	24	11	41
$PhCH_2OH$	$Pd(OCOCH_3)_2$–Ph_3P 0.05 0.1	85	2.5	76	52	2	11
$PhCH_2OH$	$PdCl_2$ — PhONa 0.05 0.5	85	2.5	0	—	—	—
$PhCH_2OH$	$Pt(Ph_3P)_4$ 0.05	85	2.5	89	19	15	44
$PhCH_2OH$	$PtCl_2(Ph_3P)_2$–PhONa 0.05 0.5	85	2.5	93	43	10	25

a) 5.05 g (0.025 mol) of a mixture of 1-phenoxy-2,7-octadiene (92%) and 3-phenoxy-1,7-octadiene (8%).
b) 0.05 mol. c) Conversion of phenoxyoctadiene. d) Based on phenoxyoctadiene.

TABLE 3. REACTION OF PHENOXYOCTADIENE WITH BENZYL ALCOHOL[a)]

Time min	Reaction products,[b)] g				
	1,3,7-Octatriene	$\text{PhOCH}_2\text{CH=CHC}_5\text{H}_9$	$\text{PhOCH(CH=CH}_2\text{)C}_5\text{H}_9$	$\text{PhCH}_2\text{OCH}_2\text{CH=CH}_5\text{CH}_9$	$\text{PhCH}_2\text{OCH-(CH=CH}_2\text{)C}_5\text{H}_9$
0	0	4.65	0.40	0	0
10	0.97	2.34	0.56	0.42	0.03
30	0.80	1.14	0.44	1.40	0.07
90	0.78	0.39	0.16	3.16	0.11

a) Reaction conditions: $\text{PdCl}_2(\text{Ph}_3\text{P})_2$ 0.05 mmol, PhONa 0.5 mmol, Phenoxyoctadiene 5.05 g (0.025 mol) and benzyl alcohol 0.05 mol, 85°C

b) $\text{C}_5\text{H}_9 = \text{-CH}_2\text{CH}_2\text{CH}_2\text{CH=CH}_2$

greater than that of ethanol, isopropyl alcohol and benzyl alcohol. The reaction of isopropyl alcohol gave only 1,3,7-octatriene in a 13% yield. It seems that the acidity of alcohol has a large effect on the reactivity. A similar tendency has been observed in the dimerization of 1,3-butadiene in the alcohols by the palladium catalyst.[7)]

The reaction of the phenoxyoctadienes with benzyl alcohol by the $\text{PdCl}_2(\text{Ph}_3\text{P})_2$-PhONa catalyst was studied as a function of time. The result is shown in Table 3. The products, IIk and IIIk, were formed in 58 and 2% yields, respectively. This shows that the ratio of 3-phenoxy-1,7-octadiene to 1-phenoxy-2,7-octadiene changed from 0.09 to 0.24 in ten minutes after the beginning of the reaction with the formation of 1,3,7-octatriene. This indicates the rearrangement of 1-phenoxy-2,7-octadiene to 3-phenoxy-1,7-octadiene with the catalyst. The initial formation of 1,3,7-octatriene was rapid. However, the amount of the triene decreased gradually. The decrease seems to be due to the consumption of 1,3,7-octatriene for the formation of its adducts by the reaction of the triene with benzyl alcohol. Vpc showed an unidentified peak near that of 1-benzyloxy-2,7-octadiene.

Results of the reactions of benzyl alcohol with phenoxyoctadiene by several palladium and platinum catalysts are shown in Table 2. Platinum catalysts and a mixture of palladium acetate and triphenylphosphine are also effective, but a combination of palladium chloride and sodium phenoxide did not show any catalytic activity. Apparently, the reaction by tetrakistriphenylphosphine complexes of Pd(0) and Pt(0) gives a larger amount of 1,3,7-octatriene than bistriphenylphosphine complexes of Pd(II) and Pt(II), and the reaction by the platinum catalysts affords a much larger amount of the branched product (IIIk) than the palladium catalysts. The allyl group of 1-phenoxy-2-propene also migrated to benzyl alcohol in the presence of $\text{PdCl}_2(\text{Ph}_3\text{P})_2$ and sodium phenoxide to give 1-benzyloxy-2-propene (IIl) in an 82% yield.

