

4-Carboxybenzyl Methyl Ketone. A reaction mixture containing 10 mmol of 4-chloromercuribenzoic acid, 2 ml of isopropenyl acetate, 5 ml of water, and 100 ml of 0.1 *M* Li_2PdCl_4 in acetic acid was stirred at room temperature for 3 days. The reaction mixture was then filtered to remove precipitated palladium metal and evaporated under reduced pressure. The residue remaining was extracted with hot hexane. On cooling, the hexane solution deposited crystals of the product. Two further recrystallizations from hexane gave 62 mg of colorless needles, mp 143–144°.

Benzyl Phenyl Ketone. A reaction mixture containing 0.10 mol of phenylmercuric chloride, 0.10 mol of cupric chloride, 20 ml of acetophenone enol benzoate⁶ and 100 ml of 0.1 *M* Li_2PdCl_4 in acetone was stirred at room temperature for 3 hr. Gas chromatographic analysis then showed that the solution was 0.33 *M* in benzyl phenyl ketone. Isolation of the product by adding water and extracting with pentane as in the 2-*p*-anisylpropionaldehyde preparation above gave 10.8 g of product, bp 105–165° (4 mm), which was a mixture of the desired ketone and unreacted acetophenone enol benzoate. Two recrystallizations from pentane gave 5.4 g of colorless crystals, mp 50.5–52.5°. The melting point rose to 55–56° after several more recrystallizations from hexane.

3-Nitrobenzyl Phenyl Ketone. A mixture of 8.8 mmol of 3-nitrophenylmercuric chloride, 1.1 ml of acetophenone enol acetate,⁶ 5 ml of water, and 100 ml of 0.1 *M* Li_2PdCl_4 in methanol was stirred at room temperature overnight. The reaction mixture was then filtered and the solvent was removed under reduced pressure. The product was extracted from the residue with hot hexane. On cooling, sticky crystals separated from the hexane solution. Two recrystallizations from aqueous methanol gave 0.20 g of colorless needles, mp 79.5–80.5°.

***p*-Anisyl 3,4-Dichlorobenzyl Ketone.** A reaction mixture containing 1.5 g (4 mmol) of 4-chloromercuric-1,2-dichlorobenzene, 0.54 g of *p*-methoxyacetophenone enol acetate (mp 68–70°),⁶ 2 ml of water, and 5 ml of 0.1 *M* Li_2PdCl_4 in methanol was stirred at room temperature overnight. Isolation of the product as in the 3-nitrobenzyl phenyl ketone preparation above and three recrystallizations from aqueous methanol gave 92 mg of colorless needles of product, mp 113.0–113.5°.

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

(5) F. Lees, *J. Chem. Soc.*, **83**, 145 (1903).

(6) Prepared by the procedure of P. A. Bedoukian, *J. Amer. Chem. Soc.*, **67**, 1430 (1945).

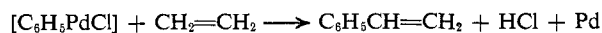
Aromatic Haloethylation with Palladium and Copper Halides

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Abstract: Aryl derivatives of group VIII metal compounds, prepared from group VIII metal salts and mercury, tin, or lead aryls, react with olefins in the presence of cupric halides to form 2-arylethyl halides. Chlorides are formed in higher yields than bromides. The most generally useful and readily obtainable reactants were arylmercuric halides, with lithium palladium chloride as the group VIII metal compound. Since only catalytic amounts of the palladium salt are required, this reaction provides a convenient method for introducing 2-haloethyl groups into aromatic systems.

Aryl derivatives of the group VIII metals react with olefins to form arylated olefins, an acid, and a reduced metal salt or the metal itself.¹ For example, "phenylpalladium chloride," prepared from phenylmercuric chloride and lithium palladium chloride *in situ*, reacts with ethylene to form styrene, hydrogen chloride, and palladium metal. The reaction can be



made catalytic with respect to palladium if certain oxidizing agents are included in the reaction mixture to reoxidize elemental palladium. Cupric chloride was a very effective reoxidant in this reaction at relatively low (<0.5 *M*) concentrations. At higher concentrations, reoxidation of the palladium still occurred, but a side reaction became important. As the concentration of cupric chloride was increased, increasing amounts of arylolethyl chlorides were formed at the expense of the arylated olefin. A study of this aromatic haloethylation reaction is the subject of this paper.

