REACTIONS OF ORGANOMETALLIC COMPOUNDS, CATALYZED BY TRANSITION METAL COMPLEXES.

7. OXIDATIVE DEMERCURATION OF ARYLMERCURY IN THE PRESENCE OF COMPLEXES OF PALLADIUM AND RHODIUM

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We have previously shown [1] that the cross-coupling of organomercury compounds R_2Hg and RHgX with aryl halides ArI in the catalytic system palladium complex–halide ion proceeds under mild conditions, and is a convenient method for the synthesis of nonsymmetrical diaryls. A by-product of these reactions with arylmercury compounds is the product of oxidative demercuration (OD) R_2, the yields of which are dependent on the nature of R in R_2Hg (RHgX), ArX, the solvent, and the ligand in the Pd complex. Furthermore, it is known that the OD of arylmercury compounds, catalyzed by Rh and Pd complexes [2, 3], takes place under conditions which are much more severe than those required for cross-coupling [1]. We assume that the addition of halide ion accelerates both cross-coupling and the oxidative demercuration of organomercury compounds.

It has been found that the demercuration of Ph_2Hg (I) in the presence of 2 mole % of $Pd(PPh_3)_4$ (II) and 1 equiv. of Bu_4NI in acetonitrile at 20°C for 4 h affords 42% of Ph_2 (73% after 24 h), whereas, according to Takagi et al. [2], in the absence of iodide ion 31% of Ph_2 was obtained after 8 h at 80°C (2.6 mole % of (II)).

To compare the catalytic activities of Pd and Rh complexes, we carried out the OD of (I) and PhHgCl (III) in the presence of added Bu_4NI. As will be seen from Table 1, in the case of the organomercury salt the Rh complex was the most active, whereas in the case of the symmetrical organomercury compound the palladium complex $PhPdI(PPh_3)_2$ was the more active, demercuration of (III) being most rapid when catalyzed by $[Rh(CO)_2Cl]_2$ (V).

$$Ph_2Hg \xrightarrow{(IV),\ I^-} Ph_2 + Hg \tag{1}$$

$$2PhHgCl \xrightarrow{(V),\ I^-} Ph_2 + Hg + HgCl_2 \tag{2}$$

To establish the optimum conditions for the demercuration of organomercury salts by reaction (2), the effects of type and amount of halide ion and type of solvent on the yields of R_2 were studied (Table 2). The presence of halide ion is necessary for the reaction to occur under mild conditions, since in the absence of halide ion not even a trace of product was obtained after 3 h at 20°C in DMF, whereas in the presence of 1 equiv. of Bu_4NI 93% of Ph_2 was obtained after 1 h. It was found that the rate of OD was virtually independent of the type of halide ion if it was added in the form of Bu_4NX, and addition of bromide and chloride was also very effective. It is noteworthy that in the presence of 2 equiv. of LiCl the demercuration of (III) catalyzed by (V) required more severe conditions (80°C, 24 h) [3], apparently owing to the lesser extent of dissociation of LiCl in comparison with Bu_4NCl [4]. As the concentration of iodide ion is increased, the rate of demercuration of (III) also increases (Table 2).

The Wilkinson complex $RhCl(PPh_3)_3$ does not catalyze the OD of (III) at 20°C, even in the presence of iodide. This implies that the presence of stabilizing ligands substantially reduces the reactivity of Rh in the OD reaction.