The reaction of the phenoxyoctadienes consisting of 1-phenoxy-2,7-octadiene(92%) and 3-phenoxy-1,7-octadiene(8%), with acetic acid in the presence of palladium acetate and triphenylphosphine proceeded to give octadienyl acetate(IIm) and (IIIm) in 32 and 6% yields based on the phenoxyoctadienes, respectively, and a small amount of 1,3,7-octatriene. The reaction in dimethylformamide as a solvent proceeded more smoothly to give IIm and IIIm in 40 and 16% yields, respectively.

Easy fission of the allylic carbon-oxygen bond is shown by the reversibility of the above reaction. It is interesting to note that the reverse reaction using a 74:26 mixture of IIm and IIIm resulted in a predominant formation of 1-phenoxy-2,7-octadiene (ratio of the linear to the branched 97:3).

$$\text{PhOCH}_2\text{CH=CH(CH}_2\text{)}_3\text{CH=CH}_2$$

$$\underset{\text{PhOH}}{\overset{\text{CH}_3\text{COOH}}{\rightleftarrows}} \underset{\text{IIm}}{\text{CH}_3\text{CO}_2\text{CH}_2\text{CH=CHCH}_2\text{CH}_2\text{CH}_2\text{CH=CH}_2}$$

$$+ \underset{\text{IIIm}}{\text{CH}_3\text{CO}_2\text{CH(CH=CH}_2\text{)CH}_2\text{CH}_2\text{CH}_2\text{CH=CH}_2}$$

Benzoic acid reacted similarly with the phenoxyoctadienes in the presence of palladium acetate and triphenylphosphine to afford a 70:30 mixture of octadienyl benzoate (IIn) and (IIIn) in a 60% yield.

Reaction of Allyl and Substituted-allyl Alkoxides. 1-Phenoxy-2,7-octadiene reacts readily with active hydrogen compounds in the presence of palladium catalysts to give 2,7-octadienyl derivatives of the active hydrogen compounds. However, 1-alkoxy-2,7-octadienes such as 1-methoxy-2,7-octadiene and 1-benzyloxy-2,7-octadiene did not react with amines and active methylene compounds under similar conditions. It was found, however, that the alkoxyoctadienes react with phenol to give 1-phenoxy-2,7-octadiene and alcohols, and that the reaction is reversible although the equilibrium exists between the alkoxyoctadienes and phenol. The reaction of the benzyloxyoctadienes(a 97:3 mixture of IIk and IIIk) with phenol by the $\text{PdCl}_2(\text{Ph}_3\text{P})_2$-sodium phenoxide catalyst gave an 86:14 mixture of 1-phenoxy-2,7-octadiene and 3-phenoxy-1,7-octadiene in a 7% yield. The reaction of methoxyoctadienes with phenol afforded phenoxyoctadienes in a 3% yield.

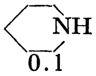
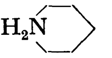
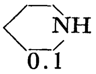
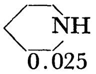
The results suggest that the presence of phenol makes it possible for the reaction of the alkoxyoctadienes with amines and active methylene compounds to give the corresponding octadienyl derivatives of the active hydrogen compounds through the two successive exchanges of the octadienyl group, as shown by the following equation.

$$\text{R}'\text{-O-C}_8\text{H}_{13} + \text{Ph-OH} \rightleftarrows \text{PhO-C}_8\text{H}_{13} + \text{R}'\text{-OH}$$

$$\text{PhO-C}_8\text{H}_{13} + \text{R}''\text{-H} \longrightarrow \text{R}''\text{-C}_8\text{H}_{13} + \text{PhOH}$$