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

Results

A study of the variables in the reaction of phenylmercuric chloride, cupric chloride, and ethylene with a lithium palladium chloride catalyst revealed that 2-phenethyl chloride could be produced in 76% yield under practical conditions. Acetic acid or aqueous acetic acid is the best solvent, and the concentration of cupric chloride should be about 2 *M*. The inclusion of lithium chloride in the reaction mixture had a beneficial effect, presumably because it solubilized the cupric chloride. The reaction was found to be quite general. Arylethyl bromides were obtained by the same procedure with cupric bromide but in lower yields. Aryl-tin and -lead compounds could also be used as well as mercurials as the arylating agents, and salts of group VIII metals other than palladium, particularly rhodium and ruthenium, were also catalysts for the reaction. Some of the reactions carried out are summarized in Table I.

By-products in the haloethylation reaction include arylated olefins, aryl halides, α -haloarylethanes, and biaryls. In alcoholic solvents, the halides were sometimes converted into ethers under the reaction conditions if the halides were unusually reactive. Olefins

Table I. Catalytic Aromatic Haloethylation

Arylating agent	Olefin ^c	Catalyst	Cupric halide	Salt added	Solvent ^a	Product	Yield, ^b %
C ₆ H ₅ HgCl	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Cl C ₆ H ₅ CH=CH ₂	76 (69) ^d 2
C ₆ H ₅ HgCl	Ethylene	RhCl ₃ ·3H ₂ O	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Cl	32
C ₆ H ₅ HgCl	Ethylene	RuCl ₃	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Cl	25
C ₆ H ₅ HgCl	Ethylene	FeCl ₃	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Cl	3
C ₆ H ₅ SnCl ₃	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Cl	5
(C ₆ H ₅) ₄ Sn	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Cl	34
(C ₆ H ₅) ₄ Pb	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Cl	23
C ₆ H ₅ HgBr	Ethylene	Pd(NO ₃) ₂	CuBr ₂	LiBr	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Br	12
C ₆ H ₅ HgBr	Ethylene	Pd(OAc) ₂	CuBr ₂	LiBr	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CH ₂ Br	14
C ₆ H ₅ HgCl	Propylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ Br C ₆ H ₅ CH ₂ CHClCH ₃ C ₆ H ₅ CH=CHCH ₃	~50 50 30
C ₆ H ₅ HgCl	Acrolein	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CHClCHO	63 ^d
C ₆ H ₅ HgCl	Methyl acrylate	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (85:15)	C ₆ H ₅ CH=CHCOOCH ₃ C ₆ H ₅ CH ₂ CHClCOOCH ₃	85 ~10
C ₆ H ₅ HgCl	1-Buten-3-one	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (85:15)	C ₆ H ₅ CH ₂ CHClCOCH ₃ C ₆ H ₅ CH=CHCOCH ₃	~80 ^d ~20
C ₆ H ₅ HgCl	Crotonaldehyde	Li ₂ PdCl ₄	CuCl ₂	LiCl	CH ₃ OH	C ₆ H ₅ CH(CH ₃)CHClCHO C ₆ H ₅ C(CH ₃)=CHCHO	22 19
C ₆ H ₅ HgCl	Methyl acrylate	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	C ₆ H ₅ CH ₂ CHClCOOCH ₃ C ₆ H ₅ CH=CHCOOCH ₃	10 85
4-HOCOC ₆ H ₄ HgCl	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	4-HOCOC ₆ H ₄ CH ₂ CH ₂ Cl	72 ^d
4-HOCOC ₆ H ₄ HgCl	1-Buten-3-one	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (85:15)	4-HOCOC ₆ H ₄ CH ₂ CHClCOCH ₃	5 ^d
4-(C ₂ H ₅) ₂ NC ₆ H ₄ HgCl	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	4-(C ₂ H ₅) ₂ NC ₆ H ₄ CH ₂ CH ₂ Cl	20 ^d
3-NO ₂ C ₆ H ₄ HgCl	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	3-NO ₂ C ₆ H ₄ CH ₂ CH ₂ Cl	47 (16) ^d
2-C ₁₀ H ₇ HgCl	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (85:15)	2-C ₁₀ H ₇ CH ₂ CH ₂ Cl	30 ^d
2-C ₄ H ₉ SHgCl	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (85:15)	2-C ₄ H ₉ SCH ₂ CH ₂ Cl [2-C ₄ H ₉ S] ₂	13 ^d 13 ^d
1,3,5-(CH ₃) ₃ C ₆ H ₂ HgCl	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (90:10)	1,3,5-(CH ₃) ₃ C ₆ H ₂ CH ₂ CH ₂ Cl	2 ^d
1,3,5-(CH ₃) ₃ C ₆ H- (HgOCOCH ₃) ₂	Ethylene	Li ₂ PdCl ₄	CuCl ₂	LiCl	HOAc-H ₂ O (85:15)	1,3,5-(CH ₃) ₃ C ₆ H(CH ₂ CH ₂ Cl) ₂	0.2 ^d

