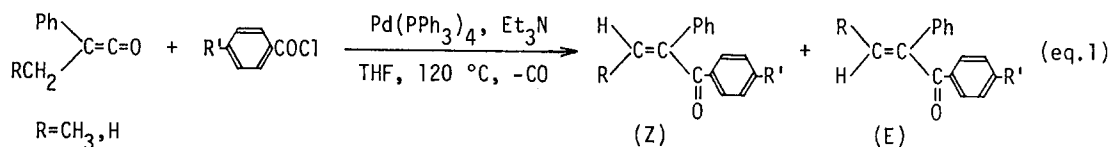


PALLADIUM COMPLEX CATALYZED SYNTHESIS OF α,β -UNSATURATED KETONES
FROM ALKYLPHENYLKETENE AND AROYL CHLORIDE

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Summary: α,β -Unsaturated ketones were obtained from alkylphenylketene and aroyl chloride via decarbonylation reaction in the presence of catalytic amounts of tetrakis(triphenylphosphine) palladium.

Although a number of synthetic reactions using ketenes have been reported,¹⁾ little is known about catalytic reactions by transition metal complexes.²⁾ Recently we reported a palladium complex catalyzed reaction of diphenylketene with terminal acetylenes giving disubstituted acetylenes derived by catalytic decarbonylation of diphenylketene.³⁾ In a course of further study on the utilization of catalytic decarbonylation reaction of ketenes for organic synthesis, we found a novel synthetic method of α,β -unsaturated ketones from alkylphenylketenes and aroyl chloride (eq. 1).



The reaction of ethylphenylketene with 4-methoxybenzoyl chloride is typical. A mixture of ethylphenylketene (1 mmol), 4-methoxybenzoyl chloride (1 mmol), triethylamine (2 mmol), and Pd(PPh₃)₄ (0.03 mmol) in 2.5 ml THF was placed in a 50 ml stainless steel autoclave under an argon atmosphere and stirred at 120 °C for 5 h. The product was isolated by a column chromatography (silica gel) and identified as a mixture of (Z) and (E)-1-(4-methoxyphenyl)-2-phenyl-2-butene-1-one by means of ¹H NMR, ¹³C NMR, FT-IR, and MS.

As shown in Table, α,β -unsaturated ketones were obtained in moderate to high yields. The (Z)/(E) ratios of products were determined by 300MHz ¹H NMR. Substituents at para position of benzoyl chloride affected yields of products, namely, electron releasing ones such as methoxy and methyl groups gave good results. Use of aliphatic acid chloride was unsuccessful.

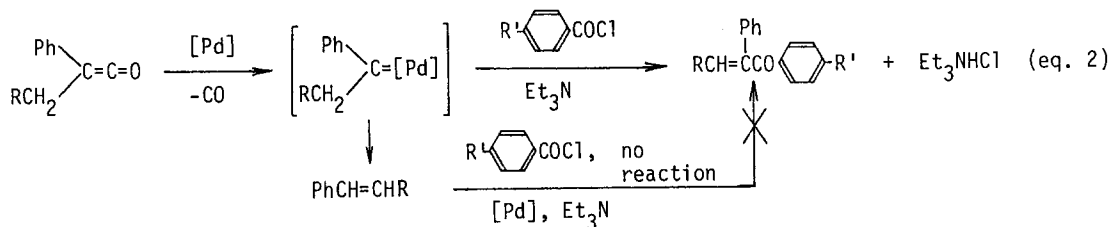
Table. Palladium Catalyzed Reaction of Alkylphenylketene with Aryl Chloride.^{a)}

run	ketene	aryl chloride	product	(Z):(E)	yield(%) ^{b)}
1	$\text{CH}_3\text{CH}_2\overset{\text{Ph}}{\underset{ }{\text{C}}}=\text{C}=\text{O}$	p-MeOC ₆ H ₄ COCl	$\text{CH}_3\text{CH}=\overset{\text{Ph}}{\underset{ }{\text{C}}}\text{COC}_6\text{H}_4\text{OMe}$	39:61	86(74)
2	$\text{CH}_3\text{CH}_2\overset{\text{Ph}}{\underset{ }{\text{C}}}=\text{C}=\text{O}$	p-MeC ₆ H ₄ COCl	$\text{CH}_3\text{CH}=\overset{\text{Ph}}{\underset{ }{\text{C}}}\text{COC}_6\text{H}_4\text{Me}$	36:64	77(60)
3	$\text{CH}_3\text{CH}_2\overset{\text{Ph}}{\underset{ }{\text{C}}}=\text{C}=\text{O}$	p-C ₆ H ₅ C ₆ H ₄ COCl	$\text{CH}_3\text{CH}=\overset{\text{Ph}}{\underset{ }{\text{C}}}\text{COC}_6\text{H}_4\text{C}_6\text{H}_5$	49:51	66(32)
4	$\text{CH}_3\text{CH}_2\overset{\text{Ph}}{\underset{ }{\text{C}}}=\text{C}=\text{O}$	C ₆ H ₅ COCl	$\text{CH}_3\text{CH}=\overset{\text{Ph}}{\underset{ }{\text{C}}}\text{COC}_6\text{H}_5$	59:41	46
5	$\text{CH}_3\text{CH}_2\overset{\text{Ph}}{\underset{ }{\text{C}}}=\text{C}=\text{O}$	p-ClC ₆ H ₄ COCl	$\text{CH}_3\text{CH}=\overset{\text{Ph}}{\underset{ }{\text{C}}}\text{COC}_6\text{H}_4\text{Cl}$	49:51	32(30)
6	$\text{CH}_3\overset{\text{Ph}}{\underset{ }{\text{C}}}=\text{C}=\text{O}$	p-MeOC ₆ H ₄ COCl	$\text{CH}_2=\overset{\text{Ph}}{\underset{ }{\text{C}}}\text{COC}_6\text{H}_4\text{OMe}$	—	43

a) Alkylphenylketene (1 mmol), aryl chloride (1 mmol), triethylamine (2 mmol), Pd(PPh₃)₄ (0.03 mmol), THF 2.5 ml, 120 °C, 5 h.

b) Determined by glc using an internal standard. Isolated yields are given in parentheses.

In all cases, in which ethylphenylketene was used (runs 1-5), a small amount of 1-phenyl-1-propene was obtained. When 1-phenyl-1-propene was allowed to react with aryl chloride under same conditions, α,β -unsaturated ketone was not produced. This fact shows that 1-phenyl-1-propene is not a reaction intermediate. At present, the mechanism of the reaction is not clear. One of the plausible mechanisms would be that ketene was catalytically decarbonylated to give a palladium carbene intermediate³⁾ and that the carbonyl group in a product was derived from aryl chloride (eq. 2).



Application and modification of the present reaction, and studies on the reaction mechanism are now in progress.

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