$\text{R}' = \text{CH}_3, \text{C}_6\text{H}_5\text{CH}_2$
$\text{R}''\text{-H}$ = active hydrogen compounds
C_8H_{13} = 2,7-octadienyl group

TABLE 4. REACTION OF ALLYL AND SUBSTITUTED-ALLYL ALKOXIDES WITH ACTIVE HYDROGEN COMPOUNDS

Alkoxy compound mol	Active hydrogen compound mol	Catalyst[c] mmol PdCl$_2$(Ph$_3$P)$_2$-	PhONa	Temp. °C	Time hr	Product	Yield[d] %
PhCH$_2$OC$_8$H$_{13}$[a] 0.05	CH$_3$COCH$_2$CO$_2$CH$_3$ 0.1	0.1	1.0	85	18	CH$_2$=CH(CH$_2$)$_3$CH=CHCH$_2$-CH(COCH$_3$)CO$_2$CH$_3$	46
CH$_3$OC$_8$H$_{13}$[b] 0.05	CH$_3$COCH$_2$CO$_2$CH$_3$ 0.1	0.1	1.0	85	16	CH$_2$=CH(CH$_2$)$_3$CH=CHCH$_2$-CH(COCH$_3$)CO$_2$CH$_3$	74
PhCH$_2$OCH$_2$CH=CH$_2$ 0.025	CH$_3$COCH$_2$CO$_2$CH$_3$ 0.05	0.05	0.5	85	15	CH$_2$=CHCH$_2$CH(COCH$_3$)-CO$_2$CH$_3$	42
						(CH$_2$=CHCH$_2$)$_2$C(COCH$_3$)-CO$_2$CH$_3$	4
PhCH$_2$OC$_8$H$_{13}$ 0.05	 0.1	0.1	1.0	80	40	CH$_2$=CH(CH$_2$)$_3$CH=CHCH$_2$	78
CH$_3$OC$_8$H$_{13}$ 0.05	 0.1	0.1	1.0	85	24	CH$_2$=CH(CH$_2$)$_3$CH=CHCH$_2$	57
CH$_2$=CHCH$_2$OCH$_2$CH=CH(CH$_2$)$_3$-CH=CH$_2$ 0.025	 0.025	0.05	0.5	95	36	CH$_2$=CH(CH$_2$)$_3$CH=CHCH$_2$	12
						CH$_2$=CHCH$_2$	24

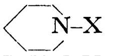
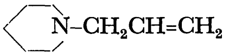
a) A mixture of 1-benzyloxy-2,7-octadiene (97%) and 3-benzyloxy-1,7-octadiene (3%)

b) A mixture of 1-methoxy-2,7-octadiene (99%) and 3-methoxy-1,7-octadiene (1%)

c) The reaction was carried out in the presence of an equivalent amount of phenol to that of the active hydrogen compounds.

