Ready Coupling of Acid Chlorides with Tetra-alkyl-lead Derivatives Catalysed by Palladium

Jun-ichi Yamada and Yoshinori Yamamoto*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Palladium-catalysed coupling of acid chlorides with tetra-alkyl-lead derivatives gives the corresponding ketones in high yields under mild conditions.

The palladium-catalysed coupling reactions between organotin derivatives and organic halides have been of great interest in modern synthetic organic chemistry.[1] Unfortunately, however, the reaction between tetra-alkyltin derivatives and acid chlorides is relatively slow, and requires higher temperatures. In particular, the reaction of tetra-alkyltin derivatives bearing long alkyl chains is sluggish. We report here that the palladium-catalysed reaction of acid chlorides with tetra-alkyl-

Table 1. Coupling of acid chlorides with tetra-alkyl-lead reagents.[a]

Entry	RCOCl	$R^2{}_4Pb$ (equiv.)	Method[b]	Reaction time/h	Yield of ketone R^1COR^2 (%)
1	PhCOCl	Bu_4Pb (1.3)	A	12[c]	99
2	PhCOCl	Bu_4Pb (0.6)	A	6	78
3	PhCOCl	Bu_4Pb (0.3)	A	12[c]	37
4	PhCOCl	Bu_4Pb (0.6)	B	6	99
5	PhCOCl	Bu_4Pb (0.6)	C	6	81
6	PhCOCl	Bu_4Pb (0.3)	C	12[c]	43
7	PhCOCl	Et_4Pb (0.6)	A	3	84
8	$Me[CH_2]_6COCl$	Bu_4Pb (0.6)	A	9	60
9	$Me[CH_2]_6COCl$	Bu_4Pb (0.6)	B	16	49[d]
10	$Me[CH_2]_6COCl$	Bu_4Pb (0.6)	C	12	50[d]
11	$Me[CH_2]_3CHEtCOCl$	Bu_4Pb (0.6)	A	4	72
12	PhCH=CHCOCl	Bu_4Pb (0.6)	A	7	65
13	PhCH=CHCOCl	Bu_4Pb (0.6)	B	2	82

[a] All reactions were carried out on 1 mmol scale under argon. [b] Method A: $Pd(PPh_3)_4$ (1 mol %), THF, 65 °C. Method B: $Pd(PPh_3)_4$ (1 mol %), C_6H_6, reflux. Method C: $PhCH_2Pd(PPh_3)_2Cl$ (1 mol %), $CHCl_3$, reflux. [c] The reaction time was not optimized. [d] The isolated ketone contained small amounts of impurities.

lead derivatives proceeeds smoothly and rapidly under milder conditions than the reaction with tetra-alkyltin derivatives [equation (1)]. The results are summarized in Table 1.

$$\mathrm{R^1COCl + R^2{}_4Pb \xrightarrow[Pd^0]{} R^1COR^2 + R^2{}_3PbCl} \qquad (1)$$

$$\mathrm{2R^2{}_3PbCl \rightleftharpoons R^2{}_4Pb + R^2{}_2PbCl_2} \qquad (2)$$

Butyl transfer from $\mathrm{Bu_4Pb}$ to benzoyl chloride in the presence of $\mathrm{Pd(Ph_3P)_4}$ took place rapidly and smoothly in comparison with transfer from $\mathrm{Bu_4Sn}$ (entries 1—6), and the desired ketone was obtained in essentially quantitative yield (entries 1 and 4). Use of only 0.6 equiv. of $\mathrm{R^2{}_4Pb}$ also gave the ketone in high yields (entries 2, 4, 5, and 7—13). This presumably reflects the ready disproportionation of $\mathrm{R^2{}_3PbCl}$ [equation (2)].[2] Use of 0.3 equiv. of $\mathrm{R_4Pb}$ resulted in low yields (entries 3 and 6). Thus two alkyl groups of $\mathrm{R^2{}_4Pb}$ can be utilized effectively for the coupling reaction. This is in marked contrast to the reaction of $\mathrm{R_4Sn}$ in which only one group is transferred.[3] The coupling reaction was also applicable to aliphatic acid chlorides and to an α,β-unsaturated derivative (entries 8—13). Needless to say, the reaction did not occur without palladium catalyst.†

The present finding not only provides a new route to ketones from acid chlorides, but also opens a door to new synthetic applications of organolead compounds.[5]

Received, 14th April 1987; Com. 501

References

1 (*a*) M. Kosugi, K. Sasazawa, Y. Shimizu, and T. Migita, *Chem. Lett.*, 1977, 1423; (*b*) D. Milstein and J. K. Stille, *J. Org. Chem.*, 1979, **44**, 1613; (*c*) For a review, see J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508.
2 P. R. Austin, *J. Am. Chem. Soc.*, 1932, **54**, 3287.
3 J. W. Labadie, D. Tueting, and J. K. Stille, *J. Org. Chem.*, 1983, **48**, 4634.
4 A. G. Davis and R. J. Puddephatt, *J. Chem. Soc. (C)*, 1968, 317.
5 Y. Yamamoto and J. Yamada, *J. Am. Chem. Soc.*, 1987, **109**, 4395.

---

† Trialkylalkynyl-lead derivatives react with acetyl chloride without palladium catalysts to produce alkynyl methyl ketones.[4]