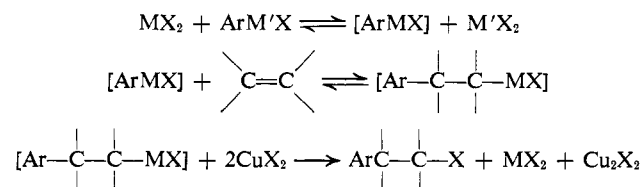
^a Reactions were all carried out for about 15–20 hr at room temperature. ^b Yields are based upon the arylating agent used and were determined by gas chromatography unless otherwise noted. ^c Ethylene and propylene gas used at 30 psig. ^d Yield of isolated product.

which isomerized easily gave complicated mixtures of products presumably because isomerization occurred under haloethylation conditions and each isomer gave different haloethylation products.

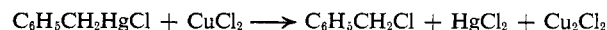
Discussion of Results

The mechanism of the aromatic haloethylation reaction appears closely related to that of the olefin arylation reaction.¹ The group VIII salt is probably converted to a metal aryl. This aryl metal compound then can add to the olefin to produce an aryylethyl derivative of the group VIII metal salt. The direction of addition in all examples is the same as was observed in the olefin arylation reaction,¹ namely, that the aryl group went on the least substituted carbon of the double bond. The observed haloethylation products would not be formed if elimination to arylated olefin occurred followed by addition of hydrogen chloride to the double bond. The aryl and halogen groups always add to different carbon atoms, and in many examples this is not the product expected in the HCl addition (e.g., styrene and hydrogen chloride give α -phenethyl chloride rather than β isomer which is observed in the haloethylation reaction). The reaction of the intermediate aryylethyl group VIII metal compound with hydrogen chloride, on the basis of known reactions of group VIII metal compounds,² would be expected to produce arylethanes, rather than halides, also. Since cupric halides are required, the aryylethyl metal complex

may react directly with cupric halide, perhaps by way of an aryylethylcupric halide, to form the β -arylethyl halide.



Support for this mechanism is found in the reaction of benzylmercuric chloride with cupric chloride with or without lithium palladium chloride. Here, even in the presence of an olefin and a palladium salt, the major product is benzyl chloride. Clearly aliphatic alkylating



agents are much more reactive toward cupric halides than the aryl derivatives, otherwise aryl halides would have been major products of haloethylation. Cupric bromide appears much less selective than cupric chloride, since, under comparable conditions, the bromoethylation of phenylmercuric bromide gave 50% bromobenzene and 10% 2-phenethyl bromide while chloroethylation of phenylmercuric chloride gave only traces of chlorobenzene and 76% 2-phenethyl chloride.

There is much to be learned about the stereochemistry of the haloethylation reaction. Phenylmercuric chloride, cupric chloride, and norbornene yield a product, in about 5% yield, whose nmr spectrum suggested that it was probably an *exo*-2-chloro-7-phenyl-

(2) G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960).

Table II. Analyses and Properties of Haloethylation Products

Compound	Bp (mm) or mp (lit.), °C	Formula	Found, %			Calcd, %		
			C	H	Cl	C	H	Cl
$C_6H_5CH_2CH_2Cl$	105–115 (41 mm)	C_8H_9Cl	68.92	6.89	25.30	68.33	6.45	25.22
$C_6H_5CH_2CHClCH_3$	59–160 (16 mm) ^a	$C_9H_{11}Cl$	69.97	7.63	23.00	69.90	7.17	22.93
$C_6H_5CH_2CHClCHO$	100–101.5 (7.5 mm)	C_9H_9ClO	63.99	5.72	21.60	64.11	5.38	21.02
$C_6H_5CH_2CHClCOCH_3$	100 (5 mm)	$C_{10}H_{11}ClO$	65.16	6.38	17.30	65.75	6.07	19.41
$4-HOCOC_6H_4CH_2CH_2Cl$	200–201	$C_9H_9ClO_2$	58.88	5.21	19.15	58.55	4.91	19.21
$4-HOCOC_6H_4CH_2CHClCOCH_3$	133.0–133.5	$C_{11}H_{11}ClO_3$	58.81	5.36	15.80	58.29	4.89	15.64
$4-(C_2H_5)_2NC_6H_4CH_2CH_2Cl$...	$C_{13}H_{15}ClN$	67.62	8.79	15.80	68.07	8.57	16.75
$3-O_2NC_6H_4CH_2CH_2Cl$	28–29	$C_8H_8O_2NCl$	51.48	4.69	19.70	51.76	4.34	19.10
$2-C_{10}H_7CH_2CH_2Cl$	47.0–47.5	$C_{12}H_{11}Cl$	74.98	5.99	18.70	75.59	5.82	18.60
$2-C_4H_9SCH_2CH_2Cl$	69–70 (7 mm)	C_6H_7SCl	48.66	5.11	23.70 ^b	49.14	4.81	24.18
$1,3,5-(CH_3)_3C_6H_2CH_2CH_2Cl$	56.0–56.5	$C_{11}H_{13}Cl$	71.82	8.49	19.10	72.31	8.28	19.41
$1,3,5-(CH_3)_3C_6H_2(CH_2CH_2Cl)_2$	115.5–116.5	$C_{13}H_{15}Cl_2$	61.57	7.63	27.30	63.68	7.40	28.92