d) Based on the alkoxy compounds

TABLE 5. REACTION OF ALLYL AND SUBSTITUTED-ALLYL CARBOXYLATES WITH ACTIVE-HYDROGEN COMPOUNDS

Carboxylate[a]	Active hydrogen Compound[c]	Catalyst mmol PdCl$_2$(Ph$_3$P)$_2$-	PhONa	Temp. °C	Time hr	Product[f]	Yield[g] %
CH$_3$CO$_2$C$_8$H$_{13}$[b]	CH$_3$CH$_2$CO$_2$H	0.05[d]	0.2[e]	85	15	CH$_3$CH$_2$CO$_2$X	37
						CH$_3$CH$_2$CO$_2$Y	13
						1,3,7-OT	trace
CH$_3$CO$_2$C$_8$H$_{13}$	PhCO$_2$H	0.05[d]	0.2[c]	85	15	PhCO$_2$X	27
						PhCO$_2$Y	16
						1,3,7-OT	12
CH$_3$CO$_2$C$_8$H$_{13}$*1	PhOH*2	0.1	1.0	85	24	PhOX	27
						PhOY	1
						1,3,7-OT	24
CH$_3$CO$_2$CH$_2$CH=CH$_2$	PhOH	0.05	0.5	85	17	PhOCH$_2$CH=CH$_2$	14
CH$_3$CO$_2$CH$_2$CH=CH$_2$	PhCH$_2$OH	0.05	0.5	70	20	PhCH$_2$OCH$_2$CH=CH$_2$	10
CH$_3$CO$_2$C$_8$H$_{13}$	PhCH$_2$OH	0.05	0.5	85	24	PhCH$_2$OX	19
CH$_3$CO$_2$C$_8$H$_{13}$	CH$_3$OH	0.05	0.5	70	18	CH$_3$OX	7
CH$_3$CO$_2$CH$_2$CH=CH$_2$	CH$_3$COCH$_2$CO$_2$CH$_3$	0.05	0.5	85	20	CH$_2$=CHCH$_2$CH(COCH$_3$)-CO$_2$CH$_3$	17
CH$_3$CO$_2$C$_8$H$_{13}$	CH$_3$COCH$_2$CO$_2$CH$_3$	0.05	0.5	85	20	X-CH(COCH$_3$)CO$_2$CH$_3$	15
CH$_3$CO$_2$C$_8$H$_{13}$		0.05	0.5	85	1		93
CH$_3$CO$_2$C$_8$H$_{13}$	PhNH$_2$	0.05	0.5	85	1	PhNH-X	89
CH$_3$CO$_2$C$_8$H$_{13}$	cyclo-C$_6$H$_{11}$NH$_2$	0.05	0.5	100	1	cyclo-C$_6$H$_{11}$NH-X	31
CH$_3$CO$_2$CH$_2$CH=CH$_2$		0.05	0.5	85	1		90
CH$_3$CO$_2$CH$_2$CH=CH$_2$	*t*-C$_4$H$_9$NH$_2$	0.05	0.5	85	1	*t*-C$_4$H$_9$NHCH$_2$CH=CH$_2$	46

a) 0.025 mol except *1 (0.05 mol)

b) Octadienyl acetate (CH$_3$CO$_2$C$_8$H$_{13}$) was a mixture of 2,7-octadienyl acetate (74%) and 1-vinyl-5-hexenyl acetate (26%).

c) 0.05 mol except *2 (0.1 mol)

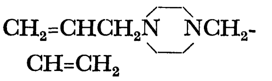
d) Pd (OAc)$_2$

e) Ph$_3$P

f) X=CH$_2$=(CH$_2$)$_3$CH=CHCH$_2$-, Y=CH$_2$=CH(CH$_2$)$_3$CH(CH=CH$_2$)-, 1,3,7-OT=CH$_2$=CHCH=CHCH$_2$CH$_2$CH=CH$_2$

g) Based on the allyl or substituted-allyl carboxylate employed.

