Hydrogenation and Carbonylation of Organomercury Compounds Catalyzed by Group 8 Metal Complexes

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Replacement of mercury by hydrogen in organomercurials has traditionally been accomplished by cleavage with mineral acids[2] or by reduction with a chemical reducing agent[3]. Cleavage of the carbon–mercury bond by molecular hydrogen has not been described with the single exception of diphenylmercury, which gave benzene and mercury at 750 psig and 175–200°; catalysis by noble metals had no impact on the resistance of organomercurials to hydrogenation.[4]

The selective functionalization of hydrocarbons via their organomercury salts has been explored in these laboratories. As part of this program the reaction of arylmercurials with hydrogen was studied to determine if such a reduction could be induced. Control experiments with phenylmercury acetate in methanol failed to occur at room temperature at hydrogen pressures up to 50 psig for reaction periods up to 3 days.[5] The addition of Pt/C and Pd/C as catalysts did not promote hydrogenation, and the formation of benzene and mercury was not observed.[7]

The inability of supported catalysts to hydrogenate phenylmercury acetate was attributed to improper substrate–catalyst interactions and/or catalyst poisoning by mercury released by reduction of a fraction of the mercurial. Homogeneous hydrogenation catalysts afforded the prospect of resolving this dilemma, for both of these complications would be avoided. Hydrogenation of phenylmercury acetate proceeded smoothly over tris(triphenylphosphine)rhodium(I) chloride[8] to give an 85% yield of benzene and an 82% yield of mercury (eq 1). The triphenylphos-

$$C_6H_5HgOAc + H_2 \xrightarrow[\substack{30-50\ \text{psig} \\ 25^\circ}]{[(C_6H_5)_3P]_3RhCl} C_6H_6 + Hg + HOAc \quad (1)$$

$$\text{mole ratio Hg/Rh} = 178:1$$

phine complexes of ruthenium,[9] platinum,[10] and palladium[10] also catalyzed this reaction, although the yields (15–25%) were depressed relative to rhodium. Hydrogenation over the rhodium catalyst was relatively insensitive to the mercury anion and the solvent; limited data indicate that ring substituents will exert some influence, but this feature has not been broadly explored. Table I summarizes some typical results. Optimum yields were provided by acetate and trifluoroacetate, a fact which complements the facile mercuration of aromatics by these mercury(II) salts.[11] The reduction of di(acetoxymercuri)benzene illustrated that this reaction was applicable to polymercurated substrates. The mercuration–hydromercuration sequence may permit the use of mercury as a blocking agent in organic synthesis, since the carbon–mercury bond can be cleaved under mild conditions with reagents that do not normally alter other functional groups.

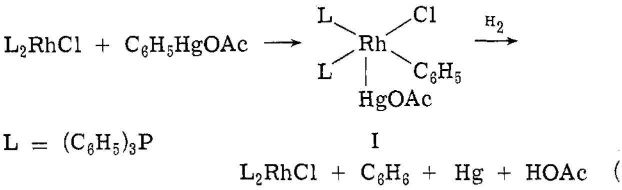
Table I
Hydrogenation of Arylmercury Salts

$$YC_6H_4HgX \xrightarrow[\text{solvent}]{H_2,\ \text{Rh catalyst}} YC_6H_5 + Hg + HX$$

Registry no.	X	Y	Solvent	Yield of YC_6H_5[a]
62-38-4	OAc	H	CH_3OH	85
100-56-1	Cl	H	CH_3OH	73
332-11-6	$OOCCF_3$	H	CH_3OH	98
55-68-5	NO_3	H	CH_3COOH	40
	OAc	H	CH_2Cl_2	70
54446-55-8	Br	CH_3	$C_2H_5OOCCH_3$	80
34012-18-5	OAc	HgOAc	CH_3OH	61 (Y = H)
54446-56-9	OAc	COOH	CH_3OH	20

[a] Based on arylmercury salt.

The mechanism of this reduction has not been studied, but oxidative addition of the mercury salt to the rhodium complex followed by hydrogen insertion into the carbon–rhodium bond appears reasonable (eq 2).[12] Oxidative addition analogous to eq 2 to yield a bimetallic complex comparable to I has been briefly described.[13] In this work a stable compound has been isolated from the reaction of phenylmercury acetate and tris(triphenylphosphine)rhodium(I) chloride; elemental analysis and spectral properties were consistent with formula I. Reaction of I with hydrogen gave benzene and mercury.