^a Product purified by preparative-scale gas chromatography. ^b S: calcd, 21.87; found, 21.75.

norbornene. The same reaction with cyclohexene instead of norbornene gave only very minor amounts of chloride. The major product was a mixture of phenylcyclohexenes.¹

The aromatic haloethylation reaction is quite general. Increasing substitution at the olefin carbons, however, seems to favor formation of arylated olefin. For example, under the same conditions chloroethylation of phenylmercuric chloride gave 76% 2-phenylethyl chloride while 2-chloropropylation gave only 50% of 1-phenyl-2-propyl chloride. The α,β -unsaturated esters gave only low yields of haloethylation products presumably because the carboxyl group coordinates with the group VIII metal in the arylethyl intermediate and this complex decomposes mainly to olefin. The α,β -unsaturated aldehydes react well in the reaction, however, so that the α -halo acid derivatives are readily available indirectly. The haloethylation reaction will be useful in synthetic organic chemistry because the 2-haloethyl group previously could not be added by a simple one-step procedure.

Experimental Section

The mercurials and other arylating agents as well as the other reagents employed were the same as described in a previous publication.¹ Gas chromatographic analyses were carried out on a 6-ft Carbowax 20M column.

2-Phenethyl Chloride. A mixture of 15.70 g (50 mmol) of phenylmercuric chloride, 2.10 g (50 mmol) of lithium chloride, and 13.40 g (100 mmol) of anhydrous cupric chloride was placed in a heavy-walled Pyrex pressure bottle with a magnetic stirring bar. The bottle was then capped with a rubber-lined metal cap with two small holes in the metal for "hypodermic" injections. The air was replaced with ethylene by evacuating and filling the bottle with ethylene several times through a hypodermic needle inserted through the rubber liner of the cap. Then 40 ml of acetic acid, 5 ml of water, and 5 ml of 0.1 M Li_2PdCl_4 in acetic acid were injected. The mixture was stirred and the pressure of ethylene in the bottle was kept at 30 psig overnight. After about 20 hr, gas chromatography indicated that the reaction mixture was 0.755 M in 2-phenethyl chloride and 0.016 M in styrene. Two such reaction mixtures were combined, poured into a mixture of water and pentane, and filtered. The solids were extracted with fresh pentane, and the aqueous layer was extracted three more times with pentane. The combined pentane extracts were washed with water, dried over anhydrous magnesium sulfate, and distilled under reduced pressure. There was obtained 13.2 g of product, bp 105–115° (41 mm), which was more than 95% 2-phenethyl chloride by gas chromatographic analysis, and 3 g of a fraction, bp 115–120° (41 mm), which was 70% 2-phenethyl chloride by analysis.

2-Phenethyl Bromide. In a pressure bottle with a stirring bar were placed 10 mmol of phenylmercuric bromide, 20 mmol of cupric bromide, and 10 mmol of lithium bromide. The bottle was capped and the air in it was replaced by ethylene. Then 7 ml of acetic acid, 1 ml of water, and 1 ml of a 0.1 M slurry of palladium

nitrate in acetic acid were added. The reaction mixture was stirred under 30 psig of ethylene overnight. Gas chromatographic analyses indicated that the solution was now 0.135 M in 2-phenethyl bromide (13.5% of theory) and about 0.5 M in bromobenzene.

1-Phenyl-2-propyl chloride was prepared like 2-phenethyl chloride except propylene was used in place of ethylene. The reaction mixture became quite warm after mixing, and propylene absorption stopped after about 45 min. Three such reaction mixtures were combined, and the products were isolated as in the 2-phenethyl chloride reaction. Vacuum distillation of the reaction product gave 17 g of colorless liquid, bp 59–160° (6 mm), which was about one-third propenylbenzene and two-thirds 1-phenyl-2-propyl chloride by gas chromatography (a 48% yield of 1-phenyl-2-propyl chloride). The two products were separated by preparative-scale gas chromatography. *Anal.* Calcd for propenyl benzene: C, 91.54; H, 8.53. Found: C, 91.16; H, 9.06. The analysis of the chloride fraction is in Table II. The nmr spectrum of the chloride supported the expected structure. The compound in deuteriochloroform solution had bands at -7.15 (singlet of relative intensity 5, aromatic protons), at -4.07 (sextet of relative intensity 1, proton α to chlorine group), at -2.94 (an AB quartet doubled, with relative intensity 2, the methylene group) and at -1.42 ppm (a doublet of relative intensity 3, the methyl group).

