Palladium-catalysed Reactions of Ketenes with Allyl Acetates or Allyl Carbonates: Novel Syntheses of 1,3-Dienes and Allylated Esters

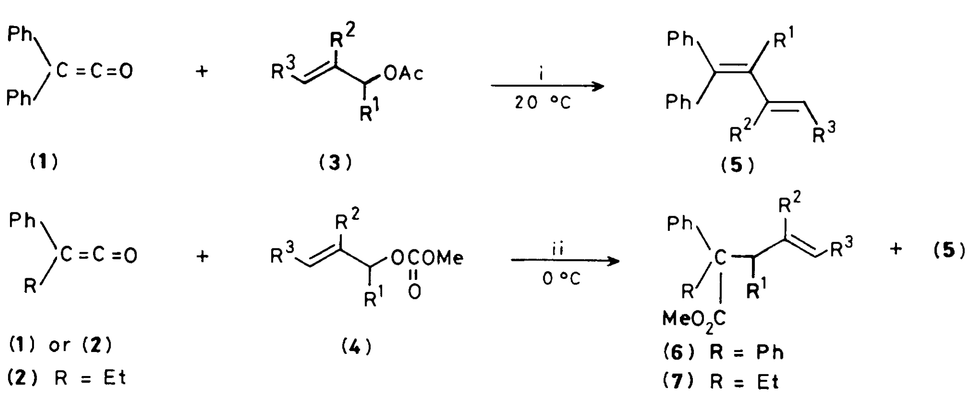
Take-aki Mitsudo, Mamoru Kadokura, and Yoshihisa Watanabe*

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

The reaction of arylketenes with allyl acetates or allyl carbonates catalysed by tetrakis(triphenylphosphine)palladium selectively gives 1,3-dienes or allylated esters, respectively, in high yields.

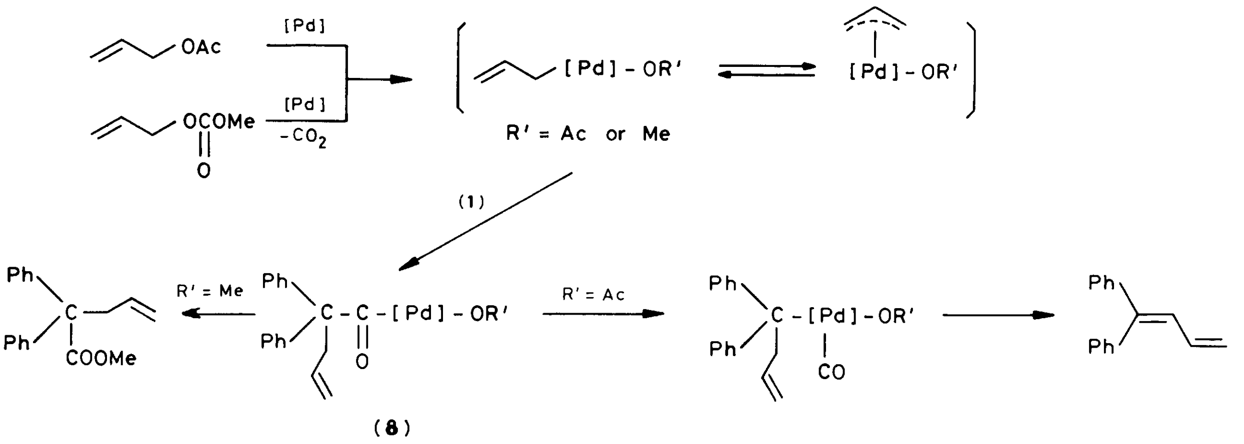
Ketenes are proposed to be one of the key intermediates in the activation of carbon monoxide;[1] however, only a few examples of catalytic reactions have been investigated.[2] Recently we have reported palladium complex catalysed reactions of arylketenes with terminal acetylenes or aroyl chlorides giving disubstituted acetylenes[3] or α,β-unsaturated ketones,[4] respectively. In the course of our study, we found two types of novel palladium catalysed reactions of arylketenes with allyl compounds, preliminary results of which are described below.

The reaction of arylketene, (**1**) or (**2**), with allyl acetates, (**3**), or allyl carbonates, (**4**), in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) selec-



a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^3 = H, R^2 = Me$
c; $R^1 = R^2 = H, R^3 = Me$
d; $R^1 = Me, R^2 = R^3 = H$
e; $R^1 = R^2 = H, R^3 = n\text{-}C_3H_7$
f; $R^1 = R^2 = H, R^3 = Ph$

Scheme 1. *Reagents:* i, $Pd(PPh_3)_4$, in benzene, 1—20 h; ii, $Pd(PPh_3)_4$, in DMF, 0.5 h, $-CO_2$.