$L_2RhCl + C_6H_5HgOAc \longrightarrow$ I $\xrightarrow{H_2}$ $L_2RhCl + C_6H_6 + Hg + HOAc$ (2)

$L = (C_6H_5)_3P$

The rhodium–mercury bimetallic complex (I) was tested for carbonylation activity. The hydroformylation of 1-hexene gave a 98% yield of C_7 aldehydes in which the normal/branched ratio was 70:30. The isomer distribution was nearly identical with that produced by bis(triphenylphosphine)rhodium(I) carbonyl chloride,[14] indicating the formation of this rhodium complex from I under reaction conditions. Complex I was inactive for the carbonylation of methanol to acetic acid.[15] Analysis of the recovered methanol by gas chromatography revealed the trace presence of a material with retention time different from that of methanol or acetic acid. Stripping the methanol provided no isolable product, but the flask possessed an odor characteristic of methyl benzoate, suggesting that carbonylation of the rhodium–carbon bond present in the bimetallic catalyst (I) had occurred to yield a tiny quantity of this ester. Carbonylation of phenylmercury acetate in methanol catalyzed by tris(triphenylphosphine)rhodium(I) chloride (mole ratio Hg/Rh 500:1) proceeded smoothly to give an 88% yield of methyl benzoate (38%) and benzoic acid (50%) (eq 3). A comparable yield of mercury was recovered as a shiny pool.

$$C_6H_5HgOAc + CO + CH_3OH \xrightarrow[\substack{100\ \text{psig} \\ 85^\circ}]{\text{catalyst}} C_6H_5COOCH_3 + C_6H_5COOH + Hg + HOAc \quad (3)$$

Subsequent study of this reaction has shown that the carbonylation of organomercurials catalyzed by group 8 metal complexes represents a new, general synthesis of carboxylic acids–esters from hydrocarbons. The details of this chemistry and its synthetic utility will be fully presented in a future publication.

Experimental Section

All reagents were obtained from commercial sources and used as received. Arylmercury salts were prepared by published procedures.[1a] Group 8 metal complexes were purchased from commercial suppliers or synthesized by published techniques.[8–10] Infrared spectra were recorded on a Beckman IR-5A spectrophotometer; NMR spectra were measured on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Vapor phase chromatography was performed on a Perkin-Elmer Model 226 capillary gas chromatograph equipped with 300 ft × 0.01 in. DC-550 silicone columns.

Hydrogenation of Phenylmercury Acetate. In a typical experiment a Parr low-pressure reactor[16] was charged with 6 g (17.8 mmol) of phenylmercury acetate, 90 mg (0.1 mmol) of tris(triphenylphosphine)rhodium(I) chloride, and 100 ml of methanol. The clear, yellow solution was pressurized with hydrogen to 36 psig at room temperature, and the reaction mixture was shaken overnight. The reactor pressure declined to ~19 psig, corresponding to the consumption of ~20 mmol of hydrogen. From the reaction was recovered 2.9 g of mercury (82%). The methanol was poured into water and was extracted with pentane. The extract was dried over magnesium sulfate and analyzed for benzene by VPC using *p*-xylene as an internal standard. The benzene yield was 1.2 g (85%).

Under similar conditions the following catalysts gave the benzene yields shown: tris(triphenylphosphine)ruthenium(II) chloride, 13%; hydridotris(triphenylphosphine)ruthenium(II) chloride, 17%; tetrakis(triphenylphosphine)palladium(0), 24%; tetrakis(triphenylphosphine)platinum(0), 16%; bis(triphenylphosphine)platinum(II) chloride, 14%.

Preparation of Bimetallic Complex (I). A solution of 264 mg (0.78 mmol) of phenylmercury acetate in 5 ml of chloroform was added to a solution of 691 mg (0.75 mmol) of tris(triphenylphosphine)rhodium(I) chloride in 5 ml of chloroform. The solution was stirred at room temperature for 15 min and the chloroform was removed by evaporation. The residue was recrystallized from 25 ml of methanol to yield 474 mg (63%) of yellow crystals, mp 184–186°.

Anal. Calcd for $C_{44}H_{38}ClO_2P_2HgRh$: C, 52.86; H, 3.83; Cl, 3.55; P, 6.20; Rh, Hg, 30.36. Found: C, 52.99; H, 3.93; Cl, 3.92; P, 6.79; Rh, Hg, 28.6.

The NMR spectrum ($CDCl_3$) showed a methyl singlet at 48 Hz and a broad multiplet of aromatic protons at 445 Hz. The observed proton areas were 6 (CH_3) and 94% (CH); the calculated values were 7.8 and 92.2%, respectively. The NMR and infrared spectra of the starting materials and product were totally different.

