and 14% methyl 2-methoxy-3-phenylpropionate. A sample of the latter was isolated by preparative-scale gas chromatography.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.38; H, 7.34.

The nmr spectrum of this compound in deuteriochloroform at 60 Mc had bands at −150 cps (multiplet of relative area 2 from the benzylic protons), −185 cps (singlet of relative area 3 from the methoxyl group), −210 cps (singlet of relative area 3 from the ester group), and at −266 cps (four lines, J_1 = 5.3, J_2 = 7.9, of relative area 1 from the tertiary proton).

Measurements of Relative Rates of Reaction of Various Olefins with Phenylmercuric Chloride. 1. Ethylene *vs.* Propylene. In a 200-ml Pyrex pressure bottle containing a magnetic stirring bar was placed 1.0 mmol of phenylmercuric chloride. The bottle was closed, evacuated, and pressured to 5 psig with propylene and 25 psig with ethylene. The mixture was stirred and thermostated at 25.0°, and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solution was injected by hypodermic syringe through the rubber-lined bottle cap. After 1 hr, reaction was complete. Gas chromatographic analyses showed that the solution contained 22 times as much styrene as 1-phenyl-1-propene and the concentration of styrene was very near 0.1 *M*. At 25.0° and 750 mm pressure 10 ml of acetonitrile dissolves 24.3 ml of ethylene and 69.3 ml of propylene. Thus, ethylene is about 60 times more reactive than propylene under these conditions.

2. Styrene *vs.* Propylene. In a 200-ml Pyrex pressure bottle containing a stirring bar was placed 1.0 mmol of phenylmercuric chloride. The bottle was closed, flushed with propylene, and pressured to 25 psig with propylene. Then 0.5 ml of styrene was added at 25.0°, followed by 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile solution. After 1 hr of stirring at 25.0°, analyses by gas chromatography showed that the solution was 0.063 *M* in 1-phenyl-1-propene (*trans*) and 0.0086 *M* in stilbene (*trans*). In a blank run under the same conditions, without the palladium or mercury compounds, the solution was found to be 0.60 *M* in propylene as determined by pressure drop. Since the styrene was initially present as a 0.41 *M* solution, propylene is about five times more reactive than styrene.

3. Methyl Acrylate *vs.* Styrene. A reaction was carried out as in the example above using 0.5 ml of methyl acrylate instead of propylene. After overnight stirring, gas chromatographic analyses showed that the solution was 0.050 *M* in methyl cinnamate and 0.017 *M* in stilbene (*trans*). Since the solution contained 5.55 mmol of methyl acrylate and 4.36 mmol of styrene initially, the relative rates of reaction are 2.3:1, respectively.

4. α-Methylstyrene *vs.* Styrene. A reaction was carried out as in the preceding example with 0.5 ml of α-methylstyrene in place of methyl acrylate. The reaction mixture was analyzed by gas chromatography and found to be 0.078 *M* in stilbene (*trans*) and 0.0017 *M* in 1,2-diphenyl-1-propene. Since the solution initially contained 3.87 mmol of α-methylstyrene and 4.36 mmol of styrene, the relative rates of reaction are 1:42, respectively.

Acknowledgments. The author gratefully acknowledges the assistance of Mr. Joseph Keelins with the experimental work. The nmr spectra were measured by Drs. M. M. Anderson and G. A. Ward.

The Arylation of Allylic Alcohols with Organopalladium Compounds. A New Synthesis of 3-Aryl Aldehydes and Ketones

R. F. Heck

Contribution from the Research Center of Hercules Inc.,
Wilmington, Delaware 19899. Received December 7, 1967

Abstract: Arylpalladium salts, prepared *in situ* from arylmercuric salts and a palladium salt, react with primary or secondary allylic alcohols to produce 3-aryl aldehydes or ketones in low to high yields depending upon the mercurial and allylic alcohol used. Since the reaction is tolerant of most substituents, it provides a very convenient and useful new method for preparing a wide variety of 3-aryl aldehydes and ketones.

The arylation of olefins with aryl derivatives of the group VIII metals is a general reaction. Certain allylic compounds undergo reactions different from those of simple olefins because of the allylic substituent. Allylic ethers and esters react normally, producing cinnamyl ethers and esters, respectively,[1] but allylic halides lose halogen, forming allylaromatic compounds.[2] In this paper is reported another example of an unusual arylation reaction, the arylation of allylic alcohols.

