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REACTIONS OF ORGANOMETALLIC COMPOUNDS CATALYZED BY TRANSITION-METAL COMPLEXES

XI *. THE PALLADIUM-CATALYZED REACTION OF ACYL CHLORIDES WITH Et_6Sn_2 AS A ROUTE TO SYMMETRICAL KETONES AND α-DIKETONES

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Summary

The reaction of aroyl chlorides (ArCOCl) with Et_6Sn_2 gives symmetrical ketones (Ar_2CO) or α-diketones ($(ArCO)_2$), depending on the nature of the palladium catalyst and the reaction conditions. The synthesis of α-diketones from AlkCOCl and HetCOCl has been performed for Alk = $n\text{-}C_7H_{15}$ and Het = $2\text{-}C_4H_3O$ (furyl). The palladium-catalyzed carbonylation of aryl iodides in the presence of Et_6Sn_2 may serve as another route to symmetrical α-diketones. Such a possibility has been demonstrated for the preparation of 4,4′-dimethoxybenzil from 4-iodoanisole, carbon monoxide, and Et_6Sn_2.

Introduction

Aryl, vinyl, benzyl, and allyl halides RX react with hexaalkyldistannanes, R'_6Sn_2 (R′ = Me, Et, or Bu), in the presence of palladium catalysts to form $RSnR'_3$ [1–3]. Earlier we found [4] that cross-coupling of the obtained in situ tetraorganostannanes with organic halides (R″X) catalyzed by palladium complexes gives RR″ in high yields (eq. 1).

$$\begin{aligned} &RX + R'_6Sn_2 \xrightarrow{Pd} RSnR'_3 + R'_3SnX \\ &RSnR'_3 + R''X \xrightarrow{Pd} RR' + R'_3SnX \end{aligned} \qquad (1)$$

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When R = R″, reaction 1 is the common method of reductive coupling of RX in the presence of distannanes (eq. 2).

$$2RX + R'_6Sn_2 \xrightarrow{Pd} R_2 + 2R'_3SnX \qquad (2)$$

When carboxylic acid chlorides (RCOCl) are used instead of RX in the reaction with distannanes, one may expect that symmetrical α-diketones will be obtained in one stage (formation of the products of decarbonylation, R_2CO and R_2, is also possible) (eq. 3).

$$2\ RCOCl + R'_6Sn_2 \xrightarrow{Pd} (RCO)_2 + R_2CO + R_2 + R'_3SnCl \qquad (3)$$

The reaction of RCOCl with distannanes catalyzed by palladium complexes has not yet been studied.

Results and discussion

The reaction of substituted benzoyl chlorides, ArCOCl (2 equiv.), with Et_6Sn_2 in toluene catalyzed by $PhPdI(PPh_3)_2$ yields symmetrical ketones, Ar_2CO (47–68%), after 1 h under reflux (Table 1). Along with Ar_2CO, diketones ($(ArCO)_2$) and diaryls (Ar_2) are also formed. The nature of the substituents on the aroyl chlorides has practically no effect on the reaction rate but influences the ratio of the products. The decarbonylation process is facilitated by electron-withdrawing substituents: the yield of α-diketone decreases and that of Ar_2 rises. Decarbonylation, apparently, partially takes place even at the first stage of the reaction, giving $ArSnEt_3$ (the formation of $PhSnEt_3$ was observed by TLC in the course of the reaction of PhCOCl with Et_6Sn_2).

One might expect that an increase of the PPh_3/Pd ratio or milder reaction conditions (reflux in benzene) would inhibit the decarbonylation processes. However, it turned out that neither the yield nor the ratio of the products depended on these factors. The nature of the ligand used is of much greater importance. For instance, when PPh_3 was replaced by $P(OEt)_3$, approximately equal amounts of benzophenone and benzil were obtained from benzoyl chloride. No diphenyl was

TABLE 1

PALLADIUM-CATALYZED SYNTHESIS OF DIARYLKETONES FROM AROYL CHLORIDES

Ar in ArCOCl	*t* (h)	Yield (%)		
		Ar_2CO	$(ArCO)_2$	Ar_2
$4\text{-}MeOC_6H_4$	1	60	25	3
$4\text{-}MeC_6H_4$	1	67	14	9
C_6H_5	1	66	4	19
C_6H_5 [a]	7	68	5	12
C_6H_6 [b]	1.5	57	4	22
C_6H_5 [c]	1	32	41	0
$4\text{-}ClC_6H_4$	1	47	3	30

[a] 80°C, in benzene. [b] PPh_3 (2×10^{-2} mmol) was added. [c] (η^3-$C_3H_5PdCl)_2$ (0.5×10^{-2} mmol) and $P(OEt)_3$ (2×10^{-2} mmol) were used instead of $PhPdI(PPh_3)_2$.

formed under the above conditions (during the reaction, the formation of $PhSnEt_3$ was not observed either). When the synthesis was performed under a carbon monoxide pressure of 8 atm, decarbonylation was inhibited to a much greater extent and the yield of benzil increased to 70%.