In the catalytic system (V)–Bu_4NI, the demercuration of (III) takes place rapidly and in high yield in a variety of solvents (HMPA, DMF, MeCN, acetone, THF, and CH_2Cl_2). Even in benzene, in which the reaction is heterogeneous, the yield of Ph_2 was 84% after 1 h. The reaction was much slower in methanol, in which the

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TABLE 1. Oxidative Demercuration of Ph_2Hg and PhHgCl Catalyzed by $PhPdI(PPh_3)_2$ (1 mole %) or $[Rh(CO)_2Cl]_2$ (0.5 mole %) and 1-2 equiv. of Bu_4NI* (HMPA, C_0 = 0.25 mole/liter, 20°C, Ar)

Organomercury compound	Catalyst	Reaction time, h	Yield of Ph_2, %
Ph_2Hg (I)	$[Rh(CO_2)Cl]_2$ (V)	20	21
	$PhPdI(PPh_3)_2$ (IV)	22	69
PhHgCl (III)	$[Rh(CO)_2Cl]_2$ (V)	2	98
	$PhPdI(PPh_3)_2$ (IV)	22	32

* 1 equiv. in the case of Ph_2Hg, and 2 equiv. in the case of PhHgCl.

TABLE 2. Effect of Solvent for Catalyst and Type and Amount of Halide Ion on the Demercuration of Organomercury Salts Catalyzed by 0.5 mole % of $[Rh(CO)_2Cl]_2$ and Bu_4NI (C_0 = 0.25 mole/liter, 20°C, 1 h, Ar)

Organomercury compound	Solvent	Equiv. of halide ion	Yield of Ph_2, %
PhHgCl	DMF	1	93
Ditto [a]	»	1	Trace
»	»	2	98
»	»	0,5	78
»	»	0,25	15
» [b]	»	0	0
» [c]	»	1	89
» [d]	»	1	93
» [e]	»	1	83
»	Acetone	1	96
» [f]	Methanol	1	40
»	HMPA	1	88
»	DMSO	1	Trace
»	MeCN	1	92
»	THF	1	96
» [f]	Benzene	1	84
»	CH_2Cl_2	1	95
» [g]	Acetone	2	53
PhHgI [h]	DMF	1	48
PhHgOAc [i]	»	2	75

[a] Catalyst 1 mole % of $RhCl(PPh_3)_3$. [b] Reaction time 3 h. [c] In air. [d,e] In place of Bu_4NI, Bu_4NBr used (d), or Bu_4NCl (e). [f] Reaction was heterogeneous. [g] NaI used. [h] 91% Ph_2 formed after 7 h. [i] Reaction time 24 h.

limiting factor is probably the dissolution of (III). It could be that DMSO is a good stabilizing ligand for Rh, as is PPh_3, resulting in the formation of an inactive Rh complex.

Less active than (III) in demercuration was PhHgI (VII). The reason for this is probably that (VII) more readily undergoes symmetrization in the presence of iodide than does (III), i.e., equilibrium (3) is shifted further to the right when X = I:

$$2PhHgX + I^- \rightleftarrows Ph_2Hg + HgX_2I^- \tag{3}$$

It was in fact established by TLC on Silufol (developer iodine vapor) that in the presence of Bu_4NI (VII) symmetrizes to (I). Consequently, the concentration of the organomercury salt when X = I is small compared with when X = Cl, and the OD of (VII) is much slower. Similar behavior is also seen in the demercuration of (III) in the presence of NaI in acetone. It is necessary to use 2 equiv. of NaI in this reaction, since one equiv. is consumed in the formation of (VII). In the case of PhHgOAc, the reaction also occurs much more slowly than with (III), probably owing to the lower reactivity of organomercury acetates in their oxidative addition to the Rh complex (see below).

Atmospheric oxygen has no appreciable effect on the rate of demercuration of (III) (Table 2).

As mentioned above, the OD of symmetrical organomercury compounds proceeds most rapidly in the presence of the Rh complex. From the results presented in Table 3, it will be seen that the demercuration of (I) catalyzed by Pd complexes containing the PPh_3 ligand proceeds in high yield in acetone, benzene, and THF

TABLE 3. Effect of Type of Solvent, Catalyst, and Type and Amount of Halide Ion on the Demercuration of Ph Hg in the Presence of 1 mole % of a Palladium Complex and NaI (C_0 = 0.25 mole/liter, 20°C)