Results

The arylation of primary and secondary allylic alcohols leads to the formation of 3-aryl aldehydes or ketones in low to high yields. Arylpalladium salts were found to be the most useful arylating agents. They were most conveniently prepared from arylmercuric salts, and palladium salts in the presence of the allylic alcohol. Various solvents, such as acetone, acetic acid, methanol, and ethanol, could be used but the preferred solvent was acetonitrile. A variety of allylic alcohols have been arylated with various arylmercuric compounds and palladium salts. The results are summarized in Table I. Yields determined by gas chromatography were considerably higher than those found by isolation. Separation of the products from insoluble inorganic salts was probably not complete in most examples. As in the allyl ether arylations with chloride-containing systems,[1] dicyclohexylethylamine favored the reaction. It appears to prevent formation of halides from the allylic alcohol and by-product hydrogen chloride. These allylic halides react with the arylpalladium compounds to form allylic aromatics.[2] The amine also probably minimizes condensation of the product aldehyde because it neutralizes hydrogen chloride.

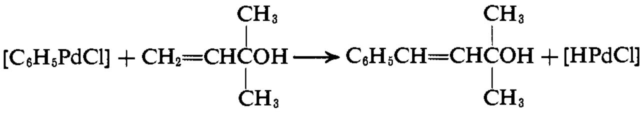
Little can be concluded about the effects of structure of the arylating group or of the allylic alcohol upon the reaction because of the limited amount of work done, but presumably the effects are similar to those found in the simple olefin arylation.[1] The reaction variables have by no means been exhaustively studied

---

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

and considerable improvement in yields may be possible. Even with the yields already obtained, the reaction is clearly a useful and convenient one for obtaining many 3-aryl ketones and aldehydes.

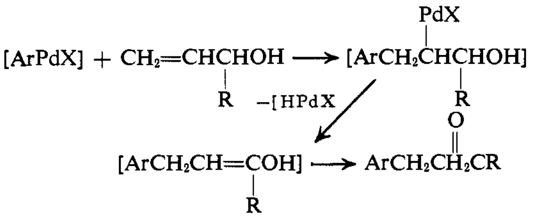
Tertiary allylic alcohols react with "arylpalladium salts," as simple olefins do, giving arylated derivatives. "Phenylpalladium chloride," prepared from phenylmercuric chloride and lithium palladium chloride, reacted with 2-methyl-3-buten-2-ol to form 2-methyl-4-phenyl-3-buten-2-ol in 83% yield as determined by gas chromatography. The pure product was isolated in 44.5% yield. The properties of the compounds prepared are given in Table II.



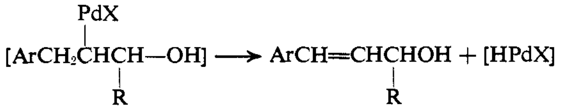
$$[C_6H_5PdCl] + CH_2{=}CH\overset{CH_3}{\underset{CH_3}{C}}OH \longrightarrow C_6H_5CH{=}CH\overset{CH_3}{\underset{CH_3}{C}}OH + [HPdCl]$$

Discussion

The mechanism of the allylic alcohol arylation reaction appears to be related to simple olefin arylation. The arylpalladium compound probably adds to the allylic double bond and then the hydride group on the hydroxyl-substituted carbon is eliminated, producing the enol of the 3-aryl aldehyde or ketone. On the basis of this mechanism, several additional products might be expected.

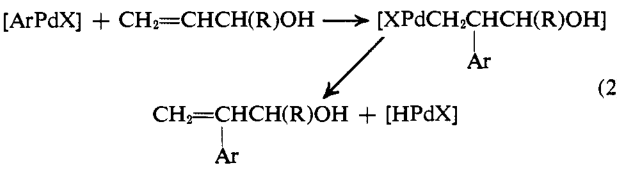


(1) Elimination of the hydrogen on the aryl-substituted carbon could occur to form cinnamyl-type alcohols.



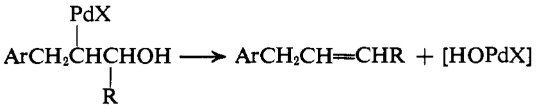
$$[ArCH_2\overset{PdX}{C}H\underset{R}{C}H{-}OH] \longrightarrow ArCH{=}CH\underset{R}{C}HOH + [HPdX] \qquad (1)$$

(2) Addition of [ArPdX] in the reverse direction followed by elimination of a hydride group might occur to produce a 2-aryl-2-propen-1-ol derivative.



