

REACTIONS OF ORGANOMETALLIC COMPOUNDS CATALYZED
BY TRANSITION METAL COMPLEXES.

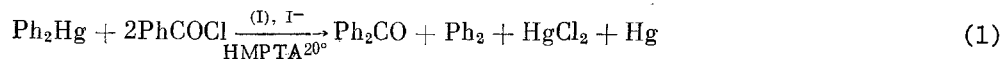
COMMUNICATION 6. REACTIONS OF ORGANOMERCURY COMPOUNDS
WITH ACID CHLORIDES IN THE PRESENCE OF PALLADIUM,
NICKEL, AND RHODIUM COMPLEXES

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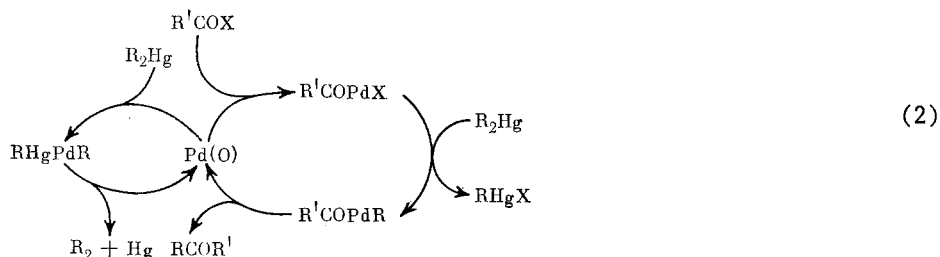
We recently reported the cross coupling of organomercury compounds (OMC), R_2Hg , and $RHgX$, with aryl iodides in a catalytic system consisting of a palladium complex and halide ion [1]. The halide ion is a nucleophilic catalyst [2] and permits carrying out the reaction of R_2Hg and $RHgX$ with ArI under mild conditions in high yield. In the present work, this approach was used for the development of a synthetic method for unsymmetrical ketones $RCOR'$ from OMC R_2Hg or $RHgX$ and acid chlorides $R'COCl$.

We found that Ph_2Hg reacts with benzoyl chloride in HMPMA at about $20^\circ C$ in the presence of $PhPdI(PPh_3)_2$ (I) (1 mole %) and Bu_4NI (2 equivalents relative to $R'COCl$). The reaction is complete in 75 min and leads to the formation of benzophenone (80% relative to both Ph groups in Ph_2Hg), 11% diphenyl, and a small amount of metallic mercury



In the absence of the iodide ion, 66% benzophenone and 12% diphenyl are formed in the reaction of Ph_2Hg with $PhCOBr$ catalyzed by $Pd(PPh_3)_4$ in HMPMA at $60^\circ C$ for 30 min. In this case, only one organic group of Ph_2Hg participates in the reaction, since the organomercury salt which forms under these conditions $RHgBr$ does not react with benzoyl bromide.

The formation of a dimeric product R_2 in the reactions of R_2Hg with $R'COX$ in the presence of a palladium complex in addition to the ketone $RCOR'$ is apparently related to catalysis of both acyldemetallation (ADM) [4] and oxidative demercuration (OD) [5, 6] by the palladium complex [Scheme (2), the ligands are omitted].



The ratio of $RCOR'$ to R_2 depends primarily on the nature of the R and R' groups as well as on the nature of the solvent and the type of catalyst used. In order to determine the optimal conditions for the ADM reaction and suppressing the OD reaction, we studied the effect of these factors on the reaction time and relative yields of $RCOR'$ and R_2 in the case of reaction (1).

The data in Table 1 indicate that the highest rate and selectivity for reaction (1) is found when using THF as the solvent. The ADM reaction also proceeds with rather high selectivity in HMPMA and acetone. The acyldemetallation of Ph_2Hg in the nonpolar solvents (benzene and CH_2Cl_2) proceeds more slowly, and the fraction of the OD product (diphenyl) is greater. This finding may be the result of a relative increase in the rate of the OD reaction in these solvents relative to the rate of ADM.

