Palladium-catalysed Decarbonylative Cross Condensation of Acyl Halides

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

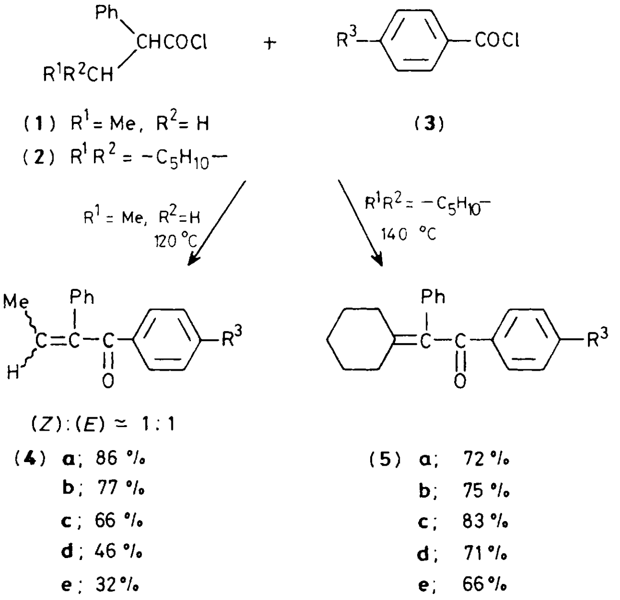
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

The reaction of alkylphenylacetyl chlorides with aroyl chlorides catalysed by tetrakis(triphenylphosphine)palladium gives α,β-unsaturated ketones selectively *via* a decarbonylative cross condensation reaction.

Recent years have seen extensive progress in selective organic syntheses catalysed by palladium complexes.[1] Recently we have reported novel palladium-catalysed reactions of arylketenes with terminal acetylenes or aroyl chlorides giving disubstituted acetylenes[2] or α,β-unsaturated ketones,[3] respectively. In the course of these studies, we have found an unusual decarbonylative cross condensation reaction of acyl halides catalysed by tetrakis(triphenylphosphine)palladium.

The reaction of alkylphenylacetyl chlorides (**1**) and (**2**) with aroyl chlorides (**3a**—**e**) in the presence of a catalytic amount of $Pd(PPh_3)_4$ proceeds selectively affording α,β-unsaturated ketones (**4**) and (**5**) in moderate to high yields (Scheme 1). A typical procedure is as follows. A mixture of (**1**) (1 mmol), (**3**) (1 mmol), triethylamine (3 mmol), and $Pd(PPh_3)_4$ (0.03 mmol) in 3 ml dry tetrahydrofuran (THF) was placed in a stainless steel autoclave under an argon atmosphere and stirred at 120 °C for 5 h.† The product was isolated by column chromatography or distillation *in vacuo*.

This reaction is a cross condensation reaction between two kinds of acyl halides accompanied by decarbonylation and elimination of two moles of hydrogen chloride. The selectivity for the cross condensation was very high and ketones derived by homo condensation were not detected at all. Only slight amounts of by-products resulting from decarbonylation of the starting materials, such as (*E*)- and (*Z*)-3,4-diphenyl-3-