(2)

(3) Elimination of hydroxyl instead of hydride could take place to form an allylaromatic compound.



$$ArCH_2\overset{PdX}{C}H\underset{R}{C}HOH \longrightarrow ArCH_2CH{=}CHR + [HOPdX] \qquad (3)$$

A search for these possible products has been made in the reaction of "phenylpalladium chloride" with allyl alcohol. From reaction 1 cinnamyl alcohol is expected. This product was identified in the reaction mixture as its acetate by acetylating a portion of the reaction mixture with acetic anhydride, and isolating the product by preparative gas chromatography. The free alcohol apparently decomposed on heating in the gas chromatography column. Cinnamyl alcohol was calculated to be formed in the arylation reaction to the extent of one-tenth the amount of the 3-phenylpropionaldehyde. Reaction 2 should form 2-phenylallyl alcohol. Attempts to find this product as its acetate were not successful, although small amounts of compounds with similar retention times were present. Reaction 3 would form allylbenzene. This was found to be present to the extent of about one-third of the amount of 3-phenylpropionaldehyde. There was no propenylbenzene in the reaction mixture. The presence of allylbenzene, however, does not necessarily confirm reaction 3. Allylbenzene could result from the arylation of by-product allyl chloride. The latter possibility seems more likely since little or no allylbenzene is formed in chloride-free arylations with acetate as the counterion. The same reaction carried out with crotyl alcohol in place of allyl alcohol produced about one-third as much 2-aryl aldehyde as 3-aryl aldehyde. Apparently addition occurred both ways in this example and the palladium group migrated, probably by a hydride elimination–addition mechanism, to produce the 2-aryl aldehyde.

Experimental Section

Arylmercuric Salts. These compounds were all obtained as described previously.[1]

3-Phenylpropionaldehyde. 1. A mixture of 10 mmol of phenylmercuric acetate, 6 ml of allyl alcohol, and 110 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 1 hr. Gas chromatographic analysis of the reaction mixture indicated that the solution was now 0.03 *M* in 3-phenylpropionaldehyde.

2. A reaction mixture containing 10 mmol of phenylmercuric chloride, 10 mmol of cupric chloride, 10 ml of acetonitrile, 1 ml of allyl alcohol, and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. Analyses by gas chromatography showed the solution to be 0.25 *M* in 3-phenylpropionaldehyde.

3. An experiment identical with the preceding one, carried out in acetone solution, gave a reaction mixture which was 0.13 *M* in 3-phenylpropionaldehyde.

4. Another experiment identical with expt 2 was carried out in acetic acid solution. The reaction mixture was found to be 0.17 *M* in 3-phenylpropionaldehyde.

5. A mixture of 10 mmol of phenylmercuric acetate, 5 mmol of mercuric acetate (reoxidant), 10 ml of acetonitrile, 1 ml of allyl alcohol, and 1 mmol of palladium acetate was stirred at room temperature for 2 days. Gas chromatographic analyses indicated that the solution was 0.24 *M* in 3-phenylpropionaldehyde. There was no allyl- or propenylbenzene present.

6. A mixture of 10 mmol of phenylmercuric chloride, 10 mmol of cupric chloride, 10 ml of acetonitrile, 1 ml of allyl alcohol, and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. The solution was then 0.25 *M* in 3-phenylpropionaldehyde and 0.077 *M* in allylbenzene. No propenylbenzene was found. A 2-ml portion of the reaction solution was removed and added to 0.5 ml of acetic anhydride in a tube. The tube was capped and heated for 1 hr in a steam bath. Analyses by gas chromatography then showed the presence of cinnamyl acetate, 0.013 *M*. A small sample of cinnamyl acetate was also isolated from the reaction mixture by gas chromatography and identified by its infrared spectrum. 2-Phenylallyl acetate was not found although small amounts of materials with similar retention times were present.

7. A reaction mixture of 0.20 mol of phenylmercuric chloride, 0.20 mol of cupric chloride, 0.25 mol of allyl alcohol, 390 ml of acetonitrile and 10 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 3 hr. The solution was now 0.15 *M* in 3-phenylpropionaldehyde as determined by gas chromatographic analysis. The product was isolated by diluting the reaction mixture with water and pentane, filtering to remove insoluble material, and separating the pentane layer. The insoluble material and the aqueous solution were extracted several times more with pentane,

Table I. 3-Aryl Aldehydes and Ketones Prepared by the Arylation of Allylic Alcohols