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TABLE 1. Solvent Effect on Reaction (1) in the Presence of Two Equivalents of Bu₄Ni and 1 mole % (I), C₀ = 0.25 mole/liter, argon, 20°C

Solvent	Reaction time, min	Yield, %	
		Ph ₂ CO	Ph ₂
HMPTA	75	80	11
THF	60	94	6
Acetone	90	86	11
CH ₂ Cl ₂	90	51	30
Benzene	180	65	35

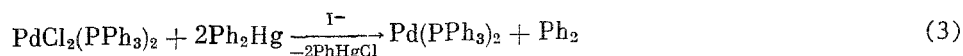
TABLE 2. Comparison of the Catalytic Activity of Pd and Ni Complexes in Reaction (1) in THF at 20°C (2 eq. Bu₄Ni, 1 mole % complex, C₀ = 0.25 mole/liter, argon)

Catalyst	Reaction time, min	Yield, %		Catalyst	Reaction time, min	Yield, %	
		Ph ₂ CO	Ph ₂			Ph ₂ CO	Ph ₂
(I) PdCl ₂ (PPh ₃) ₂	60	94	6	(Ph ₃ As) ₂ PdCl ₂	15	60	-†
	120	94	6		70	73	-†
(II)* (III)	45	15	-†	NiCl ₂ (PPh ₃) ₂	35	0	0
	15	37	-†				
	70	40	-†				

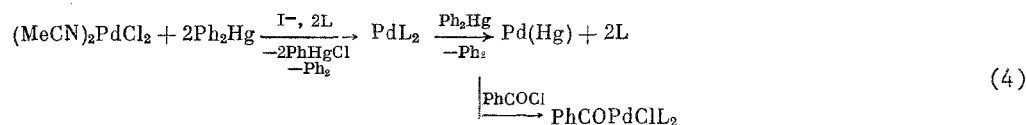
*0.5 mole % complex.

†A small amount of Ph₂ was formed, but its yield was not determined.

Since the best results were obtained in THF, the catalytic activity of various Pd complexes was compared in this solvent (Table 2). The most active catalyst studied was (I). The lower activity of PdCl₂(PPh₃)₂ may be related to its poor solubility in organic solvents and thus slow conversion to Pd(PPh₃)₂ which is the catalyst for both the ADM and OD reactions



Unexpectedly low catalytic activity was found for (π-C₃H₅PdCl)₂ (II) and (MeCN)₂PdCl₂ (III), which have the highest activity in the ADM reactions of organotin compounds [7]. Reaction (1) in the presence of complexes (II) and (III) gives only about 15% conversion for (II) and about 40% conversion for (III), and then stops. Amalgamation of "ligandless"* Pd(0) by metallic mercury may occur in this case; the OD reaction of Ph₂Hg results in the separation of metallic mercury. The catalyst is thus removed from the reaction sphere



L = solvent.

Inhibition of the reaction is also found in the case of the palladium complex containing the Ph₃As ligand, which is less basic than PPh₃.

If the deactivation of the palladium complexes is indeed related to amalgamation of Pd(0), its suppression would require either the use of stabilizing ligands or an increase in the capacity of RCOX to undergo oxidative addition to the Pd(0) complex.

*RPdXL₂, PdL_n, and other such complexes, in which the solvent molecules act as a weakly coordinating ligand, are termed "ligandless" palladium.