TABLE 6. PHYSICAL AND ANALYTICAL DATA OF THE PRODUCTS

Product[a)]	Bp °C/mmHg	n_D^{25}	Empirical formula	Calcd				Found			
				C (%)	H (%)	N (%)	Mol wt	C (%)	H (%)	N (%)	Mol wt
$(C_2H_5)_2NCH_2CH{=}CH_2$	112	1.4186	$C_7H_{15}N$	74.27	13.36	12.37	113	74.05	13.34	12.29	113[c)]
$(C_2H_5)_2NCH_2CH{=}CHCH_3$	135	1.4298	$C_8H_{17}N$	75.52	13.47	11.01	127	75.32	13.47	11.07	127[c)]
$(C_2H_5)_2NCH_2C(CH_3){=}CH_2$	123.5	1.4208	$C_8H_{17}N$	75.52	13.47	11.01	127	75.64	13.57	11.01	127[c)]
$t\text{-}C_4H_9NHCH_2CH{=}CH_2$	107.5	1.4162	$C_7H_{15}N$	74.27	13.36	12.37	113	74.06	13.45	12.50	113[c)]
$t\text{-}C_4H_9N(CH_2CH{=}CH_2)_2$	164	1.4428	$C_{10}H_{19}N$	78.36	12.50	9.14	153	78.27	12.51	9.29	153[c)]
 $CH_2{=}CHCH_2N\quad NCH_2\text{-}CH{=}CH_2$	200	1.4748	$C_{10}H_{18}N_2$	72.24	10.91	16.85	166	71.95	10.84	16.70	166[c)]
cyclo-C_6H_{11}–NH–X	117—118/2	1.4813	$C_{14}H_{25}N$	81.09	12.15	6.76	205	81.06	12.18	6.49	207
$CH_2{=}CHCH_2CH(COCH_3)\text{-}CO_2CH_3$	188	1.4398	$C_8H_{12}O_3$	61.52	7.75		156	61.31	8.02		156[c)]
$(CH_2{=}CHCH_2)_2C(COCH_3)\text{-}CO_2CH_3$	131/38	1.4576	$C_{11}H_{16}O_3$	67.32	8.27		196	67.66	8.27		196
$p\text{-}CH_3C_6H_4OCH_2CH{=}CH_2$	95/12	1.5163	$C_{10}H_{12}O$	81.04	8.16		148	81.04	7.93		153
$p\text{-}ClC_6H_4OCH_2CH{=}CH_2$	107/12	1.5342	C_9H_9OCl	64.11	5.38	21.03[b)]	167	64.30	5.63	20.75[b)]	172
$PhCH_2O$–X	126—129/3	1.5050	$C_{15}H_{20}O$	83.28	9.32		216	83.26	9.33		212
$PhCH_2O$–Y	102—104/1.8	1.4990	$C_{15}H_{20}O$	83.28	9.32		216	82.91	9.08		216
PhCOO–X	143—144/5	1.5136	$C_{15}H_{18}O_2$	78.23	7.88		230	78.34	7.99		226
PhCOO–Y	79/0.1	1.5081	$C_{15}H_{18}O_2$	78.23	7.88		230	77.83	8.03		222
CH_3CH_2COO–X	80—84/5[d)]	1.4481	$C_{11}H_{18}O_2$	72.49	9.96		182	72.46	9.71		186
CH_3CH_2COO–Y		1.4370	$C_{11}H_{18}O_2$	72.49	9.96		182	72.37	9.71		185
$PhCH_2OCH_2CH{=}CH_2$	87—88/10	1.5079	$C_{10}H_{12}O$	81.04	8.16		148	80.89	8.12		154
 $N\text{-}CH_2CH{=}CH_2$	62/50	1.4608	$C_8H_{15}N$	76.73	12.08	11.19	125	76.41	12.28	11.03	125[c)]

a) $X = CH_2{=}CH(CH_2)_3CH{=}CHCH_2\text{-}$, $Y = CH_2{=}CH(CH_2)_3CH(CH{=}CH)\text{-}$,

b) Cl

c) Determined by mass spectroscopy. The other quantities were measured by vapor pressure osmometry.

d) Mixture of linear and branched compounds.

The reaction of the benzyloxyoctadiene with piperidine in the presence of phenol and a palladium catalyst gave the expected octadienyl piperidine. The reaction is applicable to 1-alkoxy-2-alkenes. The reaction of 1-benzyloxy-2-propene with methyl acetoacetate in the presence of the palladium catalyst and phenol afforded methyl 2-acetyl-4-pentenoate and methyl 2-acetyl-2-(2-propenyl)-4-pentenoate. The results are summarized in Table 4. The reaction was much slower than that of 1-phenoxy-2-propene with methyl acetoacetate.

The reaction of 1-(2-propenyloxy)-2,7-octadiene with piperidine proceeded to give two products, *N*-(2,7-octadienyl)piperidine and *N*-(2-propenyl)piperidine, in 12 and 24% yields, respectively, which shows that the reactivity of the propenyl group is larger than that of the octadienyl group.