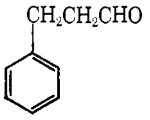
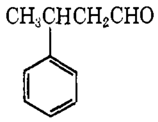
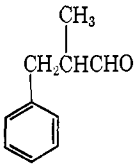
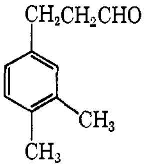
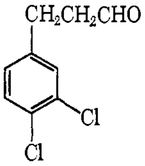
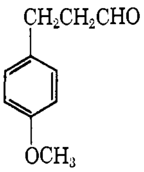
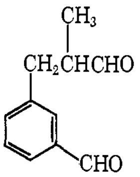
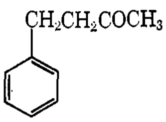
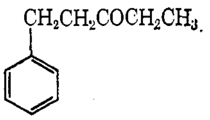
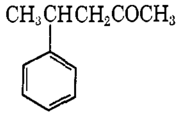
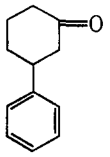
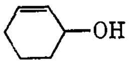
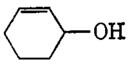
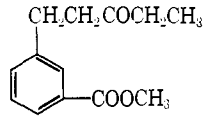
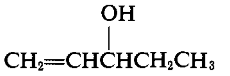
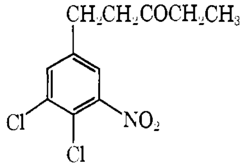
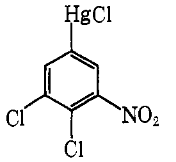
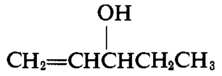
		Prepared from[a]				
Compound	Yield, %	Mercurial	Allylic alcohol	Other reagent[c]	Catalyst	Solvent
	35[d]	C_6H_5HgCl	$CH_2{=}CHCH_2OH$	...	$LiPdCl_3$	CH_3CN
	27[d]	C_6H_5HgCl	$CH_2{=}CHCH_2OH$	...	$CuCl_2$-Li_2PdCl_4	CH_3COCH_3
	36[d]	C_6H_5HgCl	$CH_2{=}CHCH_2OH$	...	$CuCl_2$-Li_2PdCl_4	CH_3COOH
	10[b] (30[c]) (53[d])	C_6H_5HgCl	$CH_2{=}CHCH_2OH$	...	$CuCl_2$-$LiPdCl_3$	CH_3CN
	26[d]	$C_6H_5HgOCOCH_3$	$CH_2{=}CHCH_2OH$	...	$Hg(OAc)_2$-$Pd(OAc)_2$	CH_3CN
	14.2[b]	C_6H_5HgCl	$CH_3CH{=}CHCH_2OH$	DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	42.5[b] (53[d])	C_6H_5HgCl	$CH_2{=}\overset{CH_3}{\overset{\vert}{C}}CH_2OH$	DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	47.5[d]	C_6H_5HgCl	$CH_2{=}\overset{CH_3}{\overset{\vert}{C}}CH_2OH$		$CuCl_2$-$LiPdCl_3$	CH_3CN
	13.3[b]	3,4-$(CH_3)_2C_6H_3HgCl$	$CH_2{=}CHCH_2OH$	...	$CuCl_2$-$LiPdCl_3$	CH_3CN
	10.5[b]	3,4-$Cl_2C_6H_3HgCl$	$CH_2{=}CHCH_2OH$	DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	8.5[b]	4-$CH_3OC_6H_4HgCl$	$CH_2{=}CHCH_2OH$	DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	2.5[b]	3-$OCHC_6H_4HgCl$	$CH_2{=}\overset{CH_3}{\overset{\vert}{C}}CH_2OH$	DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	20[b] (46[d])	C_6H_5HgCl	$CH_2{=}CH\overset{OH}{\overset{\vert}{C}}HCH_3$	DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	12[b] (32[d])	C_6H_5HgCl	$CH_2{=}CH\overset{OH}{\overset{\vert}{C}}HCH_2CH_3$	DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	12.5[b]	C_6H_5HgCl	$CH_3CH{=}CH\overset{OH}{\overset{\vert}{C}}HCH_3$	DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	24.5[b] (45.5[d])	C_6H_5HgCl		DCHEA	$CuCl_2$-$LiPdCl_3$	CH_3CN
	26[d]	C_6H_5HgCl		...	$CuCl_2$-$LiPdCl_3$	CH_3CN

Table I (*Continued*)

Compound	Yield, %	Prepared from^a			Catalyst	Solvent
		Mercurial	Allylic alcohol	Other reagent^c		
	6.6^b	$3\text{-}CH_3OCOC_6H_4HgCl$	 $CH_2{=}CH\overset{\overset{OH}{\vert}}{C}HCH_2CH_3$	DCHEA	$CuCl_2\text{-}LiPdCl_3$	CH_3CN
	4.6^b (15.7^e)		 $CH_2{=}CH\overset{\overset{OH}{\vert}}{C}HCH_2CH_3$	...	$CuCl_2\text{-}LiPdCl_3$	CH_3CN

^{a} All reactions were carried out at room temperature. ^{b} Yield of isolated product. ^{c} DCHEA = dicyclohexylethylamine. ^{d} Yield found by gas phase chromatographic analyses. ^{e} Yield of product isolated as the 2,4-dinitrophenylhydrazone.

and the combined extracts were washed twice with water and dried over anhydrous magnesium sulfate. The pentane was distilled from the product through a long Vigreux column, and the residue was distilled under reduced pressure. There was obtained 2.7 g of colorless liquid, bp 81–120° (4.5 mm), which was about 90% 3-phenylpropionaldehyde by gas chromatographic analyses. The product gave a yellow 2,4-dinitrophenylhydrazone, mp 151.0–151.5° (lit.[3] mp 149°).