2-Naphthylethyl Chloride. A reaction mixture containing 10 mmol of 2-naphthylmercuric chloride, 10 mmol of lithium chloride, 20 mmol of cupric chloride, 7 ml of acetic acid, 1 ml of water, and 1 ml of 0.1 M Li_2PdCl_4 in acetic acid was stirred at room temperature in a pressure bottle under 30 psig of ethylene overnight. The product was isolated by diluting the reaction mixture with water and methylene chloride. Insoluble material was removed by filtration, and the methylene chloride layer was separated. The insoluble material and the aqueous phase were extracted three more times with methylene chloride. The combined methylene chloride extracts were then washed twice with water, dried over anhydrous magnesium sulfate, and evaporated at room temperature under reduced pressure. The solid residue remaining after evaporation of the solvent was recrystallized twice from pentane. There was obtained 0.57 g of colorless solid, mp 46.5–47.5° (30% of theory). Another recrystallization sharpened the melting point to 47.0–47.5°. The nmr spectrum in deuteriochloroform solution had bands at -1.89 (distorted triplet of relative intensity 2, methylene on naphthylene group), at -3.15 (distorted triplet of relative intensity 2, chloromethylene group), and at -1.70 ppm (multiplet of relative intensity 7 from the naphthylene protons).

p-(2-Chloroethyl)benzoic Acid. A reaction mixture containing 10 mmol of p-chloromercuricbenzoic acid, 20 mmol of cupric chloride, 10 mmol of lithium chloride, 8 ml of acetic acid, 1 ml of water, and 1.0 ml of 0.1 M Li_2PdCl_4 in acetic acid was stirred at room temperature overnight under 30 psig of ethylene. Isolation of the product as in the 2-naphthylethyl chloride reaction above and recrystallization from aqueous methanol gave 1.33 g of colorless crystals of mp 200–201° (72% of theory). Another recrystallization from aqueous methanol did not change the melting point.

2-Thienylethyl Chloride. A reaction mixture containing 15.95 g (50 mmol) of 2-chloromercurithiophene, 13.4 g (100 mmol) of cupric chloride, 2.1 g (50 mmol) of lithium chloride, 40 ml of acetic acid, 5 ml of water, and 5 ml of 0.1 M Li_2PdCl_4 in acetic acid was stirred at room temperature overnight under 30 psig of ethylene. Three such reaction mixtures were combined, and the product was isolated as in the 2-naphthylethyl chloride reaction above. Dis-

tillation of the product gave 3.2 g of material of bp 63–93° (7 mm) (90% pure by gas chromatography), 4.0 g of material of bp 100–130° (7 mm) (75% the same material by gas chromatography), and a considerable amount of higher boiling material. Redistillation of the first fraction gave a pure sample of bp 69–70° (7 mm) which proved to be 2-thienylethyl chloride. The nmr spectrum of the product in deuteriochloroform solution had bands at -7.03 (multiplet of relative intensity 3, thiophene protons), at -4.51 (triplet of relative intensity 2, chloromethylene group), and at -3.24 ppm (triplet with relative intensity 2, methylene group on thiophene). The second compound isolated from this reaction mixture, bp 114–116° (7 mm), appeared to be mainly 2,2-bithiophene since it had only aromatic protons in its nmr spectrum and it contained only 2.5% chlorine by analyses.

3-Phenyl-2-chloropropionaldehyde. A reaction mixture containing 15.7 g (50 mmol) of phenylmercuric chloride, 26.8 g (200 mmol) of cupric chloride, 2.1 g (50 mmol) of lithium chloride, 35 ml of acetic acid, 5 ml of acrolein, 5 ml of water, and 5 ml of 0.1 *M* Li_2PdCl_4 in acetic acid was stirred, initially with ice cooling until the temperature no longer rose spontaneously, and then at room temperature overnight. The product from three such reactions was isolated as in the 2-naphthylethyl chloride preparation. Vacuum distillation gave two fractions: bp 80–100° (8 mm), 4.5 g, and bp 100.0–101.5° (7.5 mm), 13.8 g. Gas chromatography showed that the first fraction was about 50% the desired product compound, for a total yield of about 63.5%. Redistillation failed to produce an analytically pure sample. Purification was finally accomplished by converting the crude product into its sodium bisulfite addition product, washing it with ether, regenerating the aldehyde with aqueous sodium bicarbonate, and redistilling. The nmr spectrum of the product in deuteriochloroform solution had bands at -3.10 (AB quartet doubled, $J_{AB} = 14.5$, $J_{AX} = 8$, $J_{BX} = 6$ cps, with relative intensity 2, methylene group), at -4.15 (seven lines, $J_{AX} = 8$, $J_{BX} = 6$, $J_{YX} = 2$ cps, relative intensity 1, α -hydrogen), at -7.10 (a singlet of relative intensity 5 from the aromatic protons) and at -9.35 ppm (doublet with $J = 2$ cps, of relative intensity 1, from the aldehyde proton).

