

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 ($\text{Ar} = \text{p-C}_6\text{H}_4$, Ph, P-MeC₆H₄, p-MeOC₆H₄, p-Me₂NC₆H₄, p-H₂NC₆H₄, 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 $\text{R}_2\text{SnMe}_2-\text{R}'\text{I}$ system, catalyzed by "nonligand" palladium,* takes place with CO under atmospheric pressure at $\sim 20^\circ\text{C}$ to give the nonsymmetrical ketones RCOR' in high yields [1]. We attempted to use in this reaction, in place of R_2SnMe_2 , 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 $\text{R}_2\text{Hg}-\text{ArI}$ were the symmetrical ketones R_2CO . Thus, reaction of Ph_2Hg (I) with 2 equiv. of p- $\text{NO}_2\text{C}_6\text{H}_4\text{I}$ (1 mole % $\text{PhPdI}(\text{PPh}_3)_2$ (II), 1 equiv. Bu_4NI , 1 atm. CO, 20°C) for 24 h gave 55% of Ph_2CO , 26% of p- $\text{NO}_2\text{C}_6\text{H}_4\text{Ph}$, 11% Ph_2 , and only 8% of $\text{PhCOC}_6\text{H}_4\text{NO}_2\text{-p}$. Hence, two competing carbonylation reactions take place with organomercury compounds,

* 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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TABLE 1. Carbonylation of (I) and (V) Catalyzed by 1 mole % of (II) or 0.5 mole % of (IV), 1-2 equiv. of Bu₄Ni* (HMPA, C₀ = 0.25 mole/liter, 1 atm CO)

Organomercury compound	Catalyst	Reaction time, h	Yield, %	
			Ph ₂ CO	Ph ₂
(I)	(II)	18	70	24
(I)	(IV)	19	89	—
(V)	(II)	19	98	—
(V)	(IV)	18	57	41

* 1 equiv. in the case of (I), and 2 equiv. in the case of (V).

TABLE 2. Effect of Type of Solvent, Catalyst, and Type and Amount of Halide Ion on the Carbonylation of Organomercury Compounds (C₀ = 0.25 mole/liter, 20°C, 1 atm CO)

Organomercury compound	Catalyst	Solvent	Reaction time, h	Yield, %	
				Ph ₂ CO	Ph ₂
(V) *	(II)	THF (1) †	6	80	—
			20	97	—
(V) ‡	(II)	Ditto	6	29	—
(V)	(II)	Acetone(2)	2	93	7
(V)	(II)	Acetone(3)	2	55	43
(I) *	(IV)	DMF (1)	4	90	—
(I) *	(IV)	THF (1)	4	69	—
(I) *	(IV)	Acetone (1)	4	89	—
(I) *	(IV)	Benzene(1)	4	95	—
(I)	(IV)	Acetone (0)	24	84	—
(I)	(IV)	Acetone (1)	2,5	85	—
(I)	(IV)	Acetone (0,5)	2,5	83	—
(I)	(IV)	Acetone (0,25)	2,5	84	—
			5	97	—
(I)	(IV)	Acetone (0,05)	2,5	90	—
			5	98	—
(I)	(IV)	Acetone (0,02)	2,5	90	—
			5	97	—
(I)	RhCl(PPh ₃) ₃	Acetone (1)	6	65	—
(V)	(IV)	Acetone (2)	2,5	97	—
PhHgOAc	(IV)	Acetone (3)	2,5	84	—

* Bu₄Ni used instead of NaI.

† Number of equivalents of NaI shown in parentheses after the solvent.

‡ Bu₄NBr used instead of NaI.

namely, carbonylation of the R₂Hg-ArI system, and carbonylation of R₂Hg to give R₂CO, the latter reaction predominating. This finding leads to the conclusion that it is possible to carbonylate mercury compounds under very mild conditions (1 atm CO, 20°C) in the presence of iodide. It is known that in the absence of iodide, the carbonylation of ArHgX catalyzed by Pd and Rh compounds (1-3 atm, 20-100°C) gives a mixture of Ar₂CO, Ar₂, and ArCOCl, the yield of ketone not exceeding 50% [3]. The addition of LiCl considerably increases the selectivity of the reaction, enabling the carbonylation of ArHgX catalyzed by [Rh(CO)₂Cl]₂ (IV) to be carried out in high yield, but the reaction conditions were severe (70°C, 68-100 atm [4]). It is noteworthy that symmetrical organomercury compounds do not undergo carbonylation in the presence of Pd and Rh complexes.

