BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1012—1013 (1973)

Palladium-catalyzed Exchange of Allylic Groups of Ethers and Esters with Carboxylic Anhydrides

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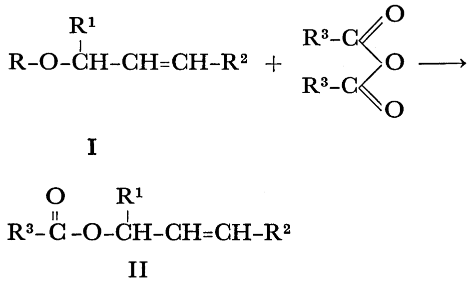
(Received October 12, 1972)

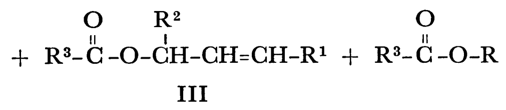
Previously we have reported[1,2] the palladium-catalyzed exchange reaction of allylic groups of ethers and esters with active-hydrogen compounds. In the course of the studies, it has been found that the reaction of the allylic compounds (I) with carboxylic anhydrides in the presense of palladium catalysts also gives the exchanged products (II and III) of allylic groups.



I

II

$$R\text{-}O\text{-}\overset{R^1}{\overset{|}{C}}H\text{-}CH{=}CH\text{-}R^2 + (R^3CO)_2O \longrightarrow R^3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{R^1}{\overset{|}{C}}H\text{-}CH{=}CH\text{-}R^2$$



III

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

$R = C_6H_5$, CH_3CO, CH_3CH_2CO
$R^1 = H$, $CH_2CH_2CH_2CH{=}CH_2$
$R^2 = H$, $CH_2CH_2CH_2CH{=}CH_2$
$R^3 = CH_3$, C_6H_5

An active and easily available catalyst is prepared by mixing palladium acetate and triphenylphosphine. Tetrakis(triphenylphosphine)palladium(0) is also an effective catalyst. However, the catalytic activity of the combination of dichlorobis(triphenylphosphine)-palladium (II) and sodium phenoxide is much smaller than that of the above two catalysts. Some platinum catalysts also showed the catalytic activity, but it was smaller than that of palladium catalysts.

The results on the reaction of allylic ethers and

TABLE 1. REACTIONS OF ALLYLIC ETHERS AND ESTERS WITH CARBOXYLIC ANHYDLIDES[a)]

Anhydride (mol)	Allylic compound (mol)	Catalyst (mmol)	Time (hr)	Products[e)] and yields[f)] (%)
$(CH_3CO)_2O$	$C_6H_5OC_8H_{13}$[b)]	$Pd(OCOCH_3)_2$-Ph_3P	40	CH_3CO_2X, CH_3CO_2Y 57 24
$(CH_3CO)_2O$	$C_6H_5OC_8H_{13}$[b)]	$PdCl_2(Ph_3P)_2$-PhONa	40	CH_3CO_2X, CH_3CO_2Y 18 8
$(CH_3CO)_2O$	$C_6H_5OC_8H_{13}$[b)]	$Pd(Ph_3P)_4$	40	CH_3CO_2X, CH_3CO_2Y 36 15
$(CH_3CO)_2O$	$C_6H_5OC_8H_{13}$[b)]	$PtCl_2(Ph_3P)_2$-PhONa	40	CH_3CO_2X, CH_3CO_2Y 10 2
$(CH_3CO)_2O$	$C_6H_5OC_8H_{13}$[b)]	$Pt(Ph_3P)_4$	40	CH_3CO_2X, CH_3CO_2Y 33 14
$(C_6H_5CO)_2O$	$C_6H_5OC_8H_{13}$[b)]	$Pd(OCOCH_3)_2$-Ph_3P	40	$C_6H_5CO_2X$, $C_6H_5CO_2Y$ 42 14
$(C_6H_5CO)_2O$	$C_6H_5OCH_2CH{=}CH_2$*	$Pd(OCOCH_3)_2$-Ph_3P	40	$C_6H_5CO_2CH_2CH{=}CH_2$ 17
$(CH_3CO)_2O$	$C_2H_5CO_2C_8H_{13}$[c)]	$Pd(OCOCH_3)_2$-Ph_3P	16	CH_3CO_2X, CH_3CO_2Y 55 22
$(C_6H_5CO)_2O$	$CH_3CO_2C_8H_{13}$[d)]	$Pd(OCOCH_3)_2$-Ph_3P	16	$C_6H_5CO_2X$, $C_6H_5CO_2Y$ 50 25
$(C_6H_5CO)_2O$	$CH_3CO_2CH_2CH{=}CH_2$	$Pd(OCOCH_3)_2$-Ph_3P	16	$C_6H_5CO_2CH_2CH{=}CH_2$ 33

a) Reaction conditions: anhydride 0.05 mol, allylic compound 0.025 mol (* 0.05 mol), palladium and platinum complex 0.05 mmol, Ph_3P 0.2 mmol, PhONa 0.5 mmol, reaction temperature 85°C, dimethylformamide 5 ml.
b) 1-Phenoxy-2,7-octadiene containing 1.3% of 3-phenoxy-1,7-octadiene.
c) A mixture of $C_2H_5CO_2X$(69%) and $C_2H_5CO_2Y$(31%).
d) A mixture of CH_3CO_2X(76%) and CH_3CO_2Y(24%).
e) $X = \text{-}CH_2CH{=}CHCH_2CH_2CH_2CH{=}CH_2$, $Y = \text{-}CH(CH{=}CH_2)CH_2CH_2CH_2CH{=}CH_2$.
f) Based on the allylic compound employed.

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[1] G. Hata, K. Takahashi, and A. Miyake, *Chem. Commun.*, **1970**, 1392.

[2] K. Takahashi, A. Miyake, and G. Hata, This Bulletin, **45**, 230 (1972).

esters with carboxylic anhydrides are shown in Table 1.

Experimental

Reagents. $Pd(OAc)_2$[3], $PdCl_2(Ph_3P)_2$,[4] $Pd(Ph_3P)_4$,[4] $PtCl_2(Ph_3P)_2$[5] $Pt(Ph_3P)_4$,[5] 1-phenoxy-2,7-octadiene,[6] 1-phenoxy-2-propene,[7] octadienyl carboxylate[8] were prepared by previously reported methods. Carboxylic anhydrides and allyl acetate were purified by distillation. Dimethylformamide was dried on calcium hydride and purified by distillation.

Reaction Procedure. All the reactions were carried out under an argon atmosphere. In a 50 ml two necked flask, catalysts, reagents, and dimethylformamide were charged and the reaction mixture was stirred at 85°C. The reaction products were characterized by elemental analysis, molecular weight measurement, and IR and NMR spectral measurement or by comparison with authentic samples. The gas chromatography was used for the quantitative analysis of products.

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6) E. J. Smutny, *J. Amer. Chem. Soc.*, **89**, 6793 (1968).

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