Anal. Calcd for $C_{15}H_{14}N_4O_4$: C, 57.32; H, 4.49; N, 17.83. Found: C, 57.69; H, 4.47; N, 17.43.

3-Phenylbutyraldehyde. A mixture of 0.10 mol of phenylmercuric chloride, 0.10 mol of cupric chloride, 20 ml of dicyclohexylethylamine, 80 ml of acetonitrile, 10 ml of crotyl alcohol, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 2 hr. Initial cooling with ice water was necessary to keep the temperature from going above 25°. The reaction products were isolated as in expt 7, but with an additional acid wash before the bicarbonate wash to remove any unreacted amine present. There was obtained 2.8 g of colorless liquid product, bp 68–72° (3 mm). Gas chromatographic analyses showed the material to be a mixture of two products in the ratio of about 3:1. Both gave positive tests with 2,4-dinitrophenylhydrazine in alcoholic sulfuric acid solution. The products were isolated by preparative scale gas chromatography. The nmr spectrum confirmed that the major product was 3-phenylbutyraldehyde. The minor product was 2-phenylbutylaldehyde judging from its nmr spectrum and analyses.

2-Methyl-3-phenylpropionaldehyde. A reaction mixture of 0.10 mol of phenylmercuric chloride, 0.10 mol of cupric chloride, 10 ml of methallyl alcohol, 100 ml of acetonitrile, 10 ml of dicyclohexylethylamine, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 2 hr. Initial cooling was necessary to keep the reaction temperature below 25°. The reaction was completed by warming to 40–45° for 1 hr. Gas chromatographic analysis indicated that a 53% yield of 2-methyl-3-phenylpropionaldehyde had been obtained. The product was isolated as in expt 7. There was obtained 6.3 g of colorless liquid, bp 71–75° (3 mm), which was 99% pure 2-methyl-3-phenylpropionaldehyde by gas chromatographic analyses. The product gave a yellow 2,4-dinitrophenylhydrazone, mp 104–105° after recrystallization from ethanol.

In identical experiments, with and without added dicyclohexylethylamine, a slightly lower yield of aldehyde was obtained without the amine, but the difference was probably not significant in this reaction.

3-(3,4-Dimethylphenyl)propionaldehyde. A reaction mixture containing 0.20 mol of 4-chloromercuri-1,2-dimethylbenzene, 0.20 mol of cupric chloride, 225 ml of acetonitrile, 16.5 ml of allyl alcohol, and 160 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred overnight at room temperature. The temperature rose to 40° initially and the mixture was cooled with ice water to 25°. The reaction was apparently complete in 2 hr because the gas chromatogram of the reaction mixture did not change after that. Isolation of the product as in the 3-phenylpropionaldehyde preparation (expt 7) gave 8.6 g of colorless liquid, bp 90–120° (3 mm), which was about 50% 3-(3,4-dimethylphenyl)propionaldehyde. One of the several impurities in the product was probably 3-(2,3-dimethylphenyl)propionaldehyde judging from the nmr spectrum of the crude product. This product no doubt arose from a minor amount of 3-chloromercuri-1,2-dimethylbenzene in the starting mercurial. A pure sample of the 3,4-dimethyl isomer was isolated by preparative scale gas chromatography, n^{25}D 1.5225.

3-(3,4-Dichlorophenyl)propionaldehyde. A reaction mixture of 0.10 mol of 4-chloromercuri-1,2-dichlorobenzene, 0.10 mol of cupric chloride, 20 ml of dicyclohexylethylamine, 10 ml of allyl alcohol, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 2 hr. Initial cooling was necessary to keep the temperature from rising above 25°. The product was isolated as in the 3-phenylpropionaldehyde reaction (expt 7). Distillation of the product under reduced pressure gave 3.0 g of colorless liquid, bp 133–135° (4 mm). This material was about 70% 3-(3,4-dichlorophenyl)propionaldehyde by gas chromatographic analyses. A pure sample was isolated by preparative scale gas chromatography.

3-*p*-Anisylpropionaldehyde. A mixture of 0.10 mol of *p*-chloromercurianisole, 0.10 mol of cupric chloride, 20 ml of dicyclohexylethylamine, 70 ml of acetonitrile, 10 ml of allyl alcohol, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 3 hr, with initial cooling to keep the temperature from rising above 25°. Isolation of the product as in the 3-phenylpropionaldehyde preparation gave 2.14 g of brown liquid, bp 106–120° (3 mm), which was 65% pure by gas chromatography. A sample was purified by preparative scale gas chromatography, n^{25}D 1.5331. There were infrared bands from the product in carbon tetrachloride solution at 2800, 2700, and 1730 cm^{-1}.

