Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE PREPARATION OF KETENE DERIVATIVES FROM α,β-UNSATURATED ACID CHLORIDES AND "ARYLPALLADIUM CHLORIDES"*

R. F. HECK
Research Center, Hercules Incorporated, Wilmington, Delaware 19899 (U.S.A.)

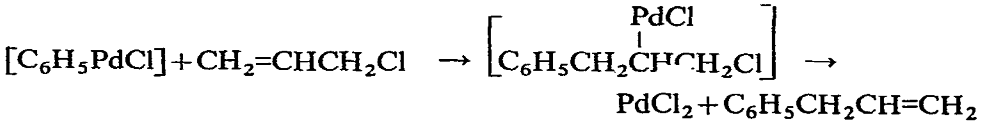
(Received June 8th, 1971)

SUMMARY

Ketene derivatives are obtained in low yields from the reaction of an arylmercuric chloride, an α,β-unsaturated acid chloride, and a catalytic amount of palladium chloride. The products were isolated and identified as esters formed by reacting the ketenes with alcohols.

INTRODUCTION

"Arylpalladium chlorides" generally add very readily to carbon–carbon double bonds, presumably forming "(2-arylethyl)palladium chlorides". The latter compounds then decompose spontaneously, usually by eliminating a β hydrogen with the chloropalladium group[1]. If a β chloro group is present, however, the elimination of palladium dichloride is preferred. This occurs, for example, when allylic chlorides are treated with "arylpalladium chlorides"[2].



$$[C_6H_5PdCl]+CH_2{=}CHCH_2Cl \rightarrow \left[C_6H_5CH_2\overset{\overset{PdCl}{|}}{C}HCH_2Cl\right] \rightarrow PdCl_2+C_6H_5CH_2CH{=}CH_2$$

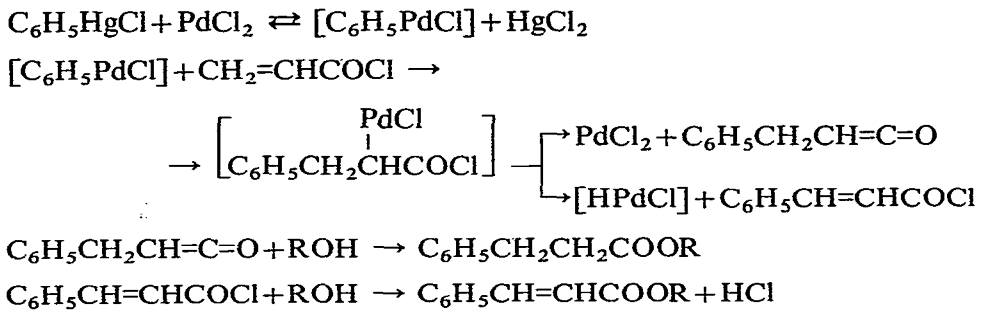
Experiments have now been carried out to determine whether α,β-unsaturated acid chlorides react analogously to allylic chlorides with "arylpalladium chlorides" and form ketene derivatives.

RESULTS AND DISCUSSION

"Phenylpalladium chloride," prepared *in situ*, from phenylmercuric chloride and palladium chloride, did react readily with various α,β-unsaturated acid chlorides. Ketene derivatives were presumably formed but they were not identified as such. Various alcohols were added to the reaction mixtures and the ketenes were converted into esters which were easily isolated and identified. Minor amounts of arylated α,β-unsaturated esters were also formed; presumably they were formed by the competing hydride elimination.

---

* Hercules Research Center Contribution No. 1556.



$$C_6H_5HgCl + PdCl_2 \rightleftharpoons [C_6H_5PdCl] + HgCl_2$$

$$[C_6H_5PdCl] + CH_2{=}CHCOCl \rightarrow$$

$$\rightarrow \left[C_6H_5CH_2\overset{\overset{PdCl}{|}}{C}HCOCl \right] \rightarrow \begin{cases} PdCl_2 + C_6H_5CH_2CH{=}C{=}O \\ [HPdCl] + C_6H_5CH{=}CHCOCl \end{cases}$$

$$C_6H_5CH_2CH{=}C{=}O + ROH \rightarrow C_6H_5CH_2CH_2COOR$$

$$C_6H_5CH{=}CHCOCl + ROH \rightarrow C_6H_5CH{=}CHCOOR + HCl$$

Methacryloyl and crotonoyl chloride reacted in the same way as acryloyl chloride. Unfortunately, yields of the esters have been only 10–16% of theory based upon the mercurial used, although the reactions were catalytic in palladium chloride. The reaction as it now stands, however, will not be very useful synthetically because of the low yields. An attempt to isolate benzylketene, as the dimer, was unsuccessful; only high-boiling complicated mixtures of products were isolated in low yields. Apparently, polymerization of the ketene occurred to a significant extent under the reaction conditions. The reactions which have been carried out are summarized in Table 1.

TABLE 1

PHENYLATION OF α,β-UNSATURATED ACID CHLORIDES

Arylating agent: C_6H_5HgCl (0.10 mole); palladium salt: $LiPdCl_3$ (2 mmoles); solvent: CH_3CN (200 ml).

Acid chloride (ml)		Products[a] (%)	
$CH_2{=}CHCOCl$	(10)	$C_6H_5CH_2CH_2CO_2CH_3$	(10.5)
		$C_6H_5CH{=}CHCO_2CH_3$	(1.0)
$CH_2{=}CHCOCl$	(20)	$C_6H_5CH_2CH_2CO_2CH(CH_3)_2$	(16.0)
		$C_6H_5CH{=}CHCO_2CH(CH_3)_2$	(1.0)
$CH_2{=}CH(CH_3)COCl$	(20)	$C_6H_5CH_2CH(CH_3)CO_2CH_2CH_3$	(12.5)
$CH_3CH{=}CHCOCl$	(20)[b]	$C_6H_5CH(CH_3)CH_2CO_2CH_3$	(12.0)

[a] Products after reaction with methanol, ethanol or isopropanol. [b] Palladium salt: $LiPdCl_3$ (2 mmoles) + $PdCl_2$ (10 mmoles).

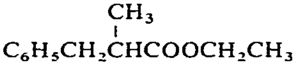
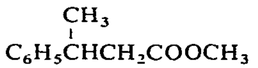
EXPERIMENTAL

General procedure for the arylation of α,β-unsaturated acid chlorides

A 500-ml 3-necked round-bottomed flask was equipped with a condenser with a calcium chloride drying tube attached, a stirring motor and a thermometer. A mixture of 31.3 g (0.10 mole) phenylmercuric chloride (Aldrich Chemical Company, Inc.), 180 ml of acetonitrile (dried by passage over molecular sieves) and 20 ml of the freshly distilled acid chloride was added. The mixture was stirred in an ice bath, and 20 ml of a 0.1 *M* solution of $LiPdCl_3$ in acetonitrile[1] was added. The reaction mixture was then stirred for 30 min in an ice bath and at room temperature overnight. The progress of the reaction could be followed by diluting a sample of the reaction mixture with methanol and analyzing by gas chromotography for the expected ester. In the reaction with crotonoyl chloride little product had been formed at this stage: there-

TABLE 2

ANALYTICAL DATA FOR REACTION PRODUCTS

Compound	b.p. (°C)[a]	Analyses: Found (calcd.) (%)		NMR data, δ (ppm)[b]
		C	H	
$C_6H_5CH_2CH_2COOCH_3$	90–115° (3 mm)	72.82 (73.14)	7.42 (7.37)	7.15 (s, 5 protons), 3.60 (s, 3 protons), 2.72 (m, 4 protons)
$C_6H_5CH_2CH_2COOCH(CH_3)_2$	105–120° (2 mm)	74.82 (74.96)	8.46 (8.26)	7.16 (s, 5 protons), 4.97 (sp, $J=6$, 1 proton), 2.70 (m, 4 protons), 1.14 (d, $J=6$, 6 protons)
 $C_6H_5CH_2\overset{CH_3}{\overset{\vert}{C}}HCOOCH_2CH_3$	100–115° (2 mm)	74.68 (74.96)	8.16 (8.26)	7.18 (s, 5 protons), 4.08 (q, $J=7$, 2 protons), 2.70 (m, 3 protons), 1.14 (t, $J=7$, 3 protons), 1.12 (d, $J=8$, 3 protons)
 $C_6H_5\overset{CH_3}{\overset{\vert}{C}}HCH_2COOCH_3$	82– 92° (2 mm)	73.80	7.71	7.19 (s, 5 protons), 3.54 (s, 3 protons), 3.27 (m X of ABX pattern, 2 protons), 1.24 (d, $J=7.0$, 3 protons)
$C_6H_5CH{=}CHCOOCH_3$	90–115° (3 mm)	73.99 (74.05)	6.33 (6.22)	7.70 (d, $J=16$, 1 proton), 7.40 (m, 5 protons), 6.42 (d, $J=16$, 1 proton), 3.78 (s, 3 protons).
$C_6H_5CH{=}CHCOOCH(CH_3)_2$	105–120° (2 mm)	—	—	7.68 (d, $J=16$,1 proton), 7.42 (m, 5 protons), 6.39 (d, $J=16$, 1 proton), 5.09 (m, 1 proton), 1.28 (d, $J=6$, 6 protons)

[a] Boiling points of crude products. Analytical and NMR samples were purified by gas chromatography.
[b] d, doublet; m, multiplet; q, quartet; s, singlet; sp, septet; t, triplet.

fore, 10 mmoles palladium chloride was added and reaction was continued for another day. The ketenes were then converted into esters by the addition of 20 ml of the appropriate alcohol. After stirring for about 15 min, the reaction mixtures were filtered through celite and concentrated on the steam bath to remove the solvents. The residue was dissolved in ether, chromatographed on 200 g of activated alumina to remove mercuric chloride, using 2 l of ether as eluant, and distilled under reduced pressure after removal of the ether at atmospheric pressure. The products were generally quite pure except for the presence in some cases of unsaturated esters. Pure samples were isolated by preparative gas chromatography on a 6′ Carbowax 20 M on Chromosorb W column. Analytical results for the products isolated are given in Table 2.

ACKNOWLEDGEMENT

Laboratory assistance was provided by Mr. A. G. Fleming and NMR spectra were taken by Mr. Lawrence Haas.

REFERENCES

1 R. F. Heck, *J. Amer. Chem. Soc.*, 90 (1968) 5518.
2 R. F. Heck, *J. Amer. Chem. Soc.*, 90 (1968) 5531.