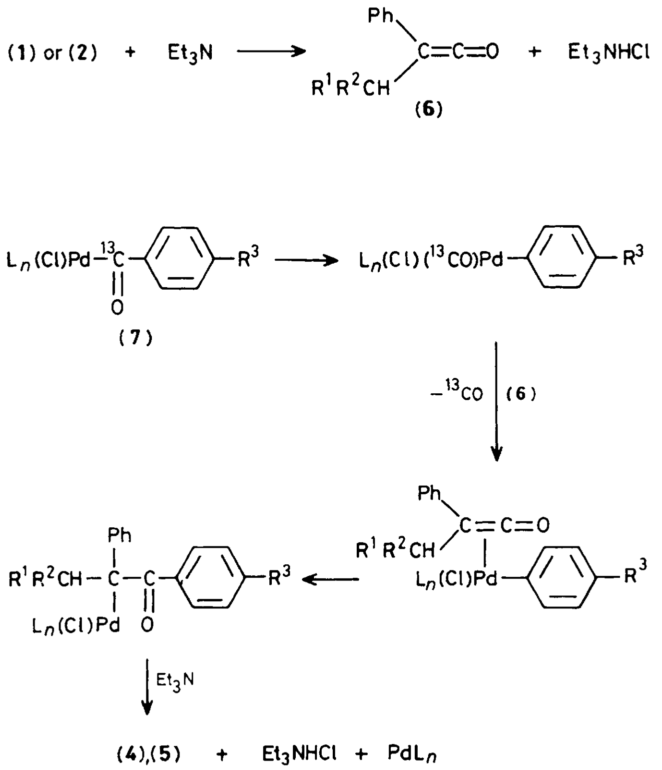


a; $R^3 = OMe$
b; $R^3 = Me$
c; $R^3 = Ph$
d; $R^3 = H$
e; $R^3 = Cl$

Scheme 1. *Reagents:* $Pd(PPh_3)_4$, Et_3N, THF, 5 h, $-CO$, $-Et_3NHCl$.

---

† This reaction also can be carried out in 1,4-dioxane under reflux. In this case, a longer reaction time than 12 h is required to complete the reaction.



PdL$_n$ = Pd(PPh$_3$)$_4$

Scheme 2

hexene, were detected. The (*Z*) : (*E*) ratios of (**4a**—**e**) were almost 1 : 1 (determined by 300 MHz ^{1}H n.m.r. spectroscopy). The reaction using cinnamoyl chloride and aliphatic acyl halides, such as pivaloyl chloride and acetyl chloride, instead of (**3**) was unsuccessful under the same conditions. Although the present reaction was also catalysed by Pd(OAc)$_2$–PPh$_3$, the yields of products were slightly lower with this catalyst.

The reaction using ^{13}C-enriched benzoyl chloride (**3d**) with (**1**) or (**2**) revealed that the carbonyl group in the product must arise from (**1**) or (**2**), because no isotope enrichment was observed in the products by ^{13}C n.m.r. spectroscopy. This shows therefore that (**3**) is catalytically decarbonylated by the palladium complex and based on these results, we postulate the mechanism shown in Scheme 2. Initially, dehydrochlorination of (**1**) or (**2**) by triethylamine affords the corresponding alkylphenylketene (**6**).[3,4] The oxidative addition of (**3**) to Pd(PPh$_3$)$_4$ gives an acyl–Pd complex (**7**) and decarbonylation of (**7**) occurs *via* a phenyl–Pd species[5] followed by insertion of ketene (**6**) and then β-elimination to afford the product. When the present reaction is performed with iodo- or bromobenzene, the yields are very low (less than 23%).‡ Thus, the use of aroyl chloride instead of aryl halide as a precursor of phenyl–Pd species gives higher yields as well as selectivities for the cross condensation products.

In conclusion, a versatile new palladium-catalysed cross condensation reaction of acyl halides leading to α,β-unsaturated ketones, which are difficult to obtain by other methods, is now available.

Received, 14th October 1985; Com. 1464

References

1 For example; J. Tsuji, 'Organic Synthesis with Palladium Compounds,' Springer-Verlag, New York, 1980; R. F. Heck, 'Palladium Reagents in Organic Syntheses,' Academic Press, New York, 1985.
2 T. Mitsudo, M. Kadokura, and Y. Watanabe, *Tetrahedron Lett.*, 1985, **26**, 3697.
3 T. Mitsudo, M. Kadokura, and Y. Watanabe, *Tetrahedron Lett.*, 1985, **26**, 5143.
4 W. T. Brady, in 'The Chemistry of Ketenes, Allenes, and Related Compounds,' ed. S. Patai, Wiley, New York, 1980, p. 279.
5 J. Tsuji and K. Ohno, *J. Am. Chem. Soc.*, 1968, **90**, 94.

---

‡ A considerable amount of biphenyl was formed.