TABLE 3. Comparison of the Catalytic Activity of Group VIII Metal Compounds in Reaction (1) in Acetone at 20°C (2 eq. NaI, 1 mole % complex, C₀ = 0.25 mole/liter, argon)

Catalyst	Reaction time, min	Yield, %		Catalyst	Reaction time, min	Yield, %	
		Ph ₂ CO	Ph ₂			Ph ₂ CO	Ph ₂
PhPdI(PPh ₃) ₂ (I)	30	93	6	PdCl ₂	7	94	6
(I) a	120	74	25	[Rh(CO) ₂ Cl] ₂ ^d	7	75	23
PdCl ₂ (PPh ₃) ₂	120	93	7	RhCl(PPh ₃) ₃	35	8	- e
(MeCN) ₂ PdCl ₂ (III)	7	93	6	NiCl ₂ (PPh ₃) ₂	15	71	27
(III) b	30	32	52	NiBr ₂	7	70	27
(III) c	60	10	30	CoCl ₂	7	26	- e
(II) d	7	94	6	FeCl ₃	7	10	- e
(Ph ₃ As) ₂ PdCl ₂	7	85	12				

^a2 eq. BuNBr instead of NaI.

^b2 eq. LiBr instead of NaI.

^c2 eq. LiCl instead of NaI.

^d0.5 mole % complex.

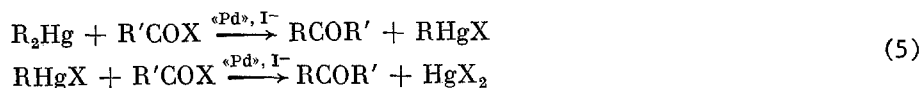
^eA small amount of Ph₂ was formed, but its yield was not determined.

In order to increase this capacity, we used acetone as the solvent. Acyl chlorides in acetone upon the action of NaI, which is a more available and inexpensive iodide ion source than Bu₄NI, are converted into acid iodides which are more active in oxidative addition reactions than acid chlorides.

Indeed, the efficiency of palladium complexes not containing phosphine ligands is significantly enhanced upon going from the THF-Bu₄NI system to the acetone-NaI system. In the presence of (II), (III), and the more available and inexpensive palladium compound PdCl₂, the ADM reaction is complete in several minutes and leads to the formation of benzophenone in virtually quantitative yield (Table 3).

Rhodium and nickel compounds may be used as catalysts for the ADM reaction for OMC in the acetone-NaI system, but the reactions with the participation of such compounds proceed less selectively than in the case of palladium complexes. In addition, in contrast to the reactions catalyzed by the palladium catalysts, atmospheric oxygen in the case of catalysis by nickel compounds has a significant effect on the ratio of the competing processes leading to RCOR' and R₂. Thus, the ketone yield upon carrying out the reaction of Ph₂Hg with PhCOCl catalyzed by NiCl₂(PPh₃)₂ in atmospheric oxygen was reduced from 71% to 47% and the diphenyl yield was enhanced from 27% to 50%.


As noted above, both organic groups in R₂Hg participate in the reaction with R'COX in the presence of iodide ion. This finding indicates that the organomercury salt intermediate is also active in the ADM reaction



Thus, not only symmetrical OMC but also organomercury salts may be used in this reaction. However, the byproduct R₂ is formed in significantly greater amounts in ADM reactions with the participation of organomercury salts than in the case of R₂Hg. For example, the reaction of p-MeC₆H₄HgCl with p-O₂NC₆H₄COCl gives 51% p-MeC₆H₄COC₆H₄NO₂NO₂-p and 38% (p-MeC₆H₄)₂, while in the case of (p-MeC₆H₄)₂Hg, the ketone yield is quantitative (Table 4). The reaction selectivity may be increased if the reaction mixture containing RHgCl and NaI is stirred for 20-30 min prior to the addition of R'COCl and the palladium complex. This apparently occurs because the organomercury salt symmetrizes to give R₂Hg in the presence of NaI in acetone [8].