Under these experimental conditions (8 atm of CO, catalytic system $(\eta^3\text{-}C_3H_5PdCl)_2 + 4P(OEt)_3$), the reaction of Et_6Sn_2 with substituted benzoyl chlorides (ArCOCl) proceeds smoothly and gives α-diketones in good yields (Table 2). Bu_6Sn_2 reacts with acyl chlorides in a similar way, although the selectivity of the reaction and the yield of diketone is not as high. The reaction of aroyl chlorides with distannanes under carbon monoxide gives, together with α-diketone, small amounts of Ar_2CO. On passing from benzoyl chloride to aroyl chlorides containing electron-donating substituents, the yield of $(ArCO)_2$ increases. In a similar fashion, heterocyclic and alkanecarboxylic acid chlorides can be converted into symmetrical α-diketones by their reaction with distannanes under CO atmosphere. Such a possibility has been demonstrated using the reaction of 2-furoyl and octanoyl chlorides with Et_6Sn_2 as an example.

Only a few examples of the reduction of acyl chlorides to α-diketones [5,6] or symmetrical ketones [7] have been described in the literature. The reaction of RCOCl with Be via the corresponding acylberyllium chloride gives $(RCO)_2$ [5]. This method has not found a wide application, however, because of the poor reproducibility of the results [8]. When Na is used (the known acyloin condensation), no intermediate α-diketone can be isolated. Under the reaction conditions, $(RCO)_2$ is reduced further to α-ketol, RCH(OH)COR. It has recently been found that the reaction of RCOCl with SmI_2, which is a milder one-electron reducing agent, gives $(RCO)_2$ as the main product [6].

It is noteworthy that no decarbonylation products are formed in the course of the reduction of acyl chlorides by Be, Na, or SmI_2. Moreover, the interaction between aroyl chlorides and Et_6Sn_2 in the absence of the palladium catalyst gives only α,α'-bis(aroyloxy)stilbenes [9,10]. Neither α-diketones, ketones, nor diaryls have been obtained. On the basis of these facts, it seems reasonable to propose that in our case the mechanism of the reduction is quite different and includes intermediate organopalladium compounds. From the mechanistic point of view, the nearest literature analogue is, perhaps, the preparation of symmetrical ketones by the

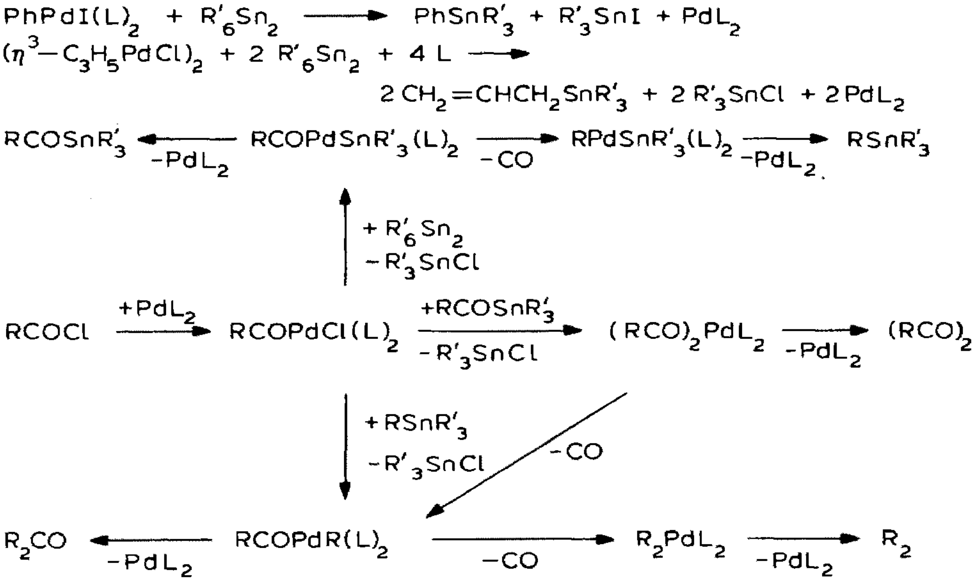
TABLE 2

SYNTHESIS OF SYMMETRICAL α-DIKETONES VIA THE PALLADIUM-CATALYZED REACTION OF ACYL CHLORIDES WITH Et_6Sn_2

R in RCOCl	Yield (%)	
	$(RCO)_2$	R_2CO
$4\text{-}MeOC_6H_4$	76	5
$4\text{-}MeC_6H_4$	73	9
C_6H_5	70	12
C_6H_5 [a]	50	14
$4\text{-}ClC_6H_4$	63	13
2-Furyl	41	–
$n\text{-}C_7H_{15}$	78 [b]	–

[a] Bu_6Sn_2 was used instead of Et_6Sn_2. [b] The yield was determined by GLC.

reaction of aliphatic acid chlorides with transition-metal carbonyls, viz. iron and nickel [7]. The most plausible mechanism for the palladium-promoted reaction of RCOCl with R'_6Sn_2 is shown in Scheme 1 (L = PPh_3, $P(OEt)_3$, or CO).