Solvent	Equiv. of halide ion	Catalyst	Reaction time, h	Yield of Ph_2, %.
Acetone	1	$PhPdI(PPh_3)_2$ (IV)	2,5	30
			24	80
»	0,25	Ditto	2,5	24
»	0,5	»	2,5	30
»	2	»	2,5	27
»	3	»	2,5	21
»	4	»	2,5	20
Benzene$^{a)}$	1	»	24	83
THF$^{a)}$	1	»	17	76
THF$^{b)}$	1	»	17	83
Benzene$^{a)}$	1	$PdCl_2(PPh_3)_2$	24	75
»	1	$PdCl_2(AsPh_3)_2$	24	32

a,b) In place of NaI, Bu_4NI (a) or Bu_4NBr (b) used.

in the presence of iodide and bromide (Bu_4NX, X = Br, I in benzene and THF; NaI in acetone). In the presence of Pd complexes, however, the demercuration of R_2Hg is much retarded, and the reaction does not proceed to completion. It appears that all the Pd gradually leaves the reaction zone as a result of the amalgamization of Pd(O) by metallic Hg, formed during the OD reaction (reaction (4)):

$$PdL_2 + Hg \rightarrow Pd(Hg) + 2L \tag{4}$$

When the complex $(Ph_3As)_2PdCl_2$, which contains a ligand less basic than PPh_3, is used as the catalyst, this reaction is even slower, ~30% reaction being reached after 2 h, whereupon the reaction almost ceased. It is noteworthy that when PdX_2L_2 or $RPdXL_2$ (L is the ligand) is used as the Pd complex, the active species PdL_2 is first formed, and this also catalyzes the demercuration:

$$PdX_2L_2 \xrightarrow[-2RHgX]{2R_2Hg} R_2PdL_2 \rightarrow R_2 + PdL_2 \tag{5}$$

It was found that the concentration of iodide had little effect on the rate of demercuration of R_2Hg in the presence of a Pd complex. When the concentration was varied by a factor of 16 in the reaction involving (I) (acetone and NaI), the yield of Ph_2 did not vary by more than a factor of 1.5. A possible explanation for this is that in this case the limiting step in the reaction is the reductive elimination of Ph_2 from Ph_2PdL_2, which is independent of iodide concentration (see below, Eq. (7)).

As has already been noted, in the absence of added halide ion the OD of arylmercury compounds catalyzed by Pd and Rh complexes requires relatively severe conditions. Thus, the demercuration of Ar_2Hg in the presence of (VI) takes place at 80°C for several hours [2], Pd complexes being inefficient catalysts. The OD of arylmercury salts in the presence of 0.5 mole % of (V) and 2 equiv. of LiCl also requires a temperature of 80°C for 24 h [3]. It will be seen from Table 4 that the addition of iodide ion enables the OD of ArHgX and Ar_2Hg, catalyzed by Rh and Pd complexes, to be effected in high yields at ~20°C. This reaction can be profitably used for the synthesis of symmetrical diaryls containing either electron-acceptor or electron-donor groups. For instance, we have obtained the substituted diaryls $(p\text{-}XC_6H_4)_2$ (X = Cl, Me, MeO) in 74–99% yield. Demercuration of p-aminophenyl- and p-dimethylaminophenylmercury acetates affords 63–69% of benzidine and 4,4'-bis(dimethylamino)diphenyl. In the demercuration of di-(2-thienyl)mercury, 83% of the symmetrical diheteryl di-2-thieyl was obtained

$$\begin{gathered} Ar_2Hg \xrightarrow{«Pd»} Ar_2 + Hg \\ 2Ar'HgX \xrightarrow{«Pd» \text{ or } «Rh»} Ar_2' + Hg + HgX_2 \\ Ar = p\text{-}ClC_6H_4,\ Ph,\ p\text{-}MeOC_6H_4,\ 2\text{-thienyl}; \\ Ar' = Ph,\ p\text{-}MeOC_6H_4,\ p\text{-}MeC_6H_4, \\ p\text{-}H_2NC_6H_4,\ p\text{-}Me_2NC_6H_4;\ X = Cl,\ OAc \end{gathered} \tag{6}$$