Reaction of Allyl and Substituted-allyl Carboxylates. As described, 2,7-octadienyl acetate and benzoate react with phenol in the presence of the palladium catalysts to afford 1-phenoxy-2,7-octadiene. The same type of reaction occurred between 2-propenyl acetate and active hydrogen compounds such as phenol, carboxylic acids, alcohols, amines and active methylene compounds. Results of the reactions of allyl and substituted-allyl carboxylates with the active hydrogen compounds are summarized in Table 5. The reactions proceed usually much more slowly than those of 1-phenoxy-2-propene and its derivatives, but the reaction with amines proceeds at a moderate rate.

Experimental

Reagents. $PdCl_2(Ph_3P)_2$,[12)] $PdCl_2(Ph_3As)_2$,[13)] $Pd(OAc)_2$,[14)] $Pd(Ph_3P)_4$,[12)] $Pd(Ph_3P)_2$(maleic anhydride),[15)] $PtCl_2(Ph_3P)_2$[16)] and $Pt(Ph_3P)_4$[16)] were prepared by previously reported methods.

Methyl acetoacetate, 2-propenyl acetate and all the phenols, alcohols, amines and carboxylic acids were purified by distillation. 1-Phenoxy-2,7-octadiene,[8)] 1-alkoxy-2,7-octadienes[7)] and 2,7-octadienyl carboxylates[17)] were prepared by the reaction of 1,3-butadiene with phenol, alcohols and carboxylic acids, respectively, in the presence of the palladium catalyst. 1-Phenoxy-2-propene,[18)] 1-phenoxy-2-methyl-2-propene[18)] and 1-phenoxy-2-butene[18)] were prepared by the reactions of phenol with allyl chloride, methallyl chloride and crotyl chloride, respectively, in the presence of potassium carbonate. 1-Benzyloxy-2-propene was prepared by the reaction of benzyl alcohol with 1-phenoxy-2-propene in the presence of $PdCl_2(Ph_3P)_2$ and sodium phenoxide. All the reactions were carried out under argon atmosphere.

Reaction of 1-Phenoxy-2-propene with Methyl Acetoacetate. A

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mixture of 0.05 mol of methyl acetoacetate, 0.1 mol of 1-phenoxy-2-propene, 0.05 mmol of $PdCl_2(Ph_3P)_2$ and 0.5 mmol of sodium phenoxide was stirred at 85° for 8.5 hr under argon atmosphere. The reaction mixture was subjected to distillation and the ratio of the products was determined by vpc. The product consisted of IIc(2.8 g, 18%) and IId(4.6 g, 47%). The yields were calculated on the basis of 1-phenoxy-2-propene. IIc, IR(neat)cm^{-1}: 1745 and 1722(keto ester), 1646, 995 and 922(–$CH{=}CH_2$). NMR(CCl_4) τ: 7.86(s, CH_3CO–), 7.47(t, $J=7.0$ Hz, =C–CH–C), 6.50(t, $J=7.0$ Hz, C–CH–CO), 6.34(s, CH_3O–) and 4.06—5.05(m, olefinic protons). IId, IR(neat)cm^{-1}: 1744 and 1714(keto ester), 1644, 993 and 921($CH_2{=}CH$–). NMR(CCl_4)τ: 7.97(s, CH_3CO–), 7.46 (d, $J=7.0$ Hz, =C–CH_2–C), 6.34(s, CH_3O) and 4.22—5.03 (m, olefinic protons).

Reaction of 1-Phenoxy-2,7-octadiene with Cyclohexylamine. A mixture of 0.05 mol of 1-phenoxy-2,7-octadiene, 0.1 mol of cyclohexylamine, 0.1 mmol of $PdCl_2(Ph_3P)_2$ and 1.0 mmol of sodium phenoxide was stirred at 85° for 2 hr to give IIe (10.4 g, 69%). IR(neat)cm^{-1}: 1644, 991 and 911($CH_2{=}CH$–), 968(*trans*-CH=CH–). NMR(CCl_4) τ: 9.24(s, –NH), 7.5—8.9(m, –$(CH_2)_3$– and cyclo-C_6H_{11}), 6.84(d, $J=4.0$ Hz, N–CH_2–C=) and 4.01—5.12(m, olefinic protons).

