

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

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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.<sup>1</sup> Unfortunately, however, the reaction between tetra-alkyltin derivatives and

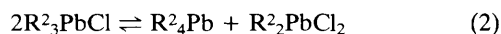
acid chlorides is relatively slow, and requires higher temperatures. In particular, the reaction of tetra-alkyltin derivatives bearing long alkyl chains is sluggish. We report here that the palladium-catalysed reaction of acid chlorides with tetra-alkyl-

Table 1. Coupling of acid chlorides with tetra-alkyl-lead reagents.<sup>a</sup>

Entry	RCOCl	R <sub>2</sub> Pb (equiv.)	Method <sup>b</sup>	Reaction time/h	Yield of ketone R <sup>1</sup> COR <sup>2</sup> (%)
1	PhCOCl	Bu <sub>4</sub> Pb (1.3)	A	12 <sup>c</sup>	99
2	PhCOCl	Bu <sub>4</sub> Pb (0.6)	A	6	78
3	PhCOCl	Bu <sub>4</sub> Pb (0.3)	A	12 <sup>c</sup>	37
4	PhCOCl	Bu <sub>4</sub> Pb (0.6)	B	6	99
5	PhCOCl	Bu <sub>4</sub> Pb (0.6)	C	6	81
6	PhCOCl	Bu <sub>4</sub> Pb (0.3)	C	12 <sup>c</sup>	43
7	PhCOCl	Et <sub>4</sub> Pb (0.6)	A	3	84
8	Me[CH <sub>2</sub> ] <sub>6</sub> COCl	Bu <sub>4</sub> Pb (0.6)	A	9	60
9	Me[CH <sub>2</sub> ] <sub>6</sub> COCl	Bu <sub>4</sub> Pb (0.6)	B	16	49 <sup>d</sup>
10	Me[CH <sub>2</sub> ] <sub>6</sub> COCl	Bu <sub>4</sub> Pb (0.6)	C	12	50 <sup>d</sup>
11	Me[CH <sub>2</sub> ] <sub>3</sub> CHEtCOCl	Bu <sub>4</sub> Pb (0.6)	A	4	72
12	PhCH=CHCOCl	Bu <sub>4</sub> Pb (0.6)	A	7	65
13	PhCH=CHCOCl	Bu <sub>4</sub> Pb (0.6)	B	2	82

<sup>a</sup> All reactions were carried out on 1 mmol scale under argon. <sup>b</sup> Method A: Pd(PPh<sub>3</sub>)<sub>4</sub> (1 mol %), THF, 65 °C. Method B: Pd(PPh<sub>3</sub>)<sub>4</sub> (1 mol %), C<sub>6</sub>H<sub>6</sub>, reflux. Method C: PhCH<sub>2</sub>Pd(PPh<sub>3</sub>)<sub>2</sub>Cl (1 mol %), CHCl<sub>3</sub>, reflux. <sup>c</sup> The reaction time was not optimized. <sup>d</sup> The isolated ketone contained small amounts of impurities.

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



Butyl transfer from  $\text{Bu}_4\text{Pb}$  to benzoyl chloride in the presence of  $\text{Pd}(\text{Ph}_3\text{P})_4$  took place rapidly and smoothly in comparison with transfer from  $\text{Bu}_4\text{Sn}$  (entries 1–6), and the desired ketone was obtained in essentially quantitative yield (entries 1 and 4). Use of only 0.6 equiv. of  $\text{R}^2_4\text{Pb}$  also gave the ketone in high yields (entries 2, 4, 5, and 7–13). This presumably reflects the ready disproportionation of  $\text{R}^2_3\text{PbCl}$  [equation (2)].<sup>2</sup> Use of 0.3 equiv. of  $\text{R}_4\text{Pb}$  resulted in low yields (entries 3 and 6). Thus two alkyl groups of  $\text{R}^2_4\text{Pb}$  can be utilized effectively for the coupling reaction. This is in marked contrast to the reaction of  $\text{R}_4\text{Sn}$  in which only one group is transferred.<sup>3</sup> The coupling reaction was also applicable to aliphatic acid chlorides and to an  $\alpha,\beta$ -unsaturated derivative

(entries 8–13). Needless to say, the reaction did not occur without palladium catalyst.<sup>†</sup>

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.<sup>5</sup>

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## References

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<sup>†</sup> Trialkylalkynyl-lead derivatives react with acetyl chloride without palladium catalysts to produce alkynyl methyl ketones.<sup>4</sup>