SCHEME 1

The active catalyst, PdL_2 (I), is generated from the initial palladium complexes under the reaction conditions. The acid chloride oxidatively adds to complex I, giving the acylpalladium(II) complex $RCOPdCl(L)_2$ (II), which undergoes transmetallation with R'_6Sn_2 and reductively eliminates the acyltrialkyltin $RCOSnR'_3$. The latter reacts with II to form $(RCO)_2PdL_2$ (III). Reductive elimination from III gives α-diketone, $(RCO)_2$, and the catalyst I. The reaction scheme 1 also includes the decarbonylation of the intermediate palladium complexes, as a result of which R_2CO and R_2 are obtained along with α-diketone. It is worth noting that R_2 may also be formed by palladium-catalyzed oxidative coupling of $RSnR'_3$ [11], and that the reaction of $RCOSnR'_3$ with RCOCl proceeding without a palladium catalyst is another possible route to α-diketones [12].

Since oxidative addition of alkyl and aryl halides to palladium(0) complexes and the carbonylation of palladium–carbon δ-bonds are well-known processes [13], we suggested that the carbonylation of the ArI/Et_6Sn_2 system could afford α-diketones. The reaction was realized for the synthesis of 4,4′-dimethoxybenzil via carbonylation of 4-iodoanisole (catalytic system $(\eta^3\text{-}C_3H_5PdCl)_2 + 4\ P(OEt)_3$, 8 atm of CO, 111°C). In the reaction of $4\text{-}MeOC_6H_4I$ (2 equiv.) with Et_6Sn_2, complete conversion of the distannane was observed in 2 h; 4,4′-dimethoxybenzil, $(4\text{-}MeOC_6H_4CO)_2$ (71%), and a small amount of ketone, $(4\text{-}MeOC_6H_4)_2CO$ (7%), were formed (yields based on reacted 4-iodoanisole; conversion 88%).

$$2\ 4\text{-}MeOC_6H_4I + Et_6Sn_2 \xrightarrow{\text{Pd, CO}} (4\text{-}MeOC_6H_4CO)_2 + 2\ Et_3SnI$$

Experimental

The palladium complexes $PhPdI(PPh_3)_2$ and $(\eta^3\text{-}C_3H_5PdCl)_2$ were prepared as described in refs. 14 and 15. The reactions were performed in anhydrous toluene; freshly prepared acyl chlorides were used. The distannanes, R'_6Sn_2 (R' = Et, Bu), were prepared according to ref. 3. Commercially available triethylphosphite was distilled from sodium under argon (b.p. 49–50°C/13 mmHg) and used as a 0.1 *M* solution in toluene.

Synthesis of symmetrical diaryl ketones (Table 1). Toluene (2 ml), Et_6Sn_2(0.5 mmol), ArCOCl (1.0 mmol), and $PhPdI(PPh_3)_2$ (1×10^{-2} mmol) were placed into a flask and the reaction mixture was refluxed under argon. After 1 h the initial aroyl chloride and distannane had completely disappeared. Precipitation of palladium black indicated that the reaction had finished. The yields of products were determined by TLC with the use of UV spectroscopy and authentic compounds [16].

Synthesis of symmetrical α-diketones (Table 2). The reaction was carried out in a 5 ml glass autoclave. Toluene (1.6 ml), $(\eta^3\text{-}C_3H_5PdCl)_2$ (1×10^{-2} mmol), and a 0.1 *M* solution of $P(OEt)_3$ (0.4 ml) in toluene were placed into the argon-filled autoclave and the reaction mixture was stirred for 5 min. RCOCl (1.0 mmol) and Et_6Sn_2 (0.5 mmol) were added to the solution. Argon was then replaced by carbon monoxide (8 atm, 20°C) and the reaction mixture was heated at 111°C. In 2 h palladium black had formed, thus indicating that the reaction was completed. The yields of the products were determined by TLC, with the use of UV spectroscopy and authentic compounds; α-diketones were isolated by TLC on silica gel and characterized by physico-chemical constants which coincided with the literature data.

Reaction of 4-iodoanisole with Et_6Sn_2. The reaction was performed in a 35 ml glass autoclave. Toluene (1.6 ml), $(\eta^3\text{-}C_3H_6PdCl)_2$ (1×10^{-2} mmol), and a toluene solution of $P(OEt)_3$ (0.4 ml) were placed into the argon-filled autoclave and the mixture was stirred for 5 min. 4-Iodoanisole (1.0 mmol) and Et_6Sn_2 (0.5 mmol) were added to the solution. Argon was replaced by carbon monoxide (8 atm, 20°C) and the reaction mixture was heated at 111°C for 2 h. The yields of the products were determined by TLC, with the use of UV spectroscopy and authentic compounds: 62% $(4\text{-}MeOC_6H_4CO)_2$, 6% $(4\text{-}MeOC_6H_4)_2CO$ (conversion of $4\text{-}MeOC_6H_4I$ 88%, Et_6Sn_2 100%).

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