Thus, the highest ketone yields in the reactions of OMC with acid chlorides are achieved by using acetone as the solvent in a catalytic system consisting of NaI-PdCl₂ and (II) or (III). In the ADM reaction under these conditions, the iodide ion not only acts as a nucleophilic catalyst but also leads to the formation of the more reactive RCOI and symmetrization of the organomercury salt. In addition, in the case of RHgCl, 1 eq. NaI is consumed in the

TABLE 4. Reactions of Organomercury Compounds with Acid Chlorides in Acetone at 20°C (2-4 eq. NaI,^a 1 mole % Pd complex, 20°C, C₀ = 0.25 mole/liter)

Experiment No.	Organomercury compound	R in RCOCl	Catalyst ^b	Reaction time, min	Yield, %	
					RCOR'	R ₂
1	MeHgI	Ph	(III)	3 h	90	—
2	»	<i>p</i> -BrC ₆ H ₄	(III)	30	88	—
3	<i>n</i> -C ₃ H ₇ HgCl	Ph	(III)	1 h	80	—
4	<i>p</i> -MeOC ₆ H ₄ HgCl	<i>p</i> -NO ₂ C ₆ H ₄	PdCl ₂	5	85	15
5	<i>p</i> -MeC ₆ H ₄ HgCl	»	PdCl ₂	5	80	17
6	PhHgCl	Ph	(I)	15	72	27
7	<i>p</i> -ClC ₆ H ₄ HgCl	<i>p</i> -NO ₂ C ₆ H ₄	(III)	5	90	10
8	Ph ₂ Hg	Me	(III)	5	76	20
9	»	<i>n</i> -C ₃ H ₇ ^c	(I)	20	60	35
10	»	PhCH ₂	(III)	5	90	10
11	»	PhCH=CH ^d	(III)	10	96	3
12	»	Ph	(II)	20	94	6
13	»	<i>p</i> -FC ₆ H ₄	PdCl ₂	20	94	5
14	»	<i>o</i> -FC ₆ H ₄	PdCl ₂	20	93	6
15	»	<i>p</i> -BrC ₆ H ₄	(III)	5	90	10
16	»	<i>p</i> -ClCOC ₆ H ₄ ^e	PdCl ₂	20	85	9
17	»	<i>p</i> -NO ₂ C ₆ H ₄	(II)	15	94	6
18	(<i>o</i> -MeOC ₆ H ₄) ₂ Hg	»	(III)	10	95	—
19	(<i>p</i> -MeOC ₆ H ₄) ₂ Hg	»	(III)	10	97	—
20	() ₂ Hg	»	(III)	10	98	—
21	(Ph=C) ₂ Hg	» ^f	(III)	10	40	24
22	»	» ^f	(III)	3	58	13

^a2 eq. NaI for R₂Hg and 4 eq. NaI for RHgX.

^b0.5 mole % for (II).

^c2 eq. Bu₄NI used instead of NaI.

^d78% PhCH=CHCOPh and 13% Ph₂ were formed when using NiCl₂·

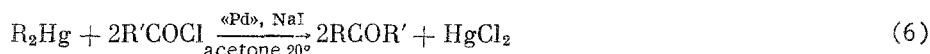
(PPh₃)₂ after 15 min at 20°C, argon atmosphere.

^eThe reaction product was *p*-PhCOC₆H₄COPh.

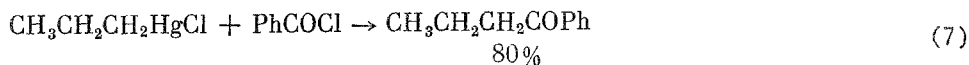
^fIn the presence of 4 eq. NaI.

formation of RHgI. Thus, the ADM reaction of organomercury salts requires a greater amount of NaI than in the case of R₂Hg.

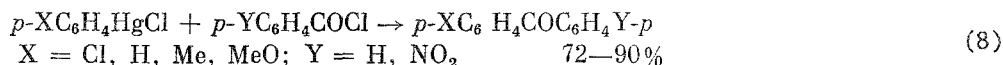
Alkyl, aryl, and ethynyl mercury derivatives and the acid chlorides of aromatic, aliphatic, and unsaturated acids were studied in the ADM reaction under the optimal conditions determined: acetone solvent, NaI, and 1 mole % palladium complex (see Table 4).