A 500 mg (0.5 mmol) sample of complex I was dissolved in methanol (50 ml) and hydrogenated at room temperature for 5 hr. Analysis of the methanol solution gave 30 mg (77%) of benzene. Filtration of the reaction mixture gave 70 mg of mercury (70%).

Hydroformylation of 1-Hexene. To an Autoclave Engineers 300-ml stainless steel autoclave were charged 30 ml of 1-hexene (20 g, 0.24 mol), 20 ml of benzene, and 0.3 g of complex I. The reaction was pressurized to 1500 psig with synthesis gas (H_2/CO 1:1) and stirred at 100° for 5 hr. Work-up of the benzene solution gave 26.8 g (98%) of C_7 aldehydes. The ratio of linear to branched isomers was 2.31.[17]

Carbonylation of Phenylmercury Acetate. To a 1-l. Parr 4500 Series autoclave was added 16.8 g (50 mmol) of phenylmercury acetate, 150 ml of methanol, and 0.1 g (0.10 mmol) of tris(triphenylphosphine)rhodium(I) chloride. The reactor was evacuated by a water aspirator, and carbon monoxide was pressured into the reactor to 110 psig. The reaction mixture was stirred at 85° for 25 min. Filtration of the reaction mixture gave 8.5 g (85%) of metallic mercury. From the methanol solution were recovered 2.5 g (38%) of methyl benzoate and 3.1 g (50%) of benzoic acid. The products were identified by comparison with authentic samples.

Registry No.—I, 54446-57-0; tris(triphenylphosphine)ruthenium(II) chloride, 15529-49-4; hydridotris(triphenylphosphine)ruthenium(II) chloride, 19631-00-6; tetrakis(triphenylphosphine)palladium(0), 14221-01-3; tetrakis(triphenylphosphine)platinum(0), 14221-02-4; bis(triphenylphosphine)platinum(II) chloride, 10199-34-5.

References and Notes

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(5) Reaction conditions were purposely mild to avoid complications arising from dimerization and coupling reactions of the mercury compound.[4,6]

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(7) Coupling reactions typical of diarylmercurials in the presence of palladium or platinum at 25° were not detected. See ref 3, Chapter 8.

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(17) Products analyzed by comparative VPC with authentic samples. The authors thank Dr. L. B. Taranko, Exxon Chemical Co., for performing this experiment.

Palladium-Promoted Cyclization of Diphenyl Ether, Diphenylamine, and Related Compounds

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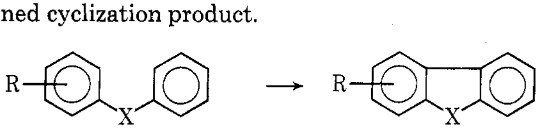
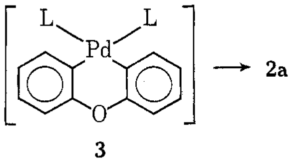
Aromatic compounds may be oxidatively coupled to biaryls and polyaryls by reaction with palladium acetate.[1–4] If diphenyl ether is used, a small amount of dibenzofuran, the product of intramolecular cyclization, is formed in addition to products from intermolecular coupling.[5] In fact, we have earlier shown that dibenzofuran is the only product if the reaction conditions are slightly modified.[6]

We now wish to present results which show that intramolecular cyclization is of general synthetic interest. When heated in acetic acid solution, which contained palladium acetate, diphenyl ether (**1a**), diphenylamine (**1b**), benzophenone (**1c**), and benzanilide (**1d**) gave high yields of cyclized products of the general structure **2** (Table I). An exception was diphenyl sulfide, which failed to yield a defined cyclization product.



1a, X = O; R = H	2a, X = O; R = H
b, X = NH; R = H	b, X = NH; R = H
c, X = CO; R = H	c, X = CO; R = H
d, X = CONH; R = H	d, X = CONH; R = H
e, X = NCH_3; R = H	e, X = NCH_3; R = H
f–m, X = NH; R = CH_3, CH_3O, Cl, Br, NO_2, CO_2H	f–m, X = NH; R = CH_3, CH_3O, Cl, Br, NO_2, CO_2H



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The investigation of a series of substituted diphenylamines showed that a large number of ring substituents were tolerated in the cyclization, e.g., methoxyl, methyl, carboxyl, and nitro groups (Table I). Therefore, the cyclization

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