*Asian Journal of Chemistry* Vol. 5, No. 4 (1993), 943–947

# Transition Metal Catalyzed Reactions of Organomercurials–I: Palladium-Catalyzed Acyldemetallation and Cross-Coupling Reactions

P.G. MORE* and B.J. DESAI
*Department of Chemistry*
*Shivraj College of Science*
*Gadhinglaj (Kolhapur)-416 502, India*

The palladium catalyzed acyldemetallation and cross-coupling reactions of organomercurials are discussed. The acyldemetallation reaction provide a mild, selective and general method for the synthesis of unsymmetrical ketones in high yield. The palladium catalyzed cross-coupling reactions with organic halides proceed under mild conditions to give biaryles or arylated heterocyclic compounds in good yields. It is found that, nucleophilic catalysis (iodide ion) is an efficient method for activation of organomercurials in acyldemetallation and cross-coupling reactions.

## INTRODUCTION

Organomercurials are rarely used in organic synthesis (as compared to Grignard reagents) because of their low reactivity. Organomercurials are readily available and can be synthesised easily by a number of synthetic routes. They are thermally stable and do not react with oxygen or atomspheric moisture and therefore it is of interest to use them in organic synthesis. The low reactivity of organomercurials can be easily overcome by using transition metal catalysis and nucleophilic catalysis[1–6].

The palladium catalyzed acyldemetallation and cross-coupling reactions of organomercurials proceed with low selectivity due to catalytic demercuration of organomercurials[7,8]. We studied that the selectivity of both the reactions towards the expected products can be increased in the presence of nucleophilic catalyst (iodide ion) and under mild experimental conditions[1–6]. In the present communication, we are dealing with acyldemetallation and cross coupling reactions of organomercurials.

The acyldemetallation reaction (reaction 1) proceeds in acetone in the presence of palladium catalyst (1 mol %) and iodide ion under argon atmosphere in 10–20 min to give ketone (RCOR′) along with small quantity of homocoupling product ($R_2$).

$$R_2Hg + 2R'COCl \xrightarrow[20^\circ C,\ \text{Acetone}]{\text{Pd, I}^-,\ \text{Ar}} \underset{80\text{–}98\%}{2RCOR'} + \underset{0\text{–}16\%}{R_2} \qquad (1)$$

Pd = $p\text{-}NO_2C_6H_4PdI(PPh_3)_2$

R = $2\text{-}C_4H_3O$, $2\text{-}C_4H_3S$

R′ = $C_6H_5$, $p\text{-}NO_2C_6H_4$, $2\text{-}C_4H_3O$,

The cross coupling reaction (reaction 2) proceeds in DMF in the presence of palladium catalyst (1 mol %) and iodide ion under argon atmosphere to give cross-coupling products along with small quantity of homocoupling product ($R_2$).

$$R_2Hg + R'I \xrightarrow[\text{Ar, DMF, 20°C}]{\text{Pd, I}^-} \underset{80\text{–}97\%}{2R\text{–}R'} + \underset{0\text{–}10\%}{R_2}$$

Pd = $p\text{-}NO_2C_6H_4PdI(PPh_3)_2$

R = $2\text{-}C_4H_3O$, $2\text{-}C_4H_3S$

R′ = $p\text{-}NO_2C_6H_4$, $2\text{-}C_5H_4N$, $2\text{-}C_4H_3S$

In above reactions both the organic groups of organomercurial take part in the reaction.

## EXPERIMENTAL

The palladium complex, organomercurials, acylhalides and arylhalides were prepared by standard procedures. Acetone and DMF were used after distillation. NaI was used after drying under vacuum (0.01 mm Hg) for about 2 hrs. The quantitive yields of the products were determined by TLC and UV spectroscopy. The products were isolated by TLC on silica gel and identified with the help of IR, NMR and mass spectra.

*Acyldemetallation*: A mixture of acetone (4 ml), NaI (2 mmol), acylchloride (1 mmol) $R_2Hg$ (0.5 mmol) and $ArPdI(PPh_3)_2$ (1 mol %, 0.01 mmol) was placed in a 5 ml capacity round bottom flask and stirred vigorously under argon. The quantitative yield of ketone was tested by TLC and UV spectroscopy. After the completion of the reaction, the reaction mixture was diluted with water (10 ml) and extracted with 3 × 5 ml of ether. The ether solutions were combined and washed with 2 × 5 ml of aqueous solution of NaI (to remove the traces of the mercury salt from the ether layer). The ether layer was then dried over $MgSO_4$ and evaporated to get the ketone.