Reaction of 1-Phenoxy-2-methyl-2-propene with Diethylamine. A mixture of 0.05 mol of 1-phenoxy-2-methyl-2-propene, 0.1 mol of diethylamine, 0.1 mmol of $PdCl_2(Ph_3P)_2$ and 0.5 mmol of sodium phenoxide was stirred at 85° in a 100 m*l* autoclave for 1 hr to give *N*-(2-methyl-2-propenyl)diethylamine (5.6 g, 89%). IR(neat)cm^{-1}: 1654 and 893($CH_2{=}C<$), NMR(CCl_4) τ: 9.03(t, $J=7.0$ Hz, CH_3–C–N–), 8.30 (s, CH_3–C=), 7.53(q, $J=7.0$ Hz, C–CH_2–N–), 7.14(s, –N–CH_2–C=) and 5.18—5.25($C{=}CH_2$).

Reaction of 1-Phenoxy-2-propene with p-*Cresol.* A mixture of 0.025 mol of 1-phenoxy-2-propene, 0.025 mol of *p*-cresol, 0.05 mmol of $PdCl_2(Ph_3P)_2$ and 0.5 mmol of sodium phenoxide was stirred at 85°C for 3 hr to afford IIi(1.5 g, 41%). Unreacted 1-phenyl-2-propene(1.3 g, 40%) was recovered.

Reaction of Phenoxyoctadiene with Benzyl Alcohol. A mixture of 0.025 mol of the phenoxyoctadiene(92% 1-phenoxy-2,7-octadiene and 8% 3-phenoxy-1,7-octadiene), 0.05 mol of benzyl alcohol and 0.05 mmol of $Pd(Ph_3P)_4$ was stirred at 85°C for 2.5 hr to give 1,3,7-octatriene(1.1 g, 41%), IIk(1.3 g, 24%) and IIIk(0.6 g, 11%). IIk IR(neat)cm^{-1}: 1666 and 1640 (C=C), 991 and 908(–$CH{=}CH_2$) and 970(*trans* –CH=CH–). NMR(CCl_4) τ: 7.8—8.7(6H, m, =C–$CH_2CH_2CH_2$–C=), 6.13 (2H, d, $J=5.5$ Hz, –O–CH_2–C=), 5.58(2H, s, Ph–CH_2–O–), 4.0—5.2(5H, m, olefinic protons) and 2.67(5H, s, C_6H_5–). IIIk IR(neat)cm^{-1}: 1644, 991, 922, and 915($CH_2{=}CH$–). NMR(CCl_4) τ: 7.8—8.7(6H, m, –$CH_2CH_2CH_2$–C=), 6.3(1H, m, –O–CH), 5.67 and 5.33(2H, two d, $J=12.0$ Hz, C_6H_5–CH_2–O–), 3.9—5.4(6H, m, olefinic protons) and 2.67(5H, s, C_6H_5–).

Reaction of Phenoxyoctadiene with Benzoic Acid. A mixture of 0.05 mol of the phenoxyoctadienes(92% 1-phenoxy-2,7-octadiene and 8% 3-phenoxy-1,7-octadiene), 0.1 mol of benzoic acid, 0.1 mmol of $Pd(OAc)_2$, 0.25 mmol of triphenylphosphine and 10 m*l* of dimethylformamide was stirred at 85°C for 24 hr. The product consisted of IIn(4.9 g, 42%), IIIn(2.1 g, 18%) and a trace amount of 1,3,7-octatriene. The unreacted phenoxyoctadienes(3.8 g) were recovered. IIn, IR(neat)cm^{-1}: 1720(ester), 1672 and 966(*trans* –CH=CH–), 1643, 988, and 907($CH_2{=}CH$–). NMR(CCl_4) τ: 8.25—8.75 (2H, m, –CH_2–C–C=), 7.70—8.15(4H, m, =C–CH_2–C–CH_2–C=), 5.28(2H, d, $J=6.5$ Hz, –O–CH_2–) and 3.9—5.25(5H, m, olefinic protons). IIIn, IR(neat)cm^{-1}: 1720(ester), 1644, 990, 922(sh), and 916($CH_2{=}CH$–). NMR(CCl_4) τ: 7.7—8.8 (6H, m, –$CH_2CH_2CH_2$–) and 3.85—5.25(7H, m, –O–CH– and olefinic protons).