It has been found that in the presence of iodide, the carbonylation of PhHgCl and (I), catalyzed by Rh and Pd complexes, proceeds at atmospheric CO pressure and 20°C. The best catalyst for the carbonylation of (I) was found to be the Rh complex, and for (V), the Pd complex (Table 1):



Addition of iodide is necessary for the carbonylation of (V) to proceed under mild conditions in the presence of Rh and Pd complexes, and for the carbonylation of (I) in the presence of Pd complexes. We have found that the carbonylation of (I) catalyzed by (IV) proceeds at ~20°C at atmospheric pressure of CO (Table 2). Addition of 1 equiv. of iodide ion considerably increases the reaction rate. Thus, carbonylation of (I) (0.5 mole % (IV), acetone), gave yield of up to 84% of (III) after 24 h, whereas in the presence of 1 equiv. of NaI the same yield was obtained after only 2.5 h.

It is noteworthy that the carbonylation of (V) and (I) is accompanied by oxidative demercuration [5, 6], which is also facilitated by iodide [7]



Taking the carbonylation of (V) in the presence of Pd complexes and of (I) in the presence of Rh complexes as examples, we have examined the effects of type of solvent, halide, and catalyst on the reaction rate and product yields (Table 2). It was found that for the carbonylation of (V) catalyzed by (II), the solvent used could be not only HMPA, but also THF and acetone. When the carbonylation is carried out in acetone, it is possible to use the more readily available NaI in place of Bu₄NI. In this case, it is necessary to use 2 equiv. of iodide, since 1 equiv. is consumed in forming PhHgI (VI). The carbonylation of (V) proceeds more rapidly in acetone (2 equiv. NaI) than in HMPA and THF, the reaction being complete in 2 h to give 93% of (III) and 7% of Ph₂. When 3 equiv. of NaI were used, the yield of ketone in this reaction fell sharply, and large amounts of diphenyl were formed. The decreased yields of (III) are apparently due to symmetrization of (VI) with the formation of (I) (reaction (3)), which in the presence of the Pd complex and iodide readily undergoes oxidative demercuration even in an atmosphere of CO (Table 1)



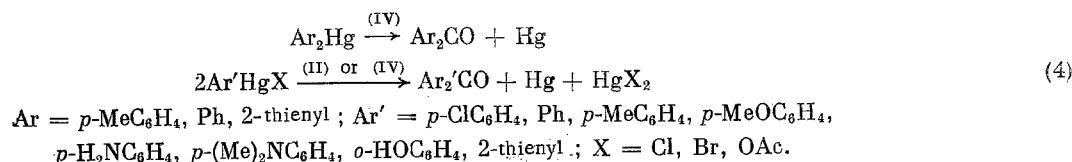
When bromide is used in place of iodide in the carbonylation of (V) in the presence of (II), the reaction proceeds much more slowly, but without affecting its selectivity (Table 2).

Complexes of Pd which do not contain phosphine ligands, such as (π -C₃H₅PdCl)₂, (MeCN)₂PdCl₂, were found to be devoid of activity in the carbonylation reaction. This is evidently due to the fact that the Pd(0) formed by the reduction of these complexes by the organomercury compound is, in the absence of stabilizing ligands, readily captured by even small amounts of metallic mercury, and is removed from the reaction zone.

It will be seen from Table 2 that carbonylation of (I) in the catalytic system iodide-(IV) proceeds rapidly in high yield both in polar solvents (DMF, THF, and acetone) and in the nonpolar benzene. When, instead of (IV), the Wilkinson catalyst RhCl(PPh₃)₃ is used as catalyst, the reaction rate is considerably reduced, i.e., the presence of phosphine ligands reduces the activity of rhodium in carbonylation.