*Cross-coupling*: A mixture of DMF (2.5 ml), NaI (2 mmol), acyl iodide (1 mmol), $R_2Hg$ (0.55 mmol) and Ph PdI $(PPh_3)_2$ (0.01 mmol) was placed in a 5 ml capacity round bottom flask and stirred vigorously under argon. The quantitative yield of the product was determined by TLC and UV spectroscopy. The reaction mixture was diluted with water (10 ml) and extracted with ether (3 × 5 ml). The ether solutions were combined and washed with an aqueous solution of NaI (to remove traces of mercury salt from the ether layer). The ether layer was dried over $MgSO_4$ and then evaporated to get the expected product.

## RESULTS AND DISCUSSION

*Acyldemetallation:* The results are summarised in Table 1. The catalytic cycle of the reaction is depicted in scheme 1. The acyldemetallation (a) and oxidative demercuration (b) processes are catalyzed by palladium complex simultaneously.

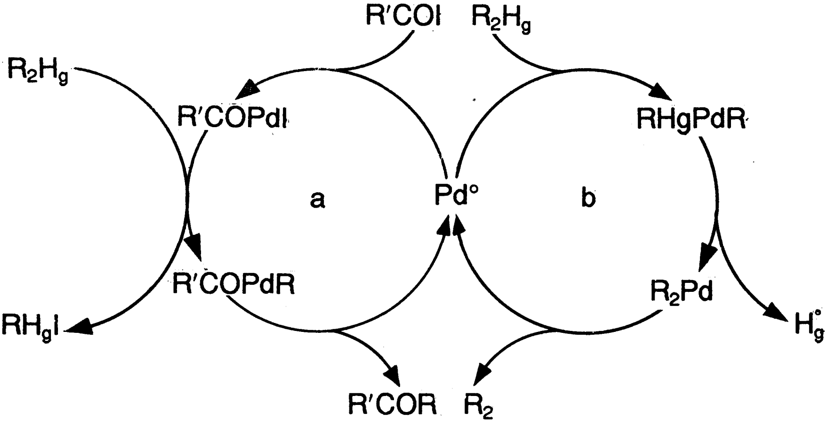


TABLE 1
REACTION OF $R_2Hg$ WITH R'COCl

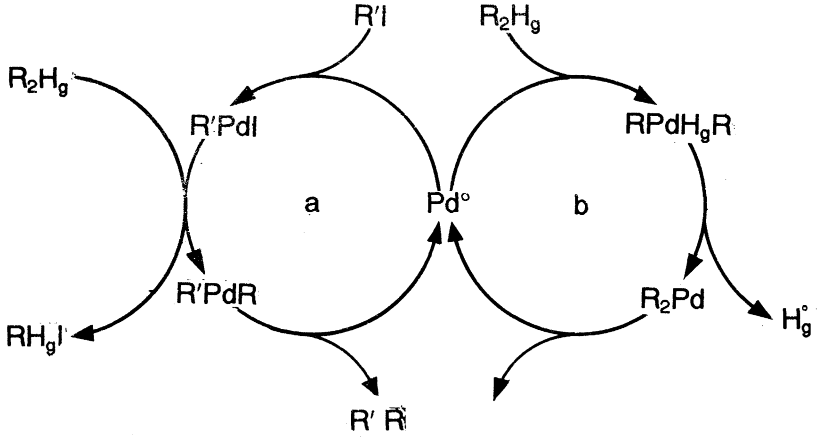
| R | R' | Reaction time (min) | Yield %[a] | |
|---|---|---|---|---|
| | | | RCOR' | $R_2$ |
| 2-$C_4H_3O$ | *p*-$NO_2C_6H_4$ | 10 | 98 (85) | — |
| 2-$C_4H_3O$ | $C_6H_5$ | 15 | 88 (80) | 6 |
| 2-$C_4H_3O$ | 2-$C_4H_3O$ | 15 | 84 (72) | 16 |
| 2-$C_4H_3S$ | $C_6H_5$ | 15 | 80 (70) | 6 |

a—Yield were determined by TLC and UV spectroscopy.
Isolated yields are given in parentheses.