2-(*p*-Diethylaminophenyl)ethyl Chloride. In a bottle with a stirring bar were placed 5 mmol of *p*-chloromercuridiethylaniline, 5 mmol of lithium chloride, 10 mmol of cupric chloride, 8 ml of acetic acid, 1 ml of water, and 1 ml of 0.1 *M* Li_2PdCl_4 in acetic acid. The reaction mixture was stirred at room temperature overnight under 30 psig of ethylene. The product was isolated by diluting the reaction mixture with methylene chloride and water. The insoluble material was filtered off, and the filtrate was made basic with sodium hydroxide. The methylene chloride layer was separated and the aqueous layer was extracted three more times with methylene chloride. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, and distilled under reduced pressure. There was too little material to obtain a boiling point. The product was redistilled to give about 0.2 g of material which was pure by gas chromatography (20% yield). The nmr spectrum in deuteriochloroform had bands at -1.10 (triplet of relative intensity 6, from methyl groups), at -2.90 (distorted triplet from benzyl methylene), at -3.30 (a quartet from aminomethylenes), at -3.58 (distorted triplet from the chloromethylene group) (total relative intensities of the last three peaks about 7), and at -6.53 and -7.13 ppm (AB quartet of relative intensity 4 from the aromatic protons).

2-(*m*-Nitrophenyl)ethyl Chloride. A reaction mixture containing 20 mmol of crude *m*-chloromercurinitrobenzene, 40 mmol of cupric chloride, 20 mmol of lithium chloride, 16 ml of acetic acid, 2 ml of water, and 1 ml of 0.1 *M* Li_2PdCl_4 in acetic acid was stirred at room temperature overnight under 30 psig of ethylene. Gas chromatography indicated that the solution was about 0.5 *M* in *m*-nitrophenethyl chloride (47% yield). The product was isolated as in the 2-naphthylethyl chloride reaction above. The crude product was distilled under reduced pressure to give 2.3 g of liquid, bp 95–145° (4.5 mm). Gas chromatography indicated the product was only 65% *m*-nitrophenethyl chloride. Two recrystallizations of the product from benzene–hexane gave 0.6 g (16%) of very pale yellow crystals of mp 28–29°. The nmr spectrum in deuteriochloroform solution had bands at -3.15 (distorted triplet of relative intensity 2, benzyl methylene group), at -3.75 (distorted triplet of relative intensity 2, chloromethylene group), and at -7.53 and -8.03 ppm (multiplets of combined relative intensities of 4 from aromatic protons).

7-*p*-Carboxyphenyl-2-chlorobicyclo[2.2.1]heptane (?). A reaction mixture containing 10 mmol of *p*-chloromercuribenzoic acid, 10 mmol of lithium chloride, 10 mmol of cupric chloride, 7 ml of acetic acid, 1 ml of water, 1 g of norbornene, and 1 ml of 0.1 *M*

Li_2PdCl_4 in acetic acid was stirred at room temperature overnight. The product was isolated as in the 2-naphthylethyl chloride reaction above. The crude product was purified by recrystallizing it twice from aqueous methanol. There was obtained 0.11 g of colorless crystals of mp 226–227.5° (4% yield). The infrared spectrum of the product in chloroform solution had a carboxyl absorption at 1695 cm^{-1} . *Anal.* Calcd: C, 67.07; H, 6.03; Cl, 14.14. Found: C, 67.02; H, 6.43; Cl, 14.9.