By carrying out the reaction in acetone in the presence of NaI and (IV), it is possible to carbonylate not only symmetrical organomercury compounds, but also organomercury salts. In the latter case, carbonylation proceeds rapidly and selectively owing to the symmetrization of R₂HgI (reaction (3)), in consequence of which the R₂Hg formed in situ undergoes reaction.

The carbonylation of ArHgX and Ar₂Hg can be used to synthesize symmetrical diaryl ketones containing either electron acceptor or electron donor groups. Thus, we have obtained 77-87% yields (Table 3) of substituted benzophenones (p-XC₆H₄)₂CO (X = Cl, Me, and MeO). Carbonylation of readily available mercury compounds containing amino-, dimethylamino-, and hydroxy-groups has given 70-97% yields of 4,4'-diaminobenzophenone, Michler's ketone, and 2,2'-dihydroxybenzophenone. Carbonylation may also be used to obtain heterocyclic ketones. For instance, 2-thienylmercury bromide and di-2-thienylmercury both afford 90% of di-2-thienyl ketone:



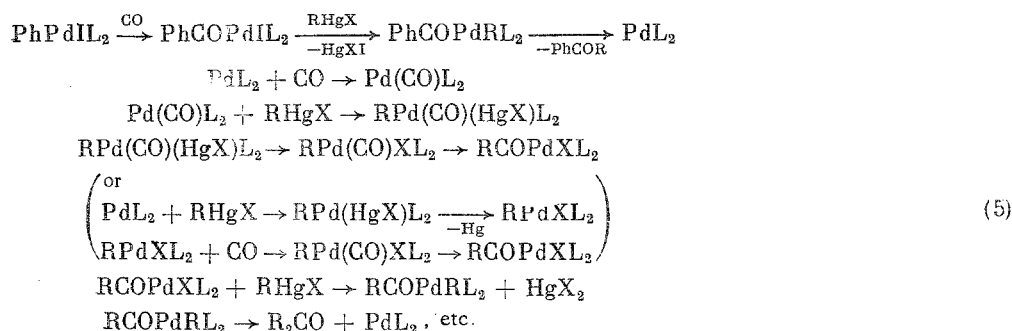
The mechanism proposed for the carbonylation of organomercury salts catalyzed by Pd complexes includes the formation of Pd(0) and Pd(II) intermediates (reaction (5)):

TABLE 3. Synthesis of Symmetrical Ketones by the Carbonylation of Arylmercury Compounds, Catalyzed by 1 mole % of (II), or 0.5 mole % of (IV), in the Presence of Bu₄Ni (C₀ = 0.25 mole/liter, 20°C, 1 atm CO)

Organomercury compound	Catalyst	Solvent	Reaction time, h	Yield, %	
				Ar ₂ CO	Ar ₂
<i>p</i> -ClC ₆ H ₄ HgCl	(II)	HMPA (2) *	40	83	17
<i>p</i> -MeOC ₆ H ₄ HgCl	(II)	Ditto	5	80	—
<i>p</i> -MeC ₆ H ₄ HgCl	(II)	»	5	87	—
(<i>p</i> -MeC ₆ H ₄) ₂ Hg	(IV)	»	10	77	—
(2-C ₄ H ₉ S) ₂ Hg	(IV)	DMF (0.5)	24	90	—
2-C ₄ H ₉ SHgBr	(II)	THF	15	90	8
<i>p</i> -Me ₂ NC ₆ H ₄ HgOAc †	(II)	DMF (2)	14	78	—
<i>p</i> -Me ₂ NC ₆ H ₄ HgOAc †	(IV)	Acetone (3)	3	72	—
<i>p</i> -H ₂ NC ₆ H ₄ HgOAc ††	(IV)	Acetone (2)	3	70	—
<i>o</i> -HOC ₆ H ₄ HgCl †	(IV)	Acetone (2)	3	95	—