It is currently believed that in the reaction of R_2Hg with Pd(0) and Pt(0) complexes the complex of Pd or Pt is first inserted into the C–Hg bond (oxidative addition of R_2Hg to the Pd(0) and Pt(0) complex), the zero-valent Pd and Pt complexes behaving as nucleophilic carbenoids [5]. If the R_2Hg compounds contain powerful electron-acceptor groups (R = CF_3, C_6F_5), the insertion products of the platinum complex RHgPt–

TABLE 4. Synthesis of Symmetrical Diaryls by the Oxidative Demercuration Arylmercury Compounds in the Presence of 1 mole% of $PhPdI(PPh_3)_2$ (IV) or 0.5 mole % of $[Rh(CO)_2Cl]_2$ (V) and NaI (C_0 = 0.25 M, 20°, Ar[a])

Organomercury compound	Solvent	Catalyst	Reaction time, h	Yield of Ar_2, %
p-MeC_6H_4HgCl[b]	HMPA (2)[c]	(V)	2	99
p-$MeOC_6H_4HgCl$[b]	»	(V)	2	98
$(p$-$MeOC_6H_4)_2Hg$	Acetone(1)	(IV)	24	74
$(p$-$ClC_6H_4)_2Hg$	»	(IV)	24	78
$(2$-$C_4H_3S)_2Hg$	»	(IV)	24	83
p-$H_2NC_6H_4HgOAc$	Acetone (3)	(IV)	3	63
p-$Me_2NC_6H_4HgOAc$[b]	DMPA (2)	(V)	24	69

[a] Reactions catalyzed by the Pd complex were carried out in air.

[b] Bu_4NI used instead of NaI.

[c] Number of equivalents of iodide ion given in parentheses after the solvent.

$R(PPh_3)_2$ are fully stable, and can be isolated (similar Pd complexes could not be isolated) [6]. The complexes $RHgPdRL_2$ formed as intermediates in the OD of R_2Hg are unstable, and form the diorganopalladium complexes R_2PdL_2 with elimination of metallic Hg, the former then undergoing reductive elimination to give R_2 and the original Pd(0) complex (equation (7))

$$\begin{gathered} R_2Hg + PdL_2 \rightarrow RHgPdRL_2 \rightarrow R_2PdL_2 + Hg \\ R_2PdL_2 \rightarrow R_2 + PdL_2 \end{gathered} \tag{7}$$

A similar mechanism for the OD of R_2Hg in the presence of Rh complexes has been proposed [2]. The addition of halide ion apparently facilitates the insertion of Pd(0) into the C−Hg bond, thus accelerating the demercuration of R_2Hg.

The OD of organomercury salts in the presence of Pd complexes must comprise three steps, including exchange of RHgX with the complex $RPdXL_2$ (Eq. (8)):

$$\begin{gathered} RHgX + PdL_2 \rightarrow RPd(HgX)\,L_2 \rightarrow RPdXL_2 + Hg \\ (\text{or}\ \ RHgPdXL_2) \\ RPdXL_2 + RHgX \rightarrow R_2PdL_2 + HgX_2 \\ R_2PdL_2 \rightarrow R_2 + PdL_2 \end{gathered} \tag{8}$$

Addition of halide, which is a nucleophilic catalyst [7], could accelerate both the insertion and the exchange stages, since it is an electrophilic substitution reaction. It is noteworthy that insertion of the Pd(0) complex could take place either at the C−Hg bond, at Hg−X. It is possible that in the latter case separation of metallic Hg could occur following the exchange step. Organomercury salts undergo OD in the presence of Pd complexes with greater difficulty than symmetrical organomercury compounds, apparently since exchange is the rate-limiting step.

A similar three-stage mechanism in which the oxidation level of the Rh varies from 1 to 3 has been proposed [3] for the OD of RHgX.

