Brief Communications

Palladium-catalyzed acyldemetallation of organomercurials in aqueous media

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Palladium- and iodide ion-catalyzed acyldemercuration of $R_2Hg(RHgI)$ by aroyl chlorides (ArCOCl) can be carried out in aqueous media. Nonsymmetrical ketones (ArCOR) are obtained in high yields along with oxidative demercuration products (R_2) in trace quantities. The possible reaction mechanism and the role of the iodide ion are discussed.

Key words: organomercurials, acyl chlorides, acyldemercuration, ketones, palladium, catalysis, aqueous medium.

The reactions of carboxylic acid chlorides with organometallic compounds are one of the most convenient methods for preparing nonsymmetrical ketones. The use of organomercurials in these reactions is of great interest, because ketones containing various functional groups can be synthesized by this method. The methods for synthesis of organomercurials are well developed, and these compounds are stable towards oxygen and moisture of air and, as a rule, are low-volatile high-melting crystalline substances. However, organomercurials because of their inertness react with aroyl chlorides only in the presence of Lewis acids.[1–3] We have previously shown that simultaneously catalyzed by palladium complex and iodide ion acyldemercuration proceeds smoothly to give nonsymmetrical ketones in high yields.[4,5] However, the reactions were performed in media of anhydrous organic solvents, and anhydrous salts (Bu_4NI or NaI) were used as the source of the iodide ion.

In this work, we have shown for the first time that aqueous acetone can be used as the medium for the reactions of organomercurials with aroyl chlorides, and the $NaI \cdot 2H_2O$ crystal hydrate can be used as the source of the iodide ion. The reactions proceed at 20 °C over 10 min in the presence of 1 mol.% $PdCl_2$ and 3 equiv. $NaI \cdot 2H_2O$ with respect to aroyl chloride to give the corresponding ketones in almost quantitative yields. The corresponding R_2 dimers are formed in trace amounts as by-products.

$$R_2Hg(2RHgI) + 2p\text{-}XC_6H_4COCl \xrightarrow{i}$$

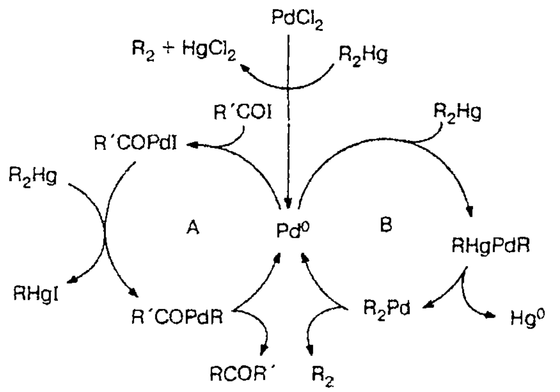
$$\longrightarrow \underset{(90\text{—}95\%)}{2p\text{-}XC_6H_4COR} + \underset{(\text{traces})}{R_2} + [HgI_2 + Hg]$$

$R = Me, Ph, 2\text{-}C_4H_3S$; $X = H, Br, Cl$

Reagents and conditions: *i.* $PdCl_2$, $NaI \cdot 2H_2O$, aqueous acetone, 20 °C, 10 min

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2065—2066, November, 1997.

Scheme 1



Unlike cross-coupling of R_2Hg with ArI,[5] acyldemercuration is slightly sensitive to atmospheric oxygen, and an inert atmosphere is not needed.

The reaction mechanism can be presented as two conjugated catalytic cycles: acyldemercuration (A) and oxidative demercuration (B) (Scheme 1).

Sodium iodide most likely performs several functions in the reaction. First, under the action of NaI, aroyl chlorides are transformed into aroyl iodides, which are more reactive at the stage of oxidative addition. Second, the iodide ion coordinating to the mercury atom favors the polarization and heterolysis of the C—Hg bond,[6] *i.e.*, facilitates the transmetallation stage in the catalytic cycle. Third, the iodide ion can form anionic complexes with Pd^0 (*cf.* Rh^1 complexes),[7] which favors the oxidative addition of aroyl iodides to Pd^0. Fourth, the coordination of the iodide ion to the mercury atoms in R_2Hg and to palladium in the Pd^0 complex, *i.e.*, the formation of the corresponding anionic $[R_2HgI]^-$ and $[Pd^0I]^-$ complexes, prevents the insertion of Pd^0 at the C—Hg bond in R_2Hg, and the oxidative demercuration (cycle B) is completely suppressed.

In the absence of the iodide ion[8] in the $Pd(PPh_3)_4$-catalyzed reactions of Ph_2Hg with PhCOBr in HMPTA at 60 °C, 66% benzophenone and 12% diphenyl are formed over 30 min. Only one Ph group of Ph_2Hg participates in the reaction, since PhHgBr formed due to the acydemercuration does not react with benzoyl bromide under these conditions.

Experimental

Acyldemetallation of R_2Hg in aqueous acetone (general procedure). Benzoyl chloride (2 mmol) and NaI · $2H_2O$ (6 mmol) were stirred at 20 °C for 30 min in aqueous acetone (4 mL, acetone : water = 9 : 1). Then bis(2-thienyl)mercury (1 mmol) and an 0.1 *M* aqueous solution (0.2 mL) of $PdCl_2$ (0.02 mmol, 1 mol.% Pd) were added, and the mixture was stirred at 20 °C for 10 min. The reaction mixture was diluted with water (40 mL) and extracted with ether (4×10 mL). The ether extract was washed with water (3×5 mL), dried with Na_2SO_4, and filtered. After the ether was removed on a rotary evaporator, 2-benzoylthiophene was obtained in 95% yield, m.p. 55 °C (*cf.* Ref. 9: 55—56 °C).

Using similar procedures, *p*-bromoacetophenone was prepared from MeHgI and *p*-bromobenzoyl chloride in 90% yield, m.p. 53—54 °C (*cf.* Ref. 10: 54 °C); benzophenone (93% yield) was obtained from Ph_2Hg and benzoyl chloride, m.p. 47—48 °C (*cf.* Ref. 11: 48.2 °C); and *p*-chlorobenzophenone (91% yield) was obtained from PhHgI and *p*-chlorobenzoyl chloride, m.p. 77 °C (*cf.* Ref. 12: 77—78 °C).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09037).

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Received January 10, 1997