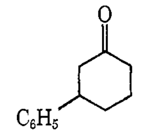
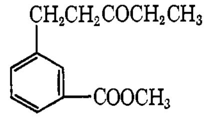
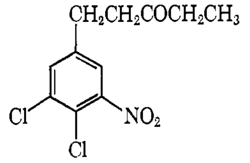
2-Methyl-3-(3-formylphenyl)propionaldehyde. A reaction mixture containing 90 mmol of 3-chloromercuribenzaldehyde, 0.10 mol of cupric chloride, 20 ml of dicyclohexylethylamine, 80 ml of acetonitrile, 10 ml of methallyl alcohol, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 2 hr. Initial cooling was necessary to keep the temperature from rising above 25°. Isolation of the product, as in the 3-phenylpropionaldehyde (expt 7), gave 0.70 g of green liquid product, bp 90–130° (2 mm), which was only about 50% pure by gas chromatographic analyses. A sample was purified further by preparative scale gas chromatography. The product had n^{25}D 1.5383 and strong infrared bands in carbon tetrachloride solution at 2810, 2720, 1730, and 1710 cm^{-1}.

1-Phenyl-3-butanone. A reaction mixture of 0.10 mol of phenylmercuric chloride, 0.10 mol of cupric chloride, 10 ml of 1-buten-3-ol, 150 ml of acetonitrile, and 50 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature with slight cooling to keep the temperature at 20–25° for 30 min. The black solution was now 0.22 *M* in 1-phenyl-3-butanone. Isolation of the product as in the 3-phenylpropionaldehyde preparation gave 2.9 g of colorless liquid, bp 97–120° (5.5 mm) which was 95% 1-phenyl-3-butanone by gas chromatographic analyses. A lower boiling fraction, 3.4 g, bp 56–98° (6 mm), was mainly crotylbenzene. A pure sample of 1-phenyl-3-butanone was isolated by preparative scale gas chromatography for analyses and determination of its nmr spectrum.

---

(3) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 171.

Table II. Properties and Analyses of 3-Arylcarbonyl Compounds

Compound	Bp (mm) or mp,[a] °C	Found, % C	Found, % H	Found, % Other	Calcd, % C	Calcd, % H	Calcd, % Other	Nmr spectrum,[c] ppm (no. of protons)
$CH_3CH(C_6H_5)CH_2CHO$	68–72 (3)	79.97 (58.50)	8.76 (4.95)	... (16.47) (N)	81.04 (58.53)	8.16 (4.91)	... (17.07) (N)[b]	−9.53, singlet (1) −7.16, singlet (5) −3.0, A_2B multiplet (3) −1.27, doublet (3)
$CH_3CH_2CH(C_6H_5)CHO$	68–62 (3)	81.28	9.33	...	81.04	8.16	...	−9.59, doublet (1) −7.20, multiplet (5) −3.34, pair of triplets (1) −1.90, multiplet (2) −0.85, triplet (3)
$C_6H_5CH_2CH(CH_3)CHO$	71–75 (3)	81.10 (58.35)	8.30 (4.84)	... (17.13) (N)	81.04 (58.35)	8.16 (4.91)	... (17.07) (N)[b]	−9.58, singlet (1) −7.17, singlet (5) −2.70, A_2B complex (3) −1.02, doublet (3)
3,4-$(CH_3)_2C_6H_3CH_2CH_2CHO$	97–106 (3)	80.99	8.53	...	81.44	8.70	...	−9.52, singlet (1) −6.83, multiplet (3) −2.60, multiplet (4) −2.11, singlet (7)
3,4-$Cl_2C_6H_3CH_2CH_2CHO$	133–135 (4)	52.86	4.24	...	53.23	3.97	...	...
4-$CH_3OC_6H_4CH_2CH_2CHO$	106–120 (3)	72.47	7.26	...	73.14	7.37	...	−9.60, singlet (1) −6.90, multiplet (4) −3.63, singlet (3) −2.70, multiplet (4)
3-$HCOC_6H_4CH_2CH(CH_3)CHO$	90–130 (2)	72.83 (51.00	6.78 3.81	... ...	74.97 51.49	6.87 4.76)[b]	... ...	...
$C_6H_5CH_2CH_2COCH_3$	97–120 (5.5)	80.87	7.91	...	81.04	8.16	...	−7.12, singlet (5) −2.65, multiplet (4) −1.95, singlet (3)
$C_6H_5CH_2CH_2COCH_2CH_3$	95–120 (3)	81.40	8.80	...	81.44	8.70	...	−7.11, singlet (5) −2.70, A_2B_2 pattern (4) −2.22, quartet (2) −0.93, triplet (3)
$CH_3CH(C_6H_5)CH_2COCH_3$	85–100 (2.5)	81.58	8.37	...	81.44	8.70	...	−7.17, singlet (5) −2.58–3.17, A_2B multiplet (3) −1.91, singlet (3) −1.20, doublet (3)
	124–130 (3)	82.51 (60.99)	8.68 (5.62)	... (15.78) (N)	82.72 (61.01)	8.10 (5.12)	... (15.81) (N)[b]	−7.17, singlet (5) −2.85, multiplet (1) −2.2, multiplet (4) −1.8, multiplet (4)
	142–150 (2)	70.93	7.08	...	70.88	7.32	...	−7.50, multiplet (4) −3.82, singlet (3) −2.80, A_2B_2 multiplet, (4) −2.48, quartet (2) −0.96, triplet (3)
	56.0–56.5	47.63 (45.15)	4.19 (3.38)	5.34 (N) (15.60) (N)	47.85 (44.75)	4.02 (3.31)	5.07 (N) (15.35) (N)[b]	...