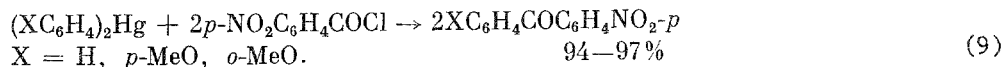
The data for experiments 1-3 in Table 4 show that alkylmercury salts may undergo the ADM reaction, including such salts containing a β-hydrogen atom



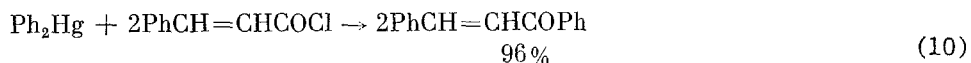
Arylmercury salts containing either electron-donor or electron-withdrawing substituents react with acid chlorides of aromatic acids to give good yields of substituted benzophenones (see experiments 4-7 in Table 4).



However, significant amounts (10-27%) of the (*p*-XC₆H₄)₂ byproduct are formed in these reactions. The ADM of symmetrical aryl mercury derivatives proceeds in quantitative yield (experiments 17-19)

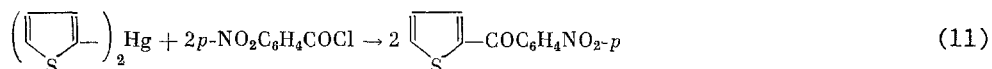


The acid chlorides of unsaturated acids may also be used for the acylation of OMC in addition to the acid chlorides of aromatic acids (experiments 13-16). Thus, chalcone is formed in quantitative yield in the reaction of Ph_2Hg with the succinyl chloride.



Aryl alkyl ketones may also be obtained in the reaction of aryl mercury derivatives with the acid chlorides of alkanecarboxylic acids. However, significant amounts of the OD product (diaryl) are formed in this reaction (experiments 8-10). The decrease in the reaction selectivity is apparently a result of the lower activity of AlkCOX in oxidative addition to $\text{Pd}(0)$ complexes relative to that of ArCOX .

The ADM permits the synthesis of ketones containing a heterocyclic fragment in high yield (experiment 20)



The reaction of $(\text{PhC}\equiv\text{C})_2\text{Hg}$ with $p\text{-NO}_2\text{C}_6\text{H}_4\text{COCl}$ carried out by the usual procedure with 2 eq. NaI relative to RCOCl gives 40% p -nitrophenyl phenylethynyl ketone, 24% bis(phenylethynyl) ketone, and a large amount of tar (experiment 21). The ketone yield in the presence of 4 eq. NaI was increased to 58% (experiment 22).



EXPERIMENTAL

The OMC, acid chlorides, and Pd , Rh , and Ni complexes were prepared by known methods. Pure-grade tetrabutylammonium iodide and bromide and LiBr were used. A pure-grade sample of NaI was dried for 2 h at 150°C (10 mm). A sample of HMPA was maintained over 13X molecular sieves for 24 h, twice distilled over CaH_2 , bp 37°C ($8 \cdot 10^{-3}$ mm), and stored over 4-Å molecular sieves. A sample of THF was maintained for 24 h over KOH and distilled over LiAlH_4 immediately prior to use. High-purity grade acetone was distilled over NaI immediately prior to use. A sample of CH_2Cl_2 was distilled over CaH_2 . A sample of benzene was distilled over sodium.

The reaction product yields were determined by thin-layer chromatography on Silufol UV-254 using UV spectroscopy. The zones appearing in UV light were cut and eluted with methanol. The UV spectra were taken on a Hitachi-124 spectrophotometer. The reaction products were identified with standard compounds relative to R_f values and UV spectra. The yields were calculated using the extinction coefficients determined for standard compounds.