Scheme 2

tively gives 1,3-dienes (**5**) or α-allylated esters, (**6**) or (**7**), respectively, in high yields (Scheme 1).†

Representative results are summarized in Tables 1 and 2. In the reaction of (**1**) with (**3**), derivatives of (*E*)-1,1-diphenylbuta-1,3-diene were selectively obtained.‡ This reaction is a rare example of a catalytic preparation of a 1,3-diene from allyl and C_1 moieties.§ Use of ethylphenylketene (**2**) resulted in the formation of several uncharacterised products. Although the reaction proceeds in tetrahydrofuran (THF), benzene is more favourable than THF. Crotyl acetate (**3c**) and 1-methylallyl acetate (**3d**) gave the same product (**5c**) showing that the reaction proceeds *via* a π-allyl palladium intermediate (entries 3 and 4). On the other hand, the reaction of (**1**) or (**2**) with (**4**) in dimethylformamide (DMF) selectively gave esters (**6**) or (**7**) by decarboxylative alkoxyallylation reaction together with a small amount of the corresponding dienes (**5**). Also in the ester formation reaction, the allyl rearrangement was observed (entries 9 and 10). The selectivity for the ester

Table 1. Palladium catalysed reactions of diphenylketene with allyl acetates.[a]

Entry	Allyl acetate	Reaction time (h)	Product	Yield(%)[b]
1	(**3a**)	1	(**5a**)	72(59)[c]
2	(**3b**)	1	(**5b**)	84(45)[c]
3	(**3c**)	20	(**5c**)	65
4	(**3d**)	6	(**5c**)	55
5	(**3e**)	4	(**5e**)	68
6	(**3f**)	5	(**5f**)	86

[a] Ketene (3 mmol), allyl acetate (3 mmol), $Pd(PPh_3)_4$ (0.15 mmol), benzene, 20 °C. [b] Determined by g.l.c. using an internal standard. [c] In THF.

---

† Satisfactory spectroscopic and analytical data for the products were obtained.

‡ As a by-product, a small amount of tetraphenylethylene which was derived *via* a decarbonylation of diphenylketene was detected.

§ *E.g.* catalytic preparation of 1,3-dienes from allyl alcohol, aldehyde and triphenylphosphine has been reported; M. Moreno-Manas and A. Trius, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2154.

Table 2. Palladium catalysed reactions of ketenes with allyl carbonates.[a]

Entry	Ketene	Allyl carbonate	Product Ester	Product Diene	Ester: Diene	Ester yield(%)[b]
7	(**1**)	(**4a**)	(**6a**)	(**5a**)	99:1(68:32)[c]	67
8	(**1**)	(**4b**)	(**6b**)	(**5b**)	99:1	80
9	(**1**)	(**4c**)	(**6c**)	(**5c**)	96:4	77
10	(**1**)	(**4d**)	(**6c**)	(**5c**)	99:1	65
11	(**1**)	(**4e**)	(**6e**)	(**5e**)	98:2	85
12	(**1**)	(**4f**)	(**6f**)	(**5f**)	95:5(39:61)[c]	87
13	(**2**)	(**4a**)	(**7a**)			28[d]
14	(**2**)	(**4f**)	(**7f**)			38[d]

[a] Ketene (3 mmol), allyl carbonate (3 mmol), $Pd(PPh_3)_4$ (0.15 mmol), DMF, 0 °C, 0.5 h. [b] Determined by g.l.c. using an internal standard. [c] In THF. [d] Isolated yield.

was significantly influenced by solvents. Namely when THF was used in the reaction of (**1**) with cinnamyl carbonate (**4f**), diene (**5f**) was the major product (entry 12).

The present two reactions may proceed *via* an acyl-Pd intermediate (**8**) which can be formed by the insertion reaction of ketene into a σ-allyl-Pd species (Scheme 2). When R′ is Ac, decarbonylation of (**8**) followed by β-hydrogen elimination would afford the diene.¶ In contrast when R′ in (**8**) is a methyl group, the reductive elimination of (**8**) or rapid nucleophilic attack of the methoxide ion on the acyl group prior to the decarbonylation reaction would give the allylated ester.

In conclusion the first palladium catalysed allylation reaction of arylketenes provides useful methods of preparing dienes and α-allylated esters.

Received, 16th June 1986; Com. 821

¶ Although i.r. spectra of the reaction mixture show carbonyl stretching absorptions at 1757 and 1826 cm^{-1} which can be assigned to carboxylic acid anhydride, the fate of the carbon monoxide and the acetate ion is ambiguous at the present time.

References

1 *E.g.* T. W. Bodnar, E. J. Crowford, and A. R. Cutler, *Organometallics,* 1986, **5**, 947.

2 *E.g.* A. Baba, Y. Ohshiro, and T. Agawa, *J. Organometal. Chem.*, 1976, **110**, 121; P. Hong, H. Yamazaki, and K. Sonogashira, *Chem. Lett.*, 1978, 535.

3 T. Mitsudo, M. Kadokura, and Y. Watanabe, *Tetrahedron Lett.*, 1985, **26**, 3697.

4 T. Mitsudo, M. Kadokura, and Y. Watanabe, *Tetrahedron Lett.*, 1985, **26**, 5143; M. Kadokura, T. Mitsudo, and Y. Watanabe, *J. Chem. Soc., Chem. Commun.*, 1986, 252.