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ALKYLATION, ARYLATION, AND VINYLATION OF ACYL CHLORIDES BY MEANS OF ORGANOTIN COMPOUNDS IN THE PRESENCE OF CATALYTIC AMOUNTS OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)

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Alkylation, arylation, and vinylation of acyl chlorides by means of organotin compounds in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium(0) were demonstrated. The corresponding ketons were obtained in fairly good yields.

Dehalogenative coupling reactions of organic halides have been effected by various reagents recently developed.[1)] Although Heck[2)] has suggested the potential utility of organotin compound for alkylation or arylation of organic halides, little attention is paid to the alkylation or arylation by means of organotin compounds. Recently, we reported the allylation and benzylation of acyl chlorides with the corresponding organotin compounds in the presence of a catalytic amount of chlorotris(triphenylphosphine)rhodium(I).[3)]

We now wish to report catalytic alkylation, arylation, and vinylation of acyl chlorides with the corresponding organotin compounds in the presence of tetrakis-(triphenylphosphine)palladium(0).

$$\mathrm{RCOCl} + \mathrm{R'_4Sn} \xrightarrow{\mathrm{Pd(0)}} \mathrm{RCOR'} + \mathrm{R'_3SnCl}$$

Palladium(0) was better catalyst than rhodium(I). The results are collected in Table I.

The reaction was carried out by heating a degassed equimolar mixture of acyl chloride and organotin compound including small amounts of the catalyst and 1 ml of benzene as solvent in a sealed tube. Products were analyzed by GLC and identified by comparing their spectroscopic data with those of the authentic samples.

As can be seen in the Table, tetraalkyl or tetraphenyltin compounds react with acyl chlorides to give the corresponding ketones in fairly good yields, and tri-n-butyltin chloride can also be used as the butylating agent. These reactions may be thought to proceed via oxidative addition of acyl chlorides to Pd(0), followed by

Table I. Reactions of acyl chlorides with organotin compounds in the presence of Pd(0) complex

Substrates m mol				Catalyst m mol	Reaction condition Temp.	Hr.	Product yield %	
Me_4Sn	2	MeCOCl	2	0.02	140°C	5	MeCOMe	53
Me_4Sn	2	PhCOCl	2	0.02	140	5	PhCOMe	54
Ph_4Sn	2	MeCOCl	2	0.02	140	5	MeCOPh	57
Ph_4Sn	2	PhCOCl	2	0.02	140	5	PhCOPh	85
Bu_4Sn	2	PhCOCl	2	0.02	140	5	PhCOBu	55
Bu_3SnCl	2	PhCOCl	2	0.02	140	5	PhCOBu	42
$Bu_3SnCH{=}CH_2$	2	PhCOCl	2	0.02	40	5	$PhCOCH{=}CH_2$	87

transmetallation with tin compounds to give acyl-alkyl-Pd(II) complexes, which undergo reductive elimination of ketones and regenerate Pd(0). Thus, as a whole, a catalytic cycle may be achieved.

These alkylation and arylation needed more drastic conditions in comparison with the allylation and benzylation reported previously.$^{3)}$ This might be due to the larger bond energies of alkyl-tin and aryl-tin bonds compared with those of allyl-tin and benzyl-tin bonds. It is interesting to note, however, that vinylation by vinyltin compound proceeds under quite mild conditions. At present, the reason for this is not clear.

There have been known several examples of alkylation and arylation of acyl halides by means of organotin compounds.$^{4,5)}$ In these reactions, about stoichiometric amounts of Lewis acids were needed. Our reaction may be more useful than these earlier examples, because the reaction proceeds very cleanly in the presence of a only catalytic amount (1 %) of the catalyst. Further studies on the scope and limitation of these reactions are now in progress.

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