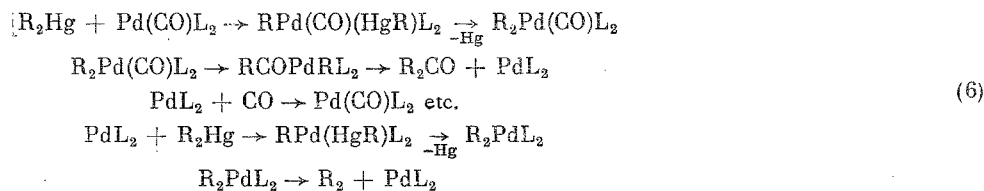
* Number of equivalents of iodide ion shown in parentheses after the solvent.

† Sodium iodide used in place of Bu₄Ni.



In the reaction sequence (5), reaction of PhPdIL₂ with CO and RHgX first results in the production of the active form of the catalyst, the coordinately unsaturated palladium complex PdL₂. This complex coordinates a molecule of CO, to give the carbonyl complex Pd(CO)L₂. Subsequently, oxidative addition of RHgX to the Pd(0) complex occurs (insertion of the Pd(0) complex into the Hg-C or Hg-X bond [8]), followed by elimination of metallic mercury. Next, insertion of CO into the C-Pd bond [9] gives an acyl Pd complex, which undergoes an exchange reaction with RHgX to give a dihydrocarbyl complex of Pd(II). Elimination of R₂CO from the dihydrocarbylpalladium complex regenerates the original complex PdL₂. Another sequence of reactions is also possible, in which the compound undergoing oxidative addition to RHgX is PdL₂, rather than the carbonyl Pd complex.

Iodide ion is a nucleophilic catalyst [10], and should accelerate the exchange step, since this is an electrophilic substitution reaction. It is also possible, however, that it also accelerates the insertion of Pd(0) into the Hg-C or Hg-X bond. This is supported by the fact that the addition of iodide also accelerates the carbonylation of organomercury compounds catalyzed by Pd complexes, in which there is no exchange step (Eq. (6)):



The formation of the oxidative demercuration product R₂ in the carbonylation of R₂Hg in the presence of Pd complexes appears to be due to the fact that R₂Hg can undergo oxidative addition to PdL₂ in addition to Pd(CO)L₂.

photometer. The reaction products were identified by comparison with authentic samples from their R_f values and UV spectra. The yields were calculated from the extinction coefficients obtained for the standard samples.

2,2'-Dihydroxybenzophenone. In a flask were placed 0.329 g (1 mmole) of *o*-hydroxyphenylmercury, 0.300 g (2 mmole) of NaI, and 4 ml of acetone. The resulting solution was stirred for 10 min in a stream of CO. The solution was then treated with 1.9 mg (0.005 mmole) of (IV) and CO introduced from a buret into the reaction mixture at 1 atm. After 3 h, TLC and UV spectroscopy showed that the mixture contained 0.102 g (95%) of the desired product. The reaction mixture was transferred without further treatment to a silica gel plate (eluent hexane- CHCl_3 , 1:1) to give 0.091 g (85%) of 2,2'-dihydroxybenzophenone, mp 61.5-62.5°C (cf. [13]).

CONCLUSIONS

1. It has been found that in the presence of iodide ion the carbonylation of arylmercury compounds $R_2\text{Hg}$ and $R\text{HgX}$ ($R = p\text{-ClC}_6\text{H}_4$, Ph, $p\text{-MeC}_6\text{H}_4$, $p\text{-MeOC}_6\text{H}_4$, $p\text{-Me}_2\text{NC}_6\text{H}_4$, $p\text{-H}_2\text{NC}_6\text{H}_4$, *o*- HOC_6H_4 , 2-thienyl; $X = \text{Cl}$, Br, OAc), catalyzed by palladium and rhodium complexes, proceeds under very mild conditions (1 atm CO, 20°C) to give high yields of symmetrical diaryl ketones.

2. The effects of type of solvent and catalyst, and the type and amount of halide ion have been examined, and the optimum conditions for carbonylation have been found.

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