EXPERIMENTAL

The organomercury compounds, Pd and Rh complexes, and Bu_4NCl were obtained by known methods. The tetrabutylammonium bromide and iodide and sodium iodide were pure grade, dried for 2 h at 150°C (10mm). Methanol was chemically pure. Purification of benzene, CH_2Cl_2, MeCN, DMSO, and DMF was carried out as described in [8]. HMPA was kept over molecular sieve 13X for 24 h, twice distilled over CaH_2, bp 37°C ($8 \cdot 10^{-3}$ mm), and stored over molecular sieve 4A. THF was kept for 24 h over KOH, and distilled from $LiAlH_4$ immediately before use. Specially pure grade acetone was redistilled from NaI.

The yields of products were determined by TLC on Silufol UV-254 in conjunction with UV spectroscopy. The bands visualized by UV were cut out, eluted with methanol, and the UV spectra recorded on a Hitachi-124 spectrophotometer. The reaction products were identified by comparing their R_f values and UV spectra with authentic samples. The yields were calculated from their extinction coefficients, determined for standard samples.

4,4'-Dimethoxydiphenyl. In a flask fitted with a magnetic stirrer were placed under a stream of argon 171 mg (0.5 mmole) of p-anisylmercury chloride, 369 mg (1 mmole) of Bu_4NI, 2 ml of HMPA, and 1.0 mg (2.5 μmole) of (V). After 2 h, TLC showed that the mixture contained 52.5 mg (98%) of the desired product. The reaction mixture was treated with 20 ml of water, extracted with 4 × 10 ml of ether, washed with 3 × 20 ml of water, and subjected to TLC on silica gel (eluent hexane–ether, 2:1) to give 47 mg (88%) of 4,4'-dimethoxydiphenyl, mp 177°C (cf. [13]).

CONCLUSIONS

1. The effects of adding halide ion, type of solvent and catalyst on the oxidative demercuration of arylmercury compounds in the presence of palladium and platinum complexes have been studied.

2. In the presence of halide ion, arylmercury compounds Ar_2Hg and ArHgX (Ar = $p\text{-}ClC_6H_4$, Ph, $P\text{-}MeC_6H_4$, $p\text{-}MeOC_6H_4$, $p\text{-}Me_2NC_6H_4$, $p\text{-}H_2NC_6H_4$, 2-thienyl; X = Cl, OAc) undergo oxidative demercuration catalyzed by palladium and rhodium complexes, under very mild conditions (20°C), to give symmetrical diaryls in high yields.

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REACTIONS OF ORGANOMETALLIC COMPOUNDS, CATALYZED BY TRANSITION METAL COMPLEXES.

8. CARBONYLATION OF ARYLMERCURY COMPOUNDS IN THE PRESENCE OF PALLADIUM AND RHODIUM

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It has previously been shown that carbonylation of the $RSnMe_3-R'I$ system, catalyzed by "nonligand" palladium,* takes place with CO under atmospheric pressure at ~ 20°C to give the nonsymmetrical ketones RCOR' in high yields [1]. We attempted to use in this reaction, in place of $RSnMe_3$, the more accessible organomercury compounds which, according to [2], in the presence of Pd complexes and iodide ion undergo cross-coupling with aryl iodides. However, the main products of carbonylation of the system $R_2Hg-ArI$ were the symmetrical ketones R_2CO. Thus, reaction of Ph_2Hg (I) with 2 equiv. of $p\text{-}NO_2C_6H_4I$ (1 mole % $PhPdI(PPh_3)_2$ (II), 1 equiv. Bu_4NI, 1 atm. CO, 20°C) for 24 h gave 55% of Ph_2CO, 26% of $p\text{-}NO_2C_6H_4Ph$, 11% Ph_2, and only 8% of $PhCOC_6H_4NO_2\text{-}p$. Hence, two competing carbonylation reactions take place with organomercury compounds,

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* By "nonligand" palladium, we mean complexes $RPdXL_2$, PdL_n, etc., in which the solvent functions as a weakly coordinating ligand.

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