1-Phenyl-2-chloro-3-butanone. A reaction mixture containing 10 mmol of phenylmercuric chloride, 10 mmol of lithium chloride, 20 mmol of cupric chloride, 7 ml of acetic acid, 1 ml of methyl vinyl ketone, 1 ml of water, and 1 ml of 0.1 *M* Li_2PdCl_4 in acetic acid was stirred at room temperature overnight. Gas chromatography indicated that the solution was about 0.8 *M* in 1-phenyl-2-chloro-3-butanone and 0.2 *M* in benzalacetones. Isolation of the product as in the 2-naphthylethyl chloride reaction gave a yellow oil after vacuum distillation at bp = 100° (5 mm). The benzalacetone in the crude product was removed by stirring with a solution of 0.5 g of potassium permanganate in 50 ml of acetone, filtering, and distilling. The distillate was free of benzalacetone but still contained a minor amount of some other impurity. The nmr spectrum of this product confirmed the proposed structure of the major product. The nmr spectrum in deuteriochloroform had bands at -2.19 (singlet of relative intensity 3 from the methyl group), at -3.15 (AB part of ABX spectrum, $J_{AB} = 14$; $J_{AX} = 8$, $J_{BX} = 6.5$ cps, with relative intensity 2 from the benzyl methylene group), at -4.35 (quartet, $J_{AX} = 8$, $J_{BX} = 6.5$ cps with relative intensity 1 from the ClCH_2 group), and at -7.15 ppm (a singlet of relative intensity 5 from the aromatic protons).

1-*p*-Carboxyphenyl-2-chloro-3-butanone. A reaction mixture containing 10 mmol of *p*-chloromercuribenzoic acid, 20 mmol of cupric chloride, 10 mmol of lithium chloride, 1 ml of water, 7 ml of acetic acid, 1 ml of methyl vinyl ketone, and 1.0 ml of 0.1 *M* Li_2PdCl_4 in acetic acid was stirred at room temperature overnight. The product was isolated as described in the preparation of 2-naphthylethyl chloride above. Recrystallization of the crude product from benzene–hexane gave 0.64 g of product, mp 120–122°. Several more recrystallizations from benzene–hexane and aqueous methanol gradually raised the melting point to 133.0–133.5° with only 0.11 g of product remaining (about 5% of theory).

2-Chloro-7-phenylbicyclo[2.2.1]heptane (?). A reaction mixture containing 10 mmol of phenylmercuric chloride, 20 mmol of cupric chloride, 20 mmol of lithium chloride, 2 g of norbornene, 8 ml of acetic acid, 1 ml of water, and 1 ml of 0.1 *M* Li_2PdCl_4 in acetic acid was stirred at room temperature overnight. The product was isolated as in the 2-naphthylethyl chloride preparation. The crude product was recrystallized three times from pentane at Dry Ice temperature to give 0.114 g of colorless solid, mp 47.5–48.0° (5.7% yield). The nmr spectrum of the product in deuteriochloroform solution had bands at -0.92 to -1.33 (multiplets of relative area 6), -2.86 (multiplets of relative area 2), -3.04 (broad singlet of relative area 1), -3.88 (X part of an ABX spectrum, $J_{AX} + J_{BX} = 11.7$ of relative area 1), and at -7.26 ppm (multiplet of relative area 5 from the phenyl protons).

2-Chloroethylmesitylene. A reaction mixture containing 2.95 g (8.3 mmol) of chloromercurimesitylene, 20 mmol of cupric chloride, 20 mmol of lithium chloride, 8 ml of acetic acid, 1 ml of water, and 1 ml of 0.1 *M* Li_2PdCl_4 in acetic acid was stirred overnight under 30 psig of ethylene at 40°. Isolation of the product as in the 2-naphthylethyl chloride preparation gave an oil which was crystallized from pentane by cooling in Dry Ice. Recrystallization from aqueous methanol gave 0.078 g of colorless needles, mp 56.0–56.5° (1.9%).

2,4-Bis(2-chloroethyl)mesitylene. A reaction mixture containing 15.92 g (25 mmol) of crude bis(acetoxymercuri)mesitylene, 100 mmol of lithium chloride, 100 mmol of cupric chloride, 40 ml of acetic acid, 5 ml of water, and 5 ml of 0.1 *M* Li_2PdCl_4 in acetic acid was stirred at room temperature overnight under 30 psig of ethylene. Then the reaction was completed by heating to 50° for 2 hr under 30 psig of ethylene. The reaction mixture was then poured into water and methylene chloride, and the product was isolated as in the 2-naphthylethyl chloride preparation. The crude product was purified by four recrystallizations from aqueous methanol and then one from pentane. There was obtained 0.078 g of colorless needles, mp 111–113° (0.8% yield). Two more recrystallizations from pentane raised the melting point to 115.5–116.5° with only 0.020 g remaining. Gas chromatography still showed the presence of a few per cent of the mono(2-chloroethyl)mesitylene. The nmr spectrum in deuteriochloroform solution had bands at -2.27 (singlet of relative area 9 from methyl groups), at -3.03 and -3.47

(symmetrical multiplets of total relative areas of 8 from the ethyl groups), and at -6.78 ppm (narrow multiplet of relative area 1 from the aromatic proton).