2-Thienyl p -Nitrophenyl Ketone. A sample of 0.457 g (1.25 mmole) di(2-thienyl)mercury, 0.750 g (5 mmoles) NaI , 0.466 g (2.5 mmoles) p -nitrobenzoyl chloride, 10 ml acetone, and 6.5 mg (0.025 mmole) (III) were added to a flask equipped with a magnetic stirrer. After 10 min, thin-layer chromatography and UV spectroscopy indicated that the reaction mixture contained 0.571 g (98%) coupling product. The reaction mixture was evaporated, 30 ml water was added, and the mixture was extracted with four 30-ml portions of ether. The combined extracts were washed with two 30-ml portions of water and the organic layer was dried over MgSO_4 . Thin-layer chromatography on silica gel using 2:1 hexane-ether as eluent gave 0.518 g (89%) product with mp $172\text{-}173^\circ\text{C}$ [9].

4-Methoxy-4'-nitrobenzophenone. A sample of 0.857 g (2.5 mmoles) p -anisylmercuric chloride, 1.50 g (10 mmoles) NaI , and 10 ml acetone were added to a flask equipped with a magnetic stirrer and stirred for 20 min. Then, 0.466 g (2.5 mmoles) p -nitrobenzoyl chloride and 4.4 mg (0.025 mmole) PdCl_2 were added. After 5 min, the reaction mixture was found to contain 0.546 g (85%) desired product and 0.040 g (15%) $(p\text{-MeOC}_6\text{H}_4)_2$. The reaction mixture was treated analogously to the previous procedure. Thin-layer chromatography on silica gel with 2:1 hexane-ether as eluent gave 0.475 g (74%) 4-methoxy-4'-nitrobenzophenone, mp 121°C [10].

CONCLUSIONS

1. A study was carried out on the effect of solvent, catalyst, and halide ion additives on the acyldemetallation of organomercury compounds in the presence of palladium, nickel, and

rhodium complexes. Optimal conditions were found for carrying out the acyldemercuration both for R_2Hg and $RHgX$, where $R = \text{aryl and alkyl groups}$.

2. Convenient methods were developed for the synthesis of substituted benzophenones, alkylaromatic, unsaturated, and heterocyclic ketones.

LITERATURE CITED

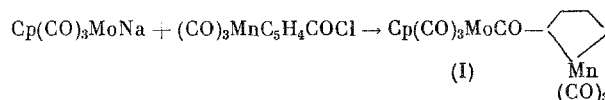
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ORGANOMOLYBDENUM DERIVATIVES OF CYMANTHRENE

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It is well known that the alkyl, aryl, and acyl σ -derivatives of cyclopentadienyltricarbonylmolybdenum $Cp(CO)_3MoR$ and $Cp(CO)_3MoCOR$ ($R = \text{Alk, Ar}$) have a low thermal and oxidation stability [1-3]. The σ -phenyl derivative of molybdenum has not been isolated at all, because rupture of the σ -bond $Mo-Ph$ and migration of the Ph -group into the cyclopentadienyl ring occur already at negative temperatures [4]. On the other hand, we have demonstrated that the σ -cymanthrenyl complexes of the transition metals ($Ni, Fe, \text{ and } W$) are much more stable than their alkyl and aryl analogs [5-7]. This led us to the conclusion that the σ -cymanthrenyl derivatives of cyclopentadienyltricarbonylmolybdenum can also be expected to be stable compounds. In the present work we have achieved the synthesis of a series of organomolybdenum derivatives of cymanthrene and investigated their properties.



The σ -acyl complex (I) has been obtained with a 55% yield by reacting the sodium cyclopentadienyltricarbonylmolybdate with the acid chloride of cymanthrenecarboxylic acid. Compound (I) is a yellow crystalline substance which melts without decomposition at 89.5-90°C. It does not change when kept in air for extended periods of time, i.e., it surpasses with respect to its stability not only the acyl derivatives of molybdenum $Cp(CO)_3MoCOAlk$, which have not been isolated in pure form, but also the perfluoroacyl compounds $Cp(CO)_3MoCOAlkF$ which start to decompose when kept in air for several hours [8].

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