Pd° is generated from the initial palladium complex under reaction conditions (Scheme 1, ligands are omitted). In cycle (a) Pd° takes part in oxidative addition with the acylhalide (R' CO I) to give R' COPd I complex, which further undergoes transmetallation with $R_2Hg$ to give RCOPdR' complex. R'COPdR complex undergoes reductive elimination to give R'COR with the recovery of Pd° complex. On the other hand, in cycle (b) the oxidative demercuration of $R_2Hg$ takes place due to insertion of Pd° into C–Hg bond to give homocoupling product ($R_2$).

*Cross-Coupling*: The results are summarized in Table 2. The catalytic cycle of the reaction is depicted in scheme 2.

Pd° is generated in the reaction mixture under reaction conditions. It catalyzes cross-coupling (a) and catalytic demercuration (b) processes simultaneously. In



cycle (a) Pd° takes part in oxidative addition with arylhalide to give arylpalladium (II) complex, R'PdI, which undergoes transmetallation with $R_2Hg$ to give R'PdR complex. R'PdR complex reductively eliminates R'–R with the recovery of Pd° complex. On the other hand, in cycle (b) oxidative demercuration of $R_2Hg$ takes place due to insertion of Pd° into C–Hg bond, to give the homocoupling product ($R_2$).

TABLE 2
REACTION OF $R_2Hg$ WITH R'I

| R | R' | Reaction time (min) | Yield %[a] | |
|---|---|---|---|---|
| | | | R–R' | $R_2$ |
| 2-$C_4H_3O$ | p-$NO_2C_6H_4$ | 10 | 97 (83) | — |
| 2-$C_4H_3O$ | 2-$C_5H_4N$ | 10 | 88 (79) | 9 |
| 2-$C_4H_3O$ | 2-$C_4H_3S$ | 10 | 82 (75) | 10 |
| 2-$C_4H_3S$ | 2-$C_4H_3S$ | 10 | 95 (80) | — |

a—Yields were determined by TLC and UV spectroscopy.
Isolated yields are given in parantheses

## Functions of Iodide ion (nucleophilic catalysis)

Iodide ion plays an important role in acyldemetallation and cross-coupling reaction. It performs several functions as under:

$$R'COCl \xrightarrow{I^-} R'COI$$

$$Pd^\circ \xrightarrow{I^-} (Pd^\circ I)^-$$

$$R_2Hg \xrightarrow{I^-} (R_2HgI)^-$$

(1) It converts acylchloride into acyl iodide(more reactive in oxidative addition step). (2) It forms an anionic complex with Pd° (as in the case of $Rh^I$ complex[9]) and hence the oxidative addition of RCOI (acyldemetallation) or R–I (cross coupling) to Pd° complex is enhanced. (3) It coordinates with mercury atom ($R_2Hg$) and helps in polarisation and heterolytic fission that taking place at transmetallation step. (4) The formation of anionic complexes $(R_2HgI)^-$ and $(Pd^\circ I)^-$ may lead to retardation of oxidative demercuration process.

## REFERENCES

1. N.A. Bumagin, P.G. More and I.P. Beletskaya, *J. Organomet, Chem.*, **365**, 379 (1989).
2. ________, *J. Organomet. Chem.*, **364**, 231 (1989).
3. ________, *Metalloorg. Khim.*, **2**, 351 (1989).
4. ________, *Metalloorg, Khim*, **2**, 530 (1989).
5. ________, Proceedings of 7th IUPAC conference on Organic Systhesis, Nancy, France (1988).
6. ________, Proceedings of 13th International Conference on Organometallic Chemistry, Torino, Italy (1988).
7. K. Tagaki, T. Okamoto, Y. Sakakibara, A. Ohno, S. Oka and N. Hayama., *Chem. Lett.*, 951 (1975).
8. N.A. Bumagin, I.O. Kalinovskii and I.P. Beletskaya, *Zh. Org. Khim.*, **18**, 1324 (1982).
9. D. Forster, *J. Am. Chem. Soc.*, **97**, 951 (1975).

(*Received*: 29 April 1992; *Accepted*: 18 February 1993) AJC–555