Reaction of Cupric Chloride with Benzylmercuric Chloride. A solution of 0.19 g (1 mmol) of dibenzylmercury, 0.14 g (1 mmol) of mercuric chloride, 0.042 g (1 mmol) of lithium chloride, and 1.0 ml of acetic acid was stirred for 5 min to form benzylmercuric chloride. Then 0.1 ml of water and 0.27 g (2 mmol) of cupric chloride were added, and the mixture was stirred magnetically for 2 days at room temperature. At the end of this time, gas chromatographic analyses showed that the solution was 0.80 *M* in benzyl chloride and that

there was also a small amount of benzyl acetate present. The same results were obtained when 0.1 ml of 0.1 *M* lithium palladium chloride in acetic acid was also added and when it and 40 psig of ethylene were present.

Acknowledgments. The author gratefully acknowledges the assistance of Mr. Joseph Keelins with the experimental work. The nmr spectra were kindly measured by Dr. M. M. Anderson of these laboratories.

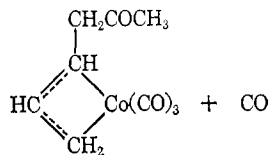
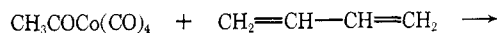
The Addition of Alkyl- and Arylpalladium Chlorides to Conjugated Dienes

R. F. Heck

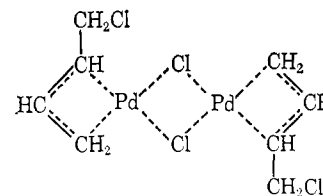
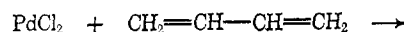
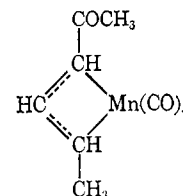
*Contribution from the Research Center of Hercules Inc.,
Wilmington, Delaware 19899. Received December 7, 1967*

Abstract: Aryl- and certain alkylpalladium chlorides, prepared *in situ* from aryl- or alkylmercury or -tin compounds and lithium palladium chloride, react readily with conjugated dienes to form 1-arylmethyl or 1-alkyl- π -allylpalladium chloride dimers, in low to moderate yields. A catalytic synthesis of arylbutenyl acetates from a conjugated diene, an arylmercuric salt, and lead tetraacetate with a catalytic amount of palladium acetate is also reported.

Addition reactions of various transition metal carbonyl derivatives to conjugated dienes are well known. Cobalt hydrocarbonyl,¹ manganese hydrocarbonyl,² and nitrosylironcarbonyl hydride³ add to butadiene to form 1-methyl- π -allylmethyl complexes, all apparently by way of 1,4-addition reactions to form σ -bonded 2-butenylmetal compounds which then cyclize to the π complexes. Methyl- or acetylcobalt tetracarbonyl reacts with butadiene to form 1-acetylmethyl- π -allylcobalt tricarbonyl.⁴ Methylmanganese pentacarbonyl reacts similarly with butadiene, but a rearrangement occurs producing 1-acetyl-3-methyl- π -



allylmanganese tetracarbonyl.⁵ Similar reactions of noncarbonyl transition metal alkyls have not been reported although there is one example of the addition of a chloride. Palladium chloride and butadiene form 1-chloromethyl- π -allylpalladium chloride dimer.⁶ We have now found that certain alkyl- and arylpalladium chlorides will also add to conjugated dienes.



Results

Alkyl- and arylpalladium chlorides are generally unstable materials. In the present investigation they were prepared by exchange reactions between lithium palladium chloride and alkyl- or arylmercury or -tin compounds in acetonitrile solution, in the presence of the conjugated dienes. Reactions were rapid at room temperature and the products were isolated by evaporating the solvent and chromatographing the crude products on alumina. In the examples tried, yellow crystalline products were isolated in low to moderate yields which, by analyses and nmr spectral studies, proved to be 1-alkyl- or 1-arylmethyl- π -allylpalladium chloride dimers. Only methyl-, benzyl-, and arylpalladium chlorides have been investigated because alkyls with β -hydrogen atoms are very unstable with respect to chloropalladium hydride and olefin and probably would not react rapidly enough with dienes

(1) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 1097 (1961).

(2) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *ibid.*, **83**, 1601 (1961).

(3) R. Bruce, F. M. Chaudhary, G. R. Knox, and P. L. Pauson, *Z. Naturforsch.*, **20b**, 73 (1965).

(4) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 3381 (1963).

(5) W. D. Bannister, M. L. H. Green, and R. N. Haszeldine, *Proc. Chem. Soc.*, 370 (1964).

(6) B. L. Shaw, *Chem. Ind. (London)*, 1190, (1962).