Reaction of 1-Methoxy-2,7-octadiene with Methyl Acetoacetate. A mixture of 0.05 mol of 1-methoxy-2,7-octadiene, 0.1 mol of methyl acetoacetate, 0.1 mmol of $PdCl_2(Ph_3P)_2$, 1.0 mmol of sodium phenoxide and 0.05 mol of phenol was stirred at 85°C for 16 hr to give IIa in a 74% yield. IR(neat)cm^{-1}: 1748 and 1724($>C{=}O$), 1644(C=C), 992 and 911(–$CH{=}CH_2$) and 971(*trans* –CH=CH–). NMR(CCl_4) τ: 8.61(2H, m, –C–CH_2–C–), 8.04(4H, m, =C–CH_2–C–CH_2–C=), 7.88(3H, s, –CO–CH_3), 7.55(2H, t, $J=7.0$ Hz, =C–CH_2–C–CO=), 6.51 (1H, t, $J=7.0$ Hz, –C–CH–CO–), 6.34(3H, s, –O–CH_3) and 3.98—5.16(5H, m, olefinic protons).

Reaction of 1-(2-Propenyloxy)-2,7-octadiene with Piperidine. A mixture of 0.025 mol of 1-(2-propenyloxy)-2,7-octadiene, 0.05 mol of piperidine, 0.1 mol of $PdCl_2(Ph_3P)_2$, 1.0 mmol of sodium phenoxide and 0.025 mol of phenol was stirred at 85°C for 20 hr and at 110°C for 16 hr. The product consisted of *N*-(2,7-octadienyl)piperidine(0.6 g, 12%) and *N*-(allyl)piperidine(0.75 g, 24%). *N*-(Allyl)piperidine showed the following spectral characteristics. IR(neat)cm^{-1}: 1643, 993, and 915($CH_2{=}CH$–). NMR(CCl_4) τ: 8.52 and 7.70(protons of piperidine ring), 7.13(2H, d, $J=7.0$ Hz, N–CH_2–) and 3.8—5.1(3H, m, olefinic protons).

Reaction of Octadienyl Acetate with Propionic Acid. A mixture of 0.025 mmol of octadienyl acetate(74% 2,7-octadienyl acetate and 26% 1-vinyl-5-hexenyl acetate), 0.05 mol of propionic acid, 0.05 mmol of $Pd(OAc)_2$, 0.2 mmol of triphenylphosphine and 5 m*l* of dimethylformamide was stirred at 85°C for 15 hr. The product consisted of 1,7-octadienyl propionate(1.7 g, 37%), 1-vinyl-5-hexenyl propionate(0.6 g, 13%) and a trace amount of 1,3,7-octatriene.

Reaction of Octadienyl Acetate with Aniline. A mixture of 0.025 mol of the octadienyl acetate(74% 2,7-octadienyl acetate and 26% 1-vinyl-5-hexenyl acetate), 0.05 mol of aniline, 0.05 mmol of $PdCl_2(Ph_3P)_2$ and 0.5 mmol of sodium phenoxide was stirred at 85°C for 1 hr. To the reaction mixture 10 m*l* of water was added, and the organic layer was extracted with ether to give *N*-(2,7-octadienyl)aniline (4.5 g, 89%).