[a] Boiling points of crude products. [b] Analyses of 2,4-dinitrophenylhydrazone are in parentheses. [c] 60 Mc with TMS as internal standard in CCl_4 solution.

1-Phenyl-3-pentanone. A reaction mixture of 0.10 mol of phenylmercuric chloride, 0.10 mol of cupric chloride, 100 ml of acetonitrile, 20 ml of dicyclohexylethylamine, 10 ml of 1-penten-3-ol, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 3 hr with initial ice cooling to keep the temperature from rising above 25°. The solution was now 0.25 *M* in 1-phenyl-3-pentanone. Isolation of the product as in the 3-phenylpropionaldehyde (expt 7) gave 2.4 g of colorless product, bp 95–120° (3 mm). The distillate was about 80% 1-phenyl-3-pentanone as determined by gas chromatographic analyses. A pure sample was isolated by preparative scale gas chromatography.

2-Phenyl-4-pentanone. A reaction mixture containing 0.10 mol of phenylmercuric chloride, 0.10 mol of cupric chloride, 20 ml of dicyclohexylethylamine, 10 ml of 3-penten-2-ol, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature for 2 hr. Initial cooling was necessary to keep the reaction mixture from warming up above 25°. Isolation of the product as in the above examples gave 2.9 g of colorless liquid, bp 85–100° (2.5 mm), which was about 70% 2-phenyl-4-pentanone by gas chromatographic analyses. A pure sample was isolated by preparative scale gas chromatography, $n^{25}D$ 1.5073.

3-Phenylcyclohexanone. A mixture of 0.10 mol of phenylmercuric chloride, 0.10 mol of cupric chloride, 20 ml of dicyclohexylethylamine, 10 ml of cyclohexenol, and 100 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred at room temperature overnight. The temperature of the reaction mixture rose initially to 37° before it could be cooled to 25° with an ice bath. The reaction mixture was found to be 0.35 *M* in 3-phenylcyclohexanone by gas chromatography. Isolation of the product as in the above examples gave 5.34 g of pale yellow liquid, bp 100–150° (3 mm), which contained about 80% of 3-phenylcyclohexanone. Redistillation gave 2.6 g of 95% pure material, bp 124–130° (3 mm). A sample was further purified by preparative scale gas chromatography. The product had a carbonyl absorption in carbon tetrachloride solution at 1720 cm^{-1}. The compound gave an orange 2,4-dinitrophenylhydrazone, mp 170.0–170.5° after recrystallization from chloroform–ethanol.

In the absence of dicyclohexylethylamine but with an equal volume of acetonitrile in its place, this reaction produced a solution that was only 0.20 *M* in 3-phenylcyclohexanone under the same reaction conditions.

1-(3-Carbomethoxyphenyl)-3-pentanone. was prepared by the same procedure used above to prepare 1-phenyl-3-pentanone, with 3-carbomethoxyphenylmercuric chloride used in place of phenylmercuric chloride. There was obtained as product, 2.43 g of an orange liquid, bp 142–150° (2 mm), which was about 60% 1-(3-carbomethoxyphenyl)-3-pentanone. A pure sample was separated by preparative scale gas chromatography.

1-(3,4-Dichloro-5-nitrophenyl)-3-pentanone. A mixture of 10 mmol of 5-chloromercuri-3-nitro-1,2-dichlorobenzene, 10 mmol of cupric chloride, 10 mmol of lithium chloride, 12 ml of 1.0 *M* 1-penten-3-ol, and 10 ml of 0.1 *M* $\mathrm{LiPdCl_3}$ in acetonitrile was stirred at room temperature overnight. The reaction mixture was concentrated at room temperature under reduced pressure and the product was extracted from the residue with boiling hexane. After concentrating and cooling, the hexane solution gave a sticky solid. Three recrystallizations from aqueous methanol gave nearly colorless needles, mp 56.0–56.5°.

In another experiment like the above the entire crude hot hexane-soluble product was converted into the 2,4-dinitrophenylhydrazone. There was obtained 0.715 g of yellow-orange crystals, mp 158–159°, after recrystallizing from chloroform–methanol.

2-Methyl-4-phenyl-3-buten-2-ol. A mixture of 0.10 mol of phenylmercuric acetate, 50 mmol of mercuric acetate, 100 ml of acetonitrile, 20 ml of 2-methyl-3-buten-2-ol, and 10 mmol of palladium acetate was stirred at room temperature overnight with initial cooling to keep temperature at about room temperature. Gas chromatographic analyses showed the solution to be 0.69 *M* in 2-methyl-4-phenyl-3-buten-2-ol. The product was isolated by adding water and extracting with pentane. After being washed with water and aqueous sodium bicarbonate, the extracts were dried with anhydrous magnesium sulfate and distilled under reduced pressure. There was obtained 8 g of product, bp 100–107° (2 mm). Recrystallization from pentane at −5° gave 6.4 g of colorless needles, mp 38.5–39.0°. In isooctane solution, the product had bands at 292 mμ (ε 900), (1270) and at 250 (18,000). The infrared spectrum of the compound in carbon tetrachloride solution had bands at 3580, 3350, and 1580 cm^{-1}. The nmr spectrum in carbon tetrachloride solution had bands at −718 ppm (singlet, five protons), −6.36 ppm (AB quarter, two protons), −3.27 ppm (singlet, one proton), and at −1.35 ppm (singlet, six protons).

Acknowledgment. The author gratefully acknowledges the assistance of Mr. Joseph Keelins with the experimental work. The nmr spectra were measured by Dr. George Ward.

Allylation of Aromatic Compounds with Organopalladium Salts

R. F. Heck

Contribution from the Research Center of Hercules Inc.,
Wilmington, Delaware 19899. *Received December 7, 1967*

Abstract: Arylpalladium salts, prepared *in situ* from arylmercuric salts and palladium(II) compounds, react with allylic halides at room temperature to produce allylaromatic derivatives. Moderate yields were obtained with a wide variety of aromatic compounds; even nitro, ester, and aldehyde groups could be present in the arylmercury compounds.

Allyl derivatives of aromatic compounds are readily obtained by the reaction of aromatic Grignard reagents or lithium compounds with allylic halides. The reaction is limited, however, because substituents which react with the Grignard reagents or lithium compounds cannot be present. A method of allylating aromatic compounds which does not have this limitation is reported in this paper.

The arylation of olefins with arylpalladium salts has been described previously.[1] We have now found that, if this reaction is carried out with an allylic halide as the olefin, an allyl group is added to the aromatic system and little or none of the arylallylic halide is formed.

$$[\mathrm{ArPdX}] + \mathrm{CH_2{=}CHCH_2X} \longrightarrow \mathrm{ArCH_2CH{=}CH_2} + \mathrm{PdX_2}$$

Results

Arylpalladium salts were prepared, *in situ*, as before, by the exchange reaction between aryltin, -lead, or particularly -mercury compounds, and palladium salts, generally lithium palladium chloride.[1] The reaction is catalytic with respect to the palladium salt. However, some side reactions occur and about 10–30 mol % of the palladium salt or 10–30 mol % of a reoxidant (cupric chloride) and a catalytic amount of the palladium salt generally must be used to obtain optimum yields. Acetonitrile, methanol, acetone, and acetic acid were used as solvents. The reaction was complete within a few hours at room temperature, producing allylated aromatics in 31–87% yields. Isomerization of the initially formed allylaromatic compound into a propenyl derivative usually occurred only if there was insufficient catalyst or reoxidant present or if the allylic halide concentration was below *ca.* 0.1 *M*. Isomerization generally did not occur unless a precipitate of palladium metal appeared in the reaction mixture. Palladium generally did not precipitate in acetonitrile solution when 10–30 mol % of cupric chloride based upon the mercurial used was present as a reoxidant and the allylic halide concentration was above 0.1 *M*. Typical examples of the aromatic allylation reaction are given in Table I. The properties of the products are given in Table II.

Discussion of Results

The allylation reaction is a quite general reaction, but rearrangements can produce unexpected products. Aside from the product isomerization to the propenyl structure mentioned